Preparation of Diarylthiolatonickel(II) Complexes, $Ni(SAr)_2L_2$, by Oxidative Addition of Diaryl Disulfides to Ni(0) Complexes and Ni-Catalyzed Coupling Reactions between Thiophenols and Aryl Halides

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Reactions of $Ni(cod)_2$ with diaryl disulfides in the presence of basic ligands proceed smoothly at room temperature to give oxidative addition products formulated as $Ni(SAr)_2L_2$ ($SAr = SC_6H_5$, SC_6H_4-p-Cl, SC_6H_4-p-CH_3, SC_6H_4-p-NO_2; L = bpy, PEt_3) in 40–79% yields. The complexes obtained have been characterized by elemental analysis, i.r. and n.m.r. spectroscopy, and by their chemical reactivities. $Ni(SPh)_2(bpy)_2$ shows paramagnetism with μ_{eff} of 3.05 B.M. in the solid state and electric conductivity in solutions. $Ni(SPh)_2(bpy)_2$ reacts with organic iodides to give the corresponding sulfides. $Ni(SPh)_2(bpy)_2$ and $NiCl_2(bpy)_2$ serve as good catalysts for coupling reactions between sodium thiophenolates and aryl halides to yield the corresponding sulfides in good yields.

Introduction

Although a number of reports have been published on the oxidative addition of disulfides, RSSR, to Fe [1], Rh [2], Mo [1c, 1d, 3] and V [4] complexes, oxidative addition of RSSR to complexes of other transition metals has not been so well explored. As for Ni, a photoinduced oxidative addition of perfluoro disulfides to $[(\eta^5\text{-}C_5H_5)Ni(CO)]$ [1c, 1d] and an oxidative addition of diphenyl disulfide, PhSSPh, to a nickel carbonyl complex have been briefly reported [5]. However, only a little is known concerning the physical properties and chemical reactivities of the dithiolatonickel complexes. In order to get more information about the oxidative addition of RSSR to Ni and to reveal the physical properties and chemical reactivities of the dithiolatonickel(II) complexes, we first investigated reactions of diaryl disulfides, ArSSAr, with bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, in the presence of basic ligands, L, to find out that ArSSAr undergoes facile oxidative addition to the highly reactive Ni(0) species [6] under mild conditions without irradiation of UV. Secondly we characterized the diarylthiolatonickel(II) complexes, $Ni(SAr)_2L_n$, and then investigated reactions of the complexes with organic iodides, R′I, to find out that the reactions afford ArSR′. Application of this reactions to an Ni-catalyzed synthesis of sulfides from thiophenols and organic halides has been also investigated. We now report the results obtained.

Results and Discussion

Oxidative Addition of ArSSAr to Ni(0) Complexes

When ArSSAr is added to a mixture of $Ni(cod)_2$ and 2,2′-bipyridine (bpy) or triethylphosphine (PEt_3) at room temperature, an instant change of color is observed, indicating that the oxidative addition of ArSSAr to the Ni(0) species is a very rapid process,

$$Ni(cod)_2 + ArSSAr + 2L \longrightarrow Ni(SAr)_2L_2 \qquad (1)$$

(*1*) Ar = Ph, L = bpy (Ph = C_6H_5)
(*2*) Ar = C_6H_4–*p*-Cl, L = bpy
(*3*) Ar = C_6H_4–*p*-NO_2, L = bpy
(*4*) Ar = Ph, L = PEt_3
(*5*) Ar = C_6H_4–*p*-CH_3, L = PEt_3

Table I shows analytical data and some physical properties of complexes (*1*)–(*5*). Yields of crude complexes (*1*)–(*3*) exceeded 80%. Even when the reaction of $Ni(cod)_2$ with diphenyl disulfide, PhSSPh, is carried out in the presence of only 1 mol of bpy per mol of $Ni(cod)_2$, the reaction affords the 20-electron complex (*1*), but a 16-electron complex having one bpy ligand, $Ni(SPh)_2(bpy)$, is not obtained; the yield of (*1*) is naturally lower than 50% under

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TABLE I. Yield, Melting Point, and Analytical Data of $Ni(SAr)_2L_2$.

