Journal of Organometallic Chemistry, 192 (1980) 265—274

LIGAND EXCHANGE REACTION BETWEEN $NiMe_2L_2$ (L = 1/2 bpy, PEt_3) AND DITERTIARY PHOSPHINES $Ph_2P(CH_2)_nPPh_2$ (n = 1—4) AND EFFECT OF LIGAND ON EASE OF REDUCTIVE ELIMINATION OF C_2H_6 FROM $NiMe_2(Ph_2P(CH_2)_nPPh_2)$

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(Received November 6th, 1979)

Summary

Reactions of the dimethylnickel(II) complexes $NiMe_2L_2$ (L = 1/2 bpy, PEt_3 (bpy = 2,2'-bipyridine)) with diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1—4) give $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ (n = 2, 3) or produce ethane and Ni^0-diphosphine complexes (n = 1, 4), depending on the chain length of $(CH_2)_n$ of the diphosphine ligand employed. The ligand exchange reaction between $NiMe_2(bpy)$ and $Ph_2P(CH_2)_3PPh_2$ (dpp) proceeds through an S_N2 process with the activation parameters $\Delta H^{\neq}$ = 8.3 kcal/mol and $\Delta S^{\neq}$ = —35 e.u. A mechanism involving coordination of dpp via one phosphorus atom and ensuing chelation of dpp accompanied by dissociation of bpy is proposed for the ligand exchange reaction. Kinetic studies on the thermal decomposition of $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ (n = 2, 3) show that the reductive elimination of C_2H_6 from $NiMe_2(Ph_2P(CH_2)_n$-$PPh_2)$ (n = 2, 3) proceeds by a unimolecular process with the activation parameters $\Delta H^{\neq}$ = 26.8 kcal/mol and $\Delta S^{\neq}$ = 1.9 e.u. for $NiMe_2(Ph_2P(CH_2)_2PPh_2)$ and $\Delta H^{\neq}$ = 25.1 kcal/mol and $\Delta S^{\neq}$ = 4.8 e.u. for $NiMe_2(Ph_2P(CH_2)_3PPh_2)$. The rate of reductive elimination of $NiMe_2(Ph_2P(CH_2)_3PPh_2)$ is 46 times faster than that of $NiMe_2(Ph_2P(CH_2)_2PPh_2)$ at 64.3°C.

Introduction

The ligand exchange reaction between a transition metal alkyl complex MR_mL_n and ligand L' serves as a convenient route to the preparation of new complexes, $MR_mL'_n$ which are difficult to prepare by other routes [1,2]. Chelating diphosphine ligands, e.g., $Ph_2P(CH_2)_nPPh_2$, having good coordinating abilities have been employed for the preparation of $PtMe_2(Ph_2P(CH_2)_nPPh_2)$ (n = 1—4) [2] from dimethylplatinum complexes with monodentate phosphine or olefin ligands. However, in the case of dialkylnickel complexes, such a ligand exchange has not been reported except for ^{31}P NMR studies of the ligand exchange reactions of alkyl or arylnickel complexes [3], although many examples of ligand exchange reactions of zero-valent nickel complexes are known [4,5]. In view of the utility of diphosphines in nickel-catalyzed reactions, such as C—C coupling between RMgX and R'X, which is considered to proceed via reductive elimination of R—R' from an intermediate NiR(R')(diphosphine) species [6], information concerning the behavior of the diphosphine-coordinated nickel alkyls is important for an understanding of the effect of the diphosphines on catalytic reactions. As a part of our program of studies of the stabilities and reactivities of alkylnickel complexes [7] we have examined the ligand exchange reactions between $NiMe_2L_2$ (L = PEt_3, 1/2 bpy (bpy = 2,2'-bipyridine)) and diphosphine ligands, $Ph_2P(CH_2)_nPPh_2$, to find the critical effect of the chain lengths of $(CH_2)_n$ for the isolation of the expected $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ complex. This paper deals with the preparation of dimethylnickel-diphosphine complexes by ligand exchange reactions, the kinetics of the ligand exchange reaction between $NiMe_2(bpy)$ and $Ph_2P(CH_2)_3PPh_2$, and the thermal stabilities of the isolated dimethylnickeldiphosphine complexes.

