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Ni-Promoted Syntheses of New 3,3′-Dichloro-5,5′-bipyrazoles and Poly(bipyrazole-5,5′-diyl)s and Isolation of Nickel Complexes Relevant to the Syntheses

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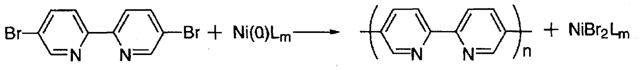
Reactions of 3,5-dichloropyrazoles and 3,3′-dichloro-5,5′-bipyrazoles with zerovalent nickel complex, Ni(0)L_m, have been studied. In cases of 3,5-dichloro-1,4-dimethylpyrazole and 3,5-dichloro-4-methoxycarbonyl-1-methylpyrazole, only the C(5)–Cl bond of the two C–Cl bonds reacts with Ni(0)L_m to afford novel bis(pyrazolyl)nickel(II) complexes with the intact C(3)–Cl bond in moderate yields. Treatment of the bis(pyrazolyl)nickel(II) complexes with H_2SO_4 gives the new dichloro monomers: 3,3′-dichloro-1,1′,4,4′-tetramethyl-5,5′-bipyrazole and its 4,4′-bis(methoxycarbonyl) analogue. These undergo dehalogenative polycondensation to give poly(1,1′,4,4′-tetramethyl-5,5′-bipyrazole-3,3′-diyl) (**6**) and its 4,4′-bis(methoxycarbonyl) analogue (**7**), respectively. Polymer **6** is soluble in formic acid, and gives an intrinsic viscosity of 39 $cm^3\,g^{-1}$ in formic acid, whereas polymer **7** is soluble in various organic solvents and has an M_n value of 8800 ($M_\mathrm{w}/M_\mathrm{n}$ = 1.56) as estimated from GPC. They show photoluminescent peaks at the onset position of the respective π–π^* absorption bands.

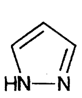
Heteroaromatic poly(arylene)s containing imine nitrogen (e.g., polypyridine, poly(2,2′-bipyridine), and poly(pyrimidine)) are the subject of recent interest. They possess high thermal stability, undergo n-doping (or reduction), and serve as chelating ligands of transition metal complexes.[1—3]

It has been reported that zerovalent nickel complexes effectively dehalogenate dihaloaromatic compounds and yield poly(arylene)s. For example the dehalogenative polycondensation of 5,5′-dibromo-2,2′-bipyridines and 5,5′-dibromo-2,2′-bithiazoles with the zerovalent nickel complex Ni(0)L_m gives poly(2,2′-bipyridine-5,5′-diyl)s and poly(2,2′-bithiazole-5,5′-diyl)s[2b—f,3] which show interesting electrical and optical properties.



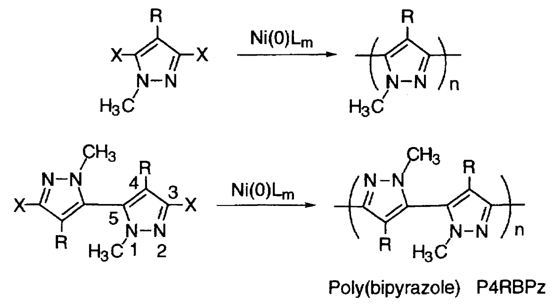
(1)

On the other hand, pyrazole



and its derivatives such as 3,3′-bipyrazole, tris(pyrazolyl) borates, and 5-arylpyrazoles are attracting growing attention because they form stable and biochemically interesting transition metal complexes and serve as agricultural medicines.[4a—f]

In order to expand the scope of the heteroaromatic poly(arylene)s, we have examined preparation of new poly(pyrazole)s and poly(bipyrazole)s by the dehalogenative polycondensation of dihalopyrazoles and dihalobipyrazoles with the zelovalent nickel complex, as shown in Scheme 1. The starting material of the polycondensation expressed by Eq. 2 is industrially produced.

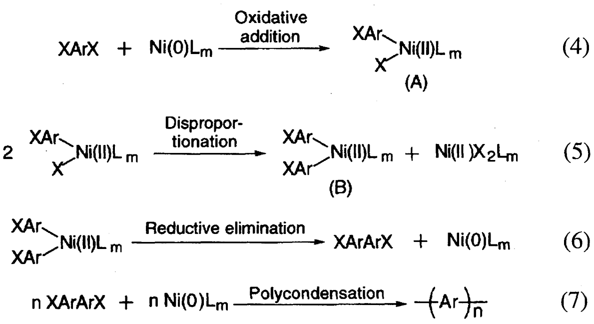


(2)

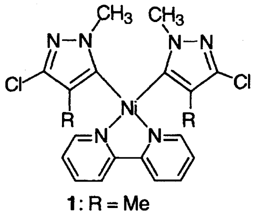
(3)

Scheme 1. Attempts for the preparation of poly(pyrazole)s and poly(bipyrazole)s by the dehologenative polycondensation. R = Me or COOMe.

The dehalogenative polycondensation of the dihaloaromatic compound is considered to proceed in DMF according to the mechanism shown in Scheme 2.[5] The polycondensation involves oxidative addition of aryl dihalide, XArX, to Ni(0)L_m to give monoarylnickel(II) intermediate (A) (Eq. 4) and its subsequent disproportionation to give Ni(II)X_2L_m and diarylnickel complex (B) (Eq. 5). The complex (B) undergoes a reductive elimination reaction and gives biaryl XArArX (Eq. 6). Repetition of the reactions expressed by Eqs. 4, 5, and 6 finally affords the poly(arylene), $-(\mathrm{Ar})_n-$ (Eq. 7). The oxidative addition (Eq. 4) usually proceeds well, however, the ease of the disproportionation and reductive elimination (Eqs. 5 and 6) seems to depend on the kind of XArX employed. For certain XArX, the reaction



Scheme 2. Fundamental processes for the polycondensation.



