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PREPARATION AND PROPERTIES OF ARYL(DIPYRIDYL)NICKEL HALIDE COMPLEXES

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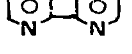
Summary

Several aryl(dipyridyl)nickel halide complexes of the composition R(dipyridyl)NiX (R = phenyl, *o*-tolyl, *m*-tolyl, *p*-tolyl and *o*-chlorophenyl, X = I, Br and Cl) have been prepared from diethyl(dipyridyl)nickel and aryl halides. The complexes were characterized by elemental analyses, NMR spectroscopy and chemical reactions. The complexes exhibited no catalytic activity for the polymerization of vinyl monomers such as acrylonitrile, methacrylonitrile and methyl methacrylate. However, in combination with Lewis acids such as $AlEtCl_2$ and $AlEt_2Cl$, the aryl(dipyridyl)nickel halide complexes show higher catalytic activity in propylene dimerization, compared to dipyridylnickel dichloride and the parent diethyl(dipyridyl)nickel. The results of the propylene dimerization experiments all favor the view that the aryl group in the nickel complex is retained in the active species in spite of the large excess of Lewis acid present in the system.

Introduction

As we previously communicated [1, 2], diethyl(dipyridyl)nickel affords aryl(dipyridyl)nickel halide complexes on reaction with aryl halides. Here, we describe the preparation and properties of several aryl (dipyridyl)nickel halide complexes, as well as the nature of the activation of the complex by Lewis acids (dipyridyl = dip = ).

Results and discussion

Diethyl(dipyridyl)nickel (I) reacts with aryl halides such as iodobenzene, bromobenzene, chlorobenzene, *o*-dichlorobenzene, *o*-chlorotoluene, *m*-chlorotoluene and *p*-chlorotoluene with evolution of n-butane, forming aryl(dipyridyl)nickel halide complexes, but does not react with fluorobenzene under similar conditions.

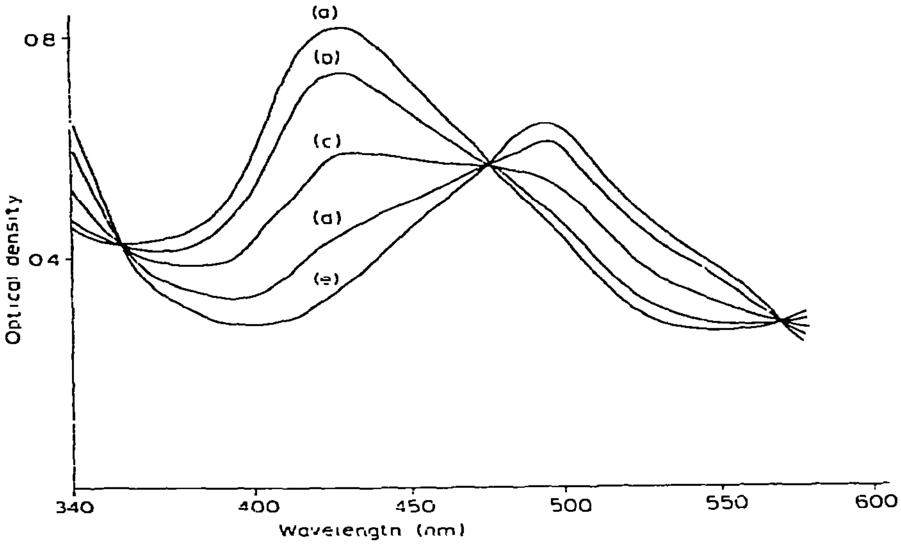


Fig. 1. Electronic spectra of the reaction of diethyl(dipyridyl)nickel with *m*-chlorotoluene at 34°. Reaction time (a) 0 min, (b) 7 min, (c) 13 min, (d) 23 min, (e) 100 min.

Et_2(dipyridyl)Ni + RX → R(dipyridyl)NiX + n-C_4H_{10}
(I)
(R = phenyl, *o*-tolyl, *m*-tolyl, *p*-tolyl and *o*-chlorophenyl;
X = I, Br and Cl)

Under well controlled conditions, no side reactions were observed, as indicated by the presence of three isosbestic points in the electronic spectra (340-600 nm) of the changing reaction mixture as shown in Fig. 1. However, the stability and the solubility of the complex formed, as well as the reactivity of the aryl halide, vary with the aryl halide employed and some variations of the preparative method are required.

