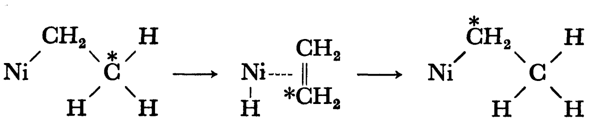
Dynamic Behavior of Acetylacetonato, Triphenylphosphine and Alkyl Ligands in $NiR(acac)(PPh_3)_n$ ($R=C_2H_5$, CH_3) in Solution and Disproportionation of the Alkylnickel Complexes in Pyridine

Takakazu Yamamoto, Toshio Saruyama, Yoshiyuki Nakamura, and Akio Yamamoto*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152

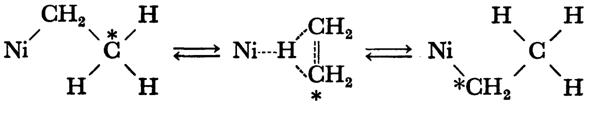
(Received August 18, 1975)

Dynamic behavior of acetylacetonato (acac), triphenylphosphine (PPh_3) and ethyl (in the case of **1**) ligands of $NiR(acac)(PPh_3)_n$ ($R=C_2H_5$, $n=1$ (**1**); $R=CH_3$, $n=2$ (**2**)) in solution has been studied. PPh_3 ligand(s) in **1** and **2** exchange rapidly on NMR time scale with free PPh_3 in solution. Addition of excess PPh_3 makes the exchange rate much faster and an S_N2 mechanism is proposed to explain the acceleration effect. ^{31}P-NMR spectrum of **1** in pyridine shows that the PPh_3 ligand is replaced by the solvent molecule. Acac ligands in **1** and **2** also undergo rapid interchange on NMR time scale. The activation energy for the acac interchange is about 10 kcal/mol. On standing a specifically deuterated ethylnickel complex, $Ni(CH_2CD_3)(acac)(PPh_3)$ **1**-d_3 in solution, the hydrogens and deuteriums in the ethyl group were scrambled. Appearance of the methyl proton signals in the ^1H-NMR spectrum of the deuterated ethylnickel complex after the treatment in solution demonstrates the occurrence of the H–D scrambling in solution. Both **1** and **2** undergo disproportionation reactions in pyridine. The rate of the disproportionation is second-order with respect to the concentration of **2**.

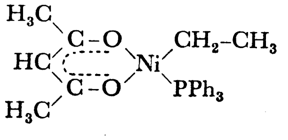
Ethyl(acetylacetonato)(triphenylphosphine)nickel(II), **1**, provides an interesting object for study of its dynamic behavior in solution. The preliminary NMR study of this complex has led us to suggest that all the ligands including ethyl, acetylacetonato and triphenylphosphine may have dynamic properties in solution.[1] The prime attention was focussed on the NMR spectrum of the ethyl group which appeared as a singlet in benzene, toluene, tetrahydrofuran and acetone and as a pair of a triplet and a quartet in pyridine (at 220 MHz). The observation of the nickel-bound ethyl group as a singlet in particular solvents appeared to suggest that this complex might afford a unique example that the ethyl group undergoes rapid reversible processes involving β-elimination and its reverse reaction such as:



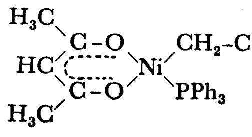
or an alternative process such as:



where the intermediacy of the ethylene-coordinated nickel hydride of any significant life time is not involved but the abstracted hydrogen is rapidly transferred in a concerted manner back and forth between two carbon atoms bonded to nickel.[12] If this should be the case the complex may be regarded as a model system for the active species of catalysts promoting various olefin catalyses such as isomerization and oligomerization. The particular feature of the complex has immediately caught attention of Cotton and coworkers who refuted the non-rigid nature of the ethyl group on the basis of ^{13}C-NMR study as well as X-ray examination of **1** which was shown to possess a normal molecular structure with a square planar configuration of the ethyl group, bidentate acetylacetonato and triphenylphosphine ligands around nickel.[2]



1



1-d_3

Our subsequent ^{13}C-NMR study of the complex also confirmed the normal ^{13}C-NMR spectrum for the ethyl group. The observation of the normal ^{13}C-ethyl signal recorded by a PFT method, however, does not warrant the complete exclusion of the possibility of proton scrambling of the ethyl group. If the chemical shift difference between CH_2 and CH_3 groups in ^{13}C-NMR is much larger than that in ^1H-NMR, and the relaxation of ^{13}C's of the ethyl group should be much faster than the rate of scrambling, the non-decoupled ^{13}C-NMR may still exhibit the triplet and quartet feature with the concomitant scrambling process taking place. In order to get an unequivocal information regarding the suspected proton scrambling process we prepared a specifically deuterated ethylnickel complex $Ni(CH_2CD_3)(acac)(PPh_3)$ **1**-d_3 and examined its behavior by spectroscopic as well as chemical means. The NMR examination of **1**-d_3 revealed that the H–D scrambling is not taking place on NMR time scale but a chemical study of **1**-d_3 in solution indicated that slow scrambling process does occur.

