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Electrochemical Reactions of Dihalobis(isocyanide)nickel(II) at Platinum and Mercury Electrodes[#]

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Electrochemical reactions of divalent nickel complexes, $NiX_2(RNC)_2$ (**1**) (X=I, Br, Cl; R=2,6-$Me_2C_6H_3$ (Xyl), 4-Br-2,6-$Me_2C_6H_2$, 2,4-*t*-Bu_2-6-MeC_6H_2, 2,4,6-*t*-$Bu_3C_6H_2$) were carried out at Hg and Pt electrodes. Cyclic voltammograms (CVs) of **1** at a Pt electrode showed a quasi-reversible redox wave at ca. −0.50 V, due to two-electron reduction $[(\mathbf{1})\rightleftharpoons(\mathbf{1})^{2-}]$. The reduction potential of the iodide (**1a**) or bromide (**1f**) complex (R=Xyl) shifted to the positive side by ca. 0.3 V in the presence of isocyanide, due to the electrochemical reaction of $NiX_2(RNC)_3$ (X=I, Br). The chloride complex (**1e**) showed a similar potential in the presence or absence of isocyanide; there exists no five-coordinated complex. The CV of **1a** at a Hg electrode showed a redox wave at −0.74 V, due to the redox reaction of the unsaturated species, "$[Ni(RNC)_2HgI_2]$" (**4**) formed from the reaction of **1a** with Hg, suggesting the CE mechanism. Compound **1a** had a redox potential at −0.72 V in the presence of 2,6-xylyl isocyanide, being responsible for $[Ni(RNC)_4HgI_2]_2$. The bromide complex showed a similar behavior, but the chloride complex underwent a very complicated reaction. The electrochemical mechanism of $NiX_2(RNC)_2$ with or without isocyanide is discussed.

There are many studies on electrochemical reactions of organometallic compounds.[1] These electrochemical studies have provided valuable information on reaction mechanisms.

Previously, we performed systematic electrochemical studies of platinum and palladium complexes such as $MCl_2(RNC)_2$ and $[M(RNC)_4]^{2+}$ (M=Pd, Pt). Polarograms of $PtCl_2(RNC)_2$ and $[Pt(RNC)_4]^{2+}$ showed irreversible two-electron reductions and their macroscopic electrolyses gave dimeric, linear trinuclear complexes and zerovalent clusters containing metal-metal bonds, depending on the potential and charge for the reduction (Scheme 1).[2,3] Polarograms of $PdCl_2(RNC)_2$ showed a different behavior from that of the Pt(II) complexes. Electron transfer from mercury to palladium(II) complexes occurred on the surface of the mercury electrode to form $HgCl_2$ and palladium metal before the electrochemical reaction proceeded, and the electrochemical reduction of $HgCl_2$ was subsequently observed; this is the so-called CE mechanism (Eqs. 1 and 2).[4]

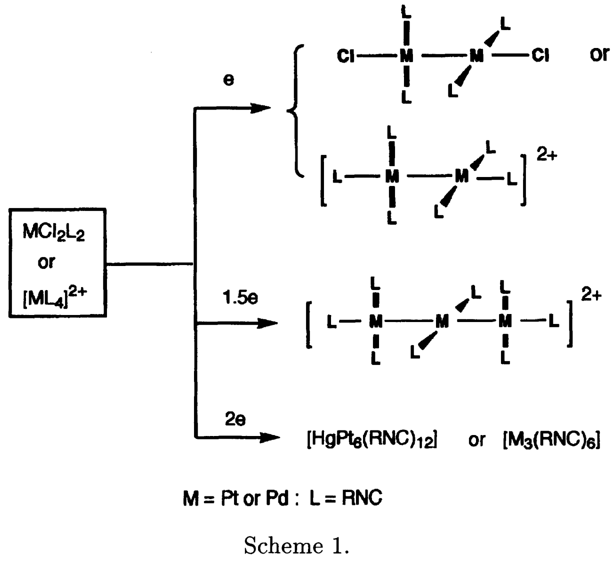
$$PdCl_2(RNC)_2 + Hg \xrightarrow{-RNC} Pd(metal) + HgCl_2 \qquad (1)$$

$$Hg^{2+} \xrightarrow{2e} Hg(0) \qquad (2)$$

On the other hand, a cyclic voltammogram at a Pt electrode showed an irreversible two-electron reduction and the macroscopic reduction by means of the platinum electrode gave dimeric and trinuclear complexes. In comparison with the isocyanide complexes of platinum(II) and palladium(II), we examined the electrochemical behavior of nickel(II) complexes $NiX_2(RNC)_2$ (X=Cl, Br, I) and their related complexes. In these reactions, particularly notable was the electrochemical response at different electrode materials. Similar electrode behaviors have been reported for a series of iron carbonyl complexes,[5] $CpM(CO)_2$ (M=Co, Rh),[6] and an osmium cluster, $[Os_{10}(CO)_{24}]^{2-}$.[7] A preliminary report of this work has already been communicated.[8]