Complex	Yield[a] (%)	M.P. (°C)	Analytical Data (%) C	H	N	S	Ni
(*1*)	52	209–210	64.9 (65.2)	4.3 (4.5)	9.4 (9.5)	10.9 (10.9)	10.3 (10.0)
(*2*)	54	177–178	58.1 (58.4)	4.0 (3.7)	8.5 (8.5)		
(*3*)	60	204–205	56.8 (56.6)	3.6 (3.6)	12.5 (12.4)	9.2 (9.4)	
(*4*)	40	110–111	55.7 (56.1)	7.5 (7.9)		12.7 (12.5)	
(*5*)	79	112–114	57.8 (57.7)	8.3 (8.2)		11.7 (11.8)	

[a] Yield after recrystallization.

the reaction conditions. This indicates that the 20-electron complex (*1*) is stabler than the 16-electron complex. Complex (*1*) can be prepared also through an ion exchange reaction between $NiCl_2(bpy)$ and $C_6H_5S^-$ in the presence of bpy,

$$NiCl_2(bpy) + 2C_6H_5SNa + bpy \longrightarrow (1) \qquad (2)$$

The formation of (*2*) having Cl-substituted aromatic ring, which is known to undergo facile oxidative addition to Ni(0) complexes [6], indicates that the oxidative addition of the S–S bond is an easier process than the oxidative addition of the C–Cl bond.

When PEt_3 is employed, the 16-electron complexes (*4*) and (*5*) are obtained exclusively. As for (*4*), its preparation through an independent reaction route (an ion exchange between $NiCl_2(PEt_3)_2$ and $C_6H_5S^-$) has been reported by Hayter and coworkers [5]. Other reaction systems, including $Ni(cod)_2$–di(*p*-tolyl) disulfide–bpy (1:1:2) and $Ni(cod)_2$–PhSSPh–dpe (dpe = 1,2-bis(diphenylphosphino)-ethane (1:1:1), also afford the oxidative addition products as revealed by (i) rapid color change of the reaction system on mixing the reactants, (ii) evolution of the corresponding thiophenol on acidolysis of the product with dry HCl (the yield of thiophenol = 80–85% of the amount calculated by assuming that the product has a composition of $Ni(SAr)_2L_n$ (n = 2 for bpy and n = 1 for dpe)), and (iii), their i.r. spectra showing absorption bands assignable to SAr and L ligands. Isolation of the complexes formed has not been successful, due to lack of suitable solvents for recrystallization. As for the $Ni(cod)_2$–PhSSPh–dpe system, the oxidative addition is retarded when 2 mol of dpe per mol of $Ni(cod)_2$ is added.

In contrast to the reaction of diaryl disulfide, a similar reaction of a dialkyl disulfide, EtSSEt, with $Ni(cod)_2$ in the presence of bpy affords a complex having no bpy ligand. Its i.r. spectrum shows only absorption bands assignable to SEt ligands at 2950, 2910, 2850, 1440, 1360, 1245, 1040, 1015, 965, 800, and 750 cm^{-1}. Since bis(ethylthiolato)nickel is known to form cluster-like $[Ni(SEt_3)_2]_6$ [7], the product obtained in the above-mentioned reaction seems to be assignable to a complex having such a cluster structure.

Properties of the Complexes

The bpy-coordinated complexes (*1*)–(*3*) are stable for about 1 h under an atmosphere of air in the solid state, but they decompose after 1 day. They are sensitive to air in solutions. The PEt_3-coordinated complexes (*4*) and (*5*) are very sensitive to air both in the solid state and in solutions.

Complexes (*1*)–(*3*) are soluble in alcohols such as methyl alcohol and ethyl alcohol. Acetone, THF, and 1,4-dioxane also dissolve them, but their solubility in these solvents is not high. The complexes are insoluble in hydrocarbons and diethyl ether. Complexes (*4*) and (*5*) are soluble in various organic solvents.

Complexes (*1*)–(*5*) have moderate thermal stability. Thermolysis of (*1*) at 250 °C for 20 min affords 0.98 mol of bpy, 0.92 mol of diphenyl sulfide, and 0.04 mol of diphenyl disulfide per mol of (*1*). The liberation of these products suggests formation of nickel sulfide in the thermolysis ((*1*) → NiS(bpy) + PhSPh + bpy).