1: R = Me
2: R = COOMe

Chart 1. Examples of isolated complexes of Type B.

may stop at the complex of Type A or Type B. Actually, we previously found that the reaction stoped at the complex of Type A when 9,10-dibromoanthracene was employed.[6a] In our preliminary communication,[6b] we reported that attempted polycondensation expressed by Eq. 2 stopped at the complex of Type B depicted in Chart 1. The Ni–C bonds in **1** and **2** have remarkably high stability, and do not undergo thermally induced reductive elimination of the expected dimer (Eq. 6).

On the other hand, complexes **1**and **2** are sensitive to protic acids to liberate the dimer XArArX,[6b] which may be usable in another type of polycondensation producing poly(bipyrazole)s (Eq. 3). Actually use of the dimer in Eq. 3 smoothly affords the expected poly(bipyrazole)s, P4RBPz's. In this paper, we describe full details of synthesis and structure of the Ni complexes and the synthesis of the novel bipyrazole-containing polymer.

Experimental

Materials. 3,5-Dichloro-1-methylpyrazoles were provided from Nissan Chemical Industries Ltd. 2,2′-Bipyridyl (bpy) was purchased from Tokyo Chemical Industry Co., Ltd. [Ni(cod)$_2$] was prepared according to the literature.[7]

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were taken by using JEOL EX-90 and EX-400 spectrometers. GLC curves, GPC curves, TGA curves, UV-vis spectra, and fluorescence spectra were obtained with a Shimadzu gas–liquid chromatography system GC-8A, a Tosoh HLC-8120 GPC unit using TSK-Gel columns (eluent = DMF containing 0.006 M LiBr; calibration = polystyrene standards), a Shimadzu thermoanalyzer DT-30, a Shimadzu UV-3100PC spectrometer, and Hitachi F-4010 spectrometer, respectively. Cyclic voltammograms were obtained by using an acetonitrile solution containing 0.1 M [Et$_4$N]BF$_4$ (1 M = 1 mol dm^{-3}). Cyclic voltammetry was carried out with a Hokuto Denko HABF-501 galvanostat/potensiostat/function generator. Microanalyses of C, H, N, and Cl were carried out with a Yanagimoto CHN Autocorder Type MT-2 or a Yanaco CHN CORDER MT-2 (C, H, and N) and a Yanaco YS-10 (Cl) by Dr. Y. Hayashi and Messrs. S. Ootake and K. Yoneyama. Mass spectra were obtained by using a JEOL Mstation / JMS-700.

Synthesis and Characterization of Complexes 1 and 2. [Ni(cod)$_2$] (3.99 g, 14.5 mmol), 3,5-dichloro-1,4-dimethylpyrazole (1.65 g, 10 mmol), and bpy (2.27 g, 14.5 mmol) were dissolved in 50 cm^3 of DMF in a Schlenk tube under nitrogen. After stirring at 60 °C for 24 h, the reaction mixture was poured into an aqueous ammonia solution to give a reddish brown powder. The powder was collected by filtration, washed with an aqueous solution of disodium dihydrogen ethylenediaminetetraacetate (Na$_2$EDTA) (once), distilled water (once), and hexane (once) in this order and dried under vacuum to obtain complex **1** (1.57 g, 66%). This complex has been characterized by IR, ^{1}H NMR, FAB-MS, elemental analysis, and X-ray crystallography.

Complex **1** (reddish brown powder; dp = 178°C under N$_2$). IR (KBr) 2918 ($\nu_{\text{aliphatic C–H}}$), 1603 ($\nu_{\text{bipyridine ring}}$), 1017 cm^{-1} ($\nu_{\text{C–Cl}}$). ^{1}H NMR (CDCl$_3$) $\delta = 2.21$ (s, 6H, C–CH$_3$), 3.89 (s, 6H, N–CH$_3$), 7.55 (m, 4H, bipyridine), 8.00 (m, 4H, bipyridine). FAB-MS (*m*-nitrobenzyl alcohol matrix): *m/z* 475 [(M+H)$^+$]. Anal. Found: C, 50.3; H, 4.1; N, 17.5%. Calcd for $C_{20}H_{20}Cl_2N_6Ni$: C, 50.7; H, 4.3; N, 17.7%. UV-vis (DMSO, nm): λ_{max}/nm = 298 (bipyridine π–π^* transition), 441 (MLCT band).

The synthesis of complex **2** was carried out in a manner similar to that applied for the preparation of **1**; yield of **2** was 74%. Complex **2** (yellow powder; dp = 306°C under N$_2$). IR (KBr) 2982, 2938 ($\nu_{\text{aliphatic C–H}}$), 1689 ($\nu_{\text{C=O}}$), 1606 ($\nu_{\text{bipyridine ring}}$), 1064 cm^{-1} ($\nu_{\text{C–Cl}}$). ^{1}H NMR (CDCl$_3$) $\delta = 3.71$ (s, 6H, COOCH$_3$), 3.93 (s, 6H, N–CH$_3$), 7.91 (m, 4H, bipyridine), 7.95 (m, 4H, bipyridine). FAB-MS (*m*-nitrobenzyl alcohol matrix): *m/z* 561 [(M+H)$^+$]. Anal. Found: C, 47.2; H, 3.5; N, 15.1%. Calcd for $C_{22}H_{20}Cl_2N_6NiO_4$: C, 47.0; H, 3.6; N, 15.0%. UV-vis (DMSO, nm): λ_{max}/nm = 294 (bipyridine π–π^* transition), 413 (MLCT band).