Results and discussion

Reactions of $NiMe_2L_2$ with $Ph_2P(CH_2)_nPPh_2$

Table 1 shows the products of the ligand exchange reactions. When $Ph_2P(CH_2)_2PPh_2$ (dpe) was added to the solution of $NiMe_2(PEt_3)_2$ or $NiMe_2(bpy)$ in a 1 : 1 molar ratio, a smooth exchange reaction of the monodentate PEt_3 ligand or of the bidentate bpy ligand with dpe took place to give the known dimethylnickel complex $NiMe_2(dpe)$ [8]. No evolution of gases (CH_4, C_2H_6) was observed. The ^1H NMR spectrum of the 1 : 1 mixture of $NiMe_2(bpy)$ and dpe, after completion of the exchange reaction, showed only peaks due to $NiMe_2(dpe)$ and free bpy. Similar results were obtained by using $Ph_2P(CH_2)_3PPh_2$(dpp) as the exchanging ligand, and a new complex, $NiMe_2(dpp)$, was obtained. However, in the case of the reaction of dpp, contamination of the

TABLE 1

PRODUCTS OF THE REACTION BETWEEN $NiMe_2L_2$ AND DIPHOSPHINES [a]

No	$NiMe_2L_2$ L =	$Ph_2P(CH_2)_nPPh_2$	Products	Yield [b] (mol %/Ni)
1	PEt_3	dpm (n = 1)	[c]	
2	PEt_3	dpe (n = 2)	$NiMe_2(dpe)$	46
3	PEt_3	dpp (n = 3)	$NiMe_2(dpp)$	69
4	PEt_3	dpb (n = 4)	$Ni(dpb)_2$	44
5	1/2 bpy	dpm	[c, d]	
6	1/2 bpy	dpe	$NiMe_2(dpe)$	80
7	1/2 bpy	dpp	$NiMe_2(dpp)$	65
8	1/2 bpy	dpb	$Ni(dpb)_2$	28 [d]

[a] Diphosphine (1 mol/Ni) was added to the solution of $NiMe_2L_2$ at —30°C and the mixture was warmed to room temperature. [b] Yield after recrystallization. [c] Ni^0 complexes such as $Ni(dpm)_n$ and $Ni(PEt_3)_m(dpm)_n$ were produced (NMR, IR), but their isolation was not feasible. [d] About a half of $NiMe_2(bpy)$ remained intact.

product with a zero-valent nickel complex, Ni(dpp)$_n$, and evolution of some ethane (0.1—0.2 mol/Ni) were observed. This is considered to be due to the partial reductive elimination of C_2H_6 from the $NiMe_2(dpp)$ formed. In fact, maintaining a toluene solution of $NiMe_2(dpp)$ for 1 h at 30°C caused partial (ca. 20%) degradation of the complex to give C_2H_6 and Ni(dpp), although $NiMe_2(bpy)$ does not decompose at this temperature.

In contrast to dpe and dpp, a diphosphine with a shorter or longer methylene chain, $Ph_2PCH_2PPh_2$ (dpm) or $Ph_2P(CH_2)_4PPh_2$(dpb), did not give the expected dimethylnickel complex. Instead, they afforded reductive elimination products, $Ni(Ph_2P(CH_2)_nPPh_2)_2$ and ethane, on reaction with $NiMe_2L_2$. This result indicates that the Ni—Me bond in $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ is unstable when $n = 1$ or 4 and that such a complex easily undergoes reductive elimination.

Thus, the ligand exchange reaction between $NiMe_2L_2$ and the diphosphine can be summarized as follows:

$$NiMe_2L_2 + Ph_2P(CH_2)_nPPh_2 \rightleftharpoons \underset{(I)}{(NiMe_2(Ph_2P(CH_2)_nPPh_2))} + 2\ L \tag{1}$$

$$I \begin{cases} \xrightarrow{n\,=\,2\ R\,=\,0} NiMe_2(dpe) \\ \xrightarrow{n\,=\,3\ R\,=\,\text{slow}} \underset{\text{major}}{NiMe_2(dpp)} + \underset{\text{minor}}{Ni(dpp)_n + C_2H_6} \\ \xrightarrow{n\,=\,1\text{ or }4\ R\,=\,\text{fast}} \begin{array}{l} Ni(dpm)_n + C_2H_6 \\ Ni(dpb)_2 + C_2H_6 \end{array} \end{cases} \tag{2}$$

R: rate of reductive elimination under preparative conditions

As for dpe and dpp, the coordinating ability of the diphosphine ligands is much greater than those of bpy and PEt_3 and the equilibrium in equation 1 lies almost completely to the right as revealed by ^1H NMR studies of the equilibrium as well as by the high yields of the exchanged products as shown in Table 1.