Complex (*1*) shows paramagnetism with μ_{eff} = 3.05 B.M. at room temperature, and consequently its NMR spectrum only shows broad signals. On the other hand, the PEt_3-coordinated complex (*4*) is diamagnetic, suggesting that the Ni(II) center has a pseudo-square planar configuration. Complex (*1*) shows some electric conductivity in a methanol

TABLE II. Reactions of $Ni(SPh)_2(bpy)_2$ with Iodides, RI.[a]

Run	Iodide[b]	Solvent	Temp. (°C)	Product (% per RI)		
				PhSR	PhSPh	PhSSPh
1	CH_3I	methanol	r.t.	62	0	20
2	C_2H_5I	methanol	r.t.	47	0	20
3	n-C_3H_7I	methanol	r.t.	47	0	17
4	CH_3I	butanol	100	82	4	13
5	C_2H_5I	butanol	100	71	1	30
6	n-C_3H_7I	butanol	100	52	3	16
7	i-C_3H_7I	butanol	100	45	0	13
8	n-C_4H_9I	butanol	100	66	0	0
9	PhI	butanol	100	50	0	0
10	TolI	butanol	100	55	17	0
11	p-$NO_2C_6H_4I$	butanol	100	70	15	8

[a] Amount of (*1*) = 0.07–0.19 mmol. Molar ratio of RI to (1) = 2.0. Reaction time: 24 h for Runs 1–3 and 8 h for Runs 4–11.
[b] PhI = phenyl iodide. TolI = tolyl iodide. p-$NO_2C_6H_4I$ = p-nitrophenyl iodide.

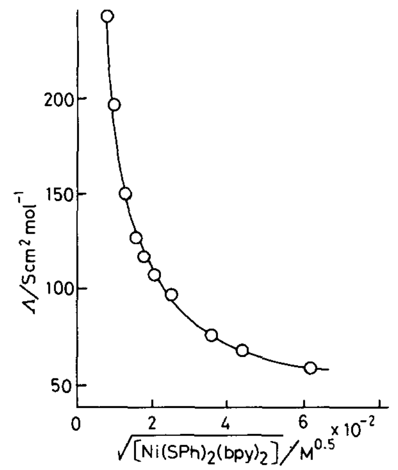

Fig. 1. Dependence of equivalent conductivity against square root of the concentration of (*1*).

solution, indicating the occurrence of the following ionic dissociation in methanol,

$$(1) \longrightarrow [Ni(SPh)(bpy)_2]^+ + PhS^- \qquad (3)$$

The dependence of the equivalent conductivity on the square root of the concentration of (*1*) is shown in Fig. 1.

I.r., ^{1}H-n.m.r., and u.v. Spectroscopy and Molecular Structure

I.r. spectra of (*1*)–(*5*) showing absorption bands due to both the thiolato and bpy or PEt_3 ligands are consistent with the formulation given in Eq. 1. The i.r. spectra show absorption bands at about 400 cm^{-1} which may be assigned to ν(Ni–S) [8]. The bands disappear on acidolysis of the complexes by dry HCl. The $\nu(NO_2)$ absorption band of (*3*) appears at the same position (1310 cm^{-1}) as those of free aromatic nitro compounds, indicating that the NO_2 group does not have interaction with the Ni of other molecules.

The ^{1}H-n.m.r. spectrum of (*4*) is consistent with the formulation. The $^{31}P\{^1H\}$-n.m.r. spectrum of (*4*) shows a sharp singlet at 9.7 ppm downfield from external PPh_3. An electron spectrum of (*1*) shows a strong (ϵ = 7000) absorption band at 488 nm, which is assigned to the lowest energy Ni → bpy CT band. The highest energy level of Ni in (*1*) estimated from the position of the CT band, 7.1 eV, is lower by about 0.5 eV than the highest occupied energy level of Ni in dialkyl(2,2′-bipyridine)nickel(II), NiR_2(bpy) [9], demonstrating a stronger electron-withdrawing effect of the SC_6H_5 ligand than the alkyl ligand.

Although a number of Ni complexes having a composition of $NiX_2(bpy)_2$ (X = Cl, Br, etc.) are known [10], it has not been established whether they actually possess 20-electron structures having σ-bonded X ligands or ionic 16-electron structures, namely $[Ni(bpy)_2]X_2$. As for the molecular structure of (*1*), it has been established by single crystal X-ray crystallography [11] that (*1*) has a pseudo octahedral structure around Ni having σ-bonded SPh ligands. This pseudo octahedral structure is, from a view point of a ligand field theory [12], consistent with the high spin character of the complex described above. The Ni–SPh bond in (*1*) is, however, cleav-

TABLE III. Ni-Catalyzed Coupling Reactions between ArSNa and Phenyl Halide or *p*-Substituted Phenyl Halides, *p*-YC_6H_4X.