In addition to the ethyl group, other ligands coordinated to nickel in **1** including the acetylacetonato and triphenylphosphine ligands show dynamic behavior amenable to NMR study. We describe here the detailed study of the dynamic behavior of **1** in solution and compare it with its methyl analog, $NiCH_3(acac)(PPh_3)_2$, **2**.

These alkylnickel complexes behave differently in pyridine and undergo a disproportionation reaction. This paper includes the kinetic study of the reaction in pyridine as followed by ^1H-NMR spectroscopy.

Experimental

Materials. $NiC_2H_5(acac)(PPh_3)$ **1**[1)] was prepared by stirring 15 g (58 mmol) of $Ni(acac)_2$, 18.6 g (71 mmol) of PPh_3 and 36 ml (240 mmol) of $Al(C_2H_5)_2(OC_2H_5)$ in 90 ml of deoxygenated and dehydrated toluene at −40 °C for 40 hr under nitrogen. The yellow-brown complex can be recrystallized from toluene, benzene, acetone or ether. Yield: about 65%; mp 93 °C (decomp.). Found: C, 66.9; H, 6.1%. Calcd for $NiC_2H_5(acac)(PPh_3)$: C, 66.9; H, 6.0%; mol wt, 449; mol wt, (cryoscopic in benzene), 450.

$NiCH_3(acac)(PPh_3)_2$ **2**[1)] was prepared and recrystallized in a similar manner by using $Ni(acac)_2$, PPh_3 and $Al(CH_3)_2(OC_2H_5)$ in a molar ratio of 1:2:4: mp 102—103 °C. Found: C, 72.5; H, 6.0%. Calcd for $NiCH_3(acac)(PPh_3)_2$: C, 72.3; H, 5.8%.

Deuterated triethylaluminum $Al(CH_2CD_3)_3$ was prepared by using commercially available CD_3COOD (150 g, 2.38 mol) as the starting material for the preparation of $Ni(CH_2CD_3)(acac)(PPh_3)$ **1**-d_3. CD_3COOD was reduced to CD_3CH_2OH by $LiAlH_4$, and the deuterated ethanol was converted to CD_3CH_2Br by treatment with PBr_3. Deuterated triethylaluminum etherate, $Al(CH_2CD_3)_3(O(C_2H_5)_2)$, was prepared and purified by distillation (91—93 °C/10 mmHg) by the method described in literature.[3)] Yield, 10.3 g (0.16 mmol, 6.6%). $Al(CH_2CD_3)_2(O(C_2H_5)_2)$ was prepared from the deuterated triethylaluminum and ethyl alcohol (1: 1) and used without purification. Acidolysis of the deuterated triethylaluminum by H_2SO_4 gave 92% of CH_3CD_3 and 8% of CH_2DCHD_2 as analyzed by mass spectroscopy, suggesting a slight H–D scrambling took place during the preparation (presumably during the distillation of $Al(CH_2CD_3)_3(O(C_2H_5)_2)$. The deuterated ethylnickel complex $NiCH_2CD_3(acac)(PPh_3)$ was prepared both in toluene, as described above, and in diethyl ether by the method described by Cotton and coworkers.[2)] Cotton's method, in which the reaction was carried out at room temperature, was modified for avoiding the possible scrambling of the ethyl group and the reaction temperature was kept below —10 °C throughout the preparation of **1**-d_3.

The mass spectrum of the ethane released by acidolysis of the deuterated ethylnickel complex with H_2SO_4 and the ^{1}H-NMR spectrum of **1**-d_3 in pyridine indicated that the H–D scrambling of the ethyl group during the preparation was negligible (see the results and discussion). The IR spectrum (KBr) of the deuterated ethylnickel complex showed ν_{C-D} at 2190, 2160, 2100, and 2040 cm^{-1}. When the preparation was carried out at room temperature (in toluene, 1 day), hydrogens and deuteriums of the ethyl group were scrambled during the preparation as proved by the evolution of CH_3CD_3 and CH_2DCHD_2 in a ratio of about 1: 1 on acidolysis of the complex by H_2SO_4.

*Reaction of **1** with Deuterium.* On treating **1** (0.75 mmol) with D_2 (2.1 mmol) in toluene (18 °C, 3 days) variously deuterated ethanes (4 mol % per **1**) were formed, whose mass spectrum (70 eV) showed the following pattern: $m/e=36$ (relative peak height=37), 35 (51), 34 (108), 33(143), 32(670), 31 (635), 30 (819), 29 (643), 28 (890), 27 (265), 26 (127). The isotopic purity of the deuterium gas employed decreased from 0.995 to 0.966 after the treatment of **1** with the deuterium gas.