(1) Phenyl(dipyridyl)nickel halide (X = Cl, Br and I)

Phenyl(dipyridyl)nickel chloride is rapidly formed in a chlorobenzene solution of I, even at room temperature, and can be isolated as Ph(dip)NiCl-($\frac{1}{2}C_6H_5Cl$) (II) (dip = dipyridyl). Ph(dip)NiBr (III), like its chloride analog, also is formed rapidly in a bromobenzene solution of I. In contrast to chlorobenzene and bromobenzene, the direct reaction of I with excess iodobenzene at room temperature afforded mixtures of unidentified products, presumably due to the high reactivity of the iodobenzene. Dropwise addition of the appropriate quantities of iodobenzene at low temperature (—30°) to a solution of I in tetrahydrofuran and subsequent gradual warming of the solution to room temperature are required for the preparation of Ph(dip)NiI (IV).

Complex II is soluble in chlorobenzene, tetrahydrofuran, acetone and toluene, but only stable in chlorobenzene. Its solutions in other solvents decompose gradually to give unidentified precipitates even at room temperature. II can be recrystallized from chlorobenzene solution as reddish-brown fine crystals.

The complexes III and IV were found to be stable in tetrahydrofuran solution from which these complexes can be recrystallized. Dark red III and IV are obtained as solvent-free crystals. The decomposition point of the complexes II, III and IV were found to be 76, 103 and 99°, respectively. The thermally most unstable complex (II) was also found to be the most unstable towards the attack by oxygen. On exposing II to air, it decomposed to a white powder in a few hours. Complexes III and IV, in the solid state, were found to be stable under air and no color changes were observed even after 24 h. The reaction of the complexes II, III and IV with olefins such as acrylonitrile, methacrylonitrile and methyl methacrylate resulted in decomposition and no polymers were formed.

Attempts to study these complexes by far infrared spectroscopy have failed. Many absorption peaks appeared in the region of the nickel—halogen stretching vibration [3] and this made unequivocal assignments a formidable problem. The complexes were characterized by elemental analyses and chemical reactions.

The presence of the Ni—Cl bond in II was confirmed by the determination of the inorganic chlorine content. The chlorine content of II determined by Fajans method agreed with the theoretical value. On reaction with dilute nitric acid, II afforded stoichiometric amounts of benzene and chlorobenzene. Toluene and benzene were detected on treatment of II with methyl iodide and ethanol, respectively.

(2) Tolyl(dipyridyl)nickel chloride (V, o-tolyl-; VI, m-tolyl-; VII, p-tolyl-)

The green solution of I in chlorotoluenes such as *o*-chlorotoluene, *m*-chlorotoluene and *p*-chlorotoluene changes at 40-50° to red with sudden evolution of n-butane. The complexes can be precipitated from the red solution by addition of n-hexane. The *o*-tolyl complex V can be recrystallized either from acetone or from chlorobenzene. The *m*- and *p*-tolyl complexes VI and VII can be recrystallized from chlorobenzene and were isolated as orange-red crystals containing the solvent of crystallization (*m*-tolyl(dip)NiCl$(C_6H_5Cl)_n$ (VIII) and *p*-tolyl(dip)-NiCl$(\frac{1}{2}C_6H_5Cl)$ (IX)). The amounts of chlorobenzene in VIII varied, depending on drying conditions.

The complexes V and VIII are stable under air and no color changes under air were observed even after 24 h. Complex IX, in contrast to V and VIII, was found to be air sensitive like complex II and it decomposed to a yellow-white powder in a few hours.

