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Note

Reductive elimination of C–CN compounds from nickel complexes as a reverse reaction for oxidative addition of benzonitriles to nickel

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Abstract

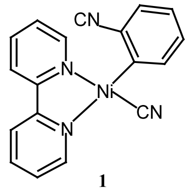
Treatment of (bpy)Ni(CN)(C_6H_4CN-*o* or -*m*) with acrylonitrile led to reductive elimination of CN–C_6H_4CN from the complex. The reductive elimination proceeded much faster for the C_6H_4CN-*m* complex.

Keywords: Nickel; Reductive elimination; Oxidative addition; C–CN compound

1. Introduction

Oxidative addition of nitriles to transition metal complexes is recently calling attention [1–3]; we have also been concerned with the oxidative addition [2].

On the other hand, reductive elimination is one of most fundamental organometallic processes. In contrast to many reports on reductive elimination of R–R [4,5], Ar–Ar [6], and C–X (X = hetero-atom [7]), report on reductive elimination of C–CN compounds, the reverse reaction of the oxidative addition of nitrile, is limited, although it is considered a key step in organic synthetic reactions concerned with nitriles [3,8]. Recently, Lewis-acid-accelerated reductive elimination of R–CN from (diphosphine)Pd(R)(CN) has been reported [9]. However, reductive elimination of Ar–CN has not been reported due to less examples of the cyano(aryl)metal complex, LnM(CN)(Ar). In addition, the M–Ar bond has usually higher stability than the M–R bond, and reversibility of the oxidative addition and reductive elimination of ArCN to and from metal complexes has not been clarified. We have previously reported preparation of cyanoaryl nickel complexes **1** and **2** according to oxidative addition of the corresponding benzonitriles to a zerovalent nickel complex, Ni(bpy)(cod) (bpy = 2,2′-bipyridyl; cod = 1,5-cyclooctadiene) [2].



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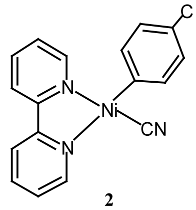

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It has been reported that coordination of electron-withdrawing molecules such as acrylonitrile [5] and protic acids [6] to Ni promote reductive elimination of R–R from (bpy)NiR_2 [5] and Ar–Ar from (bpy)NiAr_2 [6], respectively. We now report similar effect of acrylonitrile and hydrogen chloride on the reductive elimination reaction of the (bpy)Ni(CN)(aryl) type complexes.

2. Results and discussion

We first checked the generality of the oxidative addition of benzonitriles to the Ni(0)-bpy complex by examining reactions of benzonitrile and *m*-dicyanobenzene.

Reaction of Ni(bpy)(cod) with benzonitrile and *m*-dicyanobenzene also caused oxidative addition of CN–C_6H_4R (R = H, *m*-CN) to give (bpy)Ni(CN)(C_6H_4R) (**3** and **4**) as orange solids in 84% yields, respectively Eq. (1).

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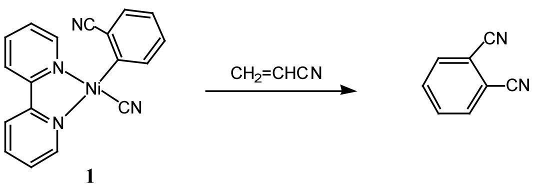
$$\mathrm{Ni(bpy)(cod)} + \underset{\mathrm{R=H},m\text{-}\mathrm{CN}}{\mathrm{CNC_6H_4R}}$$

$$\rightarrow \underset{\mathrm{R=H(3)},m\text{-}\mathrm{CN(4)}}{\mathrm{(bpy)Ni(CN)(C_6H_4R)}} + \mathrm{cod} \qquad (1)$$

IR spectrum of **3** showed a peak due to ν(C≡N) at a lower frequency (2110 $\mathrm{cm^{-1}}$) than that of benzonitrile (2228 $\mathrm{cm^{-1}}$). ν(C≡N) peaks of **4** appeared at 2219 and 2116 $\mathrm{cm^{-1}}$, which were shifted to a lower frequency from that of *m*-dicyanobenzene (2235 $\mathrm{cm^{-1}}$), similar to the cases of **1** and **2**.

Fig. 1 shows X-ray crystal structure of **3**. The bond distances between Ni- and bpy-nitrogen (1.944(4)–1.959(4)) are comparable with those found in the other square-planar nickel complexes [10]. The N–Ni–N bond angle of **3** (82.5°) is similar to those of **1** (83.0°) and **2** (82.5°). Complexes **1**, **2**, and **4** were stable under air, however, **3** was somewhat unstable under air and was stored under N_2.