Spectral Measurements and Analysis. The IR spectra of complexes were obtained by using Hitachi Model EPI-G3 spectrometer. IR spectra of deuterated ethylene evolved on standing **1**-d_3 in pyridine were recorded on Perkin Elmer Model 125. The IR spectra of specifically deuterated ethylene are given in literature.[11)] ^{1}H-, ^{31}P-, and ^{13}C-NMR spectra were measured with a Japan Electron Optics Laboratory PS-100 spectrometer. ^{31}P- and ^{13}C-NMR were obtained in the pulsed Fourier transform mode at 40.50 and 25.15 MHz, respectively. Measuring temperature of the NMR spectra was not corrected. Deuterated solvents were used as purchased from Merck and Co., Inc. The solvent and tetramethylsilane were added to an NMR tube containing $NiR(acac)(PPh_3)_n$ by a trap-to-trap distillation in vacuum and the NMR tube was sealed. ^{1}H- and ^{13}C-NMR chemical shifts are referred to internal TMS (downfield positive) and ^{31}P-NMR signals to external triphenylphosphine (downfield positive).

Mass spectra of gases were obtained with a Hitachi type RMU-5B Spectrometer. The distribution of deuterated ethanes evolved on acidolysis of the deuterated ethylnickel complex was calculated from the mass spectra. The mass spectra of specifically deuterated ethanes are given in literature.[4)]

The microanalysis of carbon and hydrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type Mt-2.

Results and Discussion

*Dynamic Behavior of Ligands in $NiC_2H_5(acac)(PPh_3)$ **1** and $NiCH_3(acac)(PPh_3)_2$ **2**. Triphenylphosphine (PPh_3) Ligand*: ^{31}P-NMR spectra of **1** in toluene and pyridine with and without addition of excess triphenylphosphine are shown in Fig. 1. In toluene, without excess PPh_3, a sharp singlet peak due to the coordinated PPh_3 ligand is observed at 44 ppm downfield from external free PPh_3 at −60 °C. At higher temperatures the singlet becomes broad with slight shift to higher field. With excess PPh_3 ($[\mathbf{1}]/[PPh_3]=1$) the ^{31}P-NMR spectrum at −80 °C shows two broad signals at 44 ppm and at the position of free PPh_3 in an area ratio of *ca.* 1: 1. These results indicate that liberation of PPh_3 from **1** at −60 °C is negligible whereas raising the temperature enhances the liberation of PPh_3 from **1** and

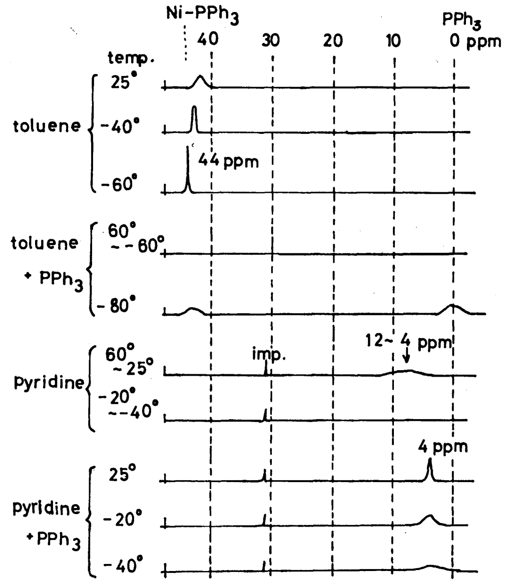


Fig. 1. ^{31}P-NMR spectra of $NiC_2H_5(acac)(PPh_3)$ under various conditions. A peak near 30 ppm which appears in pyridine is due to $Ni(C_2H_4)(PPh_3)_2$ formed by the disproportionation of **1** in pyridine (see the text).

accelerates the PPh_3 exchange of **1** with the liberated PPh_3, although the degree of dissociation is not extensive even at room temperature as revealed by the ^{31}P-NMR in toluene and molecular weight measurement of **1** in benzene. In the presence of added PPh_3, ligand exchange takes place more rapidly even at −80 °C suggesting an S_N2 mechanism, although no definite sign for the formation of $NiC_2H_5(acac)(PPh_3)_2$ corresponding to the methyl analog **2** was observed. The more rapid ligand exchange between **1** and the added PPh_3 at higher temperatures than −60 °C causes collapse of the separated two peaks.

The rate constants of the dissociation of PPh_3 from **1** (the reciprocal of the life time of PPh_3 in **1**, $1/\tau_{Ni-P}=k$ in Eq. 1) calculated

$$Ni(C_2H_5)(acac)(PPh_3) \underset{k'}{\overset{k}{\rightleftharpoons}} Ni(C_2H_5)(acac) + PPh_3 \quad (1)$$

from the half widths of the ^{31}P-NMR signals are summarized in Table 1, which includes the rate constants of dissociation of PPh_3 from **1** in acetone and pyridine and those from **2** in toluene.