Crystal Structure Determination of Complex 1. A crystal of **1** suitable for crystallography was obtained by recrystallization from chloroform/ethanol/hexane (2 : 1 : 10). The crystal was mounted in a glass capillary tube. The unit cell parameters were obtained by least-squares refinement of 2θ values of 20 reflections. Intensities were collected on Rigaku AFC-5R automated fourcycle diffractmeter by using Mo $K\alpha$ radiation (λ = 0.71069 Å) and the ω–2θ method.

Calculations were carried out by using a program package TEXSAN on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from the literature. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. The hydrogens were located by assuming ideal positions (d (C–H) = 0.95 Å) and included in the structure calculation without further refinement of the parameters.

The compound crystallizes in orthorhombic space group *Fdd*2 (No. 43) $a = 12.846(6)$, $b = 32.759(7)$, $c = 10.208(5)$ Å, $V = 4295(2)$ Å^3, $Z = 8$. The calculated density is 1.466 g m^{-3} and the total number of electrons in the cell amounts to $F(000) = 976$. $R = 5.5\%$. $R_w = 4.7\%$.

Isolation of 3-Chloro-1,4-dimethylpyrazole (3). Complex **1** (0.45 g, 1 mmol) was dissolved in N$_2$-replaced THF (30 cm^3). Hydrochloric acid (12 M, 1 cm^3) was added to the solution, and the mixture was stirred for 2 d at room temperature. The reaction mixture was then washed with brine, extracted with ether, and dried with MgSO$_4$. The solvent was removed by evaporation, and **3** was isolated by HPLC as a colorless liquid. The yield of **3** was

45%. IR (neat) 3138, 3090 ($\nu_{\text{aromatic C–H}}$), 2932 ($\nu_{\text{aliphatic C–H}}$), 1566 ($\nu_{\text{pyrazolyl ring}}$), 1112 cm^{-1}($\nu_{\text{C–Cl}}$). ^{1}H NMR ($CDCl_3$) $\delta = 2.00$ (s, 3H, C–CH_3), 3.79 (s, 3H, N–CH_3), 7.12 (s, 1H, Pyrazole-H). EI-MS *m/z* 130 (M^+).

Isolation of 3,3′-Dichloro-1,1′,4,4′-tetramethyl-5,5′-bipyrazole (4) and 3,3′-Dichloro-4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole (5). Complex **1** (0.03 g, 0.07 mmol) was dissolved in chloroform (20 cm^3) under air. The $CHCl_3$ solution was shaken with nitric acid (6 M, 10 cm^3) (once) and water (3 times) in a separating funnel under air, and the $CHCl_3$ layer was dried under vacuum to obtain crude **4**. Crude **4** was purified by column chromatography (SiO_2 : eluent = ethyl acetate) and dried under vacuum to give a white powder of **4** (55% yield). Bipyrazole **4** (mp = 87.1—88.0°C). IR (KBr) 2926 ($\nu_{\text{C–H}}$), 1117 cm^{-1} ($\nu_{\text{C–Cl}}$). ^{1}H NMR (DMSO-d_6) $\delta = 1.83$ (s, 6H, C–CH_3), 3.59 (s, 6H, N–CH_3). HRMS Found: *m/z* 258.0367. Calcd for $C_{10}H_{12}Cl_2N_4$: M, 258.0439. Anal: Found: C, 46.6; H, 4.5; N, 21.5; Cl, 27.1%. Calcd for $C_{10}H_{12}Cl_2N_4$: C, 46.4; H, 4.7; N, 21.6; Cl, 27.4%.

Complex **2** (0.062 g, 0.11 mmol) was dissolved in chloroform under air. The $CHCl_3$ solution was shaken with nitric acid in a way similar to that applied for the preparation of **4**, and the $CHCl_3$ layer was dried under vacuum to obtain pure bipyrazole **5** (97%). Bipyrazole **5** (white powder; mp = 181.0—181.9°C). IR (KBr) 2998, 2950 ($\nu_{\text{aliphatic C–H}}$), 1719 ($\nu_{\text{C=O}}$), 1079 cm^{-1} ($\nu_{\text{C–Cl}}$). ^{1}H NMR ($CHCl_3$) $\delta = 3.65$ (s, 6H, $COOCH_3$), 3.72 (s, 6H, N–CH_3). HRMS Found: *m/z* 346.0175. Calcd for $C_{12}H_{12}Cl_2N_4O_4$: M, 346.0236. Anal: Found: C, 41.2; H, 3.5; N, 16.2%. Calcd for $C_{12}H_{12}Cl_2N_4O_4$: C, 41.5; H, 3.5; N, 16.1%. A crystal of **5** suitable for crystallography was obtained by recrystallization from ethyl acetate/hexane (1 : 1). Bipyrazole **5** crystallizes in triclinic space group $P1$ (No. 2) $a = 8.468(3)$, $b = 22.923(9)$, $c = 8.189(3)$ Å, $\alpha = 93.18(3)°$, $\beta = 100.60(2)°$, $\gamma = 83.09(3)°$, $V = 1550.3(9)$ Å^3, $Z = 4$. The calculated density is 1.487 g cm^{-3} and the total number of electrons in the cell amounts to $F(000) = 712$. $R = 4.4\%$. $R_w = 4.5\%$.

