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C–C Coupling Promoted by a $NiCl_2$/bpy/Mg System in DMF and Its Application to Dehalogenative Polycondensation

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A mixture of $NiCl_2$, 2,2′-bipyridine (bpy), and Mg in DMF promoted dehalogenative homocoupling of RX (e.g., bromobenzene and *p*-tolyl bromide) efficiently. This basic coupling reaction was applied for polycondensation of dihaloorganic compounds, X–R′–X, to give poly(9,9-dioctylfluorene-2,7-diyl), poly(9,10-dioctyl-9,10-dihydrophenanthrene-2,7-diyl), and poly(pyridine-2,5-diyl).

π-Conjugated polymers are the subject of many papers,[1] and various π-conjugated polymers have been synthesized via organometallic C–C coupling reactions.[1–3] For example, the following Ni-promoted organometallic polycondensation has been reported.

$$n\ \mathrm{X{-}R'{-}X} + n\ \mathrm{Mg} \xrightarrow[\text{ethereal solvent}]{[\mathrm{Ni^{II}L}_m]} (\mathrm{R'})_n + n\ \mathrm{MgX_2} \qquad (1)^{1b,1c,2a}$$

$$n\ \mathrm{X{-}R'{-}X} + n\ \mathrm{Ni^0L}_m \xrightarrow{\text{DMF}} (\mathrm{R'})_n + n\ \mathrm{NiX_2L}_m \qquad (2)^{1b,1c,3}$$

R′: divalent organic group such as *p*-phenylene
$[Ni^{II}L_m]$: divalent nickel complex such as $[NiCl_2(bpy)]$
$[Ni^0L_m]$: zerovalent nickel complex such as a mixture
of bis(1,5-cyclooctadiene)nickel and bpy

The polycondensation expressed by eq 1 is usually carried out by adding the Ni-complex after a Grignard reagent (e.g., X–R′–MgX) is formed by the reaction between X–R′–X and Mg, and the polycondensation is believed to proceed via Ni-promoted C–C coupling[4] between the –X group and the –MgX group. However, the polycondensation can also be carried out even when the $[Ni^{II}L_m]$ catalyst, X–R′–X, and Mg are added at the same time (before formation of the Grignard reagent).[2a]

$$n\ \mathrm{X{-}R'{-}X} \xrightarrow{\substack{\mathrm{Mg} + [\mathrm{Ni^{II}L}_m]\ \text{added before} \\ \text{formation of Grignard reagent}}} (\mathrm{R'})_n \qquad (3)^{2a}$$

In this case Mg may essentially serve as a reducing reagent for $[Ni^{II}L_m]$ (e.g., $[NiCl_2(bpy)]$) to produce $[Ni^0L_m]$; the polymer may be formed by the polycondensation using the formed $[Ni^0L_m]$. Use of isolated $[Ni^0L_m]$[1,3,5] and $[Ni^0L_m]$ formed in situ[1,6] for basic C–C coupling of RX[5,6a] and dehalogenative polycondensation of X–R′–X[1,6b,6c] has been reported. Zinc has been used to reduce $[Ni^{II}L_m]$ to generate $[Ni^0L_m]$ for basic C–C coupling and dehalogenative polycondensation, which are often carried out in polar solvents such as *N*,*N*-dimethylacetamide (DMAc) and DMF. However, use of magnesium as a reducing metal for $[Ni^{II}L_m]$ has received less attention, presumably due to possibility that RX and X–R′–X react with magnesium and the formed Grignard reagent reacts with the polar solvents. If magnesium, which has stronger reducing ability than zinc,[7] can be used as a reducing metal for the $[Ni^{II}L_m]$-promoted C–C coupling and dehalogenative polycondensation of X–R′–X in polar solvent systems, the scope of the C–C coupling and dehalogenative polycondensation will be expanded.

