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Nickel(II) thiocyanate complex as a catalyst for cross-coupling reactions

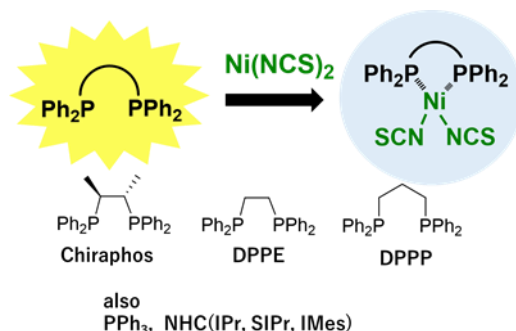
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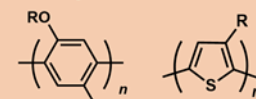
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Dedicated to Professor Hisashi Yamamoto on the occasion of his 80th birthday



Catalyze

> Polymerizations



> Coupling Reactions

- Suzuki-Miyaura cross coupling
- Buchwald-Hartwig amination

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Abstract Nickel thiocyanate complex was prepared by the reaction with Chiraphos (2S,3S-diphenylphosphinobutane) following the literature method. Thus obtained nickel complex was found to be available for the polymerization reaction of 1,4-dihalobenzene and 2-halo-3-hexylthiophene leading to poly(1,4-phenylene) and poly(3-hexylthiophene-2,5-diyl). The polymerization with other ligands such as bidentate phosphine complex of DPPE and DPPP and several N-heterocyclic carbene complexes also proceeded in a similar manner, Ni(NCS)₂ complex catalyzed Suzuki-Miyaura coupling and Buchwald-Hartwig amination to afford the corresponding biaryl and arylamine, respectively, were also found to proceed successfully.

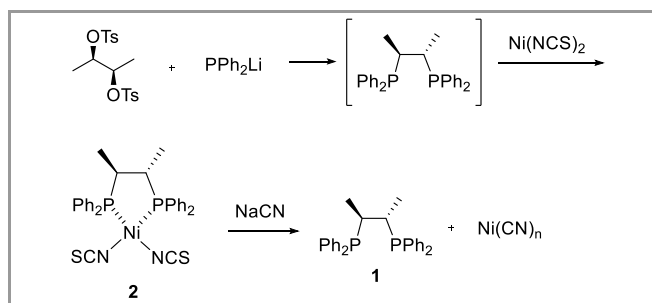
Key words Ni catalyst, thiocyanate, chiraphos, π -conjugated polymers, thiophene, phenylene, Suzuki-Miyaura cross coupling, Buchwald-Hartwig amination

Cross-coupling reaction by transition metal catalysis have attracted much attention in organic synthesis, organometallic chemistry, and materials science. A wide range of (hetero)biaryls of extended π -conjugation have been synthesized by cross coupling and thus obtained molecules were applied for biologically active compounds and electronic materials.¹ Development of effective metal catalysts and the ligand design is therefore major concern and a variety of catalytic reactions have been reported to date.²⁻⁵ We have recently shown that chiraphos **1**, a class of bidentate phosphine bearing branched structure in the bridging carbons, exhibits remarkably enhanced reactivity in cross-coupling polymerization leading to poly(1,4-phenylene)s.⁶ During the course of our synthetic study on chiraphos a precipitation protocol of chiraphos by the complexation as nickel(II) thiocyanate salt reported by Bosnich and co-workers⁷ was examined and the corresponding Ni(NCS)₂-chiraphos complex (**2**) was obtained for the use toward demetalative isolation of the free ligand **1**. Several nickel complexes involving -NCS as a counter ion have been employed for the purification of the synthesized ligand⁸ as summarized in Scheme 1, while little

attention has been paid for the utilization of the thus obtained nickel complex toward catalysis.

We have been reported also that 2-halogenated thiophene undergoes deprotonative metalation polymerization employing a bulky magnesium amide followed by the addition of a nickel(II) complex composed of halides or acetylacetonate as a catalyst for the polymerization.⁹⁻¹² The reaction was shown to proceed in a catalyst transfer manner leading to highly regioregular poly(3-substituted thiophene) when several bidentate phosphines and N-heterocyclic carbenes (NHC) are employed as a ligand¹³⁻¹⁵. We have also shown that the use of the related nickel(II) catalyst is also available for the synthesis of poly(1,4-arylene)s with dibromoarenes and bromo(chloro)arenes.¹⁶⁻¹⁸

Our interest for the application of thus obtained nickel complex of Ni(NCS)₂ was turned to the utilization of nickel complex **2** for the cross-coupling polymerization of thiophenes and phenylenes.

