

Preliminary communication

Oxidative addition of C–CN bond to nickel(0) complex: synthesis and crystal structures of $\text{Ni}(\text{CN})(o\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$ and $\text{Ni}(\text{CN})(p\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$

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Abstract

Reactions of phthalonitrile and terephthalonitrile with $\text{Ni}(\text{cod})(\text{bpy})$ in a THF solution at room temperature lead to oxidative addition of the C–CN bond to give square-planar $\text{Ni}(\text{CN})(o\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$ (**3**) and $\text{Ni}(\text{CN})(p\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$ (**4**) respectively. Data from elemental analysis, as well as their IR and NMR spectra, agree with the structures. Crystal structures of the complexes **3** and **4** have been determined by X-ray crystallography.

Keywords: Nickel; Oxidative addition; Nitrile; Crystal structure

1. Introduction

Although numerous reports have appeared concerning the oxidative addition of aryl halides to zero-valent nickel complexes [1], only a few examples of oxidative addition of aryl cyanides are known [2,3]. The C–CN bond is considered to be not so reactive [2] owing to its large bond dissociation energy. Moreover, characterization of the oxidative addition product by X-ray crystallography has not been reported. In this paper, we report that oxidative addition of aryl cyanides to electron-excessive and reactive $\text{Ni}(\text{cod})(\text{bpy})$ ($\text{cod} = 1,5\text{-cyclooctadiene}$; $\text{bpy} = 2,2'\text{-bipyridyl}$) proceeds smoothly at room temperature and the reaction products form good crystals suited for the X-ray crystallographic analysis of their molecular structures. $\text{Ni}(\text{cod})(\text{bpy})$ has only neutral ligands and is considered to have highly electron-excessive nature. In addition, the complex causes facile dissociation of the cod ligand in solutions to open a highly reactive site.

2. Results and discussion

Reactions of $\text{Ni}(\text{cod})(\text{bpy})$ prepared in situ from $\text{Ni}(\text{cod})_2$ and bpy with excess phthalonitrile and tere-

phthalonitrile at room temperature in THF lead to precipitation of yellow and greenish yellow solids respectively. Addition of hexane to the reaction mixture affords the new complexes **3** and **4** in high yields (90% and 86% respectively); see Scheme 1.

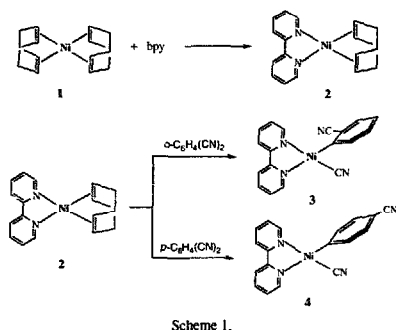
The infrared spectrum of **3** shows two sharp absorption peaks at 2114 cm^{-1} and 2210 cm^{-1} . The absorption peak at 2114 cm^{-1} is attributed to a $\nu(\text{C}\equiv\text{N})$ vibration of the $\text{C}\equiv\text{N}$ group coordinated to Ni and locates at about 100 cm^{-1} lower frequency than that of free phthalonitrile (2206 cm^{-1}). The complex **4** gives the analogous two absorption peaks at 2106 cm^{-1} and 2207 cm^{-1} .

Fig. 1 depicts the ^1H NMR spectrum of **3**, and tentative assignment of the bpy signals is shown in Fig. 1. The sharp two doublets and two triplets observed between $\delta\ 7.0\text{--}7.8\text{ ppm}$ are considered to originate from the 2-cyanophenyl group; however, assignment of each signal has not been possible. In the assignment of the bpy signals, the 6'-H and 5'-H signals are considered to receive anisotropic up-field shifts from the ring current of the 2-cyanophenyl group, and thus assignment of the signals shown in Fig. 1 is given.

Crystal structures of **3** and **4** have been established by X-ray crystallography, as shown in Figs. 2 and 3.