Based on the polymerization results expressed by eq 3, we have examined homocoupling of RX and polycondensation of X–R′–X with a mixture of $NiCl_2$, bpy, and Mg in DMF. If the reaction of RX and X–R′–X with Mg proceeds rapidly, the formed Grignard reagent will be trapped by DMF.[8] By contrast, when reduction of a $NiCl_2$–bpy complex[9] with Mg in DMF proceeds more rapidly to form $[Ni^0L_m]$ and RX and X–R′–X react smoothly with $[Ni^0L_m]$, homocoupling of RX and polycondensation of X–R′–X can be carried out with a $NiCl_2$/bpy/Mg/DMF system.

$$\mathrm{NiCl_2{-}bpy} + \mathrm{Mg} \xrightarrow{\text{DMF}} [\mathrm{Ni^0L}_m] \xrightarrow{\text{RX or X–R}'\text{–X}} \text{R–R or } (\mathrm{R'})_n \qquad (4)$$

Addition of Mg to a mixture of $NiCl_2$ and bpy in DMF at 70 °C rapidly (in about 1 min) gave a solution with deep green color typical of low-valent Ni–bpy complexes,[10,11] revealing that the reduction of $NiCl_2$–bpy with Mg in DMF is very fast. The DMF solution showed a broad UV–vis peak at about 600 nm,[10c] the peak position may be compared with that (680 nm) of $[Ni(bpy)_2]$ in hexamethylphosphoric triamide.[11] When an excess amount of Mg was added, prolonged (e.g., 20 min) reaction gave a deep reddish brown solution, which suggested formation of anionic species of a Ni–bpy complex because bpy-coordinated transition metals often give anionic complexes such as $[Ru(bpy)_3]^-$.[12]

Addition of PhBr to the deep green or deep reddish brown solution gave the C–C coupling product, biphenyl, in about 70% extraction yield when the reaction system contained 1–2 mol of $NiCl_2$ per mol of PhBr.[13] GC yield (about 90%) of the reaction was higher than the extraction yield.[13]

$$\mathrm{PhBr} \xrightarrow[\text{DMF}]{\mathrm{NiCl_2},\ \text{bpy},\ \mathrm{Mg}} \mathrm{PhPh} \qquad (5)$$

The presence of excess Mg did not affect the yield of biphenyl apparently. For example, addition of 10 mol of Mg per 1 mol $NiCl_2$ (or 20 mmol/PhBr)[14] also gave biphenyl in about 70% extraction yield; consequently it is essentially not necessary to worry about the amount of Mg and addition time of PhBr so much. Simple extraction with hexane gave almost pure biphenyl. The amount of bpy (1 or 2 mol per $NiCl_2$) gave no apparent change in the yield of biphenyl.

As described above, the C–C coupling reaction proceeded smoothly in the presence of 1–2 mol of $NiCl_2$ per PhBr. However, the C–C coupling was able to be carried out in a catalytic system to some extent. For example, addition of 0.2 mol of $NiCl_2$, 0.4 mol of bpy, and 1 mol of Mg per 1 mol of PhBr gave biphenyl in 58% extraction yield.[15] The ^1H NMR spectrum of the extracted product also agreed with that of biphenyl.

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Use of PhCl, instead of PhBr, gave analogous results to give biphenyl in an extraction yield of about 65%. By contrast PhF was not suited for the C–C coupling reaction. Use of $PhCH_2Br$ and $PhCH_2CH_2Br$ under similar reaction conditions gave $PhCH_2CH_2Ph$ and $Ph(CH_2)_4Ph$ in about 40 and 25% yields,[16] respectively; formation of these compounds was confirmed by ^1H NMR and high-resolution mass spectrometry. Use of $FeCl_3$, instead of $NiCl_2$, in the reaction of PhBr did not give biphenyl.

$CH_3C_6H_4Br$-*p* gave results analogous to those obtained with PhBr. The reaction of $CH_3C_6H_4Br$-*p* gave $CH_3(C_6H_4)_2CH_3$ in about 75% yield. The ^1H NMR spectrum of the hexane-extract revealed that $CH_3(C_6H_4)_2CH_3$ was virtually the sole hexane-extractable organic product in the reaction.

