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Homocoupling of aryl halides promoted by an $NiCl_2$/bpy/Mg system in DMF

Takakazu Yamamoto*

Homocoupling of aryl halides (2 ArX → Ar—Ar) promoted by $NiCl_2$/2,2′-bipyridine (bpy)/Mg mixtures in DMF has been studied. Mixtures of $NiCl_2$, bpy and Mg in DMF promoted homocoupling of aryl halides such as phenyl bromide and *p*-tolyl bromide to give the coupling products in good (e.g. approximately 60–75%) yields, and the homocoupling products were easily isolated from the reaction mixtures. Application of this homocoupling to dibromo-aromatic compounds (Br–arylene–Br: 2,5-dibromopyridine, 2,7-dibromo-9.9-dioctylfluorene and 2,7-dibromo-9,10-dioctyl-9,10-dihydrophenanthrene) gave the corresponding π-conjugated polymers, $-(\text{arylene})_n-$, in good yields. Organometallic processes for the homocoupling are discussed. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: homocoupling; nickel; aryl halide; magnesium; DMF

Introduction

Zerovalent nickel complexes $[Ni(0)L_m]$ have been used for homocoupling of aryl halides ArX (2 ArX + $[Ni(0)L_m]$ → Ar—Ar). Isolated Ni(0) complexes such as $[Ni(cod)_2]$[1–3] (cod = 1,5-cyclooctadiene) and Ni(0) complexes generated by reduction of Ni(II) species with Zn[4–7] have been used as the homocoupling (or condensing) agent, and the homocoupling reaction has been applied for dehalogenative polycondensation of dihaloaromatic compounds to give π-conjugated polymers (e,g. *n* X-arylene-X + *n* $[Ni(0)L_m]$ → $-(\text{arylene})_n-$; arylene = *p*-phenylene, etc.).[8–12] π-Conjugated polymers have been the focus of numerous studies because of their attractive chemical and physical properties.[13–16]

N,*N*-Dimethylformamide (DMF) is often used as the solvent for the homocoupling reaction and dehalogenative polycondensation using the isolated Ni(0) complexes. However, use of Ni(0) complexes generated by reduction of Ni(II) species with Mg in DMF has not received much attention. Mg is thought to react with both the Ni(II) species and ArX, and the Grignard reagent formed by the reaction with ArX may be trapped by DMF;[17,18] this seems to be one of reasons for less attention.

If an $NiCl_2$/ligand/Mg system in DMF is usable for the C—C coupling reaction of ArX, it will serve as a new convenient homocoupling (or condensing) reagent. Because Mg has a stronger reducing ability than Zn, the system might work as an advantageous homocoupling reagent. In addition, results of the homocoupling reactions might add new information to organometallic chemistry.

Previously we briefly reported that an $NiCl_2$/bpy/Mg (bpy = 2,2′-bipyridine) system in DMF is actually usable for homocoupling of ArX.[19] This homocoupling can be easily carried out and might expand the scope of organometallic homocoupling of ArX. We now report this homocoupling under various conditions, and discuss organometallic aspects of this homocoupling. Application of this homocoupling to dehalogenative polycondensation of dihaloaromatic compounds to give π-conjugated polymers will also be reported. Basic reactions of zero-valent nickel complexes with organic halides have been the subject of many organometallic studies.[20–24]

Experimental

Materials

Organic monohalides such as phenyl bromide and *p*-tolyl bromide, 2,7-dibromo-9,9-dioctylfluorene, 2,5-dibromopyridine, bis(1,5-cyclooctadiene)nickel(0) ($[Ni(cod)_2]$), bpy, 1,2-dimethoxybenzene, Mg turnings, $[Cu(acac)_2]$ (acac = acetylacetonato), dry solvents, poly(4-vinylpyridine) (P4VP, cross-linked) and a standard polymer (poly(9,9-dioctylfluorene-2,7-diyl)) were purchased from Tokyo Chemical Industry Co. Ltd, Sigma-Aldrich Co. LLC, Wako Pure Chemical Industries Ltd or Kanto Chemical Co. Inc. Molecular sieve-dried DMF was obtained by adding molecular sieve 4A to commercially available dry DMF. Highly pure (purity = 99.95%) 2,7-dibromo-9.9-dioctylfluorene was kindly donated by JFE Chemical Corporation. Polyethylene glycol (PEG 4000 from Tokyo Chemical Industry Co. Ltd; average molecular weight = 2600–3800) was dissolved in dry DMF under heating and this solution was dried with a 4 Å molecular sieve. The P4VP powder was dried and degassed under vacuum. Water was removed from an aqueous solution of polyethyleneimine (PEI, purchased from Wako Pure Chemical Industries Ltd; average molecular weight = 1800) under vacuum at 115°C (for 3 h). The obtained PEI solid gave N and O contents of 29.74% and 4.05%, which corresponded to an N:O ratio of about 8:1 (=29.74%/14:4.05%/16), suggesting a partly hydrated structure of $(CH_2CH_2NH.1/8H_2O)_n$.[25] 2,7-Dibromo-9,10-dioctyl-9,10-dihydrophenanthrene was prepared as previously reported.[26]