The electronic spectra of the complexes, V, VI and VII, exhibit two absorption maxima near 300 and 500 nm. Table 1 shows the measured wavelengths of these absorptions in different solvents. The position of methyl substitution in the tolyl ligand does not affect appreciably the value of λ_{max}, but λ_{max} varies considerably with the solvents used. A polar solvent seems to shift the absorption to shorter wavelength. The molar extinction coefficients of the absorptions near 300 and 500 nm were, respectively, about 6×10^3 and 2×10^3. Since the molar extinction coefficients of the two bands observed are of the same order of magnitude as the extinction coefficients of two charge transfer bands reported [4] for complex I, we consider these two bands due to charge transfer from the nickel *d*-orbitals to the two vacant π-orbitals of 2,2'-dipyridyl. The two charge

TABLE 1

λ_{max} OF TOLYL(DIPYRIDYL)NICKEL CHLORIDE COMPLEXES IN THE REGION 300—600 nm

Solvent	Complex					
	V		VI		VII	
Toluene		506	303	502	312	507
Isopropyl ether	306	508	299	511	305	510
Anisole		490		486		489
Tetrahydrofuran	303	488	305	488	308	488
Chlorobenzene	306	494	308	492	306	496
Acetone		472		472		465
Dimethylformamide		428		422		452

transfer bands [4] in the spectrum of I are at longer wavelengths (430 and 720 nm) compared to the two bands in the spectra of the aryl(dipyridyl)nickel halide complexes, but the shifts can be explained by the change in oxidation state of the nickel atom, since the nickel atom in the aryl(dipyridyl)nickel halide complex is evidently much more oxidized due to the electronegative halogen than that in I. We interpret the shift due to polar solvent in terms of stabilization of the electronic charge on nickel by electrostatic interaction.

The NMR spectrum (100 MHz) of complex V in chlorobenzene exhibits a downfield shift of the methyl proton resonance, compared to the methyl proton resonance of the parent *o*-chlorotoluene, whereas, no appreciable downfield shifts were observed for the methyl proton resonances of VIII and IX in chlorobenzene solution. The downfield shifts relative to the parent chlorotoluenes were 1.05 for *o*-CH_3, 0.10 for *m*-CH_3 and 0.08 ppm for *p*-CH_3. The downfield shift of the *o*-substituent proton resonance due to the paramagnetic anisotropy effect in analogous nickel complexes has been reported [5]. Since the rotation of the aromatic ring about the Ni—C axis in complex V can be considered to be restricted, the downfield shift of *o*-CH_3 proton resonance in V due to the paramagnetic anisotropy seems to be reasonable. The methyl group in the complex is considered to be freely rotating, since we observed a single sharp peak even for the *o*-CH_3 proton resonance.

The relative stability of the complexes, which decreases in the order of *o*-tolyl > *m*-tolyl > *p*-tolyl, suggests that the restriction of rotation of the aromatic ring increases the stability of the complex. Presumably, the restriction of rotation may favor the overlap of the nickel *d*-orbital with the aromatic π-system, as suggested by Chatt and Shaw [6].

(3) o-Chlorophenyl(dipyridyl)nickel chloride (X)

Complex X, prepared simply by warming (60°) a solution of I in *o*-dichlorobenzene, is a remarkably stable compound. Orange crystals of X, which are less soluble in most solvents than other aryl(dipyridyl)nickel halide complexes, can be recrystallized from acetone. Complex X was found to be stable in acrylonitrile and neither the complexation nor the polymerization of acrylonitrile was ob-

TABLE 2

PROPERTIES OF ARYL(DIPYRIDYL)NICKEL HALIDE COMPLEXES

Complex	Composition	Properties
II	Ph(dip)NiCl($\frac{1}{2}$ C_6H_5Cl)	Reddish-brown, air sensitive crystals recrystallized from C_6H_5Cl, m.p. 76° (dec.).
III	Ph(dip)NiBr	Dark red crystals recrystallized from THF, m.p. 103° (dec.).
IV	Ph(dip)NiI	Dark red crystals recrystallized from THF, m.p. 99° (dec.).
V	*o*-Tolyl(dip)NiCl	Red crystals recrystallized from acetone, m.p. 147° (dec.).
VI	*m*-Tolyl(dip)NiCl	Red powder precipitated by n-hexane.
VII	*p*-Tolyl(dip)NiCl	Red powder precipitated by n-hexane.
VIII	*m*-Tolyl(dip)NiCl(C_6H_5Cl)$_n$	Orange-red crystals recrystallized from C_6H_5Cl, m.p. 115° (dec.).
IX	*p*-Tolyl(dip)NiCl($\frac{1}{2}$$C_6H_5Cl$)	Orange-red crystals recrystallized from C_6H_5Cl, m.p. 75° (dec.).
X	*o*-Chlorophenyl(dip)NiCl	Orange crystals recrystallized from acetone, m.p. 172° (dec.).

served. On heating with acetylacetone, X liberated chlorobenzene and *o*-dichlorobenzene due to coupling of the chlorine atom with the *o*-chlorophenyl group. The molar ratio of chlorobenzene to *o*-dichlorobenzene liberated by acetylacetone was about 0.6.