Table 1. The rate constants of dissociation of PPh_3 from $NiR(acac)(PPh_3)_n$

Compound	Solvent	[Added PPh_3]/[**1**]	Temp (°C)	Rate constant (s^{-1})
1	Toluene	0	25	1.6×10^2
	Toluene	0	−40	4.0×10
	Toluene	1	−80	4.2×10^2
	Acetone	0	25	2.2×10^2
	Pyridine	3.4	25	1.0×10^5
	Pyridine	3.4	−20	2.6×10^4
	Pyridine	3.4	−40	1.9×10^4
			$E_a=4$ kcal/mol	
2	Toluene	0	25	2.8×10^3
	Toluene	0	−60	2.1×10^2

In pyridine the dissociation of **1** to liberate the coordinated triphenylphosphine ligand is more extensive as shown in Fig. 1. The exchange rate seems to be also high and only a broad signal was observed at 25 °C and above at a position between the coordinated PPh_3 and free PPh_3, but much closer to that of free PPh_3. Decrease of the temperature obscured the spectrum and no distinct signal was observed at −20∼−40 °C. Addition of PPh_3 to the pyridine solution containing **1** gives rise to a somewhat sharp singlet observed at 25 °C downfield from that of free PPh_3. Suppression of the exchange by lowering the temperature from 25 °C down to −40 °C makes the signal broader.

If one assumes that the chemical shift of the coordinated PPh_3 ligand of **1** in pyridine does not differ so markedly from that in toluene, the ratio of undissociated complex to the completely dissociated complex solvated with pyridine can be computed from the chemical shift of the broad signal observed in the absence of added PPh_3 as 1/10 to 1/4 in the temperature range of 60 °C to 25 °C.

The ^{31}P-NMR spectrum of the pentacoordinated methylnickel complex **2** shows somewhat different temperature dependence pattern from that of the ethyl analog **1** (Fig. 2). The single resonance which is observed as a reasonably sharp signal at −80 °C in toluene at 46 ppm downfield from free PPh_3 may be ascribed to the coordinated PPh_3 ligands in **2**. With raising the temperature to −40 °C the signal broadens and shifts to higher field indicating the exchange of the coordinated PPh_3 ligands with PPh_3 liberated from **2**. At 25 °C the signal shifts further upfield and sharpens indicating the more rapid exchange taking place. ^{31}P-NMR spectrum of the mixture of **2** and added PPh_3 in a 1:0.6 ratio in toluene is similar to the system of (**1**+PPh_3) showing broad peaks of the coordinated PPh_3 and free PPh_3 exchanging each other even at −80 °C. Raising the temperature causes collapse of the peaks and at 25 °C building up of a broad single peak can be noticed as an indication that exchange rate is enhanced by raising the temperature.

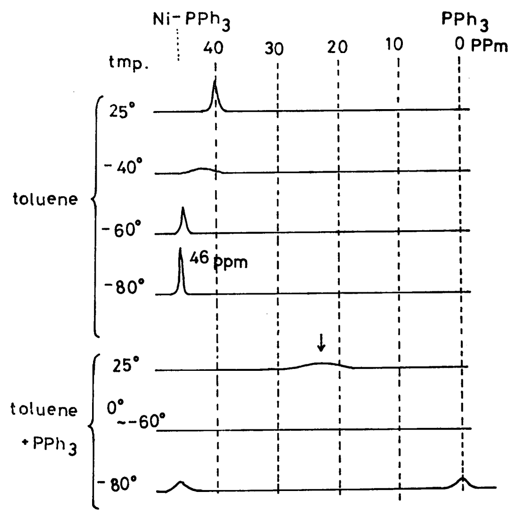
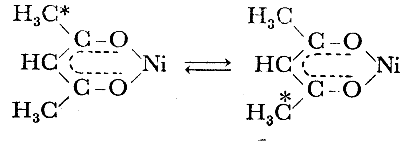


Fig. 2. ^{31}P-NMR spectra of **2** in toluene with and without addition of PPh_3.

The activation energies for dissociation of PPh_3 from **1** and **2**, roughly estimated from the data in Table 1 are in the range of 4—6 kcal/mol which are much less than the values reported for dissociation of tertiary phosphines from nickel complexes.[5]

Acetylacetonato(acac) Ligand: The ^1H-NMR spectra of **1** and **2** have been summarized in our preliminary report.[1] The ^1H-NMR spectra of **1** in acetone-d_6 and benzene-d_6 at various temperatures have been also observed by Cotton, *et al.*[2] At room temperature or below the ^1H-NMR shows two acac(CH_3) peaks. On heating **1** in the solvents these peaks undergo a continued broadening, coalescence, and then sharpening as a result of a time averaging of the two CH_3 groups. A similar temperature dependence of ^1H-NMR spectra is observed in toluene-d_8 and tetrahydrofuran-d_8. In pyridine, however, only one sharp acac(CH_3) peak appears at room temperature. On cooling the pyridine solution the peak becomes broad and then separates into two broad peaks.