Expt.	Catalyst[a] (mmol)	ArSNa[b] (mmol)	*p*-YC_6H_4X[c] (mmol)	Solvent[d]	Temp. (°C)	Time (h)	Product (%-yield based on ArSNa)		
							ArS-*p*-C_6H_4Y	ArSAr	ArSSAr
1	(*1*) 0.045	PhSNa, 2	PhI, 2	DMSO	100	10	62	e	37
2	(*1*) 0.025	PhSNa, 1	PhI, 1	DMSO	120	10	86	e	0
3	(*6*) 0.26	PhSNa, 4	PhI, 4	DMSO	100	6	66	e	4
4	(*6*) 0.26	PhSNa, 4	PhBr, 4	DMSO	100	6	24	e	34
5	(*6*) 0.26	PhSNa, 4	PhCl, 4	DMSO	100	6	6	e	37
6	(*6*) 0.26	PhSNa, 4	TolI, 4	DMSO	100	6	65	3	18
7	(*6*) 0.04	PhSNa, 2	PhI, 2	DMF	100	10	96	e	2
8	(*6*) 0.26	PhSNa, 4	TolI, 4	DMF	100	5	74	3	0
9	(*6*) 0.04	PhSNa, 2	TolI, 2	DMF	100	10	98	0	0
10	(*6*) 0.04	TolSNa, 2	TolI, 2	DMF	100	10	98	e	2
11	(*6*) 0	PhSNa, 2	TolI, 2	DMF	100	10	10	6	5
12	(*6*) 0.04	PhSNa, 2	TolBr, 2	DMF	100	10	5	4	2
13	(*6*) 0.26	PhSNa, 4	TolI, 4	DMF	120	1	67	5	14
14	(*6*) 0.04	PhSNa, 2	TolBr, 2	DMF	120	9	32	2	8
15	(*6*) 0.04	PhSNa, 2	AcC_6H_4Br, 2	DMF	120	4	98	0	0

[a] (*1*) = $Ni(SPh)_2(bpy)_2$. (*5*) = $NiCl_2(bpy)_2$. [b] ArSNa was prepared *in situ* by mixing ArSH and CH_3ONa. Tol = *p*-tolyl. [c] Tol = *p*-tolyl. AcC_6H_4 = *p*-acetylphenyl. [d] DMSO = dimethyl sulfoxide. DMF = N,N-dimethylformamide. [e] In these cases, ArSAr coincides with ArS-*p*-C_6H_4Y.

ed in polar solvents to give the electric conductivity (*vide supra*).

Chemical Reactivities

Complexes (*1*)–(*5*) release thiophenols in 96–63% yields on acidolysis of the complexes with dry HCl ($NiCl_2L_2$ is formed in the reaction),

$$Ni(SAr)_2L_2 + 2HCl \longrightarrow NiCl_2L_2 + 2\ ArSH \qquad (4)$$

Since diaryl disulfides remain intact when treated with dry HCl even in the presence of Ni compounds, the results indicate that the $(SAr)_2$ moiety in $Ni(SAr)_2L_2$ does not coordinate to Ni as a neutral non-cleaved ArSSAr ligand but it serves as the bis-arylthiolato ligand.

Treatment of (*1*) or (*4*) with various π-acids (carbon monoxide, maleic anhydride, dimethyl maleate, etc.) did not cause any apparent change, although treatment of $NiR_2(bpy)$ with the π-acid caused reductive elimination of R–R [9, 13]. The bpy ligand in (*1*) was not replaced by tertiary phosphines such as PPh_3, PEt_3, and tricyclohexylphosphine, although the bpy ligand in $NiEt_2(bpy)$ was easily replaced by PPh_3.