Reaction of **1** with acrylonitrile (excess) caused reductive elimination of *o*-dicyanobenzene (isolated yield = 0.3 mol $\mathrm{mol^{-1}}$ **1**) that was isolated by using HPLC (Eq. (2)). Determination of the yield by gas chromatography was not possible due to its high boiling point of the product.



1

(2)

Treatment of **4** with acrylonitrile also leads to reductive elimination to provide *m*-dicyanobenzene (isolated yield = 0.3 mol $\mathrm{mol^{-1}}$ **4**). The nickel complex is considered to be converted into Ni(acrylonitrile)(bpy) after the reductive elimination, similar to the case of reductive elimination reaction of $\mathrm{NiR_2(bpy)}$ caused by acrylonitrile [5a].

According to the reductive elimination, the UV–vis spectrum of an acetone solution containing **1** and acrylonitrile changes with time as depicted in Fig. 2. The change of the absorbance at 407 nm with time t obeys the first-order rate law with a rate constant of $29 \times 10^{-6}\ \mathrm{s^{-1}}$ at 35 °C. The pseudo-first-order rate constant k_{obs} increases proportionally with the concentration of acrylonitrile, indicating that the rate of the reductive elimination can be expressed by the second-order rate law.

$$\mathrm{Rate} = k[\mathbf{1}][\mathrm{CH_2{=}CHCN}] \qquad (3)$$

The k value of $29 \times 10^{-6}\ \mathrm{s^{-1}M^{-1}}$ at 35 °C is by

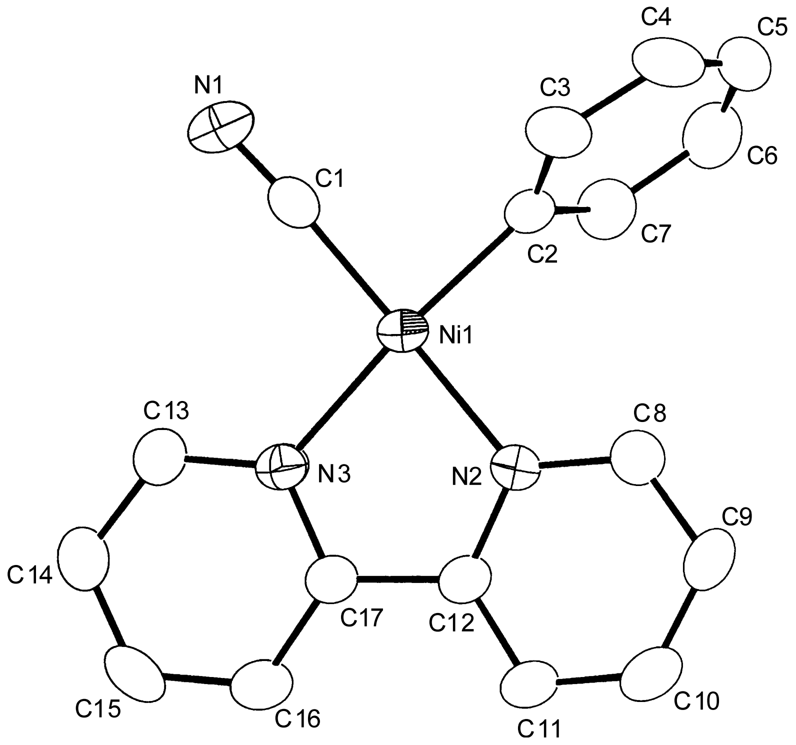


Fig. 1. Molecular structure of (bpy)Ni(CN)(Ph) (**3**). Selected bond lengths (Å) and angles (°): Ni(1)–N(2) 1.944(4), Ni(1)–N(3) 1.959(4), Ni(1)–C(1) 1.845(6), Ni(1)–C(2) 1.890(5), N(1)–C(1) 1.139(6), N(2)–Ni(1)–N(3) 82.5(2), N(2)–Ni(1)–C(1) 175.0(2), N(3)–Ni(1)–C(1) 97.3(3), N(3)–Ni(1)–C(1) 172.2(2), Ni(3)–C(2)–C(3) 121.7(5).