Measurements and General Procedures

IR and ^{1}H NMR spectra were recorded on JASCO FT-IR-460 plus and JEOL JNM-LA300 spectrometers, respectively. NMR yields of

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* *Correspondence to: Takakazu Yamamoto, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: takakazuyamamoto@kir.biglobe.ne.jp*

Chemical Resources Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama 226-8503, Japan

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coupling products were obtained by adding a measured amount of $CHCl_2CHCl_2$ to the reaction product and comparing peak areas of the product and $CHCl_2CHCl_2$.

For example, a small part of the reaction mixture obtained by the homocoupling of *p*-tolyl bromide (TolBr) was taken out, and a measured amount of $CHCl_2CHCl_2$ was added. The ^{1}H NMR spectrum of this mixture in $CDCl_3$ showed peaks of the homocoupling product (Tol–Tol) and $CHCl_2CHCl_2$. The amount of Tol–Tol was calculated from areas of a $CHCl_2CHCl_2$ peak (at around δ 6.0) and CH_3 peak of Tol–Tol (at around δ 2.4). These ^{1}H NMR peaks are sometimes somewhat broadened, presumably due to the presence of paramagnetic Ni(II) species and/or solid particles in the crude reaction mixture. Figure S1a (supporting information) shows an example of the somewhat broadened ^{1}H NMR spectrum. However, a sharper ^{1}H NMR spectrum could be obtained depending on the case, as shown in Fig. S1b. As described below, extraction of formed Tol–Tol with hexane and removal of hexane via natural evaporation gave crystals of Tol–Tol, which gave rise to a reasonable ^{1}H NMR spectrum, as shown in Fig. S2.

GC yields of the product were obtained using a Shimadzu GC 8AT chromatograph, a Chromatopac data processor, a Silicone OV-17 (5%) column and He carrier gas. A TCD detector was used. For example, a small part of the reaction mixture obtained by the homocoupling of PhBr was taken out and measured amounts of naphthalene and 1,2-diphenylethane were added. The amount of Ph—Ph formed was calculated from the GC peak areas of naphthalene, Ph—Ph and 1,2-diphenylethane (in order of retention time) and relative sensitivity of these compounds. An example of the GC curve is shown in Fig. S3.

The NMR and GC yields usually agreed with that calculated based on the weight of the product. However, sometimes a lower yield was obtained with the weighing method, compared with the NMR and GC yields. Partial loss of the product during isolation of the product (especially during drying the product under vacuum) is thought to be the reason for the lower yield.

Size-exclusion chromatography (SEC) (or gel permeation chromatography (GPC)) for poly(9,9-dioctylfluorene-2,7-diyl) (**PFlu(9,9-Oct)**; see below) and poly(9,10-dioctyl-9,10-dihydrophenanthrene-2,7-diyl) (**PH_2Ph(9,10-Oct)**) was carried out at Tosoh Analysis and Research Center Co. Ltd; the eluent was chloroform and molecular weights were estimated versus polystyrene standards. SEC of poly(pyridine-2,5-diyl) (**PPy**) was carried out at Tosoh Analysis and Research Center using a Tosoh HLC-8120GPC system with hexafluoro-*i*-propanol as the eluent[27] and poly(methyl methacrylate) standards.

The homocoupling reaction and polymerization were carried out under N_2 using standard Schlenk techniques.

Coupling Reaction

This is a typical example (No. I-11 in Table 1). A mixture of $NiCl_2$ (260 mg, 2.0 mmol), bpy (620 mg, 4.0 mmol) and dry DMF (10 ml) was stirred for 5 min at 70°C. When Mg (110 mg, 4.5 mmol) was added to this mixture under stirring, the mixture turned deep green (characteristic of low-valent Ni–bpy complexes[28,29]) rapidly. After 3 min *p*-tolyl bromide (TolBr, 263 mg, 1.54 mmol) was added and the mixture was stirred for 8 h at 70°C. After cooling to room temperature (r.t.) a small portion (0.32 g) of the reaction mixture was removed and $CHCl_2CHCl_2$ (8.2 mg) was added to this part. The ^{1}H NMR spectrum of this sample in $CDCl_3$ clearly shows peaks of 4,4′-dimethylbiphenyl, and comparison of the peak area ratio between the $CHCl_2CHCl_2$ peak and 4,4′-dimethylbiphenyl peak indicated 75% yield of 4,4′-dimethylbiphenyl. Peaks of TolBr were not observed. DMF in the remaining part of the reaction mixture was removed under vacuum, and the remaining solid was treated with diluted hydrochloric acid (4 M, 15 ml).[30] Extraction with hexane (×3) and removal of hexane by natural evaporation yielded crystals of 4,4′-dimethylbipheny (102 mg, 73% yield). IR and ^{1}H NMR spectra indicated the isolation of pure 4,4′-dimethylbiphenyl.