Of the two diphosphine ligands, dpe has a higher coordinating ability to dimethylnickel(II) and the dpp ligand in $NiMe_2(dpp)$ can be replaced by dpe. The ^1H NMR spectrum of a 1 : 1 mixture of $NiMe_2(dpp)$ and dpe after attainment of the equilibrium at —25°C in toluene-d_8 showed the CH_3 signal of $NiMe_2(dpp)$ and that of $NiMe_2(dpe)$ in a 1 : 10 ratio, indicating the preferential coordination of the dpe ligand to that of the dpp ligand.

It has been reported that the coordinating ability of monodentate phosphine ligands to transition metals is dominated by steric factors rather than by electronic factors [5] and the interpretation of the coordinating ability based on steric factors has also been applied to diphosphines such as $R_2P(CH_2)_2PR_2$ ($R = CH_3, C_6H_5$, cyclo-C_6H_{11}) [9]. As for dpe and dpp, steric factors estimated by Tolman's cone angle θ around one phosphorus atom of diphosphine (θ = 125° (dpe) ≈ 127 (dpp) [5]) and basicities are considered to be almost equal. Therefore, it is thought that the large difference in the coordinating ability between dpe and dpp is not due to steric and electronic factors around one phosphorus atom, but, probably, to the conformation of the chelate ring determined by the chain length of $(CH_2)_n$.

Thus, the ligand exchange studies reveal that the coordinating ability of the ligand to dimethylnickel(II) decreases in the order dpe > dpp >> PEt_3, bpy. Observation of the visible spectrum of a benzene solution containing $NiMe_2$(bpy) (3×10^{-4} mol/l), dpe (6.4×10^{-3} mol/l), and bpy (7.3×10^{-1} mol/l) showed that the equilibrium constant ($K = [NiMe_2(dpe)][bpy]/[NiMe_2(bpy)][dpe]$) was much greater than 10^4 at 25°C.

Mechanism of ligand exchange reaction

Among the ligand exchange reactions listed in Table 1, the one between the colored $NiMe_2$(bpy) and dpp was amenable to kinetic studies by using visible spectroscopic techniques around room temperature, whereas the exchange reaction between $NiMe_2$(bpy) and dpe was too fast to follow at that temperature. The exchange reaction of $NiMe_2$(bpy) with dpp was followed by observing the decrease in the optical density of $NiMe_2$(bpy) at 675 nm.

Figure 1 indicates that the reaction rate is first order with respect to the concentrations of $NiMe_2$(bpy) and dpp, respectively.

$$R = -\mathrm{d}[NiMe_2(bpy)]/\mathrm{d}t = k[NiMe_2(bpy)][dpp] \qquad (3)$$

In Table 2 the temperature dependence of the second-order rate constant is shown. The activation parameters computed from the temperature dependence