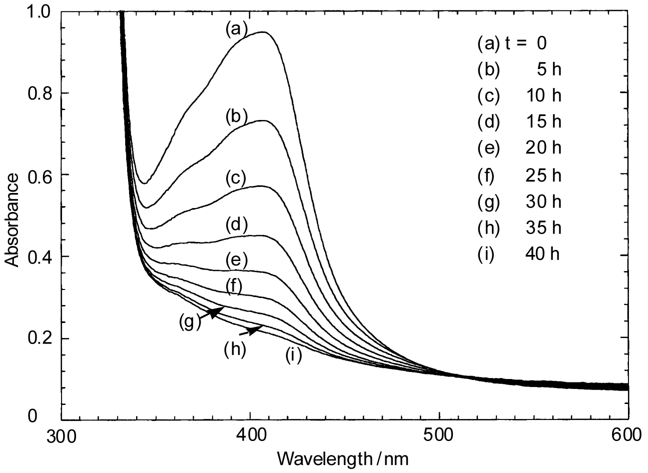


Fig. 2. Change in UV–vis spectrum during the reaction of **1** with acrylonitrile in acetone at 35 °C. [CH_2=CHCN] = 1.0 M. Under N_2.

about 10^3 times smaller than that obtained for the reductive elimination reaction of $NiEt_2$(bpy) enhanced by electron-withdrawing olefins [5,6], due to higher stability of **1** than $NiEt_2$(bpy).

The temperature dependence of the k value for the reaction with acrylonitrile gives an Arrhenius activation energy of 107 kJ mol^{-1}.

Similar reaction of **4** with acrylonitrile caused a shift of the UV–vis peak to a longer wavelength when the reductive elimination of m-CN–C_6H_4CN proceeded, as shown in Fig. 3. In this case, the UV–vis spectrum changes did not obey first-order rate law.

Scheme 1 shows a plausible reaction pathway for the acrylonitrile promoted reductive elimination of CN–C_6H_4CN from (bpy)Ni(CN)(C_6H_4CN).

The rate of the reductive elimination of CN–C_6H_4CN from **4** was by about two orders of magnitude faster than that from **1** as judged from the UV–vis change. Slower reductive elimination in **1** may be related to known o-substitution effect for stabilizing Ni-aryl compounds [11] and/or blocking of the coordination site for acrylonitrile by the o-CN group. Preliminary experiments indicated that hydrochloric acid also led to the reductive elimination of o-CN–C_6H_4CN from **1** (yield = 70%), similar to the case of Ni(aryl)$_2$(bpy) [6].

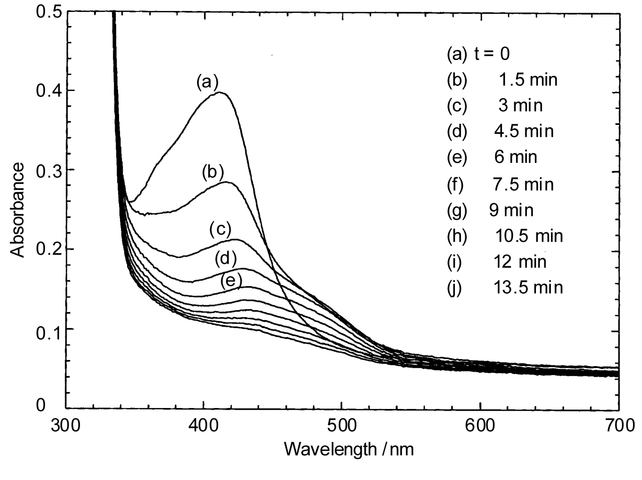


Fig. 3. Changes in UV–vis spectrum during the reaction of **4** with acrylonitrile in acetone at 35 °C. [CH_2=CHCN] = 1.0 M. Under N_2.

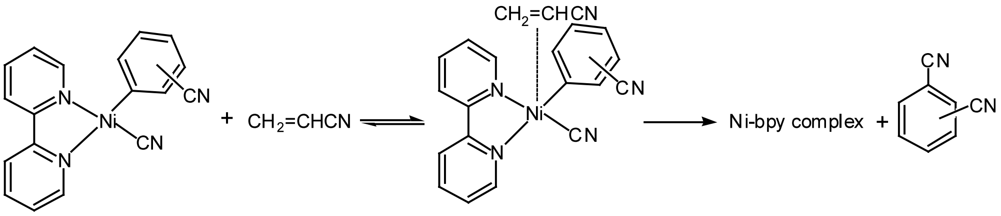
3. Experimental

All reactions and manipulations were carried out under inert gas using standard Schlenk techniques. All solvents were dried and distilled prior to use. IR and NMR spectra were recorded on a JASCO-IR 810 spectrophotometer and JEOL EX-400 spectrometer, respectively. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder.