The complexes prepared in the present work are summarized in Table 2 together with their properties.

(4) The complex activated by Lewis acid

The rate acceleration effect of the chlorinated aromatic solvents such as chlorobenzene and *o*-dichlorobenzene in propylene dimerization by nickel complex catalyst [7] is well-known and complex I, activated as a catalyst for propylene dimerization by the addition of a Lewis acid such as $AlEtCl_2$ or $AlEt_2Cl$ (Al/Ni ratio of 2 to 4), shows a high catalytic activity in chlorinated aromatic solvents only. However, the aryl(dipyridyl)nickel halide complexes, prepared previously from I and aryl halides and activated by the addition of $AlEtCl_2$, did not require such chlorinated aromatic solvents in order to exhibit high catalytic activity. Such dependence of dimerization performance on the type of nickel complex was observed even in the presence of a large excess of $AlEtCl_2$ (Al/Ni = 100). Fig. 2 compares the complexes I, X and $NiCl_2$(dip) in propylene dimerization and indicates that X shows higher catalytic activity, compared to I and $NiCl_2$(dip), even in the presence of a large excess of $AlEtCl_2$. All the aryl(dipyridyl)nickel halide complexes listed in Table 2 showed higher activities for propylene dimerization compared to the parent complex I, but the most stable catalytic activity was achieved by complex X. The yield of trimers and higher oligomers in the products was found to be independent of the degree of conversion of propylene and varied with the type of complex and with the aryl group present in the complex, as shown in Fig. 3. These observations, as well as the results shown in Fig. 2, strongly suggest the presence of the aryl group in catalytically active species.

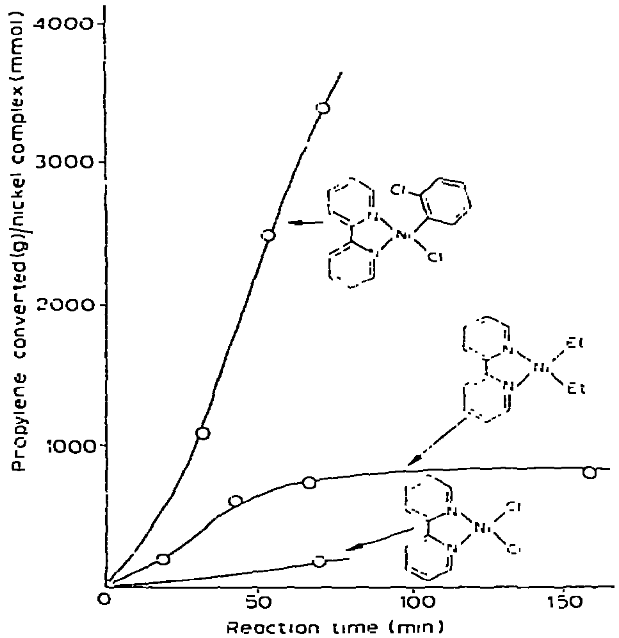


Fig. 2. The comparison of the activities of dipyridyl coordinated nickel complexes in propylene dimerization. Reaction temperature —16°, 10-30 mg nickel complexes used, Lewis acid: $AlEtCl_2$, Al/Ni = 100, 150 g initially charged propylene.

The coordination of 2,2'-dipyridyl in the active species is not clear, but the difference observed between the color of the $AlEtCl_2$—2,2'-dipyridyl mixture and that of the catalyst suggested that 2,2'-dipyridyl may not be eliminated as an adduct with $AlEtCl_2$. A detailed picture of the association of the nickel complex with the Lewis acid in the active species cannot be given on the basis