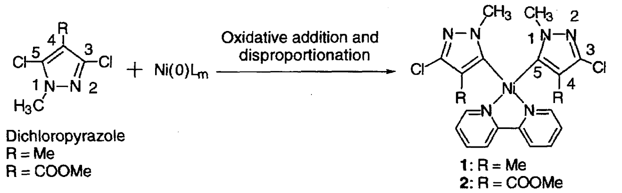
When the reactions of complex **1** (0.05 g, 0.1 mmol) with HCl_{aq} (3 M) and H_2SO_{4aq} (3 M) were conducted in DMSO (2.5 cm^3), bipyrazole **4** and **5** were also obtained in 80 and 100% GLC yields, respectively.

Synthesis of Poly(1,1′,4,4′-tetramethyl-5,5′-bipyrazole-3,3′-diyl) (6). [Ni(cod)$_2$] (1.92 g, 7 mmol) and bpy (1.09 g, 7 mmol) were dissolved in 30 cm^3 of DMF in a Shlenk type flask under N_2. To the solution was added **4** (0.50 g, 2 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 36 h. The reaction mixture was then poured into aqueous ammonia and the precipitate was separated by filtration. The residue was washed with a warm aqueous solution of Na_2EDTA (pH = 9) (three times) and methanol (once) in this order and dried under vacuum to yield white a powder of **6** (64%). IR (KBr) 2922 ($\nu_{\text{aliphatic C–H}}$), 1600 cm^{-1} ($\nu_{\text{pyrazolyl ring}}$). ^{1}H NMR (DCOOD) $\delta = 2.25$ (s, 6H, C–CH_3), 4.08 (s, 6H, N–CH_3). The intrinsic viscosity, [η], of the polymer in HCOOH at 30 °C was 39 cm^3 g^{-1}. Anal. Found: C, 62.5; H, 6.3; N, 28.7; Cl, <0.1%. Calcd for $(C_{10}H_{12}N_4)_n$: C, 63.8; H, 6.4; N, 29.8%.

Synthesis of Poly[4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole-3,3′-diyl] (7). [Ni(cod)$_2$] (1.28 g, 4.7 mmol) and bpy (0.73 g, 4.7 mmol) were dissolved in 50 cm^3 of DMF in a Shlenk type flask under N_2. To the solution was added **5** (0.40 g, 1.2 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 24 h and then poured into aqueous ammonia to yield a dark green precipitate. The precipitate was collected by filtration, washed with aqueous ammonia (twice), distilled water (once), and ether (once) in this order, and dried under vacuum to obtain a brown powder. The brown powder was dissolved in $CHCl_3$, and the solution was washed with diluted sulfuric acid in a separating funnel. The red solution lost its color. The $CHCl_3$ solution was dried to yield poly[4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole-3,3′-diyl] (**7**) in 20% yield. The low yield is ascribed to partial dissolution of the polymer in the aqueous ammonia. IR (KBr) 2952 ($\nu_{\text{alphatic C–H}}$), 1717 ($\nu_{\text{C=O}}$), 1603 cm^{-1} ($\nu_{\text{pyrazolyl ring}}$). ^{1}H NMR ($CDCl_3$) $\delta = 3.59$ (s, 6H, $COOCH_3$), 3.88 (s, 6H, N–CH_3). The M_n of **7** was 8800 ($M_w/M_n = 1.56$) as estimated by GPC (DMF containing 0.006 M LiBr; polystyrene standards).

Results and Discussion

Preparation and Properties of Bis(pyrazolyl)nickel(II) Complexes. Reactions of 3,5-dichloro-1,4-dimethylpyrazole and of 3,5-dichloro-4-methoxycarbonyl-1-methylpyrazole with a mixture of bis(1,5-cyclooctadiene)nickel(0) and 2,2′-bipyridyl (monomer : Ni : bpy = 1 : 1.5 : 1.5) in DMF for 24 h at 60 °C afford complexes **1** and **2**, respectively, in good yields.



(8)

As described above, the reactions involve oxidative addition of the C(5)–Cl bond of the substrate to the Ni(0) complex and ensuing intermolecular aryl ligand transfer. No other products from cleavage of C(3)–Cl bond by the Ni(0) center are obtained. Preferential oxidative addition of C(5)–Cl bond of the substrate can be ascribed to a lower π-electron density at the C(5) carbon than that of the C(3) carbon. It is well known that the C(5)–X bond of 3,5-dihalopyrazole is more labilized to nucleophilic reactions, like a halogen exchange reaction, than the C(3)–X bond.[8] Thus, this regioselectivity is common for both the oxidative addition of the C–Cl bond to Ni(0)L$_m$ and the S_N2 type halogen-exchanging reaction.

X-Ray crystallography of complex **1** unequivocally confirms the *cis*-type square planar structure as depicted in Fig. 1. The structure is essentially the same as that of **2** previously reported.[6b]

The ^{1}H NMR spectrum of complex **1** shows sharp signals at $\delta = 2.21$ and 3.89 due to the C–CH_3 and N–CH_3 protons, respectively. In the IR spectrum of **2**, a characteristic peak due to C=O stretching of $COOCH_3$ group is observed at 1689 cm^{-1}. In the ^{1}H NMR spectrum of **2**, signals based on the $COOCH_3$ and N–CH_3 protons are observed at $\delta = 3.71$ and 3.93, respectively. In addition, data from mass spectroscopic and elemental analyses of **1** and **2** given in the experimental part agree with the structure of the complexes. The simple ^{1}H NMR signal pattern indicates the symmetrical structure formed via the regioselective oxidative addition of 3,5-dichloro-1,4-dimethylpyrazole to Ni(0)L$_m$. These complexes are the first example of isolated *cis*-bis(heteroaryl)nickel(II) complexes.