The bond distances between Ni and bpy-nitrogen ($1.915(7)\text{--}1.961(4)\text{ \AA}$) are comparable with those found in the other square-planar nickel bpy complexes [4]. The

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Ni–N(3) distance is shorter than the Ni–N(4) distance, presumably due to a stronger trans-influence of the phenyl group than the cyano group. The N–Ni–N bond angles of **3** and **4** ($83.0(2)^\circ$ and $82.5(3)^\circ$ respectively) are also comparable with that found in Ni(cod)(bpy) [5]. The C–C and C–N distances and bond angles found for the bpy ligand are also similar to those found in the other bpy–nickel(II) complexes and free bpy [5,6]. As described above, the C–CN bonds of aryl cyanides easily add oxidatively to the reactive nickel(0) complex, and the products have been unequivocally identified by X-ray crystallography.

3. Experimental section

All reactions and manipulations were carried out under an inert gas using standard Schlenk techniques. All solvents were dried and distilled prior to use. NMR

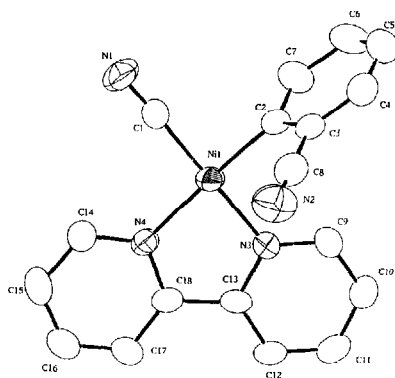


Fig. 2. Crystal structure of **3**. Selected bond lengths (Å) and angles (deg) are: Ni(1)–N(3), 1.935(4); Ni(1)–N(4), 1.961(4); Ni(1)–C(1), 1.855(7); Ni(1)–C(2), 1.894(6); N(3)–Ni(1)–N(4), $83.0(2)$; N(3)–Ni(1)–C(2), $94.7(2)$; N(4)–Ni(1)–C(1), $96.7(2)$; C(1)–Ni(1)–C(2), $85.9(2)$.

spectra were recorded on a Jeol-GX 400. Chemical shifts are reported in ppm with respect to TMS. IR spectra were recorded on a Jasco IR-810 spectrometer. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder.

3.1. Synthesis of Ni(CN)(*o*-C₆H₄CN)(bpy) (**3**) and Ni(CN)(*p*-C₆H₄CN)(bpy) (**4**)

3.1.1. Ni(CN)(*o*-C₆H₄CN)(bpy) (**3**)

A yellow THF (15 ml) solution containing Ni(cod)₂ (0.415 g, 1.5 mmol) and 0.1 ml of cod immediately

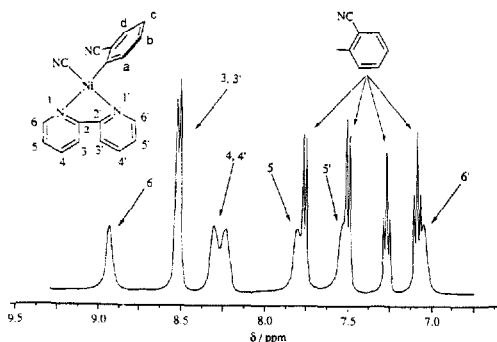


Fig. 1. ^1H NMR spectrum of **3** in DMSO-*d*₆ at room temperature (400 MHz).

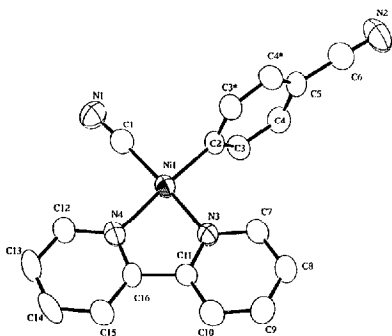


Fig. 3. Crystal structure of 4. Selected bond lengths (Å) and angles (deg) are: Ni(1)–N(3), 1.915(7); Ni(1)–N(4), 1.939(7); Ni(1)–C(1), 1.856(8); Ni(1)–C(2), 1.876(8); N(3)–Ni(1)–N(4), 82.5(3); N(3)–Ni(1)–C(2), 95.3(3); N(4)–Ni(1)–C(1), 96.6(4); C(1)–Ni(1)–C(2), 85.7(4).