Polymerization

*Preparation of **PFlu(9,9-Oct)** and **PH_2Ph(9,10-Oct)***

A mixture of $NiCl_2$ (270 mg, 2.1 mmol) and bpy (650 mg, 4.2 mmol) in dry DMF (40 ml) was stirred at 70°C for 10 min. Mg (600 mg, 25 mmol) was added, and the mixture was stirred at the temperature for several minutes. After addition of commercially available 2,7-dibromo-9.9-dioctylfluorene (**Monomer-1**, 1.17 g, ~2.1 mmol; $NiCl_2$/**Monomer-1** = ~1.0), the reaction mixture was stirred at 70°C for 18 h. The reaction mixture was poured into water (450 ml) and concentrated hydrochloric acid (50 ml) was added.[30] After stirring the mixture, the yellow precipitate was collected by filtration, and the obtained powder was washed with water and methanol. Drying under vacuum gave 800 mg (96%) of poly(9,9-dioctylfluorene-2,7-diyl), **PFlu(9,9-Oct)**. SEC data showed M_n (number average molecular weight), M_p (peak molecular weight in the SEC trace), M_w (weight average molecular weight) and M_z (z-average molecular weight) of 1000, 3000, 5700, and 18 000, respectively, with M_w/M_n of 5.7. Analogous polymerization using **Monomer-1** (580 mg, 1.1 mmol), $NiCl_2$ (270 mg, 2.1 mmol; $NiCl_2$/**Monomer-1** = 1.9), bpy (650 mg, 4.2 mmol) and Mg (600 mg, 25 mmol) gave analogous results with 90% yield and M_n, M_p, M_w and M_z of 1300, 3300, 7300 and 24 000, respectively with M_w/M_n of 5.6. The IR and ^{1}H NMR spectra of the obtained polymer essentially agreed with (or resembled) those of commercially available standard poly(9,9-dioctylfluorene-2,7-diyl). Use of highly pure **Monomer-1** (see above) gave analogous polymer.

Preparation of **PH_2Ph(9,10-Oct)** was carried out analogously (e.g. by using $NiCl_2$ (260 mg, 2.0 mmol), bpy (620 mg, 4.0 mmol), Mg (600 mg, 25 mmol) and 2,7-dibromo-9,10-dioctyl-9,10-dihydrophenanthrene (**Monomer-2**, 594 mg, 1.06 mmol; $NiCl_2$/**Monomer-2** = 1.9). Yield 91%. SEC data showed M_n and M_w of 1000 and 14 000, respectively, with M_w/M_n of 14. The ^{1}H NMR spectrum of the product essentially agreed with (or resembled) that of previously reported poly(9,10-dioctyl-9,10-dihydrophenanthrene-2,7-diyl), **PH_2Ph(9,10-Oct)**, which was prepared using $[Ni(cod)_2]$.[26]

*Preparation of **PPy***

This is a typical example. A mixture of $NiCl_2$ (260 mg, 2.0 mmol), bpy (620 mg, 4.0 mmol) and dry DMF (10 ml) was stirred at 80°C for 10 min. The color of the mixture turned from yellow to light green. When Mg (150 mg, 6.2 mmol) was added to this mixture under stirring, the mixture turned deep green rapidly. When 2,5-dibromopyridine (**Monomer-3**, 145 mg, 0.61 mmol) was added, the mixture turned blackish. After stirring for 7 h at 80°C, the reaction mixture was poured into diluted aqueous ammonia (~1.7 M, 400 ml). A yellow slurry was separated by decantation and washed with an aqueous solution of a disodium salt of ethylenediaminetetraacetic acid (EDTA.2Na) and water.