The obtained complexes **1** and **2** show high thermal stability in the TGA analysis and do not show any weight decrease

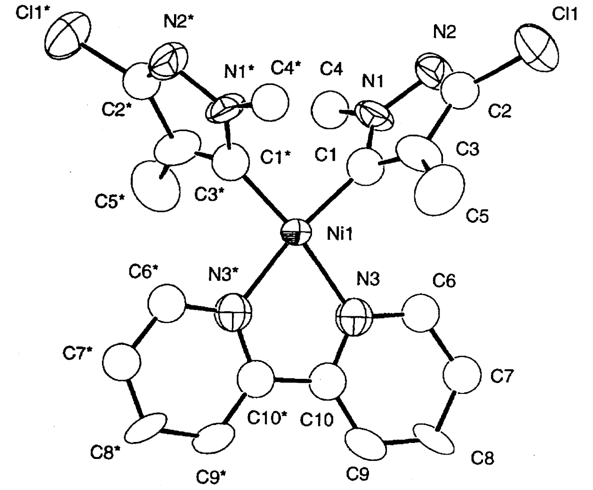
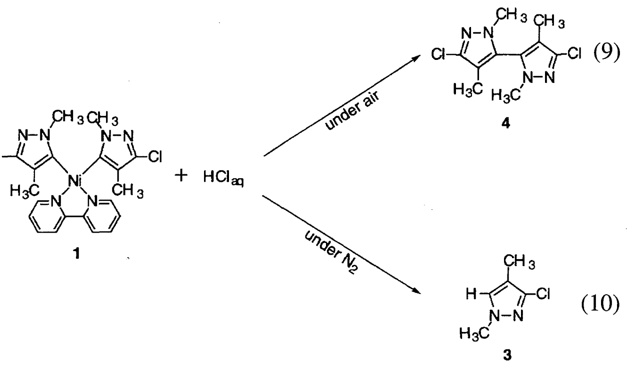


Fig. 1. Molecular structure of the complex **1**. Selected bond distance (Å), angles (°), and a torsion angle (°): Ni(1)–C(1) 1.80(3), Ni(1)–N(3) 1.95(2), C(1)–C(3) 1.36(4), C(2)–C(3) 1.49(4), C(1)–N(1) 1.34(3), C(1)–Ni(1)–C(1) 91(1), N(3)–Ni(1)–N(3) 76(1), N(3)–Ni(1)–C(1) 95(1), N(3)–Ni(1)–C(1)–C(3) 42(10).

up to 178 and 306 °C, respectively, under N_2. They are soluble in various organic solvents including, $CHCl_3$, DMSO, and DMF, and are highly stable toward air even in the solution. Heating a DMF solution of the complexes for 5 h at 60 °C under air led to quantitative recovery of the original complexes as proved by ^1H NMR spectra of the products. The complexes are stable toward various reagents such as ammonia and EDTA. *Cis*-type diarylnickel(II) complexes are usually thermally unstable and undergo facile reductive elimination;[5b] examples are known only for complexes with highly electron-accepting aryl ligands like C_6F_5[9] or aryl ligands protected by substituents at the ortho position.[10]

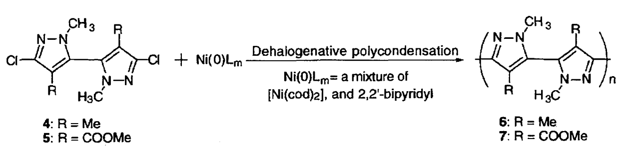
The Ni–ArX bond is polarized as $Ni^{\delta+}$–$Ar^{\delta-}$X to some extent and the reductive elimination of electrically neutral XArArX requires a partial electron transfer from the ArX ligand to Ni prior to the C–C bond formation. The exceptionally high stability of **1** and **2** among *cis*-diarylnickel(II) complexes is explained by the electron-poor character of the pyrazolyl ligands. Both the electron-withdrawing imine nitrogen and chlorine atom in the pyrazolyl ligand make the Ni–C bonds stable. Furthermore, a kinetic "*ortho* effect"[10] may also contribute to the high stability of **1** and **2**. It is known that *cis*-(diaryl)nickel(II) complexes with *ortho* substituents possess relatively high inertness toward attack by chemical reagents, due to the shielding of the nickel atom by the *ortho*-substituent.[10] In cases of complex **1** and **2**, methyl or methoxycarbonyl groups at the C(1) and C(4) position of pyrazolyl group may be protecting the Ni center from the attack by the chemical reagents.

The highly stable complexes **1** and **2**, however, react smoothly with acids such as hydrochloric acid or sulfuric acid in air to evolve the reductive coupling products, 3,3′-dichloro-1,1′,4,4′-tetramethyl-5,5′-bypyrazole (**4**) and 3,3′-dichloro-4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole (**5**), respectively.[6b] The reaction of **1** with hydrochloric and sulfuric acid under air at room temperature in DMSO proceeded smoothly to give **4** in 80 and 100% GLC yields, respectively. On the other hand, the reaction of **1** with hydrochloric acid under N_2 did not cause the reductive elimination of dichlorobipyrazoles; the reaction led to hydrolysis of the Ni–C bonds to give 3-chloro-1,4-dimethylpyrazole (**3**), as depicted in Scheme 3. Detailed analysis of the reaction will be reported elsewhere. Sulfuric acid induced the reductive elimination under air, similar to hydrochloric acid, however, **1** is inert toward sulfuric acid under N_2. Bipyrazoles **4** and **5** were also isolated from the reaction of nitric acid with complexes **1** and **2** in the respective isolated yields of 55 and 97%. These compounds were identified by various spectroscopic data (Experimental section). Figure 2 exhibits the molecular structure of **5** determined by X-ray crystallography. The unit cell contains an independent molecule with a reverse type conformation of the ester group; O(2) and O(4) take positions near to Cl(1) and Cl(2), respectively, in the independent molecule.