Results and Discussion

Electrochemistry of Isocyanide Complexes at a Platinum Electrode. A) $NiX_2(RNC)_2$ System. Orange or brown complexes of *trans*-$NiI_2(RNC)_2$ (**1a**: R=2,6-$Me_2C_6H_3$; **1b**: R=4-Br-2,6-$Me_2C_6H_2$; **1c**: R=2,4-*t*-Bu_2-6-MeC_6H_2; **1d**: R=2,4,6-*t*-$Bu_3C_6H_2$), *cis*-$NiCl_2$(2,6-$Me_2C_6H_3NC)_2$ (**1e**) and *trans*-$NiBr_2$(2,6-$Me_2C_6H_3NC)_2$ (**1f**) were used in the electrochemical reactions.[9] The cyclic voltammograms (CVs) of



Scheme 1.

[#] Electrochemical studies of organometallic compounds. Part 7. For Part 6, see: K. Ehara, K. Kumagai, Y. Yamamoto, K. Takahashi, and H. Yamazaki, *J. Organomet. Chem.*, **410**, C46 (1991).

$NiX_2(RNC)_2$ (**1**) in a $MeCN-CH_2Cl_2$ (9 : 1) solution were measured at a platinum disk electrode.

The CVs of complexes **1a**, **1b**, **1e**, and **1f** showed a quasi-reversible redox wave near −0.52 V [vs. Fc/Fc^+ (E^0 = +0.307 V vs. aq SCE); Fc = ferrocene] in addition to one or two irreversible oxidative waves at ca −0.02—+0.72 V (vs. Fc/Fc^+) (Fig. 1). For sweep rates (r) between 0.01 and 0.20 V s^{-1} the ratio $i_{pc}/r^{1/2}$ of the redox wave was constant and i_{pa}/i_{pc} = ca. 0.8—1.2, in accord with diffusion control. Potential separations between anodic and cathodic peaks were in the range of 0.08—0.15 V for a sweep rate of 0.1 V s^{-1}. Generally, the $E_{1/2}$ value is known to shift to a lower potential with a decrease in the electronegativity of a halogen. This trend was observed in the bromide and iodide complexes, but the chloride complex showed a redox potential similar to the bromide complex. This is probably due to the stereochemistry of the complexes. Thus, it is known that the reductive potential of the *cis*-isomer appears at a higher potential than that due to the *trans*-isomer in the electrochemical reactions of *trans*- and *cis*-$[PtCl_2(PPh_3)_2]$.10) Furthermore, the *cis*-isomer would be more easily reduced than the *trans*-isomer, since the LUMO energy level of the *cis*-isomer is calculated to be more stable than that of the *trans*-isomer from EHMO calculations of the model complexes. Stereochemistry-dependent behavior has also been noted in $RuX_2(RNC)_4$.11) There were no relations between the half-wave potential and the ligand (Table 1). Complex **1c** was irreversible and the i_{pa}/i_{pc} ratio was 0.38. Complex **1d** was also irreversible, and the reduction wave of **1d** was observed at −0.37 V, but an oxidative wave corresponding to the reductive wave was not observed. This electrochemical behavior suggests an EC reaction.

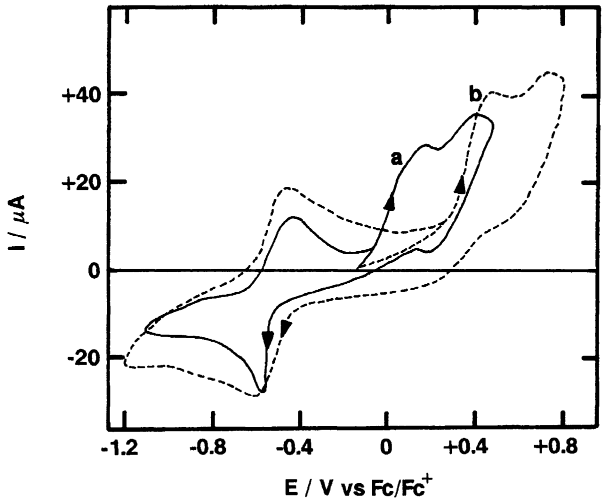


Fig. 1. Cyclic voltammograms of $NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1a**) and $NiBr_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1f**) at a Pt electrode in a 0.1 M CH_2Cl_2/MeCN (1 : 9)/[n-Bu_4N](ClO_4) solution. (a): **1a**; (b): **1f**. Measured in a 1 mM solution of sample with a scan rate of 0.1 V s^{-1}.