(2)

TABLE 2. THE RATE CONSTANTS OF THE acac INTERCHANGE IN **1**

Solvent	Additive	[Additive]/[**1**]	Temp (°C)	Rate Constant (s^{-1})
Toluene	—	—	60	1.3×10^2
Toluene	—	—	40	1.1×10
Toluene	PPh_3	4.3	70	2.1×10^2
Toluene	PPh_3	4.3	60	1.3×10^2
Toluene	PPh_3	4.3	40	1.1×10
Benzene	Ethylene	2.0	60	4.3×10^2
Benzene	Ethylene	2.0	40	9.3×10
Benzene	Ethylene	2.0	25	6.8×10
Pyridine	—	—	20	3.9×10^3
Pyridine	—	—	0	1.0×10^3
Pyridine	—	—	−20	3.0×10^2
Pyridine	—	—	−40	1.4×10^2
Pyridine	PPh_3	1.7	25	5.0×10^3
Pyridine	PPh_3	1.7	0	9.0×10^2
Pyridine	PPh_3	1.7	−20	2.1×10^2
Pyridine	PPh_3	1.7	−40	1.3×10^2

The rate constants of the acac interchange in **1** (Eq. 2) under various conditions are summarized in Table 2.

Since the addition of excess PPh_3 does not affect the rate constant, the acac interchange is independent of the exchange of PPh_3 whose exchange rate depends on the excess PPh_3 in the solutions. The mechanism for the interchange is not clear at the moment. However, a mechanism involving M–O bond rupture to form a monodentate acac complex has been proposed for the mechanism of the exchange of acac ligand in some acetylacetonato complexes,⁶⁾ and the rupture of Ni–O bond followed by a rotation of the monodentate acac around the Ni–O bond and formation of a new Ni–O bond will be one of the most probable mechanisms for the present acac interchange.

Replacement of PPh_3 in **1** by pyridine and addition of ethylene cause the acceleration of the interchange. Since attempts to obtain an ethylene-coordinated complex from a mixture of **1** and ethylene failed, the interaction between **1** and ethylene seems to be weak. However, such a weak interaction (presumably π-type interaction) makes the rate faster by a factor of 4—9. A similar acceleration effect was observed when one added stryrene or acrylonitrile into the solution of **1**.

The activation energy for the acac interchange (about 10 kcal/mol) is of the same magnitude as those obtained for various acac complexes.⁶⁾

The ^{1}H-NMR spectra of **2** at room temperature show two separate peaks for the acac CH_3 groups in toluene-d_8 and a single peak in pyridine-d_5, similarly to the ^{1}H-NMR spectra of **1** in these solvents. On cooling the pyridine solution the singlet becomes broad. However, since the acac interchange of **2** in pyridine is faster than that of **1**, separation of the peak was not observed even at the low temperatures, in contrast to the case of **1**.

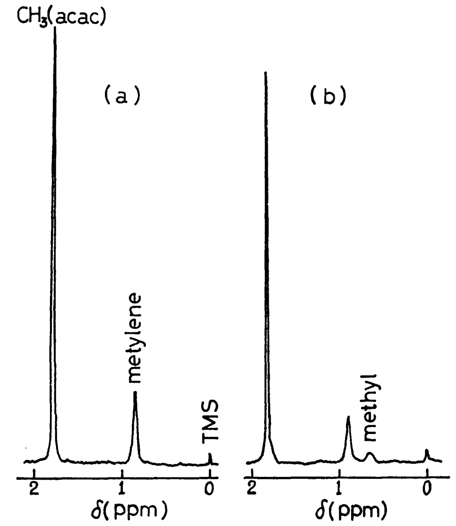


Fig. 3. ^{1}H-NMR spectra of the deuterated ethylnickel complex in pyridine (a) without treatment in solution and (b) after treatment in toluene (Room temp., 2 hr).

Ethyl Group in **1**: We prepared deuterated ethylnickel complexes from $Ni(acac)_2$, PPh_3 and $Al(CH_2CD_3)_2(OC_2H_5)(O(C_2H_5)_2)$ at −40∼−10 °C. The following three facts indicate that the H–D scrambling did not take place during the preparation. (1) The acidolysis of the complex by H_2SO_4 gives 91% of CH_3CD_3 and 9% of CH_2DCHD_2 which coincides, within experimental error, with the composition of ethane released on the acidolysis of the deuterated triethylaluminum used for the preparation. (2) The ^{1}H-NMR of the deuterated ethylnickel complex in pyridine shows a strong methylene peak, and methyl peak is not observable (Fig. 3a). (3) The ^{1}H-NMR spectrum of propionyl(acetylacetonato)(triphenylphosphine)nickel⁷⁾ prepared by the reaction of the deuterated ethylnickel complex with CO clearly demonstrates that it is composed mainly of $NiCOCH_2CD_3$ (Fig. 4a).