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Table 1. Results of C—C coupling of phenyl halides (PhX) and *p*-tolyl bromide (TolBr) using mixtures of $NiCl_2$, bpy, and Mg in DMF[a]

No.	ArX	Ni/ArX[b]	Ligand (bpy)/Ni[c]	Mg[d]/Ni	Temperature (°C)	Time (h)	Yield (%)
I-1	PhBr	1.0	2	1.5	70	8	74
I-2	PhBr	1.3	2	2.3	70	13	74
I-3	PhBr	1.9	1	5.0	70	13	68
I-4	PhBr	2.0	1	10	70	12	71
I-5	PhBr	0.2	2	4.9	70	8	58
I-6	PhBr	0.2	2	24	70	11	60
I-7	PhBr	$FeCl_3$, 1.0	2	2.5	70	7	–[e]
I-8	PhCl	1.0	2	5.0	70	11	70
I-9	PhCl	0.3	2	24	70	10	63
I-10	PhF	1.3	2	2.3	70	8	–[e]
I-11	TolBr	1.3	2	2.3	70	8	75
I-12	TolBr	1.3	2 in DMAc	2.3	70	8	68
I-13	TolBr	1.3	2 in DMSO	2.3	70	8	47
I-14	TolBr	1.3	1	Zn, 2.0	70	7	92
I-15	TolBr	1.8	0	3.1	70	7	(~10)[f]
I-16	TolBr	2.0	0	3.0	90	4	(~10)[f]
I-17	TolBr	2.0	0	Zn, 3.0	90	4	–[e]
I-18	TolBr	1.9	PEG, 5	3.1	70	7	(~10)[f]
I-19	TolBr	2.1	P4VP, 3	2.8	70	8	(~10)[f]
I-20	TolBr	2.1	cod, 5	2.5	70	7	(~10)[f]
I-21	TolBr	2.0	DMOB, 33	3.0	90	5	0
I-22	TolBr	1.9	DMOB, 24	Zn, 3.0	90	5	0
I-23	TolBr	$[Cu(acac)_2]$, 2.0	0	3.0	100	5	0
I-24	TolBr	$[Cu(acac)_2]$, 2.0	0	Zn, 3.0	100	5	0
I-25	TolBr	$[Ni(cod)_2]$, 1.9	1	0	70	7	98
I-26	TolBr	$[Ni(cod)_2]$, 1.9	0	0	70	7	100
I-27	TolBr	$[Ni(cod)_2]$, 1.9	PEG, 5	0	70	7	98
I-28[g]	PhBr	$[Ni(cod)_2]$, 0.6	0	0	55	26	82
I-29[h]	PhBr	$[NiCl_2(PPh_3)_2]$, 1.0	PPh_3, 2	Zn, 1.0	50	24	73
I-30[h]	TolBr	$[NiCl_2(PPh_3)_2]$, 1.0	PPh_3, 2	Zn, 1.0	50	24	60

[a] Data using other reaction conditions are also shown.

[b] Molar ratio. $NiCl_2$ was used unless otherwise noted. $[Ni(cod)_2]$, bis(1,5-cyclooctadiene)nickel(0); PPh_3, triphenylphosphine.

[c] Molar ratio. Bpy (2,2′-bipyridine) was used in DMF unless otherwise noted. DMAc, *N,N*-dimethylacetamide; DMSO, dimethylsulfoxide; PEG, polyethylene glycol (molarity is based on O); P4VP, poly(4-vinylpyridine) (molarity is based on N).

[d] Molar ratio. Mg was used unless otherwise noted. For I-7, I-23, I-24, Mg/(Fe or Cu) is shown.

[e] Trace.

[f] Isolation by extraction was difficult. ^{1}H NMR data indicated about 10% yield.

[g] Data from references [1] and [2].

[h] Data from reference [4]. Reaction conditions are from a typical example in this report.

The precipitate was collected by filtration and dried under vacuum at 60°C to obtain poly(pyridine-2,5-diyl) **PPy** (40 mg, 85% yield). SEC data showed M_n, M_p and M_w of 11 000, 18 000 and 25 000, respectively with M_w/M_n of 2.2. Analogous polymerization was carried out using a mixture obtained by the reaction of $NiCl_2$ (1.63 g, 12.6 mmol), bpy (3.93 g, 25.2 mmol) and Mg (243 mg, 10 mmol) in DMF (45 ml). Raising the temperature from r.t. to 70°C gave a deep-green mixture. After the UV–visible spectrum of this deep-green reaction mixture was measured, the remaining part of the green reaction mixture was used for polymerization of **Monomer-3** (710 mg, 3.0 mmol) at 70°C for 11 h. This polymerization gave **PPy** in 34% yield, and SEC data of this polymer showed M_n, M_p and M_w of 3500, 6300 and 7100, respectively, with M_w/M_n of 2.1.[19] The molecular weight of **PPy** seemed to depend on delicate polymerization conditions. The IR spectrum supported the formation of **PPy**.[31]

Results and Discussion

Coupling of Phenyl Bromide and *p*-Tolyl Bromide and Related Reactions

Table 1 shows results of coupling of phenyl halides (PhX) and *p*-tolyl bromide (TolBr) using the Mg-reduced Ni complex in DMF under various conditions.

$$\mathrm{NiCl_2\text{-}bpy + Mg} \xrightarrow{\mathrm{DMF}} [\mathrm{Ni(0)L}_m] \xrightarrow{\mathrm{ArX}} \mathrm{Ar\text{-}Ar} \qquad (1)$$

