

Electrochemical Preparation of Tetrakis(isocyanide)-dipalladium(I) Dichloride¹⁾

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 (Received January 8, 1987)

Synopsis. The electrochemical behavior of $\text{PdCl}_2(\text{RNC})_2$ (**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, $\text{Pd}_2\text{Cl}_2(\text{RNC})_4$ (**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 $\text{Pt}_2\text{Cl}_2(\text{RNC})_4$ from $\text{PtCl}_2(\text{RNC})_2$.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 $\text{PdCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (**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 $\text{PtCl}_2(\text{RNC})_2$,⁵⁾ these waves were assigned to a two-electron reduction of the Pd(II) complexes.

When a charge-controlled electrolysis of **1a** consumed 1F ($1\text{F}=96.5$ kC) of charge per mole of the Pd(II) complex at -1.5 V, binuclear complex, $\text{Pd}_2\text{Cl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4$ (**2a**) was obtained in a 73% yield. Similar binuclear complexes were obtained in a relatively high yield by the electroreduction of $\text{PdCl}_2(\text{RNC})_2$ ($\text{R}=2,6\text{-Me}_2\text{-4-BrC}_6\text{H}_2$, $2,4\text{-}t\text{-Bu}_2\text{-6-MeC}_6\text{H}_2$, $2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$, and $t\text{-Bu}$), as shown in Table 1.

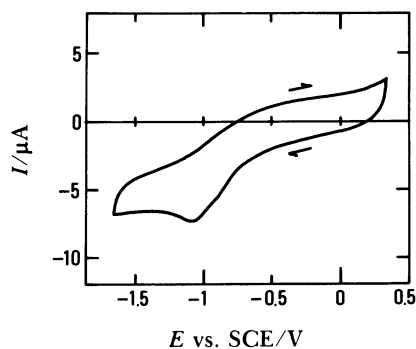
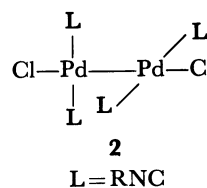


Fig. 1. Cyclic voltammogram of $\text{PdCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (0.2 mM) on a Pt-tip electrode (surface area = 0.078 cm²) in a 0.1 M $n\text{-Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ solution at 22°C . Sweep rate = 0.1 V s⁻¹.



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}) $n\text{-Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ 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 reasonably 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 $\text{PdCl}_2(\text{RNC})_2$ (**1**) on the CVM and Yields of $\text{Pd}_2\text{Cl}_2(\text{RNC})_4$ (**2**)^{a)}

	R	Electrode	$E_{\text{pc}}/\text{V}^{\text{b)}$	Yield/%
1a	2,6-Me ₂ C ₆ H ₃	Pt	-1.19	73
		Hg		23
1b	2,6-Me ₂ -4-BrC ₆ H ₂	Pt	-1.13	83
		Hg		38
1c	2,4- <i>t</i> -Bu ₂ -6-MeC ₆ H ₂	Pt	-1.18	87
		Hg		49
1d	2,4,6- <i>t</i> -Bu ₃ C ₆ H ₂	Pt	-1.15	70
		Hg		52
1e	<i>t</i> -Bu	Pt	-1.41	69

a) Reactions were carried out at -1.5 V except **1e** (-1.6 V) in a 0.1 M $\text{NaClO}_4\text{-CH}_3\text{CN}$ solution (ca. 30 cm³) 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 $n\text{-Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ solution. The potentials are shown against a saturated calomel electrode. Sample concentration: ca. $0.1\text{--}0.5$ mM; scan rate: 0.2 V s⁻¹.

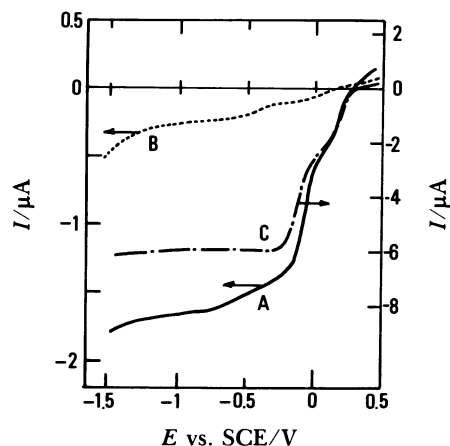
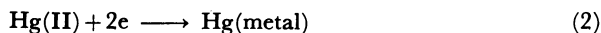
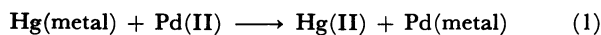


Fig. 2. d.c. Polarograms on a dropping mercury electrode ($m=0.864 \text{ mg s}^{-1}$, drop time=4 s) in a 0.1 M $n\text{-Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ solution at 23 °C. A: $\text{PdCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (0.2 mM). B: Blank (supporting electrolyte solution). C: HgCl_2 (0.5 mM).

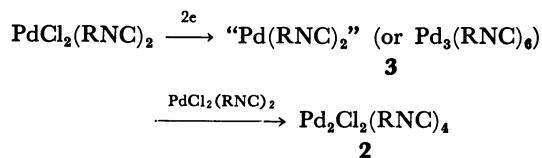
(Eq. 2).⁶⁾



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 $\text{Pd}_2\text{Cl}_2(\text{RNC})_4$ 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, $\text{Pd}_3(\text{RNC})_6$) and **1** led to a formation of **2**.



Experimental

The electrochemical apparatus has been already described.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⁾ $\text{PdCl}_2(\text{RNC})_2$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, 2,6-Me₂-4-BrC₆H₂) 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,

¹H NMR(CDCl₃) $\delta = 1.32$ (s, 4-*t*-Bu), 1.52 (s, 2-*t*-Bu), 2.43 (s, 6-Me), ca. 7.2 (aromatic protons). Anal. (C₁₆H₂₃N) C, H, N.

$\text{PdCl}_2(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{NC})_2$: IR (Nujol) 2229, 2195 cm⁻¹. Anal. (C₃₈H₅₈N₂Cl₂Pd) C, H, N.

$\text{PdCl}_2(2,4\text{-}t\text{-Bu}_2\text{-6-MeC}_6\text{H}_2\text{NC})_2$: IR (Nujol) 2205 cm⁻¹. ¹H NMR (CDCl₃) $\delta = 1.30$ (4-*t*-Bu), 1.48 (2-*t*-Bu), 2.50 (6-Me), ca. 7.3 (aromatic protons). Anal. (C₃₂H₄₆N₂Cl₂Pd) C, H, N.

$\text{Pd}_2\text{Cl}_2(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{NC})_4$: IR (Nujol) 2144 cm⁻¹. ¹H NMR (CDCl₃) $\delta = 1.29$ (s, 4-*t*-Bu), 1.65 (bs, 2 and 6-*t*-Bu), 7.32 (s, aromatic protons, 3- and 4-H). Found: C, 66.66; H, 8.54; N, 4.09%. Calcd for C₇₆H₁₁₆N₄Cl₂Pd₂: C, 66.71; H, 8.91; N, 3.90%.

$\text{Pd}_2\text{Cl}_2(2,4\text{-}t\text{-Bu}_2\text{-6-MeC}_6\text{H}_2\text{NC})_4$: IR (Nujol): 2187, 2147 cm⁻¹. ¹H NMR (CDCl₃) $\delta = 1.27$ (4-*t*-Bu), 1.46 (2-*t*-Bu), 2.47 (6-Me), ca. 7.3 (aromatic protons). Anal. (C₆₄H₉₂N₄Cl₂Pd₂) C, H, N.

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

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