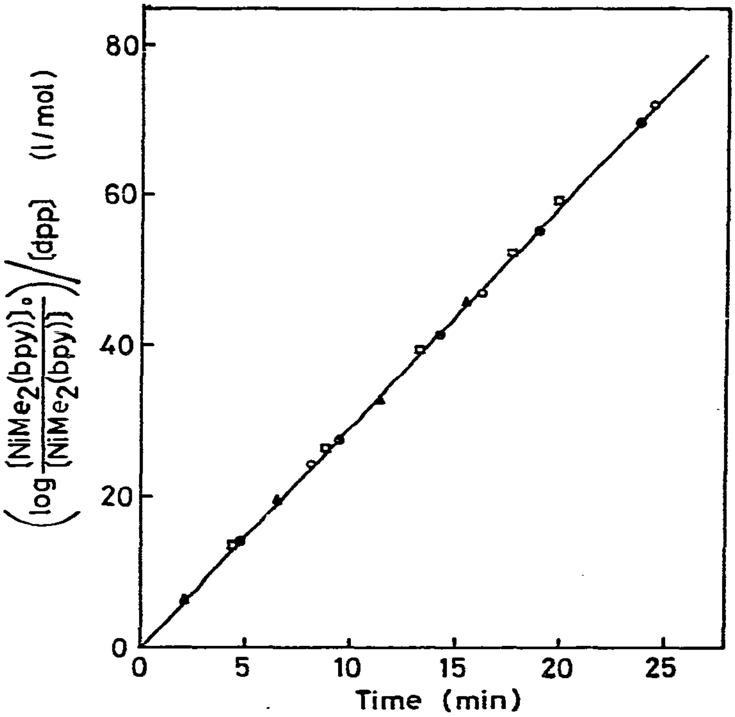


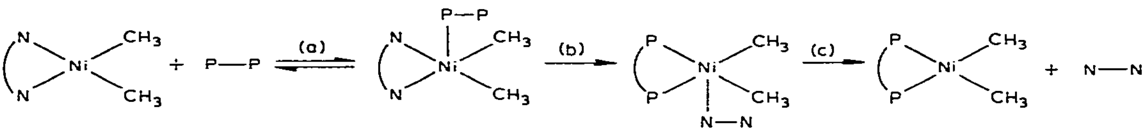
Fig. 1. Reaction of $NiMe_2$(bpy) with dpp in benzene at 27.0°C. Concentration of dpp: ○ 0.0038 mol/l, ● 0.0123 mol/l, □ 0.0188 mol/l, and ▲ 0.0233 mol/l.

TABLE 2

THE SECOND-ORDER RATE CONSTANTS IN THE LIGAND EXCHANGE REACTION OF $NiMe_2(bpy)$ WITH DPP

No	Temp. (°C)	$k \times 10^2$ (l/mol s)	E_a (kcal/mol)	$\Delta H^{\neq}_{300.0}$ (kcal/mol)	$\Delta S^{\neq}_{300.0}$ (e.u.)
1	18.4	6.98	8.9	8.3	—35
2	22.7	9.23			
3	27.0	11.2			
4	31.0	13.7			

are $\Delta H^{\neq} = 8.3$ kcal/mol and $\Delta S^{\neq} = -35$ e.u. at 27.0°C. The large negative activation entropy as well as the first-order rate dependence on the dpp concentration (Eq. 3) indicate that the ligand exchange reaction proceeds through an S_N2 mechanism. Most of the ligand exchange reactions of square planar complexes are known to proceed by S_N2 type pathways [10]. On the basis of the kinetic results we propose that the reaction proceeds through the following steps involving (a) initial coordination of dpp with nickel via one phosphorus atom, (b) partial dissociation of bpy and chelation of dpp, and (c) dissociation of bpy as shown below.



In the proposed mechanism, the difference in the chain lengths of $(CH_2)_n$ in the diphosphine (dpp and dpe) will affect step a only in a minor way because both the electronic and steric factors around the one phosphorus atom are considered to be almost equal. In considering the large difference between the rate of ligand exchange of $NiMe_2(bpy)$ and dpp and that of $NiMe_2(bpy)$ with dpe, it is thought that the rate of chelation of the diphosphine in step b is influenced by the chain lengths of $(CH_2)_n$ and probably the rate of dissociation of bpy in step c is not influenced very much by the nature of the diphosphine chelating to nickel.

Kinetics of the reductive elimination of C_2H_6 from $NiMe_2$(diphosphine)

As eq. 2 shows, the chain length of the diphosphine ligand profoundly affects the stability of the diphosphine-coordinated nickeldimethyls. Comparative kinetic studies on the thermolysis of $NiMe_2(dpe)$ and $NiMe_2(dpp)$ in diphenylmethane solution have been carried out,

$$NiMe_2(Ph_2P(CH_2)_nPPh_2) \rightarrow C_2H_6 + Ni(Ph_2P(CH_2)_nPPh_2) \quad (4)$$

The course of the evolution of C_2H_6 with time shows some deviation from the first-order rate law, presumably due to some effects of the formed $Ni(Ph_2P(CH_2)_nPPh_2)$ species on the reductive elimination (b and d in Fig. 2). Actually, in the absence of an excess of diphosphine, the thermolysis caused