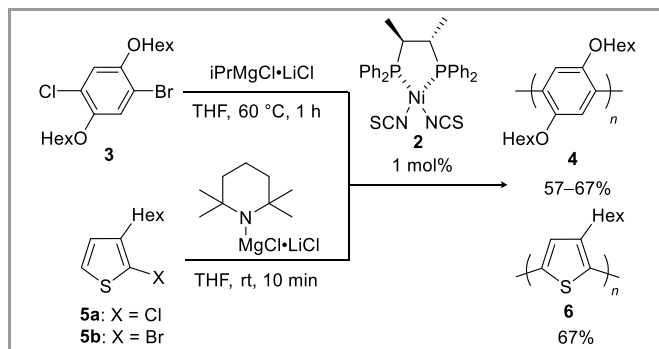


Scheme 1 Precipitation of nickel(II)NCS chiraphos complex **2** for the purification of **1** as a bidentate phosphine ligand (ref 7)

We first examined the formation of the chiraphos complex of nickel(II) thiocyanate following the literature procedure.⁷ Nickel complex **2** was prepared by the reaction of Ni(NCS)₂ and commercial chiraphos **1** in ethanol at room temperature. Formation of precipitate occurred after stirring for 12 h and

complex **2** was isolated in 74% yield. Polymerization of 2,5-di(hexyloxy)-1-bromo-4-chlorobenzene (**3**)¹⁶ was carried out with nickel complex **2** as a catalyst as shown in Scheme 2. Treatment of **3** with ⁱPrMgCl·LiCl at 60 °C for 1 h in THF underwent halogen-metal exchange at the carbon-bromine bond. Following addition of 1.0 mol% of thus obtained Ni(NCS)-chiraphos complex (**2**) and further stirring for 12 h at 60 °C afforded poly(1,4-phenylene) **4** in 57% yield. The number of molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of **4** was found to be 16000 and 1.71, respectively. It was also found that nickel complex **2** formed by the reaction mixture of 2,3-butanediol tosylate and LiPPh₂^{19,20} with Ni(NCS)₂ as shown in Scheme 1 similarly catalyzed the polymerization of **3** to afford polyphenylene **4** in 67% yield (M_n =15300 and M_w/M_n =1.80).

The nickel complex of chiraphos was also found to be available for polythiophene synthesis. The polymerization of 2-chloro-3-hexylthiophene **5a**²¹ employing nickel-chiraphos complex of chiraphos as a catalyst. Addition of **2** to the metalated thiophene, which was prepared by the reaction of **5** with magnesium amide TMPMgCl lithium salt (TMP: 2,2,6,6-tetramethylpiperidin-1-yl)²², at room temperature initiated the polymerization reaction in the presence of 1.0 mol% of catalyst **2**. The reaction was terminated after stirring for 12 h to afford polythiophene **6** in 67% yield with M_n =15800 and M_w/M_n =1.66. These results show that the nickel salt of thiocyanate, which have been employed for the isolation of a ligand by complexation, is available as a catalyst of cross-coupling polymerization reactions. The catalytic reactivity of nickel(II) thiocyanate complex **2** is similar with that of the related complexes formed by other nickel(II) salts NiCl₂, Ni(acac)₂, etc.⁶ The corresponding polymers **4** and **6** were obtained in good yields and the molecular weight and the molecular weight distribution of the obtained polymers were also comparable.



Scheme 2 Synthesis of poly(1,4-phenylene) **4** and poly(3-substituted-thiophene) **6** catalyzed by Ni(NCS)₂-chiraphos complex **2**

We next studied the effect of the bidentate phosphine ligand in the polymerization of thiophene derivative **5** employing Ni(NCS)₂. Nickel complexes composed of bidentate phosphine DPPE (**7a**)²³ and DPPP (**7b**)²⁴ were prepared in a similar manner to that of chiraphos⁷ and employed for the polymerization of thiophene **5**. As summarized in Table 1, the reaction of chlorothiophene **5a** proceeded smoothly. The reaction with Ni(NCS)₂ complex of **7a** and **7b** afforded polythiophene **6** in 66% and 74% yield, respectively with M_n 13000–18000 and M_w/M_n of 1.6–2.0. These results are comparable with that of the corresponding nickel complex of NiCl₂ bearing **7a** and **7b**. (NiCl₂(dppe) : 61% yield; M_n = 16300, M_w/M_n = 1.9, NiCl₂(dppp) : 70% yield; M_n = 15900, M_w/M_n = 1.6) It was also found that the reaction of

bromothiophene **5b** proceeded in a similar manner with DPPE or DPPP complex of Ni(NCS)₂ to afford polythiophene **6** in 78–92% yield with M_n = 15800 and M_w/M_n = 1.7 (with **7a**) and M_n = 13200 and M_w/M_n = 1.9 (with **7b**). In contrast, nickel thiocyanate salt of triphenylphosphine **8**⁷ did not undergo polymerization at all. The result was also similar to the case of NiCl₂ complex.