The reaction of yellow anhydrous $NiCl_2$ with bpy in DMF at 70°C for about 5–10 min gave a light-green suspension, which suggested the formation of $[NiCl_2(bpy)]$.[32,33] Addition of Mg to the mixture gave a deep-green solution rapidly, indicating the

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occurrence of facile reduction of [$NiCl_2$(bpy)] by Mg to give low-valent Ni complexes such as zero-valent [Ni(bpy)(solvent)$_m$].[28,29] The deep-green DMF solution was not homogeneous, and some solids were observed in the suspension. A part of this suspension was removed and diluted with DMF. The UV–visible spectrum of this diluted DMF suspension showed UV–visible peaks at 428 nm (23 400 cm^{-1}) and 600 nm (16 700 cm^{-1}), and the energy difference (6700 cm^{-1}) between the two absorption peaks suggests that the two peaks are assigned to nickel-to-bpy MLCT bands.[24,28,34] The reduction of the $NiCl_2$-bpy mixture with Mg in DMF proceeded much faster than that of the $NiCl_2$-bpy mixture in DMF with Zn, as judged from the velocity of the change of the color from light green (color of Ni(II)–bpy complex) to deep green (color of Ni(0)–bpy complex). This is reasonable because Mg is a stronger reducing agent than Zn.

The addition of PhBr or TolBr to the deep-green solution led to smooth homocoupling of these ArX. Ar—Ar was obtained in good yields. These results support the following assumption about the relative velocity of basic reactions: (i) the reduction of [$NiCl_2$(bpy)] by Mg proceeds rapidly; (ii) the homocoupling reaction of PhBr and TolBr promoted by the formed zero-valent Ni complex also proceeds rapidly; and (iii) the formation of the Grignard reagent of PhBr and TolBr and/or the trapping reaction of the Grignard reagent by DMF[17,18] is a much slower process: the rate of reduction of Ni(II) with Mg and the rate of homocoupling of ArBr by the formed Ni(0) complex are indeed much larger than the rate of reaction of ArBr with Mg and the rate of trapping of the Grignard reagent by DMF: ArBr = PhBr or TolBr.

The results shown in Table I reveal the following features (a)–(g) of the homocoupling reaction. Table 1 includes results reported by Semmelhack *et al.*[1,2] and Kende *et al.*[4] (see Nos. I-28–30) for comparison. PhBr and TolBr gave analogous results to each other; however, the isolation of the product by extraction seemed to be easier when TolBr was used.

(a) The amount of added bpy (1 mol or 2 mol of bpy/1 mol of $NiCl_2$) did not affect the yield (Nos. I-1–4). However, the reaction did not seem to proceed well in the absence of bpy (see Nos. I–15 and 16 and (e) below).

(b) PhCl also gave the coupling product. However, PhF is not active in the coupling reaction (Nos. I-8–10).

(c) Use of 0.2 mol $NiCl_2$ per PhBr also gave the coupling product in good yield (Nos. I-5 and 6). The initially formed Ni(0) complex is thought to be consumed by the reaction with PhBr to give Ph–Ph and [$NiBr_2L_m$] (L = ligand such as bpy), and [$NiBr_2L_m$] thus formed is thought to be reduced by Mg to Ni(0) complexes to make the catalytic use of Ni possible.

(d) The C—C coupling reaction also proceeded well in *N*,*N*-dimethylacetamide (DMAc) (No. I-12). Colon and Kelsey used DMAc for the C—C coupling reaction of aryl halides by the Ni (II)–L–Zn systems (L = bpy or PPh_3 (triphenylphosphine)).[5] DMSO was also usable as the solvent, although the yield of the product was lower (No. I-13).

(e) As described above, without bpy the C—C coupling did not proceed effectively (Nos. I-15 and 16). In these cases, the reaction of $NiCl_2$ with Mg rapidly gave a blackish suspension, suggesting the formation of metallic Ni. The reaction of $NiCl_2$ with Zn also gave a blackish suspension (with a slower reaction rate), and this $NiCl_2$–Zn system did not promote the C—C coupling effectively either, when bpy was absent (No. I-17).

Heating a DMF solution of [Ni(cod)$_2$] at 70°C also gave a blackish suspension, suggesting the (partial) formation of metallic Ni by liberation of cod. [Ni(cod)$_2$] solutions are stable in the presence of cod;[35,36] however, they often give blackish slurry when stored without cod.