Table 1. Redox Potentials of $NiX_2(RNC)_2$ and a $NiX_2(RNC)_2$- RNC System at Pt and Hg Electrodes^a)

Compound^b)	$E_{1/2}$/V (I_{pa}/I_{pc})		
	Reduction Pt	Oxidation Pt	Reduction Hg
1a	−0.52(1.13)	+0.17, +0.36	−0.74(1.0)
1a+XylNC	−0.48(0.78)	+0.02, +0.32	−0.72(1.01)
1b	−0.66(0.86)	−0.10	—c)
1c	−0.45(0.38)	−0.02, +0.37	—c)
1d	−0.37d)	−0.02, +0.27	—c)
1e	−0.51(0.78)	+0.88	—d)
1e+XylNC	−0.51(0.83)	+0.89	—d)
1f	−0.51(0.92)	+0.50, +0.72	—d)
1f+XylNC	−0.48(0.79)	+0.79	−0.73(0.99)

a) Measured in a 0.1 M [n-Bu_4N](ClO_4)/MeCN solution. Sample concentration: 1 mM solution. Scan rate: 0.1 V s^{-1}. E/V vs. Fc/Fc^+ (E^0 = +0.307 V). b) **1a**: *trans*-$NiI_2(XylNC)_2$; **1b**: *trans*-$NiI_2(4\text{-}Br\text{-}2,6\text{-}Me_2C_6H_2NC)_2$; **1c**: *trans*-$NiI_2(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_2$; **1d**: *trans*-$NiI_2(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_2$; **1e**: *cis*-$NiCl_2(XylNC)_2$; **1f**: *trans*-$NiBr_2(XylNc)_2$. c) Not measured. d) Irreversible.

Considering the reversibility of the complex with a series of different substituted isocyanides, the reductive species containing bulky isocyanide ligands appeared to be more unstable than those having small isocyanide ligands, suggesting a relation between the bulkiness of the reductive species and its stability.

These quasi-reversible or irreversible reductive reactions proceeded with two-electron reduction as deduces by the fact that the coulometric electrolysis of the complex **1** at ca. −1.0 V gave tetrakis(isocyanide)nickel(0).

Since the oxidative waves are in disagreement with those of halogen ions (Table 1), and conductivities of these complexes in MeCN are small enough to be a non-electrolyte, we can consider that irreversible oxidation-waves are responsible for the complex **1**. These results show that a one-electron two-step oxidation occurred for **1a**, **1c**, and **1d** (route a) (Chart 1), and that a two-electron one-step oxidation occurred for **1b** and **1e** (route b) (Chart 1).

B) $NiX_2(RNC)_2$-RNC System. When 2,6-xylyl isocyanide was added to **1a** in a mixed solvent of MeCN and CH_2Cl_2 (9 : 1), the solution changed from brown to blue. A CV of the blue solution of **1a** and 2,6-xylyl isocyanide (a 1 : 5 ratio) showed a quasi-reversible wave with a half-wave potential at −0.48 V (vs. Fc/Fc^+), higher by ca. 0.04 V than that (−0.52 V) of **1a**, suggesting the existence of a new species (Fig. 2). A blue

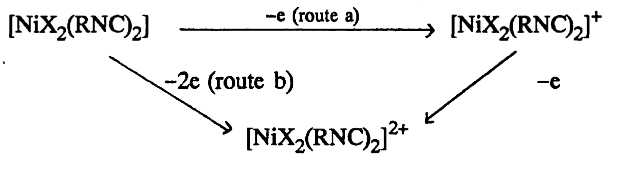


Chart 1.

complex was isolated from the blue solution quantitatively and formulated as $\mathrm{NiI_2(2,6\text{-}Me_2C_6H_3NC)_3}$ (**2a**) (vide infra).[9] When the blue complex **2a** was dissolved in a mixture of $\mathrm{MeCN\text{-}CH_2Cl_2}$ containing 0.1 M (1 M=1 mol dm^{-3})[n-$\mathrm{Bu_4N}$][$\mathrm{ClO_4}$] (complex concentration: ca 1.0 mM), the solution color changed to brown. The electronic spectrum showed a similar pattern to that of **1a**. Furthermore, the CV of the solution showed a similar wave-pattern ($E_{1/2}=-0.52$ V) to that of **1a**. These results suggested the dissociation of the ligand. Addition of RNC to the solution changed it from brown to blue, and a half-wave potential again appeared at −0.48 V. The conductivity of a mixture of **2a** and 2,6-xylyl isocyanide was small enough to be a non-electrolyte. The macroscopic electrolysis of the mixture also gave $\mathrm{Ni(2,6\text{-}Me_2C_6H_3NC)_4}$. From these electrochemical results and conductivities, the equilibrium is believed to shift to the left in the presence of RNC and to the right in the absence of RNC. The electrochemical reaction depends on the condition measured (Chart 2). The CV of **1f** and 2,6-xylyl isocyanide (a 1 : 5 ratio) showed an electrochemical behavior similar to the iodide complex. The CV of a mixture of **1e** and 2,6-xylyl isocyanide in a 1 : 5 ratio showed one redox couple at −0.51 V and an oxidative potential at +0.88 V, being in good agreement with that of **1e**. This suggested that the chloride complex **1e** existed as a four-coordinated species without association in solution. Since a mixture of **1c** and 2,4-t-$\mathrm{Bu_2\text{-}6\text{-}MeC_6H_2NC}$ did not show a color change in the solution, and the CV showed a similar pattern to that of **1c**, the five coordinated species is proposed to be nonexistent, due to the sterically bulky-substituents of the isocyanide.

