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Polymerization of aryl isocyanides by cyclopentadienylnickel–alkynyl complexes

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Abstract

(η^5-Cyclopentadienyl)nickel–alkynyl complexes, $CpNi(PPh_3)C{\equiv}CR$ ($R = Ph$, H, CO_2Et), and -methyl complex effectively catalyze the polymerization of aryl isocyanides at room temperature. Double-insertion complexes of isocyanides are isolated and characterized as an active intermediate of the polymerization, whose mechanism involving successive insertion of isocyanides into nickel–carbon σ-bonds is proposed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Nickel acetylides; Cyclopentadienylnickel; Polymerization; Isocyanides; Multiple insertion

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1. Introduction

In recent years polymerization reactions catalyzed by transition metal complexes have attracted much attention in the fields of polymer science and organometallic chemistry in terms of unique polymer synthesis and mechanistic interest. Many reports on the design and synthesis of active transition metal catalysts for polymerization of various monomers have appeared in the literature in the last few decades [1]. Such representative examples involve cyclopentadienyl-group 4 metal complexes for olefin polymerization [2], ruthenium- and tungsten–carbene complexes for ring-opening metathesis polymerization [3] and cyclopentadienyl–lanthanide complexes for vinyl polymerization [4]. In these systems the role of metal catalysts as well as the polymerization process have been well studied on the basis of organometallic chemistry and in some cases active intermediates in the polymerization reactions have been isolated and characterized.

We previously reported [5] that μ-ethynediyl palladium–palladium and palladium–platinum dinuclear complexes catalyze the living polymerization of isocyanides and the polymerization proceeds via successive and multiple insertion of isocyanides into a metal–carbon σ-bond of the ethynediyl dinuclear complexes. However, mononuclear palladium- and platinum–alkynyl complexes did not exhibit a catalytic activity for the polymerization of isocyanides although mononuclear palladium–alkyl complexes are known to be active for the polymerization of isocyanides [6]. Now we have found mononuclear cyclopentadienylnickel–alkynyl complexes to be active for the polymerization of aryl isocyanides, and successfully isolated an active intermediate in the initiation step of the polymerization.

It is well-known that nickel complexes such as $Ni(CO)_4$ [7] and NiX_2 [8] complexes exhibit a high activity for the polymerization of isocyanides, and recently Novak and co-workers have found a living polymerization system with (η^3-allyl)nickel catalysts and applied the system to a stereoselective polymerization of isocyanides [9]. We also attempted to find a new type of nickel catalysts and tried to prepare the nickel analog of μ-ethynediyl dinuclear complexes [10], but failed the preparation probably due to instability of nickel complexes in the reaction conditions. About 30 years ago Yamazaki and Yamamoto reported the reaction of cyclopentadienylnickel–alkyl and -aryl com-

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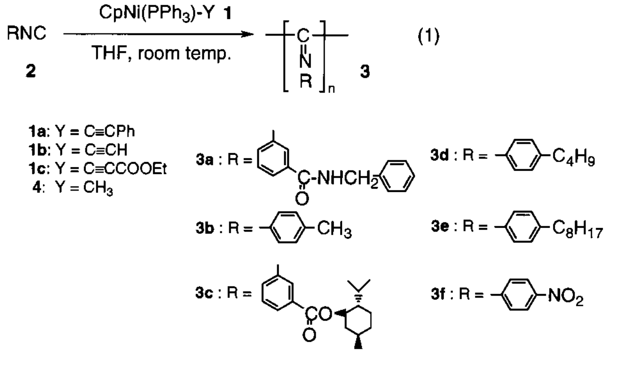
plexes with alkyl isocyanides to yield isocyanide insertion products [11]. For example, (η^5-cyclopentadienyl)(triphenylphosphine)nickel–methyl reacted with cyclohexyl isocyanide to give an insertion product, CpNi(CNC$_6$H$_{11}$)C(CH$_3$)=NC$_6$H$_{11}$, but further insertion of cyclohexyl isocyanide was not observed. Now, we have found that the nickel–methyl complex undergoes multiple insertion of aryl isocyanides and exhibit a catalytic activity for the polymerization of *p*-butylphenyl and *p*-octylphenyl isocyanide. We also found air-stable cyclopentadienylnickel–alkynyl complexes to show a high activity for the polymerization of aryl isocyanides. The latter may provide the first example of mononuclear transition metal alkynyls active for the polymerization of isocyanides. We report here the catalysis of cyclopentadienylnickel–alkynyl complexes in the polymerization of aryl isocyanides, and the polymerization mechanism will be discussed on the basis of stoichiometric reactions between the nickel complexes and isocyanides.