Table II shows results of the reactions of (*1*) with organic iodides, RI. The reactions proceed smoothly even at room temperature.

$$Ni(SAr)_2(bpy)_2 + 2RI \longrightarrow 2PhSR + NiI_2(bpy)_2 \qquad (5)$$

The yield of PhSR′ varies with change of the chain length in n-alkyl iodide. As seen from Table II, the yield-chain length profile shows decrease in the yield with increase in the chain length from methyl to n-propyl, where the yield becomes the lowest, but further increase in the chain length from n-propyl to n-butyl causes increase in the yield. This trend coincides with a known trend observed for chemical reactivities of n-alkyl halides toward S_N1 reactions [14]. Accordingly, we consider that the cross-coupling reaction 5 proceeds through an S_N1 type nucleophilic attack of the SPh ligand (or PhS^- anion liberated into the reaction mixture) at the α-carbon of R. Formation of PhSPh and PhSSPh (see Table II) seems to be due to partial degradation of (*1*) during the reactions.

Application to Catalytic Reaction

Since (*1*) reacts smoothly with R′X (Eq. 5) and $NiX_2(bpy)_2$, (*6*), formed in Eq. 5 undergoes a facile ligand exchange reaction with ArSNa (Eq. 2), combination of the two reactions is expected to lead to the following Ni-catalyzed sulfide synthetic reactions,

$$\begin{tikzcd} Ni(SAr)_2(bpy)_2 \arrow[r, bend left, "2RX \qquad 2ArSR"] & NiX_2(bpy)_2 \arrow[l, bend left, "2NaX \qquad 2ArSNa"] \end{tikzcd} \qquad (6)$$

$$\mathrm{ArSNA + RX \xrightarrow{Ni(SAr)_2(bpy)_2\ or\ NiX_2(bpy)_2} ArSR} \quad (7)$$

The catalytic reaction proceeds as shown in Table III to give the sulfides in good yields. A similar catalytic effect of a palladium complex on the coupling reaction between ArSNa and RX is reported [15], but the use of other later transition metal complexes in the coupling reaction has not been reported to our knowledge. The coupling reaction between ArSNa and RX proceeds to some extent without the Ni or Pd catalyst, but the yield obtained without the catalyst is low (see Expt. 11 in Table III and Ref. 15).

The following observations are made from Table III:

(1) Complexes (*1*) and $NiCl_2(bpy)_2$ (*6*) have catalytic activities comparable to each other.

(2) The reactivity of ArX increases in the order of ArCl < ArBr < ArI (Expts. 3–5 and Expts. 12 and 13). A similar trend of the reactivity of ArX in S_N1 type reactions is known [16].

(3) Although dimethyl sulfoxide is reported to serve as a good solvent for the Pd-catalyzed coupling reactions between ArSNa and organic halides [15], N,N-dimethylformamide seems to be a better solvent for the present coupling reaction (*e.g.*, compare Expt. 7 with Expt. 3).

(4) Formation of disulfide, ArSSAr, sometimes accompanies the coupling reaction, especially when the yield of the coupling reaction is low.

Experimental

All procedures, including preparation of diarylthiolatonickel(II) complexes and the Ni-catalyzed synthesis of sulfides, were performed under nitrogen or argon. Solvents were purified by a usual manner and stored under nitrogen. I.r. spectra were recorded on a Hitachi 295 spectrometer and ^1H n.m.r. spectra were measured on JEOL PS–100 and PMX-60 spectrometers. $^{31}P\{^1H\}$ n.m.r. spectra were recorded on a JEOL FX-90 spectrometer in FT mode. Microanalyses of C, H, N and S were carried out by Mr. T. Saito of our research laboratory using a Yanagimoto CHN Autocorder MT-2 and Yazawa sulfur microanalyzer. Electric conductivities were measured by using a TOA conductivity meter model CM-5B. Magnetic susceptibility was measured with Shimadzu MB-100 magnetic balance. Electric spectra were recorded on a Hitachi model 200-20 spectrometer. Organic compounds formed in various reactions were analyzed mainly by gas chromatography (Shimadzu GC-3BT, GC-3BF, or GC-6A gas chromatograph). Macroanalysis of Ni was performed according to literature methods [17]. Thermal analysis of complexes was performed with aid of a Shimadzu DT-30 thermal analyzer.

$Ni(cod)_2$ [6a], $NiCl_2(bpy)$ [18] and $NiCl_2(bpy)_2$ [19] were prepared according to literature methods. Commercially-available PhSSPh was recrystallized from ethyl alcohol. Thiophenols and organic halides were purchased from Tokyo Kasei Co. Ltd., and were purified by distillation. Di-*p*-tolyl disulfide and di-*p*-chlorophenyl disulfide were prepared by oxidation of the corresponding thiophenols by H_2O_2 in alkaline solutions. Recrystallization of the products from ethyl alcohol gave pure diaryl disulfides in 40–48% yields. Di-*p*-nitrophenyl disulfide was prepared according to literature methods [20]. Bpy was used as purchased from Tokyo Kasei. PEt_3 was kindly donated by the Nippon Kagaku Khogyo Co. Ltd.