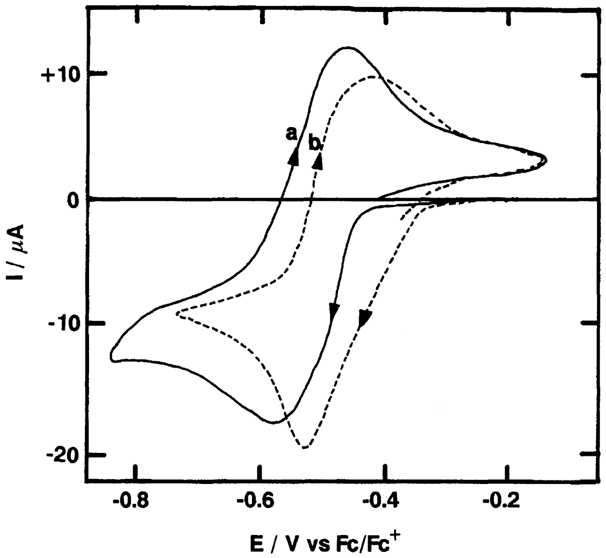


Fig. 2. Cyclic voltammograms of $\mathrm{NiI_2(2,6\text{-}Me_2C_6H_3NC)_2}$ (**1a**) with and without excess $\mathrm{2,6\text{-}Me_2C_6H_3NC}$ at Pt electrode in a 0.1 M $\mathrm{CH_2Cl_2/MeCN}$ (1 : 9)/[n-$\mathrm{Bu_4N}$]($\mathrm{ClO_4}$) solution. (a): **1a** (1.0 mM); (b): a mixture of **1a** (1.0 mM) and 2,6-xylyl isocyanide (5.0 mM). Scan rate: 0.1 V s^{-1}.

$$\begin{tikzcd}
\mathrm{NiI_2(RNC)_3} \arrow[r, shift left] \arrow[d, shift left, "+2e"] & \mathrm{NiI_2(RNC)_2} + \mathrm{RNC} \arrow[l, shift left] \arrow[d, shift left, "+2e"] \\
{[\mathrm{NiI_2(RNC)_3}]^{2-}} \arrow[u, shift left, "-2e"] & {[\mathrm{NiI_2(RNC)_2}]^{2-}} \arrow[u, shift left, "-2e"]
\end{tikzcd}$$

Chart 2.

Electrochemical Reaction at a Hanging-Mercury-Drop Electrode. The CV of **1a** at a hanging-mercury-drop electrode (HMDE) showed a redox couple at −0.74 V in the scan width from −0.42 to −0.95 V (termed as a narrow scan) (Fig. 3A and Table 2). This redox potential was lower by ca. −0.20 V than that measured at a Pt electrode (Table 2 and Fig. 3C). When the scan width was extended from −0.42 to −1.10 V (wide scan) (Fig. 3B) or when the potential was scanned again to the positive side after the potential was kept for 10 s at ca. −0.95 V (stopped scan), their CVs showed a similar wave-shape; one cathodic wave appeared at −0.79 V and two anodic waves were observed at −0.63 (a wave) and −0.66 V (b wave), being different from that (−0.69 V) of the narrow scan (from −0.42 to −0.95 V) (Fig. 3A). The oxidative wave at