3.1. Synthesis of complex 3

A yellow THF solution (15 ml) containing Ni(cod)$_2$ (0.23 g, 0.82 mmol) and 0.1 ml of cod turned to violet when bpy (0.13 g, 0.82 mmol) was added. After stirring for 2 h at room temperature (r.t.), benzonitrile (0.40 cm^3, 3.9 mmol) was added, and the reaction mixture was stirred for 4 days. The color of the reaction mixture turned to pale orange with formation of an orange precipitate. After addition of hexane (20 cm^3), the solid was separated by filtration, washed with diethyl ether, and dried under vacuum to give **3** as an orange powder (0.22 g, 84%). Crystals for microanalysis and X-ray crystallographic analysis were obtained by recrystallization from acetone at −20 °C. Element anal. Found: C, 64.00; H, 3.82; N, 13.51. Calc. for (bpy)Ni(CN)(C_6H_5): C, 64.21; H, 4.12; N, 13.21.

Complex **4** was synthesized in a similar manner by using 0.57 g (2.1 mmol) of Ni(cod)$_2$, 0.51 ml of cod, 0.33 g (2.1 mmol) of bpy, and 0.27 g (2.1 mmol) of m-dicyanobenzene in 5 ml of DMSO at r.t. An orange powder of **4** was obtained in 84% yield. ^{1}H-NMR (DMSO-d_6): δ = 8.93 (1H, 6-H of bpy); 8.48 (2H, 3- and 3′-H of bpy); 8.26 and 8.20 (2H, 4- and 4′-H of bpy); 7.84 (m, 2H, m-C_6H_4CN); 7.78 (1H, 5-H of bpy); 7.50 (1H, 5′-H of bpy); 7.34 (d, 1H, 6-H of m-C_6H_4CN); 7.18 (t, 1H, 5-H of m-C_6H_4CN); 7.13 (sh, 1H, 6′-H of bpy). The ^{1}H-NMR pattern of bpy was similar to that of reported **1**, including splitting of 6- and 6′-H [2]. The assignment of the peaks of m-C_6H_4CN is tentative, however, the ^{1}H-NMR pattern of m-C_6H_4CN is much changed from that of m-dicyanobenzene: δ = 8.47 (s, 1H, 2-H); 8.19 (m, 2H, 4- and 6-H); 7.79 (t, 1H, 5-H).



Scheme 1. A plausible reaction pathway for the reductive elimination.

3.2. Reaction of **1** with acrylonitrile

To an acetone (20 ml) solution of **1** (34 mg, 0.10 mmol) was added acrylonitrile (0.66 cm^3, 10 mmol). After the reaction mixture was stirred for 10 h, the solvent was removed by evaporation to give a light brown solid. The solid was extracted with chloroform, and removal of solvent by evaporation provided a light brown solid which was purified by using HPLC to give *o*-dicyanobenzene (4 mg).

Similar reaction of **4** with acrylonitrile gave *m*-dicyanobenzene.

3.3. Reaction of **1** with HCl

To an acetone (40 ml) solution of **1** (68 mg, 0.20 mmol) was added conc. HCl (3.3 cm^3). After the reaction mixture was stirred for 15 h, the solvent was removed by evaporation to give a light yellow solid. The solid was extracted with chloroform, and removal of solvent by evaporation provided a light brown solid which was purified by using HPLC to give *o*-dicyanobenzene (18 mg).

3.4. Crystal data for **3**

$C_{17}H_{13}N_3Ni$, $M = 318.01$, monoclinic, space group $P2_1/a$ (No. 14), $a = 8.948(6)$ Å, $b = 18.441(4)$ Å, $c = 9.266(6)$ Å, $\beta = 113.62(5)^\circ$, $V = 1400(1)$ Å^3, $Z = 4$, $D_{calc} = 1.508$ Mg m^{-3}, $F(0\,0\,0) = 656.00$. The diffraction data were collected with a Rigaku AFC5R diffractometer at ambient temperature (23 °C) using the ω scan mode ($2\theta \leqslant 55^\circ$). Correction for Lorentz and polarization effects and an empirical absorption correction (ψ scan) were applied. The structure was solved by a common combination of direct method (SAPI91) and subsequent Fourier techniques. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located by assuming the ideal geometry.

Acknowledgements

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