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Research on carbon–carbon coupling reactions of haloaromatic compounds mediated by zerovalent nickel complexes. Preparation of cyclic oligomers of thiophene and benzene and stable anthrylnickel(II) complexes

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Abstract

Dehalogenative carbon–carbon coupling reactions of 3,4-dibromothiophene, 1,2-dihalobenzenes and 9-bromoanthracene using zerovalent nickel complexes as a dehalogenating reagent produced respectively cyclotetrathiophene, triphenylene and 9,9′-bianthracene in good yields. However, two extremely stable arylnickel(II) complexes, $Ni(10\text{-}X\text{-}9\text{-anthryl})X(PPh_3)_2$ ($X = Br, Cl$), where the 10-C–X bond in the anthryl groups was inert against excess Ni^0 complexes, were obtained by oxidative addition of 9,10-dihaloanthracenes to the Ni^0 complexes. Under similar reaction conditions 9,10-dihaloanthracenes did not undergo carbon–carbon coupling reactions.

Introduction

It is well known that aryl halides react with zerovalent nickel complexes to yield dehalogenative carbon–carbon coupling products or to form organometallic complexes of nickel(II) [1,2], presumably through reductive coupling from diorganonickel(II) complexes [3]. The coupling reactions have been widely used in organic [2] as well as macromolecular [4,5] syntheses. The general patterns of these coupling reactions are shown in eq. 1 and eq. 2, respectively.

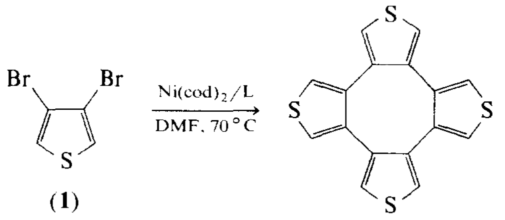
$$2\,ArX + NiL_m \longrightarrow Ar{-}Ar + NiX_2L_m \qquad (1)$$

$$n\,X{-}Ar{-}X + n NiL_m \longrightarrow {-}\!\!(Ar)\!\!{-}_n + n\,NiX_2L_m \qquad (2)$$

However, the coupling reactions of *ortho*-dihaloaromatic compounds and of bulky aromatic halides mediated by zerovalent nickel complexes have received much less attention. During our research on synthesis of new electrically conducting poly(arylene)s involving study of carbon–carbon coupling reactions of dihaloaromatic compounds, we found that Ni^0 complexes served as good reagents for the coupling of *ortho*-dihaloaromatic compounds. For example 3,4-dibromothiophene (**1**), 1,2-dibromobenzene (**3**) and 1,2-dichlorobenzene (**4**) as well as the bulky 9-bromoanthracene (**6**) react to afford the cyclic tetramer cyclotetrathiophene (**2**), the cyclic trimer triphenylene (**5**) and the dimer 9,9′-bianthracene (**7**), respectively. We also attempted to exploit the coupling reaction of 9-bromoanthracene to synthesize the π-conjugated poly(9,10-anthracenediyl) from 9,10-dihaloanthracenes by the previously developed nickel-complex coupling method [4] (eq. 2). However, the predictable carbon–carbon coupling reactions did not occur and intermediate compounds of new stable nickel(II) complexes, *trans*-Ni(10-X-9-anthryl)X$(PPh_3)_2$ (X = Br, **10**; Cl, **11**) from 9,10-dibromoanthracene **8** and 9,10-dichloroanthracene **9** were produced. Here, we report the results.

Results and discussion

Table 1 summarizes results of the treatment of 3,4-dibromothiophene (**1**), 1,2-dibromobenzene (**3**) and 1,2-dichlorobenzene (**4**) with the Ni^0 complexes, which were typically mixtures of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, and neutral ligands such as triphenylphosphine (PPh_3) and 2,2′-bipyridine (bpy). The reaction of 3,4-dibromothiophene (**1**) with zerovalent nickel complexes proceeded smoothly at 70 ° C to yield the corresponding cyclic tetramer cyclotetrathiophene (**2**) (reaction 3).