2. Results and discussion

2.1. Polymerization of isocyanides

Isocyanides have an isoelectric structure with carbon monoxide and both sometimes insert into a metal–carbon σ-bond to form an imino or carbonyl group. Transition metal–alkyl bonds often undergo isocyanide insertion, in some cases multiple insertion [12], whereas transition metal–alkynyl bonds are stable and resist isocyanide insertion except few particular cases [13]. Since multiple and successive insertion of isocyanides may lead to polymerization of isocyanides, transition metal complexes containing M–C σ-bonds have a potential to act as a catalyst (or initiator) for the polymerization of isocyanides [5,6,14]. In an attempt to find effective catalysts for isocyanide polymerization, we treated (η^5-cyclopentadienyl)nickel–phenylacetylide complex, CpNi(PPh$_3$)C≡CPh **1a**, with 100 equivalents of *m*-benzylaminocarbonylphenyl isocyanide **2a** at room temperature in THF and found that polymerization occurred smoothly to afford yellow polymer **3a** ($M_w = 27600$, $M_w/M_n = 1.46$) in 60% yield after usual work-up and precipitation with methanol. Polymer **3a** exhibits an absorption of ν(C=N) at 1650 cm^{-1} which is characteristic of isocyanide polymers. However **3a** is unable to be characterized in details by NMR spectral analyses because of its low solubility in solvents such as benzene, THF and dichloromethane. In order to improve the solubility of polymers, alkyl-substituted phenyl isocyanides are used as a monomer. *p*-Butylphenyl- (**2d**) and *p*-octylphenyl isocyanide (**2e**) were similarly polymerized in the presence of 1 mol.% of **1a** under the same reaction conditions. Polymers **3d** and **3e** thus obtained showed the typical absorption of ν(C=N) at 1650 cm^{-1} in the IR spectra, and were identified by spectral analyses as they are soluble in benzene, THF and dichloromethane. (See Section 3, Experimental) The ^{13}C-NMR spectrum of **3d** showed a broad signal due to C=N groups at 162.8 ppm. *p*-Nitrophenyl isocyanide also gave polymer **3f** in 40% yield. The low yield is due to its low solubility which causes precipitation of the polymer formed during the reaction. 2,6-Dimethylphenyl isocyanide **2g** did not give polymeric products at all and the monomer was recovered. Sterically bulky 2,6-dimethylphenyl group presumably prevents successive insertion of the isocyanide into the Ni–C bond. The results of isocyanide polymerization are summarized in Table 1, which reveals that complex **1a** is active for the polymerization of a variety of aryl isocyanides, but inactive for alkyl isocyanides. (η^5-Cyclopentadienyl)nickel–alkynyl complexes such as CpNi(PPh$_3$)C≡CH **1b** and CpNi(PPh$_3$)C≡CCOOEt **1c** as well as (η^5-cyclopentadienyl)nickel-methyl **4** also exhibited the catalytic activity towards the polymerization of aryl isocyanides.



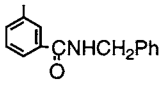
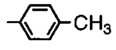
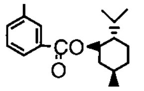
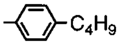
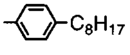
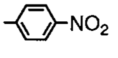
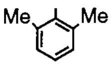
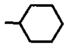
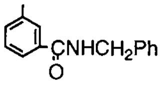
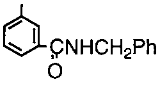
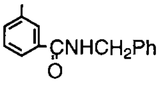
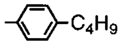
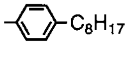
Interestingly, chiral isocyanide *m*-(−)-menthoxycarbonylphenyl isocyanide **2c** yielded polymer **3c** in 77% yield which exhibits a large optical rotation power [α]. Polyisocyanides have a 4_1 helical structure and usually exist a 1:1 mixture of two conformational isomers with right- and left-handed helices. Monomer **2c** bearing a (−)-menthyl group shows an optical rotation power of −83°, while polymer **3c** exhibits +296° with the opposite sign to the monomer, indicating that the large optical rotation power arises from a helical chirality of **3c** [15]. and that nickel complex **1a** is able to catalyze a screw-sense-selective polymerization of **2c** to give polymer **3c** having single-handed helix.