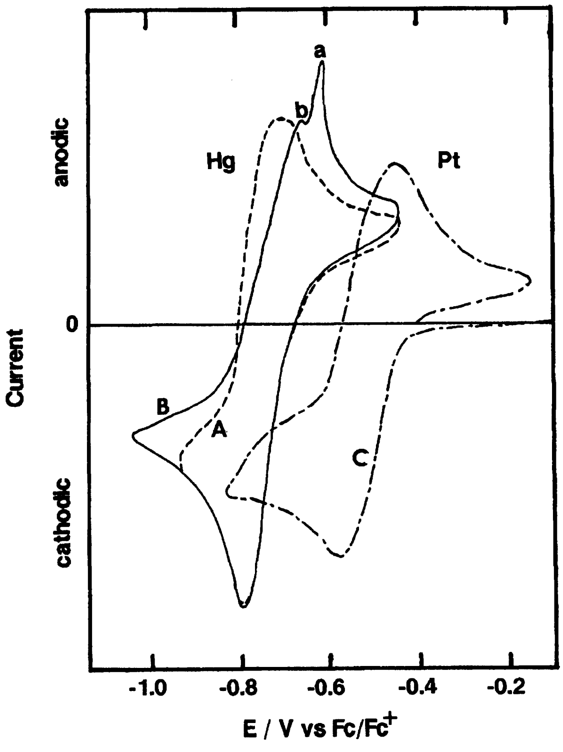


Fig. 3. Cyclic voltammograms of $\mathrm{NiI_2(2,6\text{-}Me_2C_6H_3NC)_2}$ (**1a**) at Hg and Pt electrodes in a 0.1 M $\mathrm{CH_2Cl_2/MeCN}$ (1 : 9)/[n-$\mathrm{Bu_4N}$]($\mathrm{ClO_4}$) solution. Measured in a 0.6 mM solution of the sample at a scan rate of 0.1 V s^{-1}. Hg electrode: (A: Narrow scan and B: Wide scan). Pt electrode: (C).

Table 2. Redox Potentials of $[Ni(XylNC)_4HgX_2]_2$ (**3**) at Pt and Hg Electrodes[a)]

Compound	$E_{1/2}$ (E/V)	
	Hg	Pt
$[Ni(XylNC)_4HgI_2]_2$ (**3a**)	−0.72	−0.72
$[Ni(XylNC)_4HgCl_2]_2$ (**3e**)	—[b)]	—[b)]
$[Ni(XylNC)_4HgBr_2]_2$ (**3f**)	−0.72	−0.73

a) Measured in a 0.1 M $[n\text{-}Bu_4N](ClO_4)$/MeCN solution. Sample concentration: 1 mM solution. The value I_{pa}/I_{pc} is ca. 1.0. Scan rate: 0.1 V s^{-1}. E/V vs. Fc/Fc^+ (E^0=+0.307 V vs. aq SCE). XylNC=2,6-$Me_2C_6H_3NC$.
b) Irreversible and not analyzed.

−0.63 V (a wave) was very sharp and was considered to be an adsorption wave of the oxidative product, because of its shape. The difference of the redox potentials by electrodes and scan methods suggested the formation of a new species on the Hg electrode.

In an attempt to examine the dependence on scan methods, CVs of **1a** were measured in various ratios of CH_2Cl_2 and MeCN. The CV in CH_2Cl_2 showed one redox couple even in a wide scan measurement. With the addition of MeCN to this CH_2Cl_2 solution, the wave-pattern changes and finally two anodic peaks were observed above a 7:3 ratio of CH_2Cl_2 and MeCN. Similar redox behavior was also observed in a mixture of CH_2Cl_2 and PhCN. These results are thought to be the results of the coordination of nitrile having a larger donor number than CH_2Cl_2.

In an attempt to confirm the species, CVs of $[Ni(XylNC)_4HgI_2]_2$ (**3a**),[9)] prepared from $NiI_2(XylNC)_2$, isocyanide and mercury and determined by X-ray analysis, were measured at Hg and Pt electrodes. Both $E_{1/2}$ values were −0.72 V (vs. Fc/Fc^+) (Fig. 4), indicating no interaction between the complex and electrodes.

In the CVs (wide scan) of a mixture of **1a** and 2,6-xylyl isocyanide, the cathodic peak shifted to the positive side with the addition of isocyanide to a solution of **1a** and the anodic peak to the negative side. Finally, the redox potential agreed very closely with that of **3a**. This result showed that the species **3a** is assumed to have been formed in the presence of isocyanide before the electrochemical reaction occurred (Fig. 5).

From these electrochemical behaviors, we assume that a transient species such as "$Ni(RNC)_2HgI_2$" (**4**) was initially formed by a chemical reaction. In the CV at the narrow scan width, the redox reaction of this species **4** was observed as an electrochemical reaction [(**4**)$\rightleftharpoons$(**4′**)], whereas in the CVs at the wide scan or stopped scan widths, the solvation of MeCN to the coordinatively unsaturated species **4′** occurred to form **5′**. Subsequently, **5′** was oxidized to generate **4** by two different routes. One is a direct oxidation of **5′** containing the elimination of MeCN. Another route proceeded with the oxidation of an adsorbed species **5″** to regenerate **4**. In both processes, the formation of **4** was confirmed by the fact that similar cathodic potentials in the narrow and wide scan (containing a stopped scan) measurement were observed. In the CH_2Cl_2 solution the uncoordinated species (**4′**) had a relatively long life-time, due to the weak coordination ability of CH_2Cl_2. In the presence of isocyanide, the species (**4**) captured isocyanide molecules to give the Hg–Ni complex (**3**) and the redox couple of **3** has been observed (Scheme 2).