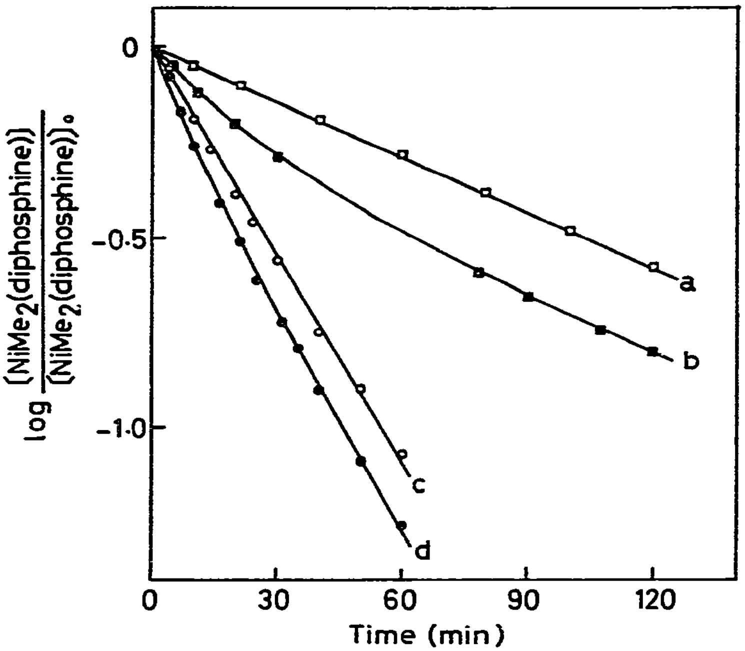


Fig. 2. Thermal decomposition of $NiMe_2$(diphosphine) in diphenylmethane. The amount of remaining $NiMe_2$(diphosphine) was calculated from the amount of ethane evolved. a, $NiMe_2$(dpe) + dpe (1 : 1.5) at 69.6°C; b, $NiMe_2$(dpe) only at 69.6°C; c, $NiMe_2$(dpp) + dpp (1 : 1.2) at 49.5°C; d, $NiMe_2$(dpp) only at 49.5°C.

deposition of black nickel metal, suggesting the occurrance of a bimolecular reaction between $NiMe_2$(diphosphine) and Ni(diphosphine) to give C_2H_6, Ni(diphosphine)$_2$, and Ni metal.

Trapping of $Ni(Ph_2P(CH_2)_nPPh_2)$ as $Ni(Ph_2P(CH_2)_nPPh_2)_2$ by addition of an excess of diphosphine prevented the deposition of nickel metal and gave the first-order rate law for the dimethylnickel(II) complex (a and c in Fig. 2),

$$NiMe_2(Ph_2P(CH_2)_nPPh_2) + Ph_2P(CH_2)_nPPh_2 \rightarrow C_2H_6 + Ni(Ph_2P(CH_2)_nPPh_2)_2 \quad (5)$$

$$d[C_2H_6]/dt = k'[NiMe_2(Ph_2P(CH_2)_nPPh_2)] \quad (6)$$

Following the reaction by ^{31}P-NMR showed the decrease of $NiMe_2$(diphosphine) and the free diphosphine as well as the increase of Ni(diphosphine)$_2$, revealing formation of no other phosphorus-containing species in the solution. The ^{31}P-NMR signal of each species was very sharp excluding the possibility of a rapid exchange on NMR time scale. The rate constants obtained under various conditions and the activation parameters are listed in Table 3. For comparison, the first-order rate constant of the thermolysis of $NiMe_2$(bpy) in diphenylmethan is also included.

It is seen that the rate of the reductive elimination of C_2H_6 from Ni is strongly affected by the diphosphine ligand attached to Ni. For example, the rate for $NiMe_2$(dpp) is 46 times faster than that for $NiMe_2$(dpe) at 64.3°C. The smaller activation enthalpy together with the larger activation entropy for the thermo-

TABLE 3

THE FIRST-ORDER RATE CONSTANTS FOR THE REDUCTIVE ELIMINATION OF C_2H_6 FROM $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ (n = 2, 3) [a]