2.2. Stoichiometric reaction of isocyanides

In order to know the polymerization mechanism, reactions of nickel catalysts with stoichiometric amounts of isocyanides were investigated. On treatment of CpNi(PPh$_3$)C≡CPh **1a** with three equivalents of *m*-PhCH$_2$NHCOC$_6$H$_4$NC **2a** in dichloromethane at room temperature, we obtained reddish-brown complex **5a** in

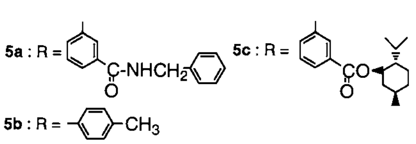
27% yield along with isocyanide oligomers and recovered **1a**. The FAB mass spectrum ($m/z = 697$, $M+1$) and elemental analysis suggested **5a** to be a product derived from an addition of two molecules of **2a** to **1a** and an elimination of the triphenylphosphine ligand from **1a**. The IR spectrum of **5a** exhibited an absorption at 2141 cm^{-1} due to v(C≡C) which appeared at a higher wave number than that of **1a** (2098 cm^{-1}). Although the absorption attributable to a C=N group was not assigned in the IR spectrum because of overlapping with the absorption of the N–H group, in the ^{13}C-NMR spectrum two signals due to C=N groups appeared at 177.6 (C=N) and 156.6 ppm (C=N), and in addition the ^{1}H-NMR spectrum clearly showed signals due to the CH_2 protons of the benzylamino groups at 4.35 and 4.62 ppm, suggesting the presence of two kinds of C=NR groups in **5a**. The IR and NMR spectra indicated that **5a** does not contain isocyanide ligands coordinated the nickel atom. The proton signal of the cyclopentadienyl group appeared at 5.30 ppm, and carbon signals assignable to the C≡C group at 98.84 and 121.49 ppm, while no peaks were observed in the ^{31}P-NMR spectrum. These data indicate **5a** to be a double-insertion product in which two molecules of isocyanide **2a** successively insert into the Ni–C bond of **1a**. Similarly the reaction of **1a** with three equivalents of *p*-tolyl isocyanide **2b** and *m*-(−)-menthoxycarbonylphenyl isocyanide **2c** gave **5b** and **5c**, respectively. Double-insertion product **5** thus obtained seems to be an apparent 16-electron complex of divalent nickel and coordinately unsaturated one (structure **5A**). A molecular structure of **5B** or **5C** seems more likely because it forms an 18-electron complex by coordination of the imino nitrogen atom or the acetylene group. However, complexes **5** showed a normal stretching frequency of the C≡C group around 2140 cm^{-1} in the IR spectra, and we did not observe a shift to lower frequencies suggesting an interaction of the C≡C group with the central nickel atom; that is, the terminal acetylenic group to be free.

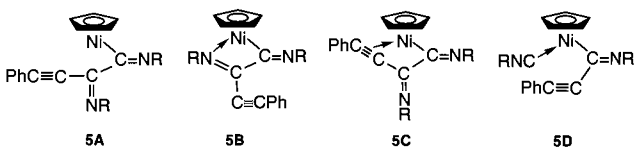
Table 1
Polymerization[a] of isocyanides RNC catalyzed by $CpNi(PPh_3)C{\equiv}CY$ **1** and $CpNi(PPh_3)CH_3$ **4**

Run	R	Catalyst[b]	Yield	M_w
1		1a	60	27600
2		1a	70	45000
3		1a	77	177000
4		1a	67	48500
5		1a	73	93400
6		1a	40	c
7		1a	0	–
8		1a	0	–
9	tert-C_4H_9	1a	0	–
10[d]		1b	85	84800
11[d]		1c	60	70600
12		5a	60	37000
13		4	67	62500
14		4	69	103300