Scheme 3. Reductive elimination and hydrolysis of **1**.

Dehalogenative Polycondensation of Dichlorobipyrazoles with the Ni(0) Complex. Polycondensation of 4 and 5. Polycondensation of **4** was carried out by using a mixture of $Ni(cod)_2$ and 2,2′-bipyridyl (bpy) as the dehalogenating reagent.[11]



(11)

The polymerization in DMF at 60 °C gives the corresponding poly(1,1′,4,4′-tetramethyl-5,5′-bipyrazole-3,3′-diyl) (**6**) in 64% yield. The ^1H NMR spectrum the polymer **6** (Fig. 3) shows the signals due to the N–CH_3 and C–CH_3 protons at $\delta = 4.08$ and 2.25, respectively. These signals appear at lower magnetic field positions than those of the monomer **4** (N–CH_3: $\delta = 3.81$ and C–CH_3: $\delta = 2.01$). Figure 4 compares the IR spectra of **4** and **6**. The characteristic ν(C–Cl) peak of the monomer at 1117 cm^{-1} is very weakened in the IR spectrum of **6**. Data of the elemental analysis essentially agree with the structure of **6**. The polymer is soluble in formic acid, and gives an intrinsic viscosity $[\eta]$ of 39 $cm^3\ g^{-1}$

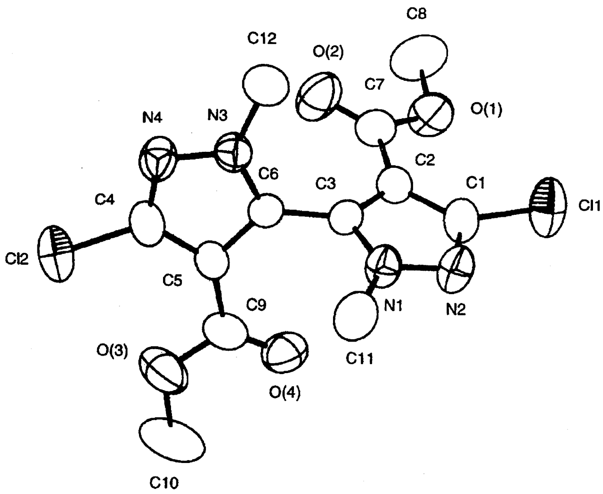


Fig. 2. Molecular structure of the bipyrazole **5**. Selected bond distance (Å), angles (°), and a torsion angle (°): C(1)–C(2) 1.405(6), C(2)–C(3) 1.385(6), C(3)–N(1) 1.349(6), N(1)–N(2) 1.355(5), C(1)–Cl(1) 1.728(5), C(1)–C(2)–C(3) 101.9(4), C(2)–C(3)–N(1) 108.1(4), C(3)–N(1)–N(2) 112.1(4), N(1)–N(2)–C(1) 103.4(4), C(2)–C(3)–C(6)–C(5) 107.0(6).

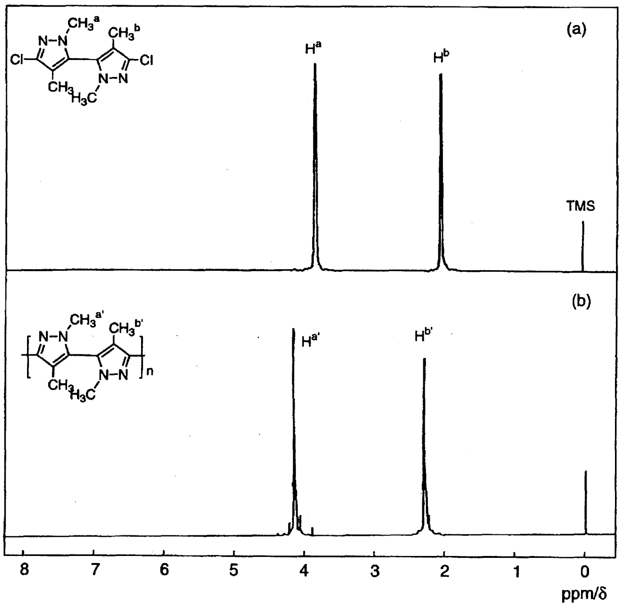


Fig. 3. ^{1}H NMR spectra of (a) 3,3′-dichloro-1,1′,4,4′-tetramethyl-5,5′-bipyrazole (**4**) and (b) poly(1,1′,4,4′-tetramethyl-5,5′-bipyrazole-3,3′-diyl) (**6**) in DCOOD.

in the solvent. This [η] value corresponds to a molecular weight of 34000 for polystylene,[12] however, determination of the molecular weight of **6** by GPC and vapor pressure osmometry has not been feasible due to the limited solubility of the polymer.

All of these data indicate that the Ni(0) complex-promoted-polycondensation of **4** proceeds smoothly to give the polymer **6**, revealing that all of the reactions shown in Scheme 2 proceed well in the polycondensation expressed by Eq. 11. This is in sharp contrast to the results that the reaction of 3, 5-dichloro-1,4-dimethylpyrazole with Ni(0)L$_m$ (Eq. 8) under similar conditions stops at the complex **1**.