No	Complex	Phosphine/Ni [b]	T (°C)	k' (min^{-1})	$\Delta H^{\neq}_{333.5}$ (kcal/mol)	$\Delta S^{\neq}_{337.5}$ (e.u.)
1	$NiMe_2$(dpe)	dpe/Ni = 1.5	64.3	0.0053	26.8	1.9
2	$NiMe_2$(dpe)	dpe/Ni = 1.5	70.0	0.0105		
3	$NiMe_2$(dpe)	dpe/Ni = 6.2	70.0	0.0109		
4	$NiMe_2$(dpe)	dpe/Ni = 1.5	78.5	0.028		
5	$NiMe_2$(dpe)	dpe/Ni = 1.5	87.0	0.070		
6	$NiMe_2$(dpp)	dpp/Ni = 1.2	45.0	0.023	25.1	4.8
7	$NiMe_2$(dpp)	dpp/Ni = 1.2	49.5	0.043		
8	$NiMe_2$(dpp)	dpp/Ni = 6.1	49.5	0.043		
9	$NiMe_2$(dpp)	dpp/Ni = 1.2	59.1	0.140		
10	$NiMe_2$(dpp)	dpp/Ni = 1.2	64.3	0.245		
11	$NiMe_2$(dpp)	PPh_3/Ni = 5.0	49.8	0.047		
12	$NiMe_2$(dpp)	PEt_3/Ni = 5.0	45.6	very fast [c]		
13	$NiMe_2(PEt_3)_2$	—	45.6	very fast [c]		
14	$NiMe_2$(bpy)	—	87.8	0.0045 [d]		

[a] The reaction was carried out in diphenylmethane solution. [b] Molar ratio of the added phosphine to $NiMe_2(Ph_2P(CH_2)_nPPh_2)$. [c] The reaction rate was too fast to be determined. [d] The rate constant for the thermolysis of solid $NiMe_2$(bpy) is given in ref. 7a.

lysis of $NiMe_2$(dpp) than those of $NiMe_2$(dpe) contribute to make $NiMe_2$(dpp) less stable than $NiMe_2$(dpe).

The independence of the rate constant on the amount of diphosphine added (No 2, 3 and 7, 8 in Table 3) excludes the possibility that the reductive elimination proceeds through a mechanism involving further coordination of diphosphine to $NiMe_2$(diphosphine) to form $NiMe_2(\text{diphosphine})_2$ or full dissociation of the diphosphine ligand from $NiMe_2$(diphosphine).

An explanation which is compatible with the experimental results is related to the inherent strength of the Ni—CH_3 bond affected by the attached bidentate diphosphine ligand.

This view reminds us of the effect of the chain length of $(CH_2)_n$ of diphosphine ligands on the geometry and electronic state of MX_2(diphosphine) type complexes. An X-ray crystallographic analysis of $PtCl_2((t\text{-}Bu)_2P(CH_2)_nP(t\text{-}Bu)_2)$ (n = 2, 3) revealed a distortion from square planar geometry toward tetrahedral when n is varied from 2 to 3 [11a]. A similar change in the geometry of $NiX_2(Ph_2P(CH_2)_nPPh_2)$ (X = Br, I; n = 2, 3) from the square planar to a square planar—tetrahedral equilibrium in solution on varing n from 2 to 3 reportedly brings about changes in the electronic state of Ni from diamagnetic to a diamagnetic—paramagnetic equilibrium [11b]. Similar changes in the geometry and electronic state of Ni are also conceivable with $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ (n = 2, 3) on varing n, and if the species distorted from square planar to tetrahedral undergoes the reductive elimination more easily than the species having the square planar configuration, the difference in the ease of reductive elimination between $NiMe_2$(dpe) and $NiMe_2$(dpp) may be explained. An alternative reason for explaining the difference in their thermal stability between $NiMe_2$(dpe) and $NiMe_2$(dpp) may be found in the assumption that the reductive elimination proceeds through a three-coordinated species formed on partial dissociation of the diphosphine ligand. It has been reported [12], on the basis of a kinetic study and theoretical calculation, that the dissociation of one ligand from four coordinate transition metal alkyls is essential for the occurrence of reductive elimination of alkanes R—R from certain four-coordinate alkyltransition metal complexes having the R groups. If one assumes an equilibrium between the four-coordinate species $NiMe_2$ (P ~ P) and a partially dissociated three-coordinate species $NiMe_2$ (P ~ P*) (P* denotes the phosphorus uncoordinated to Ni) and that the reductive elimination proceeds through the three-coordinate species, the change of the stability of $NiMe_2(Ph_2P(CH_2)_nPPh_2)$ with varying n can be reasonably explained, since the thermal stability of the complex increases with the increase in the coordinating ability of the diphosphine ligand, dpm, dpb < dpp < dpe.