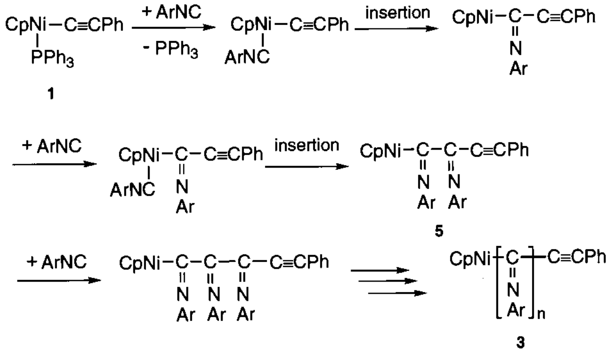
[a] Conditions: 1 mol.% of **1** in THF at room temperature.
[b] **1a**: Y = Ph, **1b**: Y = H, Y = CO_2Et.
[c] Not determined due to its low solubility in THF.
[d] 2 mol.% of **1** in THF at 40°C.

$$\underset{\mathbf{1a}}{CpNi(PPh_3)C{\equiv}CPh} + \underset{\mathbf{2}}{2\,RNC} \longrightarrow CpNi{-}\underset{\underset{R}{N}}{\overset{}{C}}{-}\underset{\underset{R}{N}}{C}{-}C{\equiv}CPh \quad \mathbf{5} \qquad (2)$$





It is known that **4** and $CpNi(PPh_3)C{\equiv}CPh$ react with cyclohexyl isocyanide to give a single-insertion product $CpNi(CNC_6H_{11})C(R){=}NC_6H_{11}$ (R = Me or Ph) with replacement of the PPh_3 ligand by the isocyanide [11]. However, the analogous form **5D** is excluded for the structure of **5** because the spectral data indicate the presence of two kinds of imino groups and the absence of a coordinated isocyanide ligand in **5** as mentioned above. Then, we added excess amounts of PPh_3 to a solution of **5a** in THF, but **5a** was recovered intact.



Scheme 1.

Addition of isocyanides to **5** caused further insertion of isocyanides leading to the polymerization (vide infra). On the basis of these facts, we tentatively propose molecular structure **5B** which involves an interaction between the imino nitrogen atom and the nickel one, although we have not yet obtained evidence for confirming such the interaction from the spectral analyses.

An experiment by monitoring with gel permeation chromatography demonstrated that the reaction of **1a** with one equivalent of isocyanide **2a** at room temperature in dichloromethane gave double-insertion product **5a** along with recovered complex **1a**, but the formation of a single-insertion product was not detected. Probably a second monomer reacts with a single-insertion complex much faster than the first one with **1a**, and the same phenomenon has been observed for the reaction of a μ-ethynediyl dipalladium complex with phenyl isocyanide [5].

2.3. Polymerization mechanism

We examined the reactivity of double-insertion complexes **5** for isocyanides and found that they can initiate the polymerization of isocyanides. When **5a** was treated with 100 equivalents of isocyanide **2a** in THF at room temperature, polymerization reaction smoothly occurred to give a yellow polymer with M_w of 37000 and M_w/M_n of 2.18 in 60% yield (Table 1, run 12). The almost same catalytic activity of **5a** as **1a** unambiguously indicates **5a** to be an active intermediate at the initial stage of the polymerization. Other double-insertion complexes **5b** and **5c** also effectively initiate the polymerization of isocyanides. Thus, we propose the polymerization mechanism involving successive insertion of isocyanides into the nickel–carbon bond. (Scheme 1) The mechanism may predict a living nature of the polymerization if the Ni–imino complexes are stable during the propagation step. Actually, after complete reaction of **1a** with 50 equivalents of **2c**, of which the GPC analysis showed the formation of polymer **3c** with $M_w = 57000$ and $M_w/M_n = 1.94$, addition of 50 equivalents of 3,5-dipropoxycarbonylphenyl isocyanide as a second monomer produced a co-polymer having $M_w = 71000$ and $M_w/M_n = 2.46$. The increase in the molecular weight of the resulting polymer suggests a living nature of the present system, however the rather large polydispersity index (M_w/M_n) means that the present polymerization is not a real living one. Then, in an attempt to stabilize the living nickel catalyst and to improve the polymerization reaction, triphenylphosphine was added to the polymerization system initiated with complex **1a**. Addition of 10 equivalents of PPh_3, however, did not affect significantly the polymerization of isocyanide **2a** and gave a polymer of $M_w = 26000$, $M_w/M_n = 1.56$. Almost no effect of the additional phosphine on the polymerization (cf. Table 1, run 1) is consistent with the proposed mechanism, in which an isocyanide monomer interacts with the active nickel complexes much more strongly than triphenylphos-phine.