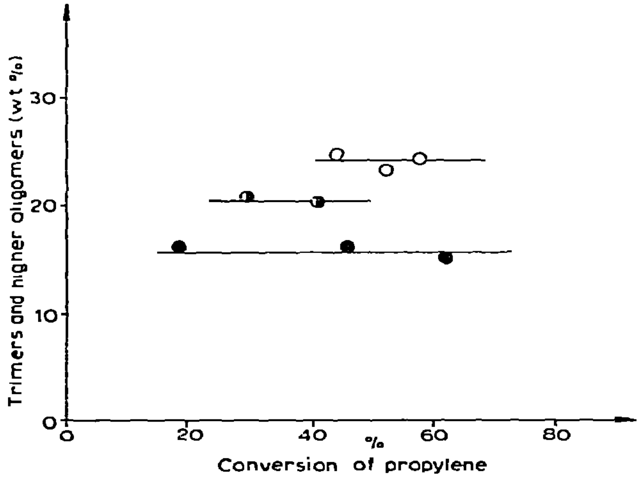


Fig. 3. The yield of trimers and higher oligomers in products of propylene dimerization. Reaction temperature —16°, Lewis acid: $AlEtCl_2$, Al/Ni = 100, nickel complexes: O, I, ◑ V; ●, X.

of the available information. Eberhardt and Griffin [7i] proposed the coordination of the ligands of the Lewis acid complexes to the catalytically active nickel, but several examples of direct transition-metal—aluminium bonding are also known [10].

The propylene dimers obtained with the present catalysts were composed of 4-methyl-2-pentene (60-70%), n-hexenes (20%), 2-methyl-2-pentene, 4-methylpentene and negligible quantities of 2,3-dimethylbutenes and of 2-methyl-1-pentene. If the propylene dimerization proceeds by insertion of propylene into the nickel—propyl bond, followed by β-elimination of the hydrogen from the hexylnickel formed, the dimers such as 2-methyl-1-pentene and n-hexenes are considered to be produced from n-propylnickel species and dimers such as 4-methyl-2-pentene, 4-methyl-1-pentene and 2,3-dimethyl-1-butene are considered to be produced from isopropylnickel species and the dominant formation observed of n-hexenes over 2-methyl-1-pentene as well as that of 4-methyl-2-pentene and 4-methyl-1-pentene over 2,3-dimethylbutenes can be explained by the favored insertion of type I, where C_3H_7 is isopropyl or n-propyl.

(1)

A simple explanation for the formation of 2-methyl-2-pentene may be the isomerization of methylpentenes during the course of dimerization of propylene, but the isomerization of methylpentenes, observed in the course of the dimerization, was only that from 4-methyl-1-pentene to 4-methyl-2-pentene and the relative quantities of the thermodynamically stable 2-methyl-2-pentene did not increase during the course of dimerization (Fig. 4), indicating that the 2-methyl-2-pentene observed is a primary product of dimerization. Since the insertion of propylene into the nickel—propyl bond, followed by β-elimination of hydrogen, cannot explain the formation of 2-methyl-2-pentene as a primary product, the

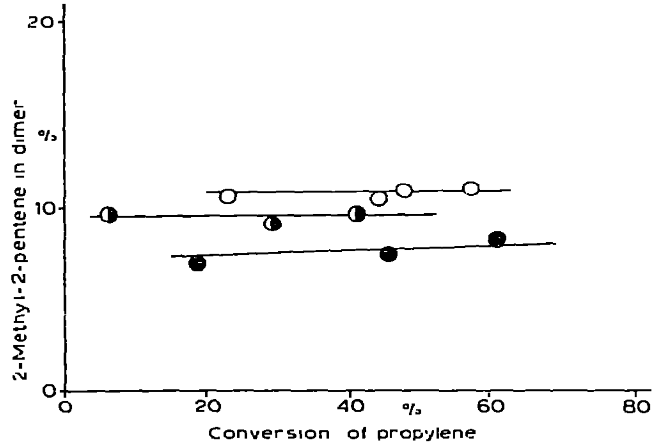
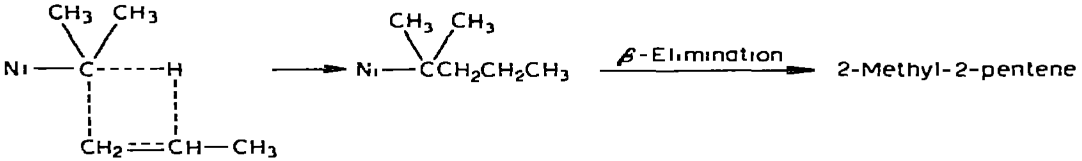