In the course of their studies on the Ni-catalyzed C—C coupling reaction between RMgX and R'X, Tamao and his coworkers found that $NiCl_2(Ph_2P(CH_2)_nPPh_2)$ (n = 2—4) exhibited remarkable activities, which decreased in the order $n = 3 > n = 2 > n = 4$ [6]. The catalytic C—C coupling reaction has been considered to proceed through the reductive elimination of R—R' from an intermediate $NiR(R')L_2$ species on interaction of R'X to form $NiR'(X)L_2$ which is alkylated to $NiR(R')L_2$ by RMgX.

It is noted that the order of the catalytic activities of the diphosphine-coordinated nickel catalyst systems with the varying CH_2 chain length differs from the order of the ease of reductive elimination with the diphosphine coordinated nickeldimethyls ($n = 2 < n = 3 \ll n = 1, 4$). Since the rate-determining step in the catalytic cycle of the C—C coupling has not been located, one cannot deduce a straightforward conclusion. It may be stated, however, that the diphosphine ligand which makes the dialkylnickels too unstable or too stable may not give the species with the highest catalytic activity.

Experimental

General and materials

All reactions were carried out under nitrogen or argon or in vacuum. The amount of gas evolved during the reaction was measured with a Toepler pump and analyzed by GLC using a Shmadzu GC-3BT gas chromatgraph. NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer (TMS as an internal standard) and visible spectra were recorded on a Hitachi 200-20 spectrophotometer.

Reactions of $NiMe_2L_2$ with diphosphines

Reaction of $NiMe_2(bpy)$ with dpp. 1,3-Bis(diphenylphosphino)propane (dpp) (254 mg, 0.62 mmol) was added to a toluene (2 ml) solution of $NiMe_2$-(bpy) (147 mg, 0.60 mmol) at —30°C. The mixture was stirred at room temperature for 1 h to give a yellow suspension with evolution of a small amount of ethane. Addition of 5 ml of hexane yielded 317 mg of a yellow solid, which was recrystallized from THF-hexane to afford $NiMe_2$(dpp) (yield = 194 mg, 65%); Anal. Found: C, 69.1; H, 6.5. $C_{29}H_{32}NiP_2$ Calcd.: C, 69.5; H, 6.4%; mp (decomp) 95°C; ^1H NMR (C_6D_6): δ: 0.69 (6 H, dd, $^3J(P^1—H) = 10$ Hz, $^3J(P^2—H) = 2$ Hz, Ni—CH_3), 1.4 (2 H, m, CH_2—CH_2—CH_2), 1.9 (4 H, m, P—CH_2), 7.1—7.7 ppm (20 H, phenyl).

Reaction of $NiMe_2(PEt_3)_2$ with dpp. To an ether (5 ml) solution of $NiMe_2(PEt_3)_2$ (233 mg, 0.69 mmol) dpp (284 mg, 0.69 mmol) was added at —30°C. The temperature was gradually raised from —30°C to 0°C and after 2 h a yellow precipitate was formed. This yellow precipitate was washed with ether to give $NiMe_2$(dpp) (yield = 238 mg, 69%).

Reaction of $NiMe_2$(bpy) with dpe. 1,2-Bis-(diphenylphosphino)ethane (dpe) (166 mg, 0.42 mmol) was added to a toluene (2 ml) solution of $NiMe_2$(bpy) (95 mg, 0.39 mmol) at room temperature. The mixture was stirred at room temperature for 30 min to give a yellow solution. Careful addition of excess hexane yielded a yellow solid, which was washed with hexane to afford the known $NiMe_2$(dpe) [8] (yield = 152 mg, 80%) as characterized with IR and NMR spectroscopy.

Reaction of $NiMe_2(PEt_3)_2$ with dpe. The reaction of $NiMe_2(PEt_3)_2$ (254 mg, 0.52 mmol) with dpe (246 mg, 0.62 mmol) was carried out in a similar manner to that of $NiMe_2(PEt_3)_2$ with dpp. $NiMe_2$(dpe) (yield = 117 mg, 46%) was obtained.