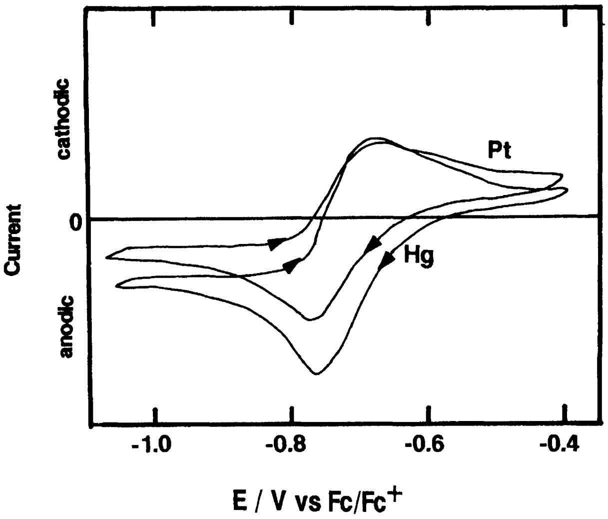


Fig. 4. Cyclic voltammograms of $[Ni(2,6\text{-}Me_2C_6H_3NC)_4HgI_2]_2$ (**3a**) at Pt and Hg electrodes in a 0.1 M CH_2Cl_2/MeCN (1:9)/$[n\text{-}Bu_4N](ClO_4)$ solution. Measured in 1.0 mM solution of the sample with a scan rate of 0.1 V s^{-1}.

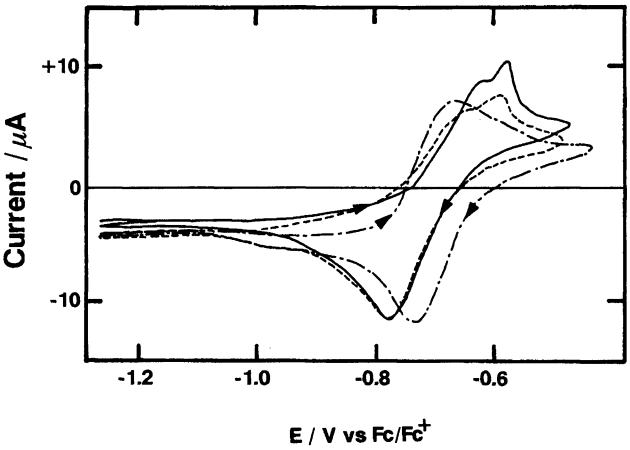
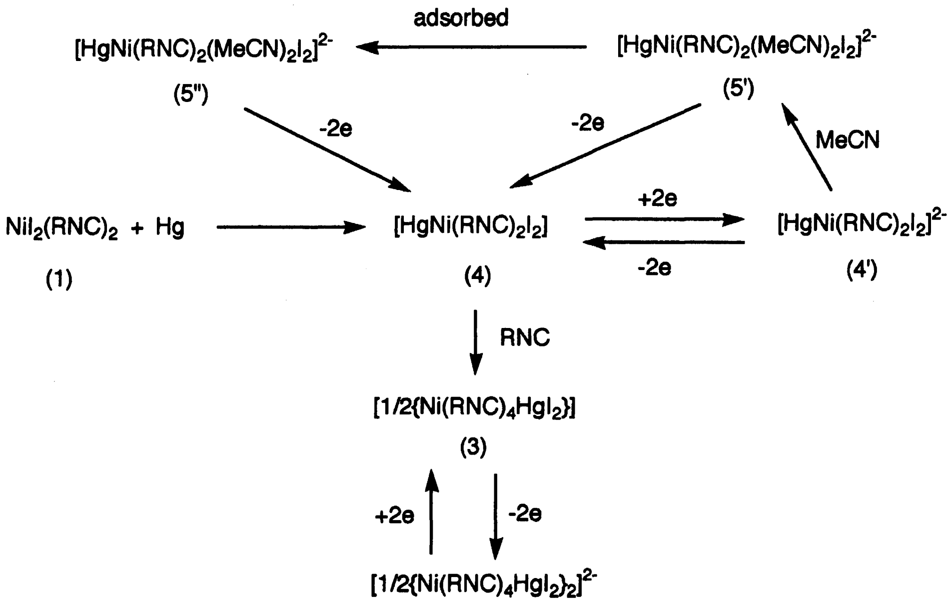


Fig. 5. Cyclic voltammograms of a mixture of $NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1a**) and 2,6-xylyl isocyanide at a wide scan. Measured by a Pt electrode. Scan rate of 0.1 V s^{-1}. (a): **1a** (1 mM). (b): **1a** (1 mM)+XylNC (1 mM). (c): **1a** (1 mM)+XylNC (ca. 3 mM).