3. Experimental

All reactions were carried out under an atmosphere of argon, but the work-up was performed in air. ^1H- and ^{13}C-NMR were recorded in $CDCl_3$ on a JEOL EX-270 (270 MHz) and JEOL JNM-LA400 (400 MHz) spectrometer using $SiMe_4$ as an internal standard, and ^{31}P-NMR (in $CDCl_3$) spectra on a JEOL JNM-LA400 (400 MHz) spectrometer against an external 85% H_3PO_4 reference. Chemical shifts are given in ppm. IR and mass spectra were taken on a Perkin–Elmer System 2000 FT-IR and JEOL JMS-600H instrument, respectively. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Molecular weight measurements were carried out by a Shimazu LC-6AD liquid chromatograph using columns of Shimazu GPC-805, -804 and -8025 with polystyrene standards.

3.1. Materials

Aryl and alkyl isocyanides were prepared according to the literature methods [16]. (η^5-Cyclopentadienyl)methyl(triphenylphosphine)nickel **4** was prepared from the reaction of $CpNi(PPh_3)Cl$ with MeMgI by the literature method [17].

3.1.1. Synthesis of $CpNi(PPh_3)C{\equiv}CPh$ (1a) [18]

To a solution of PhC≡CH (102 mg, 1 mmol) in 15 ml of a 1/2 mixture of Et_2O and Et_3N was added a solution of $CpNi(PPh_3)Cl$ (243 mg, 1 mmol) in 25 ml of Et_2O. After addition of a CuCl catalyst (5 mg) the reaction mixture was stirred for 1.5 h at room temperature. The solvent was evaporated and the residue was chromatographed on alumina with benzene. The fraction of a green band was collected, and the solvent was removed to give green crystals **1a**. (368 mg 82%) ^{13}C-NMR: (67.8 MHz, $CDCl_3$) δ 134.44–124.53 (m, Ar*C*), 119.73 (s, *C*≡CNi), 85.77 (d $J_{P-C} = 49$ Hz, C≡*C*Ni), 92.58 (s, Cp*C*); ^{1}H-NMR: (270 MHz, $CDCl_3$) δ 7.78–7.70 (m, 6H, PPh_3–*H*), 7.42–7.25 (m, 9H, PPh_3–*H*)), 6.93–6.88 (m, 3H, ≡CPh–*H*)), 6.65–6.62 (m, 2H, ≡CPh–*H*)), 5.25 (s, 5H, Cp*H*); ^{31}P-NMR: (162 MHz, $CDCl_3$) δ 41.3 (s, *P*Ph_3): IR (KBr pellet): ν(C≡C) 2098 cm^{-1}; Anal. Calcd for $C_{31}H_{25}PNi$: C, 76.42; H, 5.17; P, 6.36%; Found: C, 76.19; H, 5.22; P, 6.12%; m.p. 131–132°C (dec.).

*3.1.2. Synthesis of CpNi(PPh$_3$)C≡CY **1b** and **1c***

Alkynyl complexes CpNi(PPh_3)C≡CH **1b** and CpNi(PPh_3)C≡CCO_2Et **1c** were similarly prepared in a mixed solvent of diethyl ether and triethylamine.

1b: green crystals; yield 65%, m.p. 124–126°C (dec.); IR (KBr pellet): ν(≡C–H) 3250, ν(C≡C) 1960 cm^{-1}; ^{1}H-NMR: (270 MHz, $CDCl_3$) δ 7.8–7.7 (m, 6H, PPh_3–*H*), 7.48–7.33 (m, 9H, PPh_3–*H*), 5.18 (s, 5H, Cp*H*); 1.46 (d, $J_{P-H} = 2.64$ Hz, 1H, ≡C*H*)

1c: green crystals; yield 65%, m.p. 62–64°C (dec.); ^{1}H-NMR: (270 MHz, $CDCl_3$) δ 7.72–7.36 (m, 15H, PPh_3–*H*), 5.2 (s, 5H, Cp*H*), 3.8 (q, $J = 7.26$ Hz, 2H, O–CH_2–), 1.1 (t, $J = 7.26$ Hz, 3H, O–C–CH_3); IR: ν(C≡C) 2090 cm^{-1}, ν(C=O) 1667 cm^{-1}; Anal. Calcd for $C_{28}H_{25}O_2PNi$: C, 69.68; H, 5.18%; Found: C, 69.63; H, 5.19%.