(**1**)

(**2**)

(3)

Kauffmann and co-workers [6] reported preparation of compound **2** by treatment of a more complicated compound, 4,4′-dibromo-3,3′-bithiophene, with n-C_4H_9Li followed by oxidative coupling in the presence of $CuCl_2$ or $FeCl_3$. However, the yield was considerably lower (ca. 23%), and the method using the Ni^0 complex and

Table 1

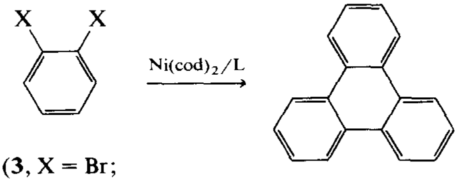
Preparation of cyclotetrathiophene (**2**) and triphenylene (**5**)

Run	Monomer	Complex/L [a]	Conditions	Product	Yield (%)
1	**1**	$Ni(cod)_2/PPh_3$	DMF, 70 °C 22 h	**2**	64 [b]
2	**1**	$Ni(cod)_2$/bpy	DMF, 70 °C 20 h	**2**	70 [b]
3	**3**	$Ni(cod)_2$/bpy	THF, reflux 20 h	**5**	37 [b]
4	**3**	$Ni(cod)_2/PPh_3$	DMF, 70 °C 26 h	**5**	60 [c]
5	**4**	$Ni(cod)_2$/bpy	DMF, 70 °C 20 h	**5**	9 [c]
6	**4**	$Ni(cod)_2$/bpy	THF, reflux 20 h	**5**	11 [c]

[a] $Ni(cod)_2$: L = 1 : 1 (molar ratio). [b] Isolated yield. [c] Measured by gas chromatography (1,3,5-triphenylbenzene used as internal standard).

3,4-dibromothiophene is more suitable to the preparation of compound **2**. Compound **2** has been characterized by elemental analysis, IR and mass spectroscopy as well as by comparison of its UV–visible and ^{1}H NMR properties with those reported in the literature [6].

The reaction of 1,2-dihalobenzenes with zerovalent nickel complexes also gave a cyclic compound (reaction 4).



(4)

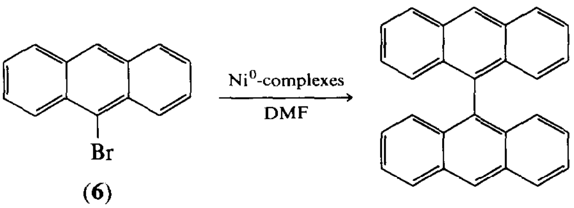
(**3**, X = Br;
4, X = Cl)

(**5**)

The product from both 1,2-dibromobenzene (**3**) and 1,2-dichlorobenzene (**4**) was a cyclotrimer, triphenylene (**5**). The main byproducts as determined by GC–mass spectroscopy were biphenyl, 2-halobiphenyl and 2,2′-dihalobiphenyl. Triphenylphosphine is a better ligand than 2,2′-bipyridine in this reaction, and triphenylene (**5**) prepared from 1,2-dibromobenzene (**3**) afforded higher yield than that prepared from 1,2-dichlorobenzene (**4**). Compound **5** has been characterized by comparison of its m.p. and ^{1}H NMR data with those reported in the literature [7] as well as by elemental analysis and mass spectroscopy. The reaction is also a more useful method for the preparation of compound **5** than the reported methods [7,8].

The results of the reaction of 3,4-dibromothiophene **1** with zerovalent nickel complexes (reaction 3) are very different from those of 1,2-dihalobenzenes **3** and **4** (reaction 4), although the coupling conditions are almost the same. Reaction 3 produces cyclotetramer **2** and the yield is almost independent of the ligand (PPh_3 or bpy) added to $Ni(cod)_2$. However, reaction 4 just produces cyclotrimer **5** and the yield is strongly dependent on the ligand. The difference may originate from the volume of a five-membered thiophene ring being smaller than that of a six-membered benzene ring, so production of the cyclotetramer is favourable for the former and of the cyclotrimer for the latter in these reactions. It is reported that cyclotetrathiophene (**2**) [9] has a tub conformation where *ortho*-thiophene rings are twisted by an angle of 53.7°, whereas triphenylene **5** probably has a more rigid planar conformation [10]. On these bases, triphenylene **5** seems to have more strict requirements for its space environment (dependent on the ligand) than cyclotetrathiophene (**2**) during its formation.

In addition, we have been interested in the coupling reaction of bulky 9-bromoanthracene (**6**) mediated by the zerovalent nickel complex. The coupling reaction from 9-bromoanthracene produced the dimeric product, 9,9′-bianthracene (**7**) (reaction 5).