turned to violet when bpy (0.235 g, 1.5 mmol) was added. After stirring for 2 h at room temperature, phthalonitrile (0.384 g, 3.0 mmol) was added, and the reaction mixture was stirred for 3 days. The color of the reaction mixture turned yellow with formation of a yellow precipitate. After an addition of hexane (20 ml), the precipitate was collected by filtration, washed with diethyl ether (5 ml; 3 times), and dried under vacuum to give 3 as a yellow powder (0.463 g, 90%). Crystals for microanalysis and the X-ray crystallographic analysis were obtained by recrystallization from DMSO–diethyl ether at room temperature. Elemental anal. Found: C, 62.74; H, 3.44; N, 16.28. Calc. for $\text{Ni}(\text{CN})(o\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$: C, 63.02; H, 3.53; N, 16.32%. IR (KBr): 2114 and 2210 cm^{-1} ($\nu(\text{C}\equiv\text{N})$). ^1H NMR (298 K, 400 MHz, $\text{DMSO}-d_6$): δ = 8.95 (b, 1H), 8.54 (d, 2H), 8.32 (b, 1H), 8.25 (b, 1H), 7.83 (b, 1H), 7.78 (d, 1H), 7.55 (b, 1H), 7.52 (d, 1H), 7.29 (t, 1H), 7.10 (t, 1H), 7.09 (b, 1H).

3.1.2. $\text{Ni}(\text{CN})(p\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$ (4)

A yellow THF (20 ml) solution containing $\text{Ni}(\text{cod})_2$ (0.235 g, 0.85 mmol) and 0.1 ml of cod immediately turned to violet when bpy (0.133 g, 0.85 mmol) was added. After stirring for 2 h at room temperature, terephthalonitrile (0.435 g, 3.4 mmol) was added and the reaction mixture was stirred for 3 days. The color of the reaction mixture turned from violet to pale yellow with formation of a greenish yellow precipitate. After an addition of hexane (20 ml), the solid was separated by filtration, washed with diethyl ether (5 ml; 3 times) and dried under vacuum to give 4 as a greenish yellow powder (0.251 g, 86%). Crystals for microanalysis and

X-ray crystallographic analysis were obtained by recrystallization from acetone at -20°C . Elemental anal. Found: C, 62.71; H, 3.54; N 16.06. Calc. for $\text{Ni}(\text{CN})(p\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$: C, 63.02; H, 3.53; N, 16.32%. IR (KBr): 2110 and 2200 cm^{-1} ($\nu(\text{C}\equiv\text{N})$). ^1H NMR(298 K, 400 MHz, $\text{DMSO}-d_6$): δ = 8.93 (b, 1H), 8.47 (b, 2H), 8.23 (b, 2H), 7.78 (d, 2H), 7.76 (b, 1H), 7.53 (b, 1H), 7.37 (d, 2H), 7.12 (b, 1H).

3.2. Single-crystal X-ray diffraction study

3.2.1. Crystal data for $\text{Ni}(\text{CN})(o\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$ (3)

$\text{C}_{18}\text{H}_{12}\text{N}_4\text{Ni}$, $M = 343.02$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.746(3)\text{ Å}$, $b = 18.765(7)\text{ Å}$, $c = 10.135(3)\text{ Å}$, $\beta = 112.74(2)^\circ$, $V = 1534.1(10)\text{ Å}^3$, $Z = 4$, $D_c = 1.485\text{ Mg m}^{-3}$, $F(000) = 704.00$, $\mu(\text{Mo K}\alpha) = 1.272\text{ mm}^{-1}$. The diffraction data were collected with a Rigaku AFC5R diffractometer at ambient temperature (23°C) using the ω scan mode ($2\theta \leq 55.0^\circ$).

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 methods (SAP91) 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.

3.2.2. Crystal data for $\text{Ni}(\text{CN})(p\text{-C}_6\text{H}_4\text{CN})(\text{bpy})$ (4)

$\text{C}_{18}\text{H}_{12}\text{N}_4\text{Ni}$, $M = 343.02$, orthorhombic, space group $Pnma$ (No. 62), $a = 14.267(10)\text{ Å}$, $b = 6.890(5)\text{ Å}$, $c = 19.468(6)\text{ Å}$, $V = 1913(3)\text{ Å}^3$, $Z = 4$, $D_c = 1.403\text{ Mg m}^{-3}$, $F(000) = 844.00$, $\mu(\text{Mo K}\alpha) = 1.032\text{ mm}^{-1}$. The diffraction data were collected with a Rigaku AFC5R diffractometer at ambient temperature (23°C) using the ω scan mode ($2\theta \leq 55.0^\circ$). 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 methods (SAP91) 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.

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