3.2. Polymerization of isocyanide

*3.2.1. Polymerization of m-benzylaminocarbonylphenyl isocyanide **2a** with catalyst **1a***

To a solution of *m*-benzylaminocarbonylphenyl isocyanide (354 mg, 1.5 mmol) in 10 ml of THF was added a solution of CpNi(PPh_3)C_2Ph **1a** (7.3 mg, 0.015 mmol) in 5 ml of THF. After stirred for 24 h at room temperature, the solution was concentrated to about 1 ml. Addition of methanol (100 ml) gave a precipitate, which was collected, washed with methanol, and dried in vacuum to afford yellow powder of **3a** (216 mg, 60%); Anal. Calcd for $(C_{15}H_{12}ON_2)_n$: C, 76.25; H, 5.12; N, 11.86%; Found: C, 76.07; H, 5.11; N, 11.93%. IR: ν(C=N) 1650 cm^{-1}.

*3.2.2. Polymerization of p-tolyl isocyanide **2b**, m-(−)-menthoxycarbonylphenyl isocyanide **2c**, p-n-buthylphenyl isocyanide **2d**, p-n-octylphenyl isocyanide **2e**, or p-nitrophenyl isocyanide **2f** with catalyst **1a***

The polymerizations of **2b**–**2f** (1.5 mmol) were carried out with **1a** (0.015 mmol) in THF at room temperature by the procedure similar to that for **2a** to give polymers **3b**–**3f**.

Polymer **3b**: yield: 70%; Anal. Calcd for $(C_8H_7N)_n$: C, 82.02; H, 6.02; N, 11.96%; Found: C, 81.80; H, 5.81; N, 11.69%; IR (KBr pellet): ν(C=N) 1650 cm^{-1}.

Polymer **3c**: yield: 77%; ^{13}C-NMR: (100 MHz, $CDCl_3$) δ 164.4 (br, Ar*C*OOC), 160.7 (br, *C*N), 150.8 (br, Ar*C*), 129.1 (br, Ar*C*), 118.6 (br, Ar*C*), 74.7 (br, *C*H_2), 47.3, 41.0, 34.4, 31.5, 31.0, 26.5, 23.7, 22.1, 20.8, 17.1, 16.5 (br, menthyl–*C*); Anal. Calcd for $(C_{18}H_{23}O_2N)_n$: C, 75.76; H, 8.12; N, 4.91%; Found: C, 75.71; H, 8.00; N, 4.71%; IR (KBr pellet): ν(C=N) 1650 cm^{-1}; $[\alpha]_D^{20} = 296°$ ($CHCl_3$, $c = 0.05$).

Polymer **3d**: yield: 67%; ^{13}C-NMR: (100 MHz, $CDCl_3$) δ 1162.8 (br, *C*N), 146.2 (br, Ar*C*) 138.0 (br, Ar*C*), 127.7 (br, Ar*C*), 118.5(br, Ar*C*), 35.5 (br, *C*H_2), 33.7 (br, *C*H_2), 22.3(br, *C*H_2), 14.0 (br, *C*H_2); Anal. Calcd for $(C_{11}H_{13}N)_n$: C, 83,03; H, 8.17; N, 8.80%; Found: C, 81.98; H, 7.76; N, 9.90%; IR (KBr pellet): ν(C=N) 1650 cm^{-1}.

Polymer **3e**: yield: 73%; Anal. Calcd for $(C_{15}H_{21}N_1)_n$: C, 83.67; H, 9.83; N, 6.50%; Found: C, 82.98; H, 9.58; N, 6.74%; IR (KBr pellet): ν(C=N) 1650 cm^{-1}.

Polymer **3f**: yield: 36%; IR (KBr pellet): ν(C=N) 1650, ν(NO_2) 1520, ν(NO_2) 1380 cm^{-1}.