(5)

(**6**)

(**7**)

Table 2

Preparation of 9,9′-bianthracene (**7**)

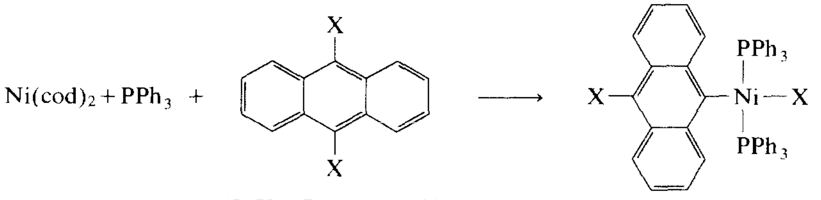
Run	Complex	9-Br-anthracene : Ni-complex	Conditions	Yield (%) [a]
1	$Ni(cod)_2$/bpy(1 : 1)	1 : 1	70 °C, 17 h	16
2	$Ni(cod)_2$/bpy(1 : 1)	2 : 1	70 °C, 9 h 100 °C, 16 h	6
3	$NiBr_2$/Zn/bpy [b]	1 : 1	70 °C, 28 h 100 °C, 3 h	9
4	$NiBr_2$/Zn/PPh_3 [b]	1 : 1	70 °C, 28 h 100 °C, 3 h	52
5	$NiBr_2$/Zn/PPh_3 [b]	2 : 1	70 °C, 28 h 100 °C, 3 h	38

[a] Isolated yield. [b] Ni^0-complex was prepared *in situ* by a reduction of $NiBr_2$ with Zn powder in the presence of bpy ($NiBr_2$: Zn : bpy = 1 : 1 : 2) or PPh_3 ($NiBr_2$: Zn : PPh_3 = 1 : 1 : 4) [17].

Compound **7** has been synthesized by several methods; one useful method was reported by Bell and Waring [11] using an oxidative coupling reaction from Grignard reagent (9-MgBr-anthracene + $CuCl_2 \rightarrow$ bianthracene).

The coupling results mediated by zerovalent nickel complexes are listed in Table 2. The yield of dimeric product was raised if excess nickel complex was used. Triphenylphosphine is better as the ligand of nickel(0) complexes than 2,2′-bipyridine. The yield of run 4 in Table 2 approaches the yield (58%) attained by Bell and Waring [11]. These results clearly indicate that the carbon–carbon coupling reaction of the anthryl group at 9 or 10-positions can proceed, mediated by zerovalent nickel complex.

Prompted by the results of coupling 9-bromoanthracene, we attempted to synthesize electrically conducting poly(9,10-anthracenediyl) from the bulky aromatic dihalides, 9,10-dibromoanthracene (**8**) and 9,10-dichloroanthracene (**9**), by a similar nickel-complex coupling method [4]. Although we treated 9,10-dihaloanthracenes with various Ni^0 complexes, the expected carbon–carbon coupling products of polymer or oligomer were not obtained. The reaction stopped at the oxidative addition of the monomer to the zerovalent nickel complex when triphenylphosphine was used as the ligand. The nickel(II) complexes **10** and **11** were thus obtained (reaction 6). When 2,2′-bipyridine was used instead of triphenylphosphine, no corresponding complexes were isolated and the starting compounds of 9,10-dihaloanthracenes were recovered.



(6)

(**8**, X = Br; **9**, X = Cl)

(**10**, X = Br; **11**, X = Cl)

Table 3 summarizes the results of reaction 6. Complex **10** is more easily produced than complex **11**. As shown in Table 3, the activity of the mixture of $Ni(cod)_2$ and

Table 3

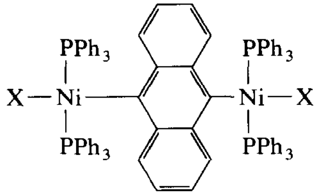
Formation of nickel complexes **10** and **11**

Run	Monomer	Complex [a]	Solvent	Conditions	Product	Yield(%)
1	**8**	$Ni(cod)_2/PPh_3$	DMF	60 °C, 5 h	**10**	58
2	**8**	$Ni(cod)_2/PPh_3$	THF	60 °C, 8 h	**10**	90
3	**8**	$Ni(cod)_2/PPh_3$	toluene	60 °C, 5 h	**10**	72
4	**9**	$Ni(cod)_2/PPh_3$	DMF	60 °C, 5 h	**11**	36
5	**9**	$Ni(PPh_3)_4$	DMF	r.t., 2 h 60 °C, 9 h	**11**	5 [b]

[a] **8** or **9**: $NiL_n = 1:1$, $Ni(cod)_2 : PPh_3 = 1:2$. [b] 90% of the starting compound of 9,10-dichloroanthracene (**9**) was recovered.