Fig. 4. The content of 2-methyl-2-pentene in propylene dimer. Reaction temperature —16°, Lewis acid $AlEtCl_2$, Al/Ni = 100, nickel complexes: ○, I; ◑, V; ●, X.

presence of the following addition reaction is suggested:



(2)

In the propylene dimerization catalyzed by the $NiX_2 2PR_3$—$AlEt_2Cl$ system [7b], the ratio of the sum of 2-methyl-1-pentene + n-hexenes to the sum of 2,3-dimethylbutenes + 4-methyl-1-pentene + 4-methyl-2-pentene remains constant, regardless of the variation of the dimer composition with the phosphine used and with the degree of conversion of propylene, suggesting the constant ratio of n-propylnickel species to isopropylnickel species in the catalytically active nickel species. The ratio of the dimers, produced from n-propylnickel species to the dimers produced from isopropylnickel species, depends neither on the complex used nor on the degree of conversion of propylene in the present study and agrees with the value observed in propylene dimerization with $NiX_2 2PR_3$—$AlEt_2Cl$ catalyst. These facts may indicate that the n-propylnickel species in the nickel complex catalyst of propylene dimerization generally exists in equilibrium with the isopropylnickel species and that the relative quantities of n-propylnickel species compared to isopropylnickel species are maintained constant in spite of the changes of the nickel complex, of the degree of the conversion of propylene and of Lewis acid. Recently Tamao et al. [8] have investigated the reaction of a Grignard reagent (isopropylmagnesium chloride) with $PhNiClL_2$ (L = ligand) and reported the isomerization equilibrium 3 in the reaction system.

$$\text{i-PrPhNiL}_2 \rightleftharpoons \text{n-PrPhNiL}_2 \qquad (3)$$

Since the active species may be very similar to the complexes in 3, it seems quite reasonable to consider such isomerization equilibrium in the present dimerization.

Experimental

All procedures for the preparation of the complexes were carried out under purified nitrogen or argon. Solvents and aryl halides, dehydrated by usual methods, were distilled and stored under nitrogen. Diethyl(dipyridyl)-nickel (I) was prepared from 2,2′-dipyridyl, nickel acetylacetonate and diethylaluminium monoethoxide in ether, as described in the literature [9]. Ethylaluminium dichloride (Texas Alkyls) was purified by distillation before use. Commercially available polymerization grade propylene was passed through a calcium hydride column before use.

Analytical methods. The gas evolved in the reaction of I with aryl halide was measured by the volumetric method and identified by gas chromatography. The organic compounds produced in the chemical reaction of II, the composition of the propylene dimers and the ratio of the propylene dimer to the higher oligomers were determined by gas chromatography. The conversion of the propylene was determined by the distillation of the unchanged propylene.

NMR spectra of the complexes were recorded on a JEOL NMR spectrometer (100 MHz). Electronic spectra were recorded on a Hitachi EPI-3 spectrometer.

Preparation of Ph(dip)NiCl($\frac{1}{2}C_6H_5Cl$) (II)

Three g of I was dissolved in chlorobenzene (about 80 ml) and the solution was stirred for 2 h at room temperature. After cooling the red reaction mixture to —10°, the red precipitate formed was filtered and dried. The red powder thus obtained was dissolved in chlorobenzene at 65° and crystallized. The reddish brown complex II was obtained in a 60% yield. (Anal.: Found: C, 59.48; H, 4.0; Cl, 14.4; N, 7.3. $C_{19}H_{16.5}Cl_{1.5}N_2Ni$ calcd.: C, 59.4; H, 4.0; Cl, 13.9; N, 7.3%.) The inorganic chlorine content determined by Fajans method. (Found: 10.3. Calcd.: 10.7%.)

Preparation of Ph(dip)NiBr (III)

I (1.1 g) was dissolved in bromobenzene (40 ml) and stirred at room temperature until the green solution became red. The red solution was concentrated to 20 ml and n-hexane (100 ml) was added. The red precipitate thus formed was filtered and crystallized from tetrahydrofuran (150 ml). Dark red crystals of III were obtained in a 45% yield. (Anal.: Found: C, 51.7; H, 3.5; Br, 22.3; N, 7.6. $C_{16}H_{13}BrN_2Ni$ calcd.: C, 51.7; H, 3.5; Br, 21.4; N, 7.5%.)