3.3. Stoichiometric reactions of complexes with isocyanides

*3.3.1. Reaction of complex **1a** with m-benzylaminocarbonylphenyl isocyanide **2a***

To a solution of *m*-benzylaminocarbonylphenyl isocyanide **2a** (354 mg, 1.5 mmol) in 15 ml of THF was added a solution of complex **1a** (243 mg, 0.5 mmol) in 10 ml of CH_2Cl_2. After stirred for 1.5 h under room temperature, the solution was chromatographed on alumina with CH_2Cl_2. After removing unreacted **1a** and an isocyanide oligomer, a mixture of CH_2Cl_2 /ethyl acetate (19/1: v/v) was use as an eluent. The fraction of the orange band was collected, and the solvent was evaporated under reduced pressure. Addition of hexane (100 ml) gave a precipitate, which was washed with hexane and dried in vacuum to afford reddish-brown powder of **5a** (95 mg, 27%).

^{13}C-NMR: (100 MHz, $CDCl_3$) (ppm) δ 177.64 (s, *C*N), 167.96 (s, Ar*C*OOC), 165.59 (s, Ar*C*OOC), 156.59 (s, *C*N), 150.42 (s, Ar*C*), 138.55–119.66 (m, Ar*C*), 92.99 (s, Cp*C*), 43.94 (s, *C*H_2); ^{1}H-NMR: (400 MHz, $CDCl_3$) δ 8.37 (s, 1H, N*H*), 7.94–7.13 (m, 23H, Ar*H*), 6.63 (s, 1H, N*H*), 5.30 (s, 5H, Cp*H*), 4.62 (d, 2H, $J = 6$ Hz, CH_2), 4.35 (d, 2H, $J = 6$ Hz, CH_2); IR (KBr pellet): ν(C≡C) 2146 cm^{-1}; Anal. Calcd for $C_{43}H_{34}O_2N_4Ni$: C, 74.05; H, 4.91; N, 8.03%; Found: C, 73.89; H, 4.67; N, 7.99%; Mass: *m*/*z* 697 (M + 1).

*3.3.2. Reaction of complex **1a** with isocyanides **2a** and **2c***

Similarly the reaction of **1a** with 3 equivalents of *p*-tolyl isocyanide **2b** and *m*-(−)-menthoxycarbonylphenyl isocyanide **2c** gave complexes **5b** and **5c**, respectively.

5b: reddish-brown oil: yield 32%; ^{13}C-NMR: (100 MHz, CDCl$_3$) δ 173.83 (s, *C*N), 153.08 (s, *C*N), 149.62 (s, Ar*C*), 139.18–120.37 (m, Ar*C*) 92.57 (s, Cp*C*), 21.34, 21.04 (s, *C*H$_3$); ^{1}H-NMR: (400 MHz, CDCl$_3$) δ 7.56–7.00 (m, 13H, Ar*H*), 5.28 (s, 5H Cp*H*), 2.35 (s, 3H, C*H*$_3$), 2.33 (s, 3H, C*H*$_3$); IR (KBr pellet): ν(C≡C) 2135, ν(C=N) 1542 cm^{-1}.

5c: reddish-brown solid: yield 61%; ^{13}C-NMR: (100 MHz, CDCl$_3$) δ 176.66 (s, *C*N), 166.0 7 (s, Ar*C*OOC), 164.02 (s, Ar*C*OOC), 155.45 (s, *C*N), 151.43 (s, Ar*C*), 133.55–121.00 (m, Ar*C*), 92.94 (s, Cp*C*), 77.00, 76.51 (s, menthyl−*C*), 47.22, 47.03, 40.95, 40.76, 34.16, 34.07, 31.47, 31.32, 26.35, 26.26, 23.37, 22.54, 21.94, 20.76, 16.28 (s, menthyl−*C*); ^{1}H-NMR: (400 MHz, CDCl$_3$) δ 8.02–7.27 (m,13H, Ar*H*), 5.36 (s, 5H, Cp*H*), 4.98–4.91 (m, 2H, menthyl−*H*)), 2.10–0.77 (m, 36H, menthyl−*H*); IR (KBr pellet): ν(C≡C) 2135 cm^{-1}; Anal. calcd for $C_{49}H_{56}O_2N_2Ni$: C, 73.96; H, 7.09; N, 3.52%; Found: C, 73,75; H, 7.09; N, 3.61%.

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