Similar electrochemical behavior has been observed in the bromide complex (**1f**). However, the chloride complex (**1e**) showed a very complicated CV. In spite of added isocyanide, the complicated CV remained unchanged. Although complex **1e** showed an unusual electrochemical behavior on the mercury surface, the com-



Scheme 2. Electrochemical reaction mechanism.

plex $\mathrm{[Ni(XylNC)_4HgCl_2]_2}$ (**3e**) could be isolated. The CV of **3e** is in good agreement with that of a mixture of **1e** and 2,6-xylyl isocyanide, suggesting that the stability in the reductive state is very low. The lower stability of the chloride complex than those of the bromide and iodide complexes probably is responsible for the stability of the five-coordinated nickel complexes, because isolation of $\mathrm{NiCl_2(RNC)_3}$ was not possible, whereas $\mathrm{NiX_2(RNC)_3}$ (X=Br and I) were isolated. We do not have further information on the electrochemical mechanism of **3e**.

Electrochemical and Chemical Preparation of $\mathrm{Ni(RNC)_4}$. The potentiostatic electrolysis of $\mathrm{NiI_2(RNC)_2}$ was carried out in the presence or absence of isocyanide by a Pt plate electrode. The results are shown in Table 3. Since coatings on the surface of the electrode were observed with an increase of charge and the electric current decreased, current efficiency became low. However, reduction of **1** with sodium amalgam gave tetrakis(isocyanide)nickel(0) in a relatively high yield. This chemical reduction presents a simple and convenient route to tetrakis(aryl isocyanide)nickel(0). Zerovalent aromatic isocyanide complexes are less sensitive than $\mathrm{Ni(\mathit{t}\text{-}BuNC)_4}$, and especially $\mathrm{Ni(2,4,6\text{-}\mathit{t}\text{-}Bu_3C_6H_2NC)_4}$ is very stable and remains unchanged in the solid state for several years. Such unusual stability has been observed in hexakis(2,4,6-tri-*t*-butylphenyl isocyanide)molybdenum(0) and -tungsten(0).[12]

Table 3. Electrochemical and Chemical Preparation of $\mathrm{Ni(RNC)_4}$[a]

R	Yeild (%)	
	Electrochemical	Chemical
$\mathrm{2,6\text{-}Me_2C_6H_3}$	33	62
$\mathrm{2,4,6\text{-}Me_3C_6H_2}$	42	75
$\mathrm{4\text{-}Br\text{-}2,6\text{-}Me_2C_6H_2}$	29	77
$\mathrm{2,4,6\text{-}\mathit{t}\text{-}Bu_3C_6H_2}$	20	80

a) Electrochemical reactions wee carried out at −1.0 V ($\mathrm{Fc/Fc^+}$), using a Pt plate electrode. Chemical reactions were carried out in THF; sodium amalgam (ca. 3%) was used as a reductive reagent.

In the ^{1}H NMR spectra of a mixture of $\mathrm{Ni(\mathit{t}\text{-}BuNC)_4}$ and *t*-BuNC in toluene-d_8, only one resonance has been observed between 20 and −120 °C showing the presence of the rapid ligand exchange.[13] The exchange reaction between $\mathrm{Ni(PhNC)_4}$ and PhNC[13] is so fast that it was impossible to measure the rate even at 4 °C.[14] The temperature dependent ^{1}H NMR spectra of $\mathrm{Ni(RNC)_4}$ obtained in these experiments were examined in the presence of excess isocyanide. The ligand exchange was found to occur only at higher temperatures. The ligand exchange was not observed until 120 °C for a $\mathrm{Ni(2,4,6\text{-}\mathit{t}\text{-}Bu_3C_6H_2NC)_4}$ and $\mathrm{2,4,6\text{-}\mathit{t}\text{-}Bu_3C_6H_2NC}$ system, due to the steric bulkiness of the isocyanide.

Interaction of Group 10 Metal Isocyanide Complexes with Mercury. In the reactions of $\mathrm{MX_2(RNC)_2}$ (M=Ni, Pd, Pt) with a Hg atom, the palladium complex led to a deposit of palladium metal (Eq. 1). The platinum complex did not react with Hg and was recovered. These results show that the chemical reactivities of $\mathrm{MX_2(RNC)_2}$ to the Hg atom is in the order Pd>Ni>Pt. This order is similar to a trend of amalgamation of the group 10 metals with the Hg atom, suggesting that an interaction between palladium and mercury is larger than nickel and platinum.[15] The large amalgamation ability of palladium may be a factor which leads to the decomposition of the palladium complex.