Table 1 Polythiophene synthesis employing Ni(NCS)₂-phosphine complex^a

thiophene	ligand	yield, % ^b	M_n^c	M_w/M_n^c
5a	DPPE(7a)	66	18000	2.02
	DPPP(7b)	74	13700	1.62
	PPh ₃ (8) ^d	8	-	-
5b	7a	78	15800	1.66
	7b	92	13200	1.87

^a The reaction was carried out with 2-halo-3-hexylthiophene (0.3 mmol) and TMPMgCl·LiCl (0.36 mmol) in THF (3.0 mL) at room temperature for 10 min followed by the addition of Ni(NCS)₂-phosphine complex (1.0 mol%) and stirring at room temperature for 12 h. ^b Isolated yield. ^c Measurement by SEC (size exclusion chromatography) analysis based on the calibration by polystyrene standards. ^d The ratio of Ni(NCS)₂/PPh₃: 1/2)

Formation of N-heterocyclic carbene (NHC)²⁵ complex of Ni(NCS)₂ was also examined by the reaction of Ni(NCS)₂ with an equimolar amount of IPr (N,N'-(2,6-diisopropylphenyl)dihydroimidazolium-1-ylidene) in ethanol in a similar manner to that of the related phosphine complex. However, precipitation was not formed after stirring for 1 h. Although concentration of the solvent was attempted to form a crude solid, further purification and characterization of the complex has not been successful (see Supporting Information). We then examined the polymerization of thiophene **5** with the in situ formed nickel complex with Ni(NCS)₂/2PPh₃ and IPr (1:1)²¹ at room temperature for 1 h in THF. When the reaction was carried out with 1 mol% of in situ formed catalyst, polymerization of chlorothiophene **5a** took place to afford polythiophene **6** in 88% yield (M_n = 14400, M_w/M_n = 1.3). Polymerization of **5a** was also examined with the in-situ formed Ni(NCS)₂ complex of bidentate phosphine ligands **7a–7c** to afford polythiophene **6** in moderate to good yield.

These results are summarized in Table 2. When DPPP (**7b**) was employed as a ligand, the polymerization proceeded in 75% yield with M_n = 15000 (M_w/M_n = 2.4). The use of DPPF (1,1'-ferrocene-bis(diphenylphosphine)) (**7c**) also proceeded the reaction in excellent yield with the reasonable average molecular weight (M_n = 18400, M_w/M_n = 2.0) whereas the reaction with the corresponding DPPE complex resulted in an inferior yield and low molecular weight. We have also examined the effect of other NHC ligands and found that the use of SIPr also promoted the polymerization. However, the reaction with IMes (bearing mesityl group as an N-substituent) as a ligand resulted in a much lower yield similar to the case of the reaction with a NiCl₂ complex we have shown previously.²¹

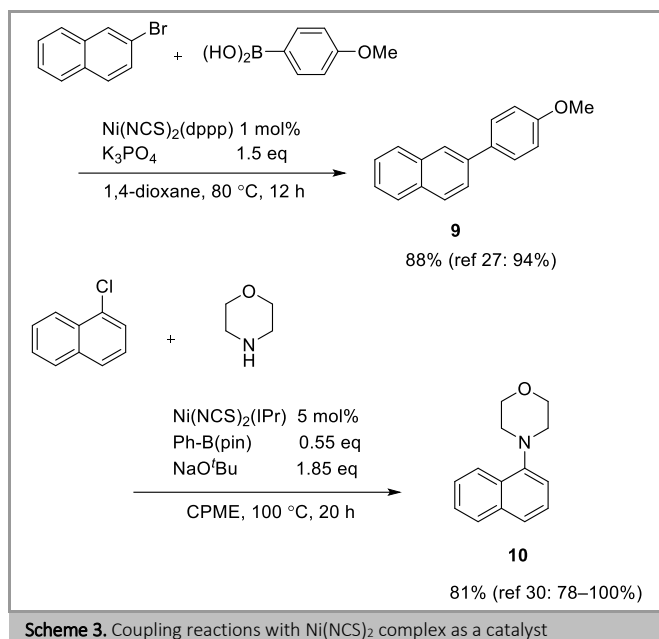
Table 2 Synthesis of polythiophene **6** with in-situ formed nickel complex of bidentate phosphine or NHC ligand^a