PPh_3 (1 : 2) is higher than that of $Ni(PPh_3)_4$ for the oxidative addition of 9,10-dihaloanthracenes, indicating that presence of an appropriate amount of PPh_3 is favoured whereas coordinatively saturated $Ni(PPh_3)_4$ has only low reactivity. THF is a better solvent than DMF and toluene. Complexes **10** and **11** have been characterized by elemental analysis and IR as well as ^1H, ^{31}P and ^{13}C NMR spectroscopy as summarized in Table 4. The ^{31}P NMR spectra of complexes **10** and **11** each show only one sharp singlet peak at 21.65 ppm and 19.50 ppm, respectively, indicating a *trans*-configuration of the complexes. The X-ray single crystal analysis of the structure of the complexes confirmed the *trans*-configuration; Fig. 1 shows molecular structure of complex **11**, $Ni(C_{14}H_8Cl)Cl(PPh_3)_2$, by X-ray crystallography *. Details of the structural analysis will be reported elsewhere.

We attempted to obtain the following binuclear complex,



by using one equivalent of monomer with two equivalents of zerovalent nickel complex. However, the products remained as the mononuclear complexes **10** and **11**. The *para*-carbon–halogen bond of the anthryl group in the complexes showed itself to the inert to the zerovalent nickel complex. A similar low reactivity of halogen–carbon bond in halopyridylnickel(II) complexes has been reported [12]. The low reactivity of C–X bond in the 10-haloanthryl group may be due to steric hindrance between the anthryl group and two triphenylphosphine ligands as shown in Fig. 1.

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* Single crystals of **11** containing two $CHCl_3$ molecules were obtained by slow evaporation of the $CHCl_3$ solution at room temperature. Crystal data: triclinic; $a = 14.135(5)$, $b = 14.807(4)$, $c = 11.954(4)$ Å, $\alpha = 99.59(2)$, $\beta = 92.94(3)$, $\gamma = 92.37(2)°$, $V = 2460.3$ Å^3; formula $C_{52}H_{40}Cl_8P_2Ni$, $M_w = 1069.2$, $d_{calc} = 1.44$ g cm^{-3}. $R = 0.128$, $R_w = 0.131$. Insufficient convergence of the structure calculation is probably due to severe disorder of the solvent molecules. Selected bond distances and angles with standard deviations in parentheses: Ni–C, 1.87(2) Å; Ni–P1, 2.223(8) Å; Ni–P2, 2.242(8) Å; Ni–Cl1, 2.225(7) Å; C–Ni–P1, 87.6(9)°; C–Ni–P2, 90.5(9)°; C–Ni–Cl, 176.2(9)°; Cl1–Ni–P1, 92.6(3)°; Cl1–Ni–P2, 89.2(3)°; P1–Ni–P2, 176.4(3)°.

Table 4

Analytical and spectroscopy data of nickel complexes **10** and **11**

complex	m.p. (°C)	elemental analysis (%) found (calc.)	IR spectra (cm^{-1})	NMR spectra ($CDCl_3$, ppm)		
				^1H	^{31}P	^{13}C
10	217 (dec.)	C 65.0 (65.3) H 4.1 (4.1) Br 17.7 (17.4)	3048, 1479, 1430, 1295, 1251, 1090, 921, 747, 690, 520.	7.14– 8.07 (m)	21.65 (s)	134.1, 132.0, 131.7, 131.6, 129.2, 128.6, 128.1, 127.1, 127.0, 126.2, 125.6, 125.3.
11	204 (dec.)	C 72.0 (72.3) H 4.8 (4.6) Cl 8.1 (8.5)	3052, 1479, 1431, 1320, 1254, 1091, 937, 747, 691, 521.	7.17– 8.09 (m)	19.50 (s)	134.2, 134.0, 133.7, 132.3, 131.9, 130.8, 129.4, 128.8, 128.3, 127.5, 127.3, 127.1.