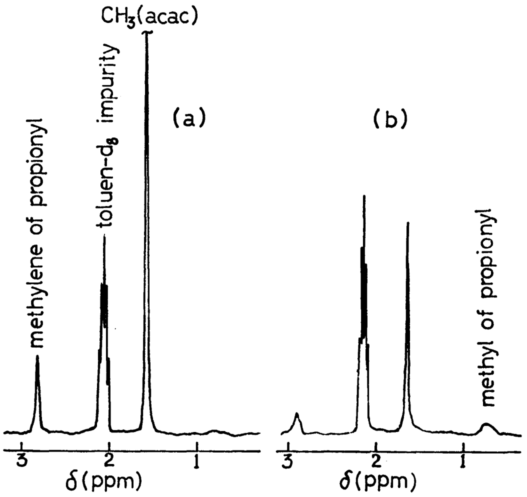


Fig. 4. ^{1}H-NMR spectra of the propionyl (acetylacetonato)(triphenylphosphine)nickel in toluene-d_8 prepared by the reaction of **1**-d_3 and CO. (a) Without treatment of **1**-d_3 in solution. (b) After treatment of **1**-d_3 in acetone (Room temp., 1.5 days).

Since the preparation of $Ni(CH_2CD_3)(acac)(PPh_3)$ **1**-d_3 was carried out at −40∼−10 °C where the ethyl signal appears as a sharp singlet in less basic solvents, the H–D scrambling should have taken place during the preparation if the rapid scrambling on NMR time scale should occur and, consequently, we can completely rule out the rapid proton scrambling on NMR time

Table 3. Composition of the deuterated ethanes evolved on acidolysis of the deuterated ethylnickel complex

No	H–D Scrabling conditions			Composition of deuterated ethanes formed on acidolysis					
	Solvent	Temp (°C)	Time	C_2HD_5	$C_2H_2D_4$	CH_3CD_3	CH_2DCHD_2	$C_2H_4D_2$[a]	C_2H_5D[a]
1	Without treatment					91	9		
2	Toluene	25.6	7.5 min			86.5	13.5		
3	Toluene	25.6	16 min			83	17		
4	Toluene	25.6	31 min			78	22		
5	Toluene	25.6	82 min			71	29		
6	Acetone	24.4	47 min		1	74	24	1	
7	Acetone	24.4	111 min	1	16	22	42	16	1
8	Acetone	Room temp.	a few hrs	2	16	12	52	16	2
9	Pyridine	Room temp.	2.5 days		3	38	56	3	

a) The following relation was assumed: the amounts of $C_2H_4D_2$ and C_2H_5D are equal to the amounts of $C_2H_2D_4$ and C_2HD_5, respectively.

scale based on the facts described above.

Although the rapid scrambling on NMR time scale does not take place, a slow H–D scrambling does occur when one allows the deuterated ethylnickel complex to stand in solutions.

Table 3 summarizes the composition of ethane evolved on acidolysis of the deuterated ethylnickel complex with H_2SO_4 after treatments in solutions.

Through an intramolecular H–D scrambling the specifically deuterated ethylnickel complex is expected to become a mixture of Ni–CH_2CD_3, Ni–$CHDCHD_2$ and Ni–CD_2CH_2D complexes; the first one will evolve CH_3CD_3 on acidolysis with H_2SO_4 and the last two CH_2DCHD_2. Therefore, an increase of CH_2DCHD_2 fraction in Table 3 is regarded as an indication of increase of the degree of internal H–D scrambling.

The random distribution of H and D without isotope effect will result in the formation of Ni–CH_2CD_3, Ni–$CHDCHD_2$ and Ni–CD_2CH_2D complexes in a ratio of 1 : 6 : 3. Such a mixture of the Ni–$C_2H_2D_3$ complexes will evolve CH_3CD_3 and CH_2DCHD_2 in a ratio of 1 : 9 on the acidolysis.

It is shown in Table 3 that the degree of the H–D scrambling increases with time. In toluene formation of Ni-ethyl-d_4 and Ni-ethyl-d_5 species is negligible and the CH_2DCHD_2 fraction increases linearly with time in the early stage (7.5—31 min). In the case of the treatments in acetone the degree of the H–D scrambling at 47 min is of the same extent as that achieved in toluene. However, after allowing the solution containing **1**-d_3 to stand for 111 min or more, considerable amounts of Ni-ethyl-d_4 and Ni-ethyl-d_5 species were formed as proved by evolution of $C_2H_2D_4$ and C_2HD_5 on acidolysis with H_2SO_4. Since the Ni-ethyl-d_4 and Ni-ethyl-d_5 species are not formed at the early stage, they may be formed through a intermolecular interaction of the deuterated ethylnickel complex catalyzed by an unknown compound which is formed during standing the complex in acetone. The H–D scrambling in pyridine is somewhat slower than in acetone and in toluene. In pyridine the ethylnickel complex undergoes disproportionation reaction (*vide infra*) and more than half of the ethylnickel complex is decomposed in a day at room temperature. Therefore most of the Ni–$C_2H_2D_3$ bond had been cleaved before the acidolysis and the data given in Table 3 (No. 9) is for the remaining ethylnickel-d_3 complex resistant to the disproportionation.