These results indicate that the homocoupling of $CH_3C_6H_4Br$-*p* (TolBr-*p*) using the $NiCl_2$/bpy/Mg/DMF mixture proceeds cleanly and rates of (a) reduction of Ni(II) species by Mg and (b) homocoupling of TolBr-*p* promoted by Ni(0) species are much faster than that of (c) the reaction of TolBr-*p* with Mg:

Rate (reduction of Ni(II)), Rate (reaction of TolBr-*p* with Ni(0)) $\gg$ Rate (reaction of TolBr-*p* with Mg)

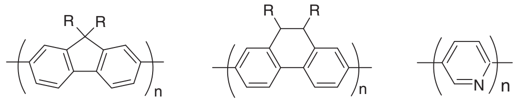
Bpy and Ni–bpy complexes were not extracted by hexane in the experimental procedures presumably due to high solubility in the aqueous solution (4 M hydrochloric acid).[13] This made the isolation of $CH_3(C_6H_4)_2CH_3$ easy, and removal of hexane by evaporation from the solution obtained by hexane-extraction gave needles or blocks of crystalline $CH_3(C_6H_4)_2CH_3$. Use of DMAc, instead of DMF, gave $CH_3(C_6H_4)_2CH_3$ in an analogous yield; however, DMSO as the solvent gave $CH_3(C_6H_4)_2CH_3$ in a lower yield (about 40%). DMF, DMAc, and DMSO, which partly remained after removal from the reaction system under reduced pressure,[13] were virtually not extracted by hexane.

The C–C coupling reaction also proceeded with $CH_3COC_6H_4Br$-*p* having a carbonyl group to give the product, $CH_3COPhPhCOCH_3$. However, the yield was much lower (about 30%).[17] Because Ni(0)-complex promoted C–C coupling of RX is thought to proceed through R–R coupling (reductive elimination) on an intermediate $[NiR_2L_m]$ species,[18] the above shown results with $PhCH_2Br$, $Ph(CH_2)_2Br$, and $CH_3COC_6H_4Br$-*p* suggest high stability of the Ni–alkyl bond as well as the Ni–aryl bond with the electron-accepting $-COCH_3$ group.[19]

Because the $NiCl_2$/bpy/Mg/DMF system promotes the C–C coupling reactions, we carried out polycondensation of X–R′–X using the $NiCl_2$/bpy/Mg mixture in DMF as the condensing reagent.

$$\text{Br–R}'\text{–Br} \xrightarrow[\text{DMF}]{\text{NiCl}_2\text{, bpy, Mg}} (\text{R}')_n \tag{6}$$

$(R')_n$:



P1 **P2** **P3**

R = octyl

For example, dehalogenative polycondensation of 2,7-dibromo-9,9-dioctylfluorene, **M1**, with the $NiCl_2$/bpy/Mg mixture in DMF gave poly(9,9-dioctylfluorene-2,7-diyl), **P1**, in good yield.[20] The IR and ^1H NMR spectra of the polymer essentially agreed with those of standard poly(9,9-dioctylfluorene-2,7-diyl) and reported data of poly(9,9-dialkylfluorene-2,7-diyl).[21] **P1** thus obtained showed M_w (weight-average molecular weight) of 5700 with a broad molecular weight distribution ($M_w/M_n = 5.6$ (M_n: number-average molecular weight)) in gel permeation chromatography (GPC, eluent: chloroform).

P2 was obtained analogously in a good yield using the $NiCl_2$/bpy/Mg system in DMF, and its IR and ^1H NMR essentially agreed with those of previously prepared poly(9,10-dioctyl-9,10-dihydrophenanthrene-2,7-diyl).[22] GPC (eluent: chloroform) of **P2** showed M_w of 14000 and a broad molecular weight distribution ($M_w/M_n = 14$). **P3** was prepared similarly with the $NiCl_2$/bpy/Mg system in DMF, and its IR spectrum essentially agreed with that of previously reported poly(pyridine-2,5-diyl).[23] The yield of **P3** was lower (34%) presumably due to partial loss of the polymer during treatment of the product, which included washing the product with aqueous ammonia and an aqueous solution of disodium salt of ethylenediaminetetraacetic acid in stirring systems. GPC (eluent: $(CF_3)_2CHOH$)[24] showed M_w of 7100 and M_w/M_n of 2.1. These results indicate that the C–C coupling using the $NiCl_2$/bpy/Mg/DMF mixture can be basically applied to the dehalogenative polycondensation. The findings that the $NiCl_2$/bpy/Mg/DMF mixture can promote the basic C–C coupling reaction and polycondensation will expand the scope of C–C coupling.