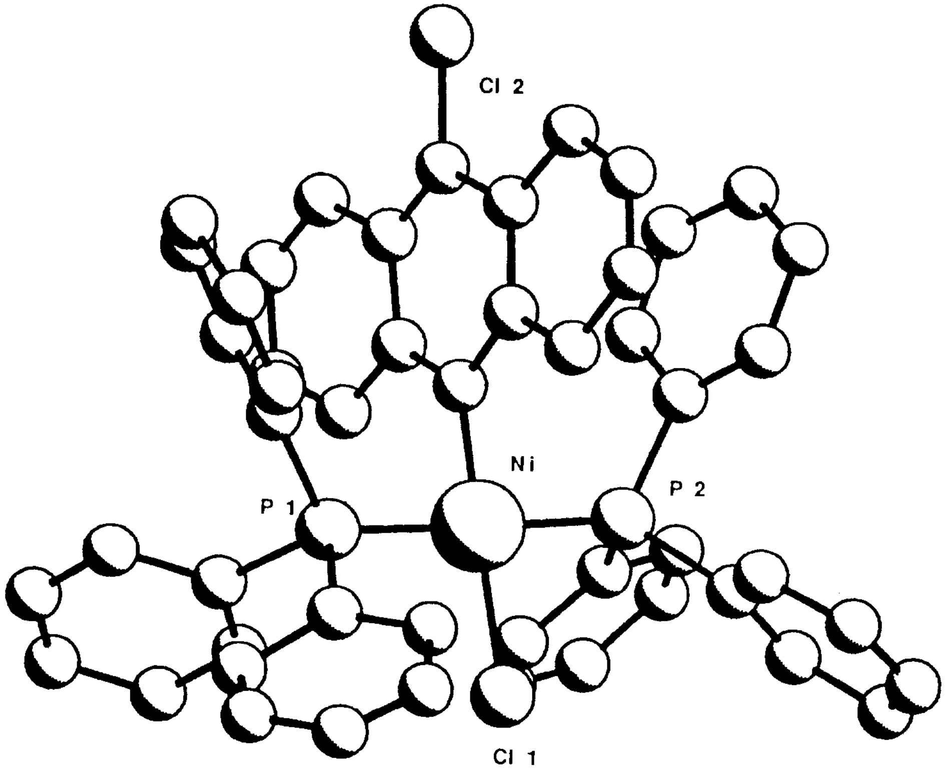

Fig. 1. Molecular structure of $Ni(C_{14}H_8Cl)Cl(PPh_3)_2$, **11**. Solvent molecules are omitted for simplicity. See footnote on previous page.

The shielding effect of phenyl groups in triphenylphosphines prevents a reaction at the 10-C–X bond in the anthryl group; the decrease in electrophilicity of the carbon at the 10-C–X bond caused by back-donation of electron from Ni to the 10-haloanthryl group will also decrease the reactivity of this C–X bond.

It is interesting that complexes **10** and **11** are very stable compared with the usual nickel(II) complexes containing a σ nickel–carbon bond. Upon reaction with hydrochloric acid (2 *M*) in a dispersion system at room temperature followed by exposure to air in boiling toluene for several hours the starting complexes were recovered almost quantitatively. As shown in the footnote on p. 123, one of the reasons for the extremely high stability of the complexes is the very short Ni–C bond length (1.87 Å [13]), which may result from the lowering of the energy of the HOMO orbital of Ni by double bonding to the anthryl group using the π-orbitals of the anthryl group as described by Chatt and Shaw [14]. The high stability of **10** and **11** may also partly originate from the steric effect. The nickel atom is surrounded by electron-rich aromatic rings of the bulky anthryl group, and six phenyl groups in two triphenylphosphine ligands will prevent the attack of a reactant at the nickel centre. As for the steric effect, it has been reported that *o*-substituted arylnickel(II) complexes have high thermal stability [1g, 14].

These results show that the failure to obtain poly(9,10-anthracenediyl) starting from 9,10-dihaloanthracenes and Ni^0 complex is attributable to the low reactivity of complexes **10** and **11**.

Experimental

Materials

Solvents were dried in the usual manner, distilled, and stored under an argon or nitrogen atmosphere. DMF was stored over 4 Å molecular sieves. 3,4-Dibromothiophene was used as purchased from Tokyo Kasei Kogyo Co. Ltd. 9,10-Dihaloanthracenes were recrystallized from toluene. $Ni(cod)_2$ [15] and $Ni(PPh_3)_4$ [16] were prepared according to literature methods.

Measurement and analysis

Infrared spectra were measured on a Jasco IR 810 spectrometer by using KBr pellets. NMR spectra were measured on a JEOL FX-100 or JEOL GX-270 spectrometer by Dr. Y. Nakamura, Ms. A. Kajiwara and Ms. H. Taniguchi of our laboratory. ^{31}P NMR signals are referenced to 85% H_3PO_4 as an external standard, GC analysis was performed on a Shimadzu GC-6A gas chromatograph using a 2% Silicone OV-1 column. GC-mass analysis was carried out with a Hitachi M-80 mass spectrometer. Microanalyses were carried out by Dr. M. Tanaka, Mr. T. Saito and Ms. H. Mochizuki of our laboratory using a Yanagimoto CHN Autocorder Type MT-2 and Yazawa Halogen Analyzer.