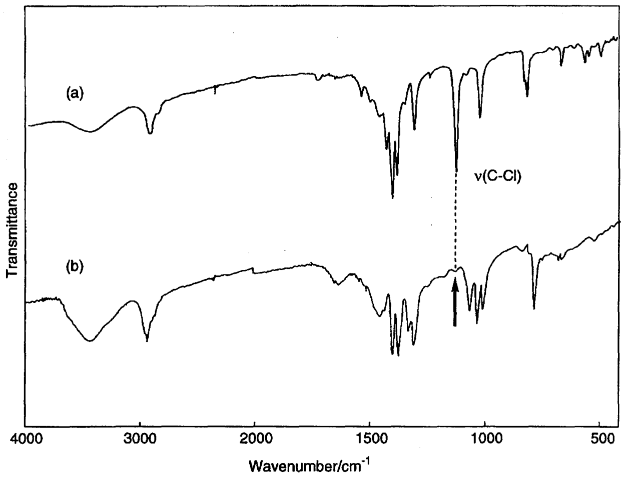


Fig. 4. IR spectra of (a) 3,3′-dichloro-1,1′,4,4′-tetramethyl-5,5′-bipyrazole (**4**) and (b) poly(1,1′,4,4′-tetramethyl-5,5′-bipyrazole-3,3′-diyl) (**6**). The ν(C–Cl) peak at 1117 cm^{-1} disappears after the polycondensation.

The acid-treatment of **2** also liberates the corresponding dimeric XArArX type monomer **5**[6b] (cf. Experimental section). The polycondensation of **5** also proceeds under similar conditions, and the corresponding polymer **7** is obtained. Figure 5 compares the IR spectra of **5** and **7**. The characteristic ν(C–Cl) peak of the monomer at 1079 cm^{-1} is not observable in the spectrum of **7**. The structure of polymer **7** was also assigned from the ^{1}H NMR spectrum (Experimental section). Polymer **7** shows an M_n value of 8800 ($M_w/M_n = 1.56$) in the GPC analysis.

Properties of the Polymers. Polymer **6** is soluble only in HCOOH among the solvents tested, whereas polymer **7** is soluble in various organic solvents such as CHCl$_3$, DMF, and DMSO. Polymers **6** and **7** show high thermal stability (5%

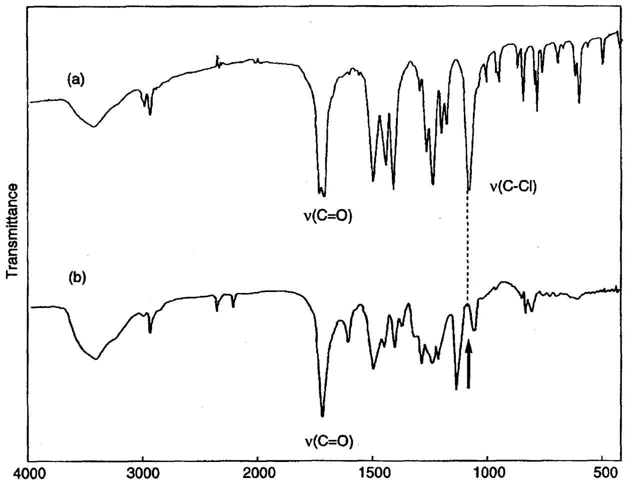


Fig. 5. IR spectra of (a) 3,3′-dichloro-4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole (**5**) and (b) poly[4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole-3,3′-diyl] (**7**). The ν(C–Cl) peak at 1079 cm^{-1} disappears after the polycondensation.

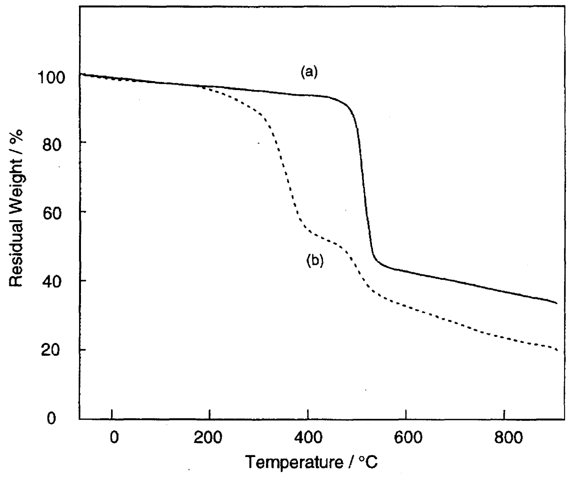


Fig. 6. TGA % loss for (a) poly(1,1′,4,4′-tetramethyl-5,5′-bipyrazole-3,3′-diyl) (**6**) and (b) poly[4,4′-bis(methoxycarbonyl)-1,1′-dimethyl-5,5′-bipyrazole-3,3′-diyl] (**7**).

weight loss at 492 and 307 °C, respectively) as estimated by thermogravometric analyses (TGA) (Fig. 6).

The UV-visible absorption peak of monomer **4** is hidden in the absorption due to HCOOH and its $\lambda_{\max}$ seems to appear at a wavelength shorter than 250 nm in HCOOH. The polymer **6** exhibits a bathochromic shift of the absorption band and its $\lambda_{\max}$ appears at 266 nm in HCOOH, presumably due to the expansion of the π-system. The polymer **7** in $CHCl_3$ gives rise to the absorption peak at 297 nm, which is red shifted by about 60 nm from that of the monomer **5** ($\lambda_{\max} < 240$ nm). The polymer **6** emits a blue-white light at $\lambda_{\max} = 386$ nm (excitation wavelength = 279 nm). Polymer **7** also fluoresces a light blue-white color in $CHCl_3$ with an emission peak at 352 nm (excitation wavelength = 264 nm).