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13 An example for the preparation of biphenyl carried out using standard Schlenk technique: A mixture of $NiCl_2$ (260 mg, 2 mmol) and bpy (624 mg, 4 mmol) in dry DMF (10 mL) was stirred for 5 min at 70 °C. After addition of Mg (75 mg, 3 mmol), the reaction mixture was stirred for 10 min. Magnesium turnings purchased from Kanto Chemical Co., Inc. were used without activation. Then PhBr (310 mg, 2 mmol) was added, and the reaction mixture was stirred for 7 h and 20 min at 70 °C. Volatile materials were removed by evaporation under reduced pressure (50 °C under vacuum). Hydrochloric acid (4 M, 15 mL) was added to the residue, and the product was extracted with hexane. Drying up the hexane solution gave a white crystalline solid (112 mg, 0.73 mmol; extraction yield: 73%), whose ^1H NMR and IR spectra indicated the extracted product was almost pure biphenyl; accurate mass measurement also supported biphenyl. During the removal process of the volatile materials a part of biphenyl seemed to be lost because standing biphenyl under vaccum at 50 °C caused a weight loss. A separate experiment under similar conditions ($NiCl_2/PhBr = 1.3$; $bpy/NiCl_2 = 2$; $Mg/PhBr = 2.9$) showed an extraction yield of 70% and a GC yield of 88% for biphenyl, supporting the notion that a part of formed biphenyl in the extraction process was lost during work-up.

14 When the reaction was carried out with excess Mg, Mg remained after the reaction. Addition of hydrochloric acid[13] caused evolution of a gas which was thought to be H_2. This should be cautioned.

15 A mixture of $NiCl_2$ (130 mg, 1 mmol) and bpy (312 mg, 2 mmol) in dry DMF (10 mL) was stirred for 5 min at 70 °C. After addition of Mg (120 mg, 4.9 mmol), the reaction mixture was stirred for 10 min. Then PhBr (800 mg, 5.1 mmol) was added, and the reaction mixture was stirred for 7 h and 20 min at 70 °C. Volatile materials were removed by evaporation under reduced pressure (50 °C under vacuum). Hydrochloric acid (4 M, 15 mL) was added to the residue, and the product was extracted with hexane. Drying up the hexane solution gave a white crystalline solid (229 mg, 1.49 mmol; extraction yield: 58% yield based on PhBr or 149% yield based on $NiCl_2$) whose ^1H NMR and IR spectra indicated the extracted product was almost pure biphenyl; accurate mass measurement also supported biphenyl.

16 Extraction-NMR yield of $Ph(CH_2)_4Ph$ was 25%. ^1H NMR spectra ($CDCl_3$) of extracts obtained in reactions of $PhCH_2Br$ and $PhCH_2CH_2Br$ showed a CH_2 peak of $PhCH_2CH_2Ph$ at δ 2.90 (s) and CH_2 peaks of $Ph(CH_2)_4Ph$ at δ 2.62 (t, $J = 7.1$ Hz) and 1.67 (multiplet) (cf. D. H. Richards, N. F. Scilly, *J. Chem. Soc. C* **1969**, 55), respectively. Accurate mass of extracted $PhCH_2CH_2Ph$ (EI) m/z: 182.1092 (found), 182.1096 (calcd). Accurate mass of extracted $Ph(CH_2)_4Ph$ (EI) m/z: 210.1406 (found), 210.1409 (calcd). Extraction-NMR yield was determined by adding $CHCl_2CHCl_2$ as an internal reference.

17 A mixture of $NiCl_2$ (260 mg, 2.0 mmol), bpy (620 mg, 4.0 mmol), Mg (110 mg, 4.5 mmol) in dry DMF (10 mL) was stirred at 70 °C for about 10 min. $CH_3COC_6H_4Br$-*p* (300 mg, 1.5 mmol) was added, and the reaction mixture was stirred at 70 °C for 7.5 h. After removal of volatile materials under reduced pressure, hydrochloric acid (4 M, 15 mL) was added to the residue, and the product was extracted with toluene. Removal of toluene gave a solid whose IR spectrum essentially agreed with that of standard $CH_3COC_6H_4COCH_3$. However, the ^1H NMR spectrum showed some additional peaks and the extraction-NMR yield was determined by adding $CHCl_2CHCl_2$ as an internal reference.

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