Reaction of $NiMe_2$(bpy) with dpm. To a toluene (1 ml) solution of $NiMe_2$(bpy) (86 mg, 0.35 mmol) diphenylphosphinomethane (146 mg, 0.38 mmol) was added at —30°C. The mixture was stirred at room temperature for 1 h to give a dark green solution with evolution of ethane. Cooling the dark green solution to —78°C yielded a deep green solid. Examination of the IR spectrum (KBr) indicated that this deep green solid was a mixture of $NiMe_2$(bpy) and dpm-coordinated Ni complex(es). The ^1H NMR spectrum of a 1 : 1 mixture of dpm and $NiMe_2$(bpy) in toluene-d_8, after 1 day, showed signals of ethane (δ = 0.80 ppm), free bpy, intact $NiMe_2$(bpy), and coordinating dpm (δ = 3.26 ppm (br, $P—CH_2—P$)) in about a 1 : 1 : 1 : 2 molar ratio.

Reaction of $NiMe_2(PEt_3)_2$ with dpm. To an ether (2 ml) solution of $NiMe_2(PEt_3)_2$ (145 mg, 0.45 mmol) dpm (220 mg, 0.58 mmol) was added at —30°C. The temperature was gradually raised from —30°C to room temperature and after 1 day a deep red solution was obtained. On cooling the solution to —78°C, red crystals were deposited (yield = 163 mg). The crystals were highly air sensitive and micro analysis was not feasible. The ^1H NMR spectrum showed signals of PEt_3 (δ = 0.8—1.8 ppm (br, $P—C_2H_5$) and dpm (δ = 4.2 ppm (br, $P—CH_2—P$), 7.1 and 7.7 ppm (br, $P—C_6H_5$)) (PEt_3/dpm = 3/1). The IR spectrum (KBr) showed only absorption bands assignable to the coordinating PEt_3 and dpm.

Reaction of $NiMe_2$(bpy) and dpb. To a toluene solution of $NiMe_2$(bpy) (69 mg, 0.28 mmol) 1,4-bis(diphenylphosphino)butane, dpb, (136 mg, 0.32 mmol) was added at —30°C. The mixture was stirred at room temperature and after 1 day an orange solid precipitated with evolution of ethane. Filtration and washing with ether gave the known $Ni(dpb)_2$ (yield = 28%) [13]. Anal. Found: C, 74.3; H, 6.2. $C_{56}H_{56}NiP_4$ Calcd.: C, 73.8; H, 6.2%.

Reaction of $NiMe_2(PEt_3)_2$ and dpb. To an ether solution of $NiMe_2(PEt_3)_2$ (161 mg, 0.50 mmol) dpb (212 mg, 0.50 mmol) was added at —40°C. The temperature was gradually raised from —40°C to room temperature and after 1 day an orange solid was obtained. Filtration gave $Ni(dpb)_2$ (yield = 44%).

Kinetic studies of the ligand exchange reaction between $NiMe_2(bpy)$ and dpp

The temperature of the benzene solution of $NiMe_2$(bpy) (2×10^{-4}—4×10^{-4} mol/l) and dpp (3×10^{-3}—4×10^{-2} mol/l) in a Schlenk type cell was controlled to ±0.5°C by passing thermostatted water around the cell. The visible spectrum of $NiMe_2$(bpy) shows an absorption maximum at 675 nm, whereas the absorption maximum of $NiMe_2$(dpp) appears at 350 nm without any absorption at 675 nm. As the ligand exchange reaction proceeds, the color of the solution changes from green to yellow and the reaction was followed by observing the decrease of the optical density at 675 nm.

Kinetic studies on the thermal decomposition of $NiMe_2(Ph_2P(CH_2)_nPPh_2)$

A 20 ml Schlenk tube containing a diphenylmethane (3—4 ml) solution of the dimethylnickel(II) complex (0.1—0.2 g) and phosphine (0—6.1 mol/Ni) was connected to a vacuum line equipped with a mercury manometer and the system was evacuated. The temperature was controlled by passing thermostatted water around the Schlenk tube. The rate constant for thermolysis was obtained by measuring the gas evolved with time.

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