ligand	yield, %	M_n^b	M_w/M_n^b

IPr	88	14400	2.33
DPPP(7b)	75	15000	2.40
DPPE(7a)	43	6500	1.29
DPPF(7c)	145	18400	2.00
SIPr ^c	84	30800	2.30
IMes ^c	13	12400	2.67

^a Unless specified, the reaction was carried out with **5a** (0.3 mmol) and TMPMgCl-LiCl (0.36 mmol) in THF (3.0 mL) at room temperature for 10 min followed by the addition of Ni(NCS)₂-ligand (1.0 mol%) and stirring at room temperature for 12 h. ^b Determined by SEC analysis based on polystyrene standards. ^c Prepared from the corresponding HCl salt.

Nickel complex formed by the reaction of Ni(NCS)₂ with a ligand was also available for other catalytic synthetic reactions. As shown in Scheme 3, Suzuki–Miyaura coupling²⁶ of 2-bromonaphthalene with 4-methylphenylboronic acid proceeded when the nickel(II) complex of Ni(NCS)₂dppp was employed as a catalyst (1 mol%). The reaction at 80 °C for 12 h in 1,4-dioxane afforded the coupling product **9** in 88% yield.²⁷ Buchwald–Hartwig coupling^{28,29} also proceeded with 5 mol% of nickel(II) complex composed of N-heterocyclic carbene ligand (Ni(NCS)₂/IPr). When the reaction was carried out with 1-chloronaphthalene and morpholine at 100 °C for 20 h in CPME, amination proceeded in 81% yield to afford the coupling product **10**.²⁹ Yields of these reactions were comparable with the reported ones employing the related nickel complexes as a catalyst^{27,30} representing that nickel thiocyanate also served as a catalyst species of these coupling reactions.



Scheme 3. Coupling reactions with Ni(NCS)₂ complex as a catalyst

In summary, we have shown that nickel(II) thiocyanate complex bearing several phosphine or NHC ligands, which have been employed for the complexation of chiral bidentate phosphine chiraphos for the isolation and purification, is available for the catalyst of polymerization and cross-coupling reactions. Although such a NCS complex has hardly been recognized for the use of catalysis, we have revealed that Ni(NCS)₂ bearing several kinds of ligand undergo cross coupling polymerization to afford poly(1,4-phenylene) and poly(3-substituted thiophene). Several catalytic coupling reactions were also shown to proceed with Ni(NCS)₂ complex. Since Ni(NCS)₂ complexes bearing a variety of

ligands are stable and easily prepared, the use of such complexes as a catalyst would be widely available for other synthetic and polymerization reactions.³¹

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Acknowledgment

Supporting Information

Supporting Information for this article is available online at <http://doi.org/@@@>

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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- (31) **General procedure for the preparation of poly(3-hexylthiophene) (6):** To 20 mL Schlenk tube equipped with a magnetic stirring bar was added 2-chloro-3-hexylthiophene (**5a**) (60.8 mg, 0.3 mmol) at room temperature followed by the addition of $\text{TMPPMgCl}\cdot\text{LiCl}$ (chloromagnesium 2,2,6,6-tetramethylpiperidine-1-yl lithium chloride salt) (1.0 M, 0.36 mL, 0.36 mmol) and 0.3 mL of THF. After stirring at room temperature for 10 min, the mixture was diluted with 3.0 mL of THF followed by the addition of $\text{Ni}(\text{NCS})_2[(S,S)\text{-chiraphos}]$ (**2**) (1.86 mg, 0.003 mmol). After the reaction mixture was stirred at room temperature for 12 h, the mixture was poured into a mixture of hydrochloric acid (0.30 mL) and methanol (1.0 mL) to form a precipitate, which was filtered off

to leave a crude solid. The residue was washed with methanol and hexanes repeatedly and dried under reduced pressure to afford 55.0 mg of **6** (67%). Spectroscopic characteristics were identical with the authentic sample. The molecular weight and the molecular weight distribution was determined by SEC analysis using chloroform as an eluent. $M_n = 15700$, $M_w/M_n = 1.7$.