The polymer **6** is electrochemically active and its electrochemical behavior has been followed by cyclic voltammetry. The cyclic voltammogram of a film of polymer **6** on a platinum electrode gives an irreversible anodic (or oxidation) peak at about 1.2 V (vs. Ag/Ag^+) in an acetonitrile solution of $[NEt_4]BF_4$ in the first cycle, revealing that the polymer receives electrochemical oxidation. However, its corresponding cathodic (reduction of the oxidized polymer) peak is not observed. This phenomenon is considered to originate from trapping of the BF_4^- dopant by the polymer presumably due to a strong interaction of BF_4^- and the chelating bipyrazole nitrogens. Similar irreversible CV behavior was reported for electrochemical p-doping of poly(3-hexylthiophene-2,5-diyl) with large anions such as $CH_3C_6H_4SO_3^-$-*p*.[11] The polymer received the electrochemical p-doping; however, the large anion had difficulty coming out from the polymer film during the p-undoping. In addition, a large potential difference between electrochemical n-doping of polythiophene bearing a crown etheral unit with Na^+ and its corresponding n-undoping was also reported.[13]

In summary this paper presents Ni(0)-complex promoted dehalogenative polycondensation of dichlorobipyrazole derivatives to afford the first polymer containing the pyrazole unit in the main chain.

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References

1 a) "Handbook of Organic Conductive Molecules and Polymers," ed by H. S. Nalwa, John Wiley, Chichester (1997), Vol. 2, Conductive Polymers, p. 171. b) T. Yamamoto, *J. Synth. Org. Chem. Jpn.*, **53**, 11 (1995). c) T. Yamamoto, *J. Polym. Chem. Soc*: *Part A*: *Polym. Chem.*, **34**, 997 (1996).

2 a) T. Yamamoto, T. Ito, and K. Kubota, *Chem. Lett.*, **1988**, 153. b) T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, F. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.*, **116**, 4832 (1994). c) T. Yamamoto, Z.-H. Zhou, T. Kanbara, and T. Maruyama, *Chem. Lett.*, **1990**, 223. d) T. Maruyama and T. Yamamoto, *Inorg. Chim. Acta*, **238**, 9 (1995). e) T. Kanbara, T. Kushida, N. Saito, I. Kuwajima, K. Kubota, and T. Yamamoto, *Chem. Lett.*, **1992**, 583. f) T. Yamamoto, H. Suganuma, T. Maruyama, T. Inoue, Y. Muramatsu, M. Arai, D. Komarudin, N. Ooba, S. Sasaki, and K. Kubota, *Chem. Mater.*, **9**, 1217 (1997). g) T. Yamamoto, Y. Yoneda, and K. Kizu, *Makromol. Chem.*, *Rapid Commun.*, **16**, 549 (1995).

3 a) T. Yamamoto, H. Suganuma, T. Maruyama, and K. Kubota, *J. Chem. Soc.*, *Chem. Commun.*, **1995**, 1613. b) J. I. Nanos, J. W. Kampf, M. D. Curtis, L. Gonzalez, and D. C. Martin, *Chem. Mater.*, **7**, 2332 (1995).

4 a) S. Trofimenko, *Chem. Rev.*, **93**, 943 (1993). b) S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972). c) N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, **43**, (1995). d) K. Yagi, T. Ogura, A. Numata, S. Ishii, and K. Arai, "72nd Ann. Meeting Chem. Soc. Jpn.," Abstr., No. 3F 312 (1997). e) C. Kashima, Y. Tsukamoto, K. Fukusaka, and S. Tsuruoka, "72nd Ann. Meeting Chem. Soc. Jpn.," Abstr., No. 3F 313 (1998). f) H. Suzuki and H. Suzuki, "75th Ann. Meeting Chem. Soc. Jpn.," Abstr., No. 2P1A 20 (1998).

5 a) T. Yamamoto, S. Wakabayashi, and K. Osakada, *J. Organomet. Chem.*, **428**, 223 (1992). b) S. Komiya, Y. Abe, A. Yamamoto, and T. Yamamoto, *Organometallics*, **2**, 1466 (1983).

6 a) Z.-H. Zhou and T. Yamamoto, *J. Organomet. Chem.*, **414**, 119 (1991). b) Y. Murakami and T. Yamamoto, *Inorg. Chem.*, **36**, 5682 (1997).

7 G. Wilke, *Angew. Chem.*, **72**, 581 (1960).

8 S. D. Braton and W. D. Ollis, "Comprehensive Organic Chemistry," ed by P. G. Sammes, Pergamon, Oxford (1979), Vol. 4, p. 382.

9 a) A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc.*, *Dalton Trans.*, **1989**, S1. b) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel," Academic Press, New York (1974), Vol. 1, p. 198. c) T. Yamamoto and M. Abla, *J. Organomet. Chem.*, **535**, 209 (1997).

10 a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1960**, 1718. b) M. L. H. Green, "Organometallic Compounds," 3rd ed, Methuen, London (1968), Vol. 2, p. 222. c) D. R. Fahey, *Organomet. Chem.*

Rev., **7**, 245 (1972). d) M. Wada, K. Kusabe, and K. Oguro, *Inorg. Chem.*, **16**, 446 (1977). e) J. M. Coronas, G. Muller, M. Rocamora, C. Miravitlles, and X. Solans, *J. Chem. Soc., Dalton Trans.*, **1985**, 2333.

11 T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992).

12 C. H. Bamford and M. J. S. Dewar, *Proc. R. Soc. London, Ser. A*, **A192**, 329 (1948).

13 T. Yamamoto, M. Omote, Y. Miyazaki, A. Kashiwazaki, B.-L. Lee, T. Kanbara, K. Osakada, T. Inoue, and K. Kubota, *Macromolecules*, **30**, 7158 (1997).