In contrast to cases of the $NiCl_2$–Mg and $NiCl_2$–Zn systems, the blackish suspension formed from [Ni(cod)$_2$] promoted the C—C coupling reaction effectively even without bpy (Nos. I-26 and 28). The difference in reactivity between [Ni(cod)$_2$] and Mg- or Zn-reduced $NiCl_2$ might be due to the difference in the state of the formed metallic Ni, although, in the case of [Ni(cod)$_2$], a main part of this complex might remain even after the formation of the blackish suspension and promote the effective coupling reaction.

For [Ni(cod)$_2$], cod may work as an effective stabilizer for the zerovalent state of nickel. However, the addition of cod to the $NiCl_2$–Mg system did not give good results for the C—C coupling reaction (No. I-20).

(f) As described above, Mg-reduced Ni species without bpy did not promote the C—C coupling reaction effectively. Bpy is thought to stabilize the Ni(0) species by coordination. Di- or polyamines such as ethylenediamine and diethers (O—O) such as dimethoxyethane can coordinate with Ni. However, addition of these types of ligands (see Experimental section and Fig. 1) did not assist the C—C coupling effectively (Nos. I-18, 19, 21 and 22).

o-Dimethoxybenzene (DMOB), polyethylene glycol (PEG) and poly(4-vinylpyridine) (P4VP) may not stabilize the zero-valent Ni, and/or the Ni(0) species coordinated with these ligand may not be active for the C—C coupling. In the case of [Ni(cod)$_2$], addition of PEG did not disturb the C—C coupling reaction (No. I-27). However, addition of polyethyleneimine (PEI) to the [Ni(cod)$_2$] system did not give good results for the formation of Tol–Tol from TolBr.

[Ni(cod)$_2$] is a superior condensing reagent for homocoupling of ArX, giving Ar—Ar in higher yields under wider reaction conditions.[1–3] Based on this, [Ni(cod)$_2$] is thought to be a better coupling agent than the Ni(0) species generated by reduction of Ni(II) species with Mg and Zn. However, the Ni(II)–Mg and Ni(II)–Zn systems are easily constructed and might be more useful in practical purposes.

(g) Because metallic Cu is used in Ullmann coupling of ArX,[37] Mg-reduced metallic Cu might be expected to promote the C—C coupling. However, the [Cu(acac)$_2$]–Mg system did not cause the C—C coupling (No. I-23). Use of Zn as the reducing agent gave analogous results (No. I-24). Iron forms various complexes with bpy. However, Mg-reduced Fe-bpy complexes did not promote the C—C coupling either (No. I-7).

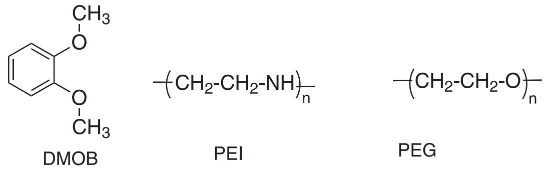

Figure 1. Examples of ligands for Ni.

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Coupling of Other Organic Halides

Table 2 shows results of the C—C coupling of *p*-bromoacetophenone, benzyl bromide and 2-phenyl-1-bromoethane. For comparison, related results reported in the literature are also shown.

As shown in No. II-1, $CH_3COC_6H_4Br$-*p* with a moderately electron-withdrawing acetyl group also underwent the C—C coupling reaction. Similar results were reported for the coupling of $CH_3COC_6H_4Br$-*p* and NCC_6H_4Br-*p* promoted by isolated Ni–cod complexes,[1,2,24] and the reported results are shown in Nos. II-4 and 5. $PhCH_2Br$ and $PhCH_2CH_2Br$ with an sp^3 C—Br bond also underwent the C—C coupling reaction (Nos. II-2 and 3).

On the Mechanism of the C—C Coupling Reaction and Effects of Substituents

As described above, the reaction of $NiCl_2$ with bpy gave a light-green product, the color being characteristic of $[NiCl_2(bpy)]$.[32,33] Reduction of this light-green product with Mg smoothly gave a deep-green product, and this color change supported the formation of low-valent Ni–bpy complex(es) such as [Ni(bpy)(solvent)] (see equation (2)):[28,29,38]

$$NiCl_2 + bpy + Mg \rightarrow [Ni(bpy)(DMF)] \qquad (2)$$

This Ni(0) complex is thought to react with organic halide (RX) to form [NiX(R)(bpy)] by oxidative addition of RX (equation (3)). Disproportionation of [NiX(R)(bpy)] seems to occur to give $[Ni(R)_2(bpy)]$ (equation (4)), and reductive elimination on $[Ni(R)_2(bpy)]$ gives the C—C coupling product, R—R (equation (5)):

$$[Ni(bpy)(DMF)] + RX \rightarrow [NiX(R)(bpy)] \qquad (3)$$

$$2[NiX(R)(bpy)] \rightarrow [Ni(R)_2(bpy)] + [NiX_2(bpy)] \qquad (4)$$

$$[Ni(R)_2(bpy)] \rightarrow R - R + [N(bpy)(solvent)] \qquad (5)$$

Total C—C coupling reaction of RX by $[Ni(0)L_m]$ is expressed as follows:

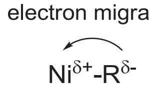
$$[Ni(0)L_m] + 2\ RX \rightarrow [Ni(II)X_2L_m] + R{—}R \qquad (6)$$

The oxidative addition (equation (3)) of RX to zero-valent nickel complexes is well known.[3,20–24,39] Disproportionation (equation (4)) of [NiCl(R)(bpy)] to $[Ni(R)_2(bpy)]$ and $[NiX_2(bpy)]$ has been reported,[33] and isolation of $[Ni(aryl)_2(bpy)]$ from $[Ni(cod)_2]$–bpy–aryl halide reaction systems has also been reported.[24,40] As described below, isolation of *cis*-$[Ni(aryl)_2L_m]$ complexes such as $[Ni(aryl)_2(bpy)]$ is possible only for selected aryl groups.

The reductive elimination (equation (5)) of R—R from diorganonickel complexes such as $[Ni(R)_2(bpy)]$ and $[Ni(R)_2(diphosphine)]$ is also known,[24,28,41] and it is proposed that the reductive elimination from $[Ni(aryl)_2(bpy)]$ is assisted by π-electron interaction[24,42,43] between the two aryl groups attached to Ni (see Fig. 2).

Such Ni complexes were isolated when the aryl group is highly electron-withdrawing (e.g., —C_6F_5[24] and chloropyrazolyl[40]). When the two aryl groups in $[Ni(aryl)_2(bpy)]$ are not highly electron-withdrawing, this Ni complex seems to undergo reductive elimination easily.

The Ni—C bond in $[Ni(R)_2L_m]$ is thought to be *polarized* as $Ni^{\delta+}$—$C^{\delta-}$ due to the difference in electronegativity between Ni and C. On the other hand, the reductive elimination releases the *neutral* molecule, R—R. Consequently, the reductive elimination is thought to involve electron migration from C to Ni:[44]



This electron migration is thought to be difficult when the aryl group is a strongly electron-withdrawing group, and the $[Ni(aryl)_2(bpy)]$ can be isolated in this case (e.g. isolated from $[Ni(cod)_2]$/bpy/ArX systems[24,40]).

Attempts to isolate *cis*-$[Ni(aryl)_2L_m]$ (e.g. from the $[Ni(cod)_2]$/bpy/ArX system) has not been successful when the aryl group is not a strongly electron group. In these cases the coupling products Ar—Ar were obtained, instead of the isolation of *cis*-$[Ni(aryl)_2L_m]$.

However, when the aryl group has two substituents at the *o*-positions, as in the case of a mesityl group, the *cis*-$[Ni(aryl)_2L_m]$ complex is isolable.[24,34,45,46] The presence of the two substituents at the *o*-positions seems to hinder the approach of C_1 and C_2 in the *cis*-$[Ni(aryl)_2L_m]$ complex (see Fig. 2). This difficulty for the reductive elimination from the *cis*-[Ni(*o*-disubstituted $Ar)_2L_m$] might be

Table 2. Results of C—C coupling of other organic bromides in DMF

No.	RX[a]	Ni/RX[b]	Bpy[c]/Ni	Mg/Ni	Temp. (°C)	Time (h)	Yield (%)
II-1	$CH_3COC_6H_4Br$-*p*	1.3	2	2.3	70	7	28
II-2	$PhCH_2Br$	1.3	2	2.3	70	13	80[g]
II-3	$PhCH_2CH_2Br$	1.3	2	2.3	70	13	21
II-4[d]	$CH_3COC_6H_4Br$-*p*	$Ni(cod)_2$, 0.6	0	0	45	36	93
II-5[e]	NCC_6H_4Cl-*p*	Ni(cod)(bpy)	(1)	0	r.t.		78
II-6[d]	$O_2NC_6H_4Br$-*p*	$Ni(cod)_2$, 0.6	0	0	40	17	0
II-7[d]	2,6-$Me_2C_6H_3Br$	$Ni(cod)_2$, 0.6	0	0	54	9.5	0
II-8[f]	Aryl halides with two *o*-substituents	$NiCl_2(PPh_3)_2$, 1.0	(PPh_3, 2)	Zn, 1.0	50	24	0

[a] 2,6-$Me_2C_6H_3Br$, 2-bromo-*m*-xylene.
[b] PPh_3, triphenylphosphine.
[c] Bpy is used unless otherwise noted.
[d] Data from reference [1]. Reaction conditions are from a typical example in this report.
[e] Data from reference [24].
[f] Data from reference [4]. Reaction conditions are from a typical example in this report.
[g] GC yield. Isolation yield was lower (~40%) because of partial loss of the product during drying of the product under vacuum.