Further evidence for the H–D scrambling was provided as follows. (1) The ^{1}H-NMR spectrum of the toluene-treated (Room temp., 2 hr) ethylnickel-d_3 complex in pyridine shows methylene and methyl peaks in an area ratio of 1 : 0.35 (Fig. 3b). (2) The ^{1}H-NMR spectra of propionyl(acetylacetonato)(triphenylphosphine)nickel prepared by the reaction of the acetone-treated (room temp, 1.5 days) ethylnickel-d_3 complex with CO shows methylene and methyl peaks of the propionyl group in an area ratio of 1 : 1.3 (Fig. 4b).

Although it has been known that the H–D scrambling in some deuterated alkylplatinum complexes occurs during their thermal decomposition,[8] this is the first report concerning the H–D scrambling in deuterated alkyltransition metal complex without its decomposition.[12]

Another feature of a dynamic behavior of hydrogens in the ethyl group was demonstrated when **1** was treated with D_2. Although the ethylnickel complex **1** reacts very slowly with D_2 at room temperature, mass spectroscopic examination of ethane gas formed revealed that it contained considerable amounts of C_2D_6, C_2D_5H, $C_2D_4H_2$, $C_2D_3H_3$ and $C_2D_2H_4$ in addition to C_2H_5D which was expected as the sole product in the absence of H–D exchange during the reaction of **1** by D_2 (see the experimental section).[9] Since the ethyl group in the remaining ethylnickel complex **1** was not deuterated at all, this type of H–D exchange is considered to take place only at the moment when the ethyl-nickel bond is cleaved by the reaction with D_2.

Disproportionation of NiR(acac)$(PPh_3)_n$ in Pyridine.

Although **1** and **2** are stable in less basic solvents (benzene, toluene, acetone, *etc.*), the complexes undergo an intermolecular reaction in pyridine. The NMR spectral change of **1** and **2** in pyridine is shown in Fig. 5. The ethyl signals of the ethylnickel complex **1** decrease with time and signals assignable to C_2H_6 and $Ni(C_2H_4)(PPh_3)_2$ increase (the molar ratio of $C_2H_6 : Ni(C_2H_4)(PPh_3)_2 \fallingdotseq 1 : 1$), although the signal of the ethylene in $Ni(C_2H_4)(PPh_3)_2$ is somewhat broadened due to exchange with uncoordinated ethylene in the solution.[10]

In the methyl complex, the methyl signal decreases and peaks assignable to CH_4 and C_2H_6 increase with time. After completion of the reaction one can isolate

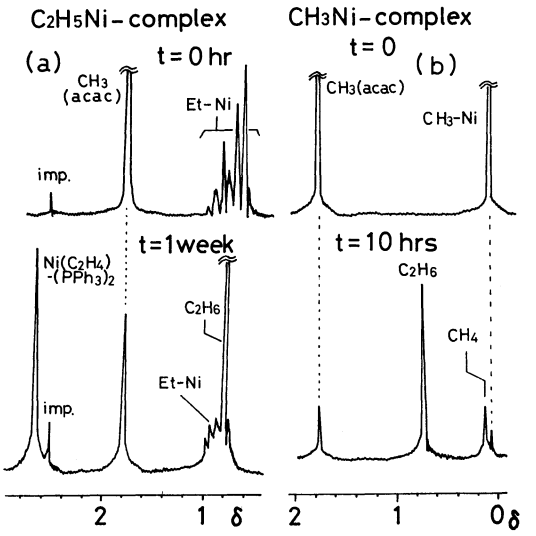
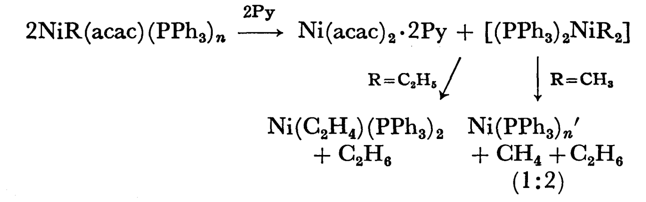


Fig. 5. Changes of ^{1}H-NMR spectra of **1** and **2** with time in pyridine. (a) $\mathrm{NiC_2H_5(acac)(PPh_3)}$; (b) $\mathrm{NiCH_3(acac)(PPh_3)_2}$.

$\mathrm{Ni(acac)_2(pyridine)_2}$ from the both systems. These results suggest that the following disproportionation reaction *via* formation of an unstable dialkylnickel complex may be taking place in pyridine.



$$\begin{array}{l}
2\mathrm{NiR(acac)(PPh_3)}_n \xrightarrow{2\mathrm{Py}} \mathrm{Ni(acac)_2\cdot 2Py} + [(\mathrm{PPh_3})_2\mathrm{NiR_2}] \\
\qquad\qquad\qquad\qquad \swarrow_{\mathrm{R=C_2H_5}} \qquad \downarrow_{\mathrm{R=CH_3}} \\
\qquad\qquad\quad \mathrm{Ni(C_2H_4)(PPh_3)_2} \quad \mathrm{Ni(PPh_3)}_{n'} \\
\qquad\qquad\qquad + \mathrm{C_2H_6} \qquad\quad + \mathrm{CH_4} + \mathrm{C_2H_6} \\
\qquad\qquad\qquad\qquad\qquad\qquad\quad (1:2)
\end{array}$$