Preparation of cyclotetrathiophene (2)

To a solution of $Ni(cod)_2$ (1.43 g, 5.2 mmol) in 12 mL of DMF at room temperature were added 1,5-cyclooctadiene (0.8 mL) and 2,2′-bipyridine (0.81 g, 5.2 mmol). Then a solution of 3,4-dibromothiophene (1.0 g, 4.1 mmol) in 8 mL of DMF was added dropwise. After stirring for 22 h at 70 °C, the mixture was added to about 100 mL of water and extracted with ether. The ether solution was dried over anhydrous $MgSO_4$, filtered and concentrated. The product was separated by column chromatography (silica gel). Hexane was used as the first developing solvent, and then ether was added. The product was recrystallized from ether; 234 mg of light yellow needles were obtained (yield 70%). M.p. 299–300 °C (lit. [6] m.p. 300–301 °C). IR (3089, 850, 787 cm^{-1}). ^1H NMR ($CDCl_3$, ppm): 7.20 (s). Mass (*m/e*): 328 (M^+, 100%). Elemental analysis. Found: C, 58.9; H, 2.6. Calc.: C, 58.5; H, 2.4%.

Preparation of triphenylene 5

The procedure was similar to the preparation of cyclotetrathiophene **2**. After completion of the reaction, the mixture was separated by column chromatography and the product was recrystallized from methanol (run 3 in Table 1). 1,3,5-Triphenylbenzene was added to the mixture as an internal standard of gas chromatography for measurement of yield of the product (runs 4, 5, 6 in Table 1). M.p. 202–203 °C (lit. [7b] m.p. 199 °C). ^1H NMR ($CDCl_3$, ppm): 8.67 (q, $J_1 = 6.1$ Hz, $J_2 = 3.4$ Hz, 6 H), 7.66 (q, $J_1 = 6.2$ Hz, $J_2 = 3.4$ Hz, 6 H). Mass (*m/e*): 228 (M^+, 100%). Elemental analysis. Found: C, 94.5; H, 5.0. Calc.: C, 94.7; H, 5.3%.

Preparation of 9,9′-bianthracene 7 (run 4 in Table 2 as an example)

To a suspension of anhydrous $NiBr_2$ (0.425 g, 1.9 mmol) in 20 mL of THF was added PPh_3 (1.99 g, 7.6 mmol). The mixture was stirred for 1 h at room temperature and then stirred at 50 °C for 2 h. Active zinc powder (0.124 g, 1.9 mmol) was then added and the mixture was allowed to react for 2 h at 60 °C. 9-Bromoanthracene (0.50 g, 1.9 mmol) was added directly to the reaction mixture and this was stirred for 28 h at 60 °C and then 3 h at 100 °C. After cooling to room temperature, the reaction mixture was added to 50 mL of a 1 : 1 mixture of concentrated ammonia and water and extracted with toluene. The toluene solution was dried over anhydrous $MgSO_4$ and concentrated. The residue was separated by PLC (Merck silica gel F-254); the developing solvent was hexane and then hexane/ether. 176 mg of dimer-product was obtained and the yield was 52%. M.p. 304–306 °C (lit. [11] m.p. 308 °C). ^1H NMR ($CDCl_3$, ppm): 8.80 (s, 2 H, 10,10′-H), 8.25 (d, $J = 7.8$ Hz, 4 H, 4,5,4′,5′-H), 7.2–7.7 (m, 12 H). Mass (*m/e*): 354 (M^+, 100%).

Preparation of trans-*halo(10-halo-9-anthryl)bis(triphenylphosphine)nickel (**10** and **11**)*

The typical procedure (run 2 in Table 3) was as follows. To a solution of $Ni(cod)_2$ (0.90 g, 3.3 mmol) in 18 mL of dry THF at room temperature were added 1,5-cyclooctadiene (0.7 mL) and PPh_3 (1.73 g, 6.6 mmol). Then a solution of 9,10-dibromoanthracene (1.0 g, 2.9 mmol) in 35 mL of THF was added dropwise. After stirring the reaction mixture for 8 h at 60 °C, a yellow precipitate was obtained. The product was separated by filtration, washed with toluene, then recrystallized from THF and dried under vacuum to obtain 2.42 g (yield 90%) of complex **10**.

Acknowledgements

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