Preparation of Ph(dip)NiI (IV)

I (1.5 g) was dissolved in tetrahydrofuran (50 ml) and the solution was cooled to —30°. After dropwise addition of iodobenzene (5 ml) to the solution at —30°, the temperature was raised gradually to room temperature. The red solution thus obtained was concentrated to about 25 ml and n-hexane (100 ml) was added. The red precipitate was crystallized from tetrahydrofuran solution, similarly to III. The red crystalline complex was obtained in 35% yield. (Anal.: Found: C, 45.8; H, 3.1; I, 30.9; N, 6.6. $C_{16}H_{13}IN_2Ni$ calcd.: C, 45.9; H, 3.1; I, 30.3; N, 6.7%.)

Preparation of o-tolyl(dip)NiCl (V)

One g of I was mixed with 30 ml of *o*-chlorotoluene and the green solution was warmed to 45° and stirred for 30 min. The color turned red with sudden evolution of n-butane. After two hours of additional stirring at 45°, the solution was cooled to room temperature and concentrated. The addition of n-hexane (100 ml) to the concentrated solution gave an orange precipitate. Recrystallization from acetone (150 ml) afforded red crystals of V in 50% yield. (Anal.: Found: C, 59.0; H, 4.2; Cl, 10.5; N, 8.4. $C_{17}H_{15}ClN_2Ni$ calcd.: C, 59.9; H, 4.4; Cl, 10.4; N, 8.2%.)

Preparation of m-tolyl(dip)NiCl(C_6H_5Cl)$_n$ (VIII)

I (1.3 g) was treated in *m*-chlorotoluene (30 ml) analogously to the preparation of V. The red precipitate, obtained by the addition of n-hexane (100 ml) to the concentrated solution, was recrystallized from chlorobenzene (150 ml). The orange red complex VIII ($n \sim 0.5$) was obtained in 42% yield. The elemental analyses varied due to chlorobenzene whose quantities changed with drying conditions.

Preparation of p-tolyl(dip)NiCl($\frac{1}{2}C_6H_5Cl$) (IX)

The complex was prepared similarly to VIII from 1.7 g of I in *p*-chlorotoluene (70 ml). Orange-red crystalline complex IX, recrystallized from chlorobenzene solution, was obtained in a 40% yield. (Anal.: Found: C, 60.9; H, 4.4; Cl, 13.7; N, 7.4. $C_{20}H_{17.5}Cl_{1.5}N_2Ni$ calcd.: C, 60.4; H, 4.4; Cl, 13.4; N, 7.0%.)

Preparation of o-ClPh(dip)NiCl (X)

I (1.5 g) was dissolved in dichlorobenzene (150 ml) and a green solution was warmed to about 50°. The red solution obtained was stirred for 3 h at 50°. Upon cooling the mixture, orange powder was precipitated. The precipitate, washed with toluene at 60°, was recrystallized from acetone (150 ml). A red-brown crystalline complex was obtained in a 70% yield. (Anal.: Found: C, 54.1; H, 3.3; Cl, 19.6; N, 8.0. $C_{16}H_{12}Cl_2N_2Ni$ calcd.: C, 53.1; H, 3.3; Cl, 19.6; N, 7.7%.)

Preparation of $NiCl_2$(dip)

To the anhydrous nickel dichloride in ethanol, nearly stoichiometric quantities (a slight excess) of 2,2'-dipyridyl in ethanol was added dropwise, under vigorous stirring, at room temperature. The precipitate obtained after several hours of stirring was washed with acetone and dried. A light green powder was obtained almost quantitatively. (Anal.: Found: C, 41.9; H, 2.9; N, 9.5. $C_{10}H_8Cl_2N_2Ni$ calcd.: C, 42.0; H, 2.8; N, 9.8%.)

Propylene dimerization procedures

The nickel complex was placed in an autoclave (350 ml) under a nitrogen atmosphere. The autoclave was sealed, evacuated, cooled to —60° and charged with propylene (150 g). Ethylaluminium dichloride diluted in n-pentane was mixed with the liquid propylene and the temperature was kept constant at —16°C by circulating the thermostatted ethanol. In the course of dimerization, the liquid phase sample (30-50 ml) was taken out and the quantities of unchanged propylene as well as the product composition were determined.

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