Although the rate of the disproportionation of **1** is very slow, that of **2** is reasonably fast and the disproportionation reaction of **2** was followed by NMR spectroscopy. Figure 6 shows the decrease of **2** with time and the second-order plot for the reaction. If we take into account the kinetic result as well as the observation of the fluxionality of the acac ligand, a partial dissociation of acac ligand from nickel and a following coordination of the partially dissociated acac ligand with another alkylnickel complex to form a binuclear complex seem to be the most probable process for the disproportionation reaction.

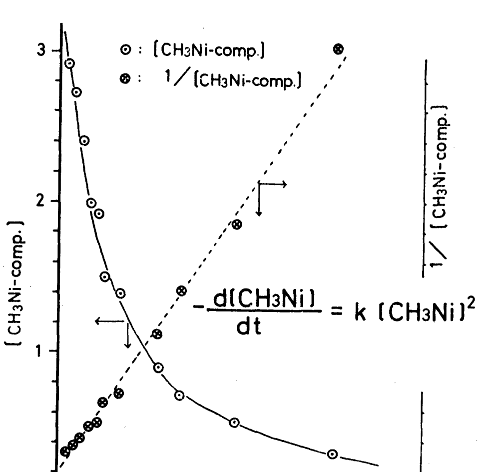


Fig. 6. Disproportionation of $\mathrm{NiCH_3(acac)(PPh_3)_2}$ in pyridine followed by ^{1}H-NMR spectroscopy. The unit of the concentration of **2** is arbitrary (peak area).

When **1**-d_3 was employed for the disproportionation reaction in pyridine, the ethylene evolved in a day at room temperature was $\mathrm{CH_2{=}CD_2}$ and other deuterated ethylene was not detected (IR spectrum). This suggests that the scission of the Ni–$\mathrm{C_2H_5}$ bonds in the supposed unstable diethylnickel complex proceeds through a β-elimination mechanism.

We are grateful for the grant support of this work by Research Grants in Basic Chemistry administered through Japan Society for Promotion of Science.

References

1) A. Yamamoto, T. Yamamoto, T. Saruyama, and Y. Nakamura, *J. Amer. Chem. Soc.*, **95**, 4073 (1973).

2) F. A. Cotton, B. A. Frenz, and D. L. Hunter, *ibid*, **96**, 4820 (1974). In the literature they claimed that the ethylene ligand formed by the β-elimination of the ethyl group should have rotated about the axis from Ni to the center of the ethylene in order to lead to scrambling of hydrogens. However, we think that the rotation of ethylene is not necessary and the reversible processes involving the β-elimination and its reverse reaction is enough to lead to scrambling of hydrogen.

3) E. Krause and B. Wendt, *Chem. Ber.*, **B56**, 466 (1923).

4) Y. Amenomiya and R. F. Pottie, *Can. J. Chem.*, **46**, 1741 (1968).

5) a) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Amer. Chem. Soc.*, **96**, 53 (1974); b) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969); c) R. D. Johnston, F. Basolo, and R. G. Pearson, *ibid.*, **10**, 247 (1971); d) C. H. Bamford and E. O. Hughes, *Proc. Roy. Soc. Ser. A*, **326**, 469 (1972).

6) a) A. C. Adams and E. N. Larsen, *Inorg. Chem.*, **5**, 814 (1966); b) G. E. Glass and R. S. Tobias, *J. Organometal. Chem.*, **15**, 481 (1968); c) N. Serpone and R. Ishayek, *Inorg. Chem.*, **13**, 52, (1974); d) G. M. Tanner, D. G. Tuck, and E. J. Wells, *Can. J. Chem.*, **50**, 3950 (1972).

7) T. Saruyama, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 546 (1976).

8) a) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.*, *A* **1968**, 190; b) G. M. Whitesides, J. F. Gaasch and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

9) A. Yamamoto, T. Yamamoto, M. Takamatsu, T. Saruyama, and Y. Nakamura, 'Organotransition-metal Chemistry,' Eds. Y. Ishii and M. Tsutsui, Plenum Publishing Coorporation, New York (1975), p. 281.

10) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, **10**, 2210 (1971).

11) R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, **18**, 118 (1950).

12) After having submitted this paper we noted Osborn and coworkers' paper in which they described that hydrogen of Mo–H in $\mathrm{MoH(C_2H_4)_2}$ (diphenylphosphinoethane)$_2$($\mathrm{CF_3COO}$) exchanged rapidly and reversibly with the half of the bound ethylene protons on NMR time scale (J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Amer. Chem. Soc.*, **97**, 3872 (1975)). They proposed that the rapid exchange proceeded *via* the insertion of ethylene into the Mo–H bond and its reverse reaction.