Experimental

Materials. Acetonitrile was purified by distillation from calcium hydride. [n-Bu_4N][ClO_4], as a supporting electrolyte, was recrystallized from ethylacetate. Isocyanides were prepared according to the literature method, some with modifications.[16,17] $NiX_2(RNC)_2$ and [$Ni(2,6\text{-}Me_2C_6H_3NC)_4HgX_2]_2$ were prepared by the literature method.[9]

Apparatus. ^1H NMR spectra were recorded on a JEOL FX100 instrument. Infrared spectra were recorded on JASCO 442 spectrometer. Conductivities were measured by an Ando Electronic Co., Ltd. LCR-10 impedance bridge. Controlled potential electrolysis with coulometry was carried out using a Huso polarography model 312A, and a potential scanning unit model 312 was employed for cyclic voltammetry. The electrolytic cell consisted of a conventional three-electrode system. Working electrodes used were a Pt disk electrode (0.14 cm^2) and HMDE (0.085 cm^2) for CV measurements and a Pt plate electrode (9.0 cm^2) for the macroscopic electrolysis. A Pt wire was used as a counter electrode. The reference electrode was an $Ag/AgNO_3$ (0.1 $mol\,dm^{-3}$)-[n-Bu_4N][ClO_4]/MeCN (0.1 $mol\,dm^{-3}$) system, whose potential was determined relative to a ferrocene (Fc)/ferrocenium (Fc^+) (1×10^{-3} $mol\,dm^{-3}$) couple ($E^0=+0.307$ V vs. aq SCE)[18] at the end of each experiment. The supporting electrolyte was tetra-n-butylammonium perchlorate. Electrochemical measurements were carried out in a 0.1 M (1 M=1 $mol\,dm^{-3}$) solution of [n-Bu_4N][ClO_4]-MeCN under an atmosphere of nitrogen at 25±1 °C after the solution was deaerated by bubbling with nitrogen. All potentials are indicated vs. Fc/Fc^+. The $Ni(RNC)_4$ complexes were electrochemically prepared according to the literature method.[4]

Preparation of $Ni(2,6\text{-}Me_2C_6H_3NC)_4$. (a) A brown solution of $NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (0.58 g, 1.0 mmol) in THF (30 ml) was stirred with Na/Hg (ca. 1%) for 2 h at room temperature. The yellow-orange solution was decanted and the solvent was removed under reduced pressure. The residue was chromatographed on deactivated alumina (containing 10% H_2O, column height ca. 3 cm), benzene being used as an eluent. Removal of the solvent and crystallization from benzene-hexane gave orange-yellow crystals (0.18 g, 62%). IR (Nujol) 1995 (N≡C) cm^{-1}. ^1H NMR (PhCl) $\delta=2.35$ (s, Me). Anal. Calcd for $C_{36}H_{36}N_4Ni$: C, 74.11; H, 6.22; N, 9.60%. Found: C, 74.12; H, 6.27; N, 9.59%.

(b) By using a strictly analogous procedure, 0.48 g (81%) of the title complex was obtained from $NiI_2(2,6\text{-}Me_2C_6H_3NC)_2$ (0.58 g, 1.0 mmol) and 2,6-xylyl isocyanide (0.47 g, 3.6 mmol). The following complexes were prepared by using method b.

$Ni(2,4,6\text{-}Me_3C_6H_2NC)_4$ (75%): IR (Nujol) 1995 cm^{-1} (N≡C). ^1H NMR (PhCl) $\delta=2.04$ (s, 4-Me), 2.31 (s, 2- and 6-Me). Anal. Calcd for $C_{40}H_{44}N_4Ni$: C, 75.12; H, 6.93; N, 8.76%. Found: C, 75.00; H, 6.99; N, 8.93%.

$Ni(4\text{-}Br\text{-}2,6\text{-}Me_2C_6H_2NC)_4$ (77%): IR (Nujol) 1990 cm^{-1} (N≡C). Anal. Calcd for $C_{36}H_{32}N_4Br_4Ni$: C, 48.10; H, 3.59; N, 6.23%. Found: C, 48.00; H, 3.61; H, 6.33%.

$Ni(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_4$ (80%): IR (KBr) 2025 cm^{-1} (N≡C). ^1H NMR (PhCl) $\delta=1.25$ (s, 4-t-Bu) and 1.61 (bs 2-and 6-t-Bu). Anal. Calcd for $C_{76}H_{116}N_4Ni$: C, 79.76; H, 10.22; N, 4.90%. Found: C, 80.03; H, 10.58; N, 4.46%.

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