Preparation of (1), (2), (3) and Related Complexes

$Ni(cod)_2$ (0.41 g, 1.5 mmol) and bpy (0.46 g, 3 mmol) were dissolved in 20 cm^3 of toluene in a 50 cm^3 Schlenk tube. When 0.32 g (1.5 mmol) of PhSSPh was added to the deep-purple solution at room temperature, a rapid reaction took place to give a brown precipitate. The precipitate was separated by filtration, washed twice with hexane, and dried under vacuum to yield a brown solid whose IR spectrum is almost identical to that of pure (*1*) (crude yield = *ca.* 90%). Recrystallization from 300 cm^3 of acetone gave analytically-pure black needles (0.45 g, 52%) of (*1*). Recrystallization from methyl alcohol containing H_2O gave prisms suitable for single X-ray crystallography [11]. A similar reaction in the presence of only 1 mol of bpy per mol of $Ni(cod)_2$ ($Ni(cod)_2$ = 2.0 mmol, bpy = 2.0 mmol, and PhSSPh = 2.0 mmol) gave the same complex (*1*) with 48% crude yield. I.r. (KBr, cm^{-1}): 3030m, 1595s, 1570s, 1445s, 1310m, 1245w, 1150s, 1080s, 1015s, 765s, 740s, 690s, 650m, 620w, 480m, 410m. A ligand-exchange reaction using $NiCl_2(bpy)$ (4.0 g, 1.4 mmol), bpy (4.4 g, 2.9 mmol) and PhSNa (2.8 mmol prepared from 3.1 g of PhSH and 1.5 g of CH_3ONa) in 40 cm^3 of dioxane also gave (*1*) in good yield (reaction conditions: 80 °C, 1 h).

$Ni(cod)_2$ (2.5 g, 9.1 mmol) and bpy (2.8 g, 18 mmol) were dissolved in 50 cm^3 of toluene in a 200 cm^3 Schlenk tube. When 2.6 g (9.1 mmol) of di-*p*-chlorophenyl disulfide was added to the deep-purple solution at room temperature, rapid formation of a dark brown precipitate was observed. The precipitate was separated by filtration, washed twice with diethyl ether, and dried under vacuum to give a black solid. The black solid was dissolved in acetone at its boiling point. Cooling the solution to –20 °C gave black (slightly reddish) prisms of (*2*). Recrystallization from methyl alcohol gave similar prisms. I.r. (KBr, cm^{-1}): 3050w, 1590s, 1555m, 1460s, 1440s, 1310m, 1245w, 1150m, 1085s, 1005m, 820s, 760s, 730s, 640w, 540s, 490s, 405m.

Complex (*3*) was prepared analogously by mixing $Ni(cod)_2$ (1.0 g, 3.6 mmol), bpy (1.1 g, 7.2 mmol), and di-*p*-nitrophenyl disulfide (1.1 g, 3.6 mmol) in 100 cm^3 of THF at room temperature. Recrystallization from acetone gave the black powder of (*3*). I.r. (KBr, cm^{-1}): 3000w, 1590m, 1560s, 1480s, 1440s, 1310vs, 1065s, 1010m, 840s, 760s, 740m, 730m, 680m, 640m, 620m, 535m, 405m.

A similar reaction using 5.0 mmol of Ni(cod)$_2$, 10 mmol of bpy, and 5.0 mmol of di-*p*-tolyl disulfide gave similar results, and acidolysis of the product by dry HCl liberated *p*-methylbenzenethiol (80% of the amount calculated by assuming that the product had a composition of Ni(STol)$_2$(bpy)$_2$). I.r. spectrum also suggested the formation of the similar complex.