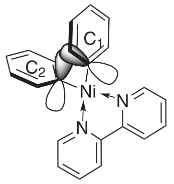


Figure 2. Postulated π-electron interaction between the two aryl groups. X-ray crystallographic data of isolated [Ni(C_6F_5)$_2$(bpy)] indicates an essentially perpendicular arrangement of the two aryl groups, which is thought to bring about the π-electron interaction shown above.

related to reported unsuccessful C—C coupling of *o*-disubstituted aryl halides by Ni(0) complexes (see II-7 and -8 in Table 2).

When an excess amount of Mg was added (No. I-4 in Table 1; Mg/$NiCl_2$ = 10), the deep-green product, which was usually formed in the reduction of the $NiCl_2$–bpy mixture, further changed to deep reddish-brown in about 10–20 min at 70°C. Because the reduction of transition metal–bpy complexes often gives anionic species such as $[Ru(bpy)_3]^-$,[47] the formation of anionic Ni–bpy complexes such as $Mg[Ni(bpy)_2]$ is suggested. The C—C coupling of PhBr also proceeded smoothly in the presence of excess Mg (No. I-4), and occurrence of reactions such as $Mg[Ni(bpy)_2] + 4\ ArX \rightarrow 2\ Ar\text{-}Ar + [NiX_2(bpy)] + MgBr_2$ is suggested.

Application to Synthesis of π-Conjugated Polymers

Usability of the $NiCl_2$–bpy–Mg mixture in DMF for the synthesis of π-conjugated polymers has been examined. As shown in Fig. 3, three kinds of Br–arylene–Br monomers were used for the preparation of **PFlu(9,9-Oct)**, **PH_2Ph(9,10-Oct)** and **PPy.**

These π-conjugated polymers show interesting electronic and optical functionalities, and numerous studies have been carried out on these types of π-conjugated polymers.[13–16,26,31,48,49] Dehalogenative organometallic polycondensation of dihalomonomers (X–(arylene)–X) is one of the most popular routes for the preparation of π-conjugated $-(arylene)_n-$,[8–16,26] and the $[Ni(cod)_2]$–bpy mixture has been used as the condensing agent for the preparation of π-conjugated $-(arylene)_n-$.[13–16,26,27,31]

The $NiCl_2$–bpy–Mg mixture in DMF gave these polymers in good yields. The IR and ^1H NMR spectra of the products essentially agreed with reported data.[26,31,50,51] **PFlu(9,9-Oct)** obtained thus showed an M_w (weight average molecular weight) of 5700. **PH_2Ph (9,10-Oct)** and **PPy** showed M_w of 14 000 and 25 000, respectively. These data indicate that the $NiCl_2$–bpy–Mg mixture in DMF is usable in the preparation of π-conjugated $-(arylene)_n-$. However, in repeated experiments, the polymer products sometimes showed additional IR and/or ^1H NMR peaks, suggesting contamination with by-product(s) by the occurrence of side reaction(s). In the case of $[Ni(cod)_2]$–bpy mixture, the polymerization product does no show such additional peaks in repeated syntheses. The polymerization results obtained by using the $NiCl_2$–bpy–Mg mixture in DMF seemed to depend on delicate reaction conditions.

Conclusions

The $NiCl_2$–bpy–Mg mixture in DMF promotes the C—C coupling of aryl halides. The results of C—C coupling of Ar—X agree with information obtained in the field of organometallic chemistry. The C—C coupling promoted by the $NiCl_2$—bpy—Mg mixture in DMF can be applicable to the preparation of π-conjugated $-(arylene)_n-$. The present findings might contribute to a better understanding of organometallic homocoupling of aryl halides and to development of new C—C coupling reactions.

$$\underset{\text{(Monomer-1 - Monomer-3)}}{\text{Br-arylene-Br}} \xrightarrow[\text{DMF}]{\text{NiCl}_2\text{, bpy, Mg}} \text{-(arylene)}_n\text{-} \qquad (7)$$

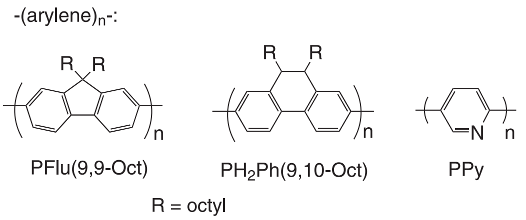


Figure 3. Application of C—C coupling to the synthesis of π-conjugated polymers. **Monomer-1** = 2,7-dibromo-9.9-dioctylfluorene; **Monomer-2** = 2,7-dibromo-9,10-dioctyl-9,10-dihydrophenanthrene; **Monomer-3** = 2,5-dibromopyridine (see Experimental section).

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