Preparation of (4), (5), and Related Complexes

Ni(cod)$_2$ (1.4 g, 5.2 mmol) and PEt$_3$ (1.5 cm^3, 1.2 g, 10 mmol) were dissolved in toluene (20 cm^3) in a 50 cm^3 Schlenk tube. When 1.1 g (5.2 mmol) of PhSSPh was added to the orange solution at room temperature, a rapid reaction occurred to give a brown homogeneous solution. The solution was condensed to 10 cm^3. After addition of 40 cm^3 of hexane to the condensed solution, the mixture was cooled to –20 °C to yield deep brown needles, which were collected by filtration and dried *in vacuo* to obtain 1.0 g of (*4*). ^{1}H n.m.r. of (*4*) (toluene-d$_8$):δ: 1.00 ppm (18H, quintet, 8 Hz), 1.56 ppm (12H, quartet, 8 Hz), *ca.* 7.0 ppm (6H, m and *p*-Ph), *ca.* 8.2 ppm (4H, *o*-Ph). I.r. (KBr, cm^{-1}): 3050w, 2960s, 2860m, 1575s, 1470s, 1415m, 1375m, 1265m, 1250m, 1085s, 1030s, 1000m, 760s, 740s, 715s, 690s, 620m, 480m, 410m.

Ni(cod)$_2$ (1.1 g, 3.9 mmol) and PEt$_3$ (1.1 cm^3, 0.92 g, 7.8 mmol) were dissolved in 10 cm^3 of toluene. Di-*p*-tolyl disulfide (0.96 g, 4.1 mmol) was added to the orange solution to initiate a rapid reaction, which led to the formation of a brown homogeneous solution. After adding 40 cm^3 of hexane to the reaction solution, the mixture was filtered. The filtrate was cooled to –20 °C to yield brown needles, which were collected by filtration and dried under vacuum to obtain 1.7 g of (*4*). I.r. (KBr, cm^{-1}); 2950s, 2850m, 1590m, 1480s, 1240m, 1080s, 1030s, 800s, 755s, 715s, 620s, 490s, 400m.

A similar reaction of Ni(cod)$_2$ (0.45 g, 1.6 mmol) with PhSSPh (0.36 g, 1.7 mmol) in the presence of dpe (1.3 g, 1.6 mmol) in THF (50 cm^3) at room temperature seems to cause similar oxidative addition of PhSSPh to Ni. Acidolysis of the product with dry HCl liberated thiophenol (85% of the amount calculated by assuming that the product had a composition of Ni(SPh)$_2$(dpe)).

Acidolysis of Complexes

Dry HCl generated by a reaction of NaCl and conc. H$_2$SO$_4$ was dissolved in dry diethyl ether by using a vacuum technique to obtain a 0.68 *M* ethereal solution of HCl. The ethereal solution (0.88 cm^3 containing 0.60 mmol of HCl) was added to 0.070 g (0.119 mmol) of (*1*) at room temperature. Stirring the mixture immediately gave a light green NiCl$_2$(bpy)$_2$. Analysis of the solution by glc showed liberation of 0.114 mmol of thiophenol. Acidolyses of other complexes were performed analogously.

*Reactions with Iodides (*cf. *Table II)*

Methyl iodide (53 mg, 0.37 mmol) was added to a methyl alcohol solution of (*1*) (109 mg, 0.185 mmol) at room temperature. After stirring the reaction mixture for 24 h, formation of 0.23 mmol (62%) of methyl phenyl sulfide and 0.037 mmol (20%) of PhSSPh was observed (glc). Other reactions with iodides were carried out analogously.

*Catalytic Reactions (*cf. *Table III)*

Expt. 2: A mixture of Ni(SPh)$_2$(bpy)$_2$ (16 mg, 0.27 mmol), thiophenol (150 mg, 1.3 mmol), CH$_3$ONa (71 mg, 1.3 mmol), and phenyl iodide (270 mg, 1.3 mmol) in 3 cm^3 of dimethyl sulfoxide was stirred at 120 °C for 10 h. Analysis of the reaction mixture by glc showed formation of PhSPh in an 86% yield. Other catalytic reactions were carried out analogously. AcC$_6$H$_4$SPh obtained in Expt. 15 was isolated by recrystallization and identified by ^{1}H-n.m.r.: δ: 2.10 ppm (3H, s, CH$_3$), 7.0–7.9 ppm (9H, m, aromatic H).

Thermolysis

Ni(SPh)$_2$(bpy)$_2$ (30 mg, 0.56 mmol) in a Schlenk tube was heated in an oil bath (250 °C) for 20 min. Analysis by glc showed formation of bpy (49%), PhSPh (92%), and PhSSPh (4%).

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