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NMR STUDIES OF PHOSPHINE—NICKEL(0) COMPLEXES OF ETHYL METHACRYLATE $Ni(PR_3)_2(CH_2{=}C(CH_3)COOC_2H_5)$

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Summary

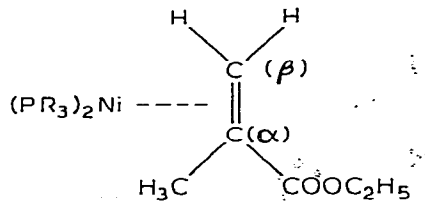
^{13}C NMR data are given for a series of phosphine—nickel(0) complexes of ethyl methacrylate (ema), $Ni(PR_3)_2(CH_2{=}C(CH_3)COOC_2H_5)$ (PR_3 = PPh_3 (Ia), $PEtPh_2$ (Ib), PEt_2Ph (Ic), PMe_2Ph (Id), PEt_3 (Ie)). The olefinic carbon signals of ema shift upfield by 71.5—86.5 ppm on coordination, the magnitude of the upfield shift increasing with increase in the bacisity of the phosphine ligand. The effect of the basicity of PR_3 is discussed on the basis of the back-bonding from Ni to ema. Variable temperature ^1H NMR studies reveal that the ema of Id, the complex having the least sterically demanding phosphine ligands, exchanges with free ema in toluene on the NMR time scale. The dependence of the rate of exchange on the concentration of ema shows that the exchange proceeds through an S_N2 mechanism. The activation parameters are: $\Delta H^{\neq}_{273}$ 2.7 kcal/mol, $\Delta G^{\neq}_{273}$ 12.7 kcal/mol, $\Delta S^{\neq}_{273}$ —37 e.u. The ^{31}P NMR spectra of the complexes show two doublets when the exchange is frozen out, indicating the inequivalence of the two phosphine ligands in the ema-coordinated complex. The difference in the ^{31}P chemical shifts of the two coordinated tertiary phosphines increases with increase in the basicity of the PR_3 ligand.

Introduction

In a previous paper we reported the preparation of a series of square-planar phosphine-nickel complexes (Ia, Ib, Id, Ie) with an ethyl methacrylate (ema) ligand and their ^1H NMR data at room temperature [1]:

The ^1H NMR data at room temperature revealed that: (i) The olefinic proton signals of ema shift upfield on coordination, the magnitude of the upfield shift increasing with increase in the basicity of the phosphine ligand. The increase in the basicity of PR_3 was considered to enhance the Ni→ema back-bonding and increase the shielding of the olefinic protons. (ii) The ema ligand

$Ni(cod)_2$ + tertiary phosphine (PR_3) + ema ⟶



(1)

(PR_3 = PPh_3 (Ia), $PEtPh_2$ (Ib), PEt_2Ph (Ic), PMe_2Ph (Id), PEt_3 (Ie))

in Id is exchanged on the NMR time scale with free ema partly liberated from Id. In contrast, the ema ligand in the other complexes is rigidly bonded to Ni.

This paper reports further studies on the bonding between Ni and ema by means of ^{13}C and ^{31}P NMR spectroscopy and detailed examination on the dynamic behavior of the complexes in solutions with variable temperature ^1H and ^{31}P NMR spectroscopy. Our attention is focused primarily on the effect of the phosphine ligand on (i) the bonding between Ni and the ema ligand and (ii) the dynamic behavior of the complexes in solution.

Results and discussion

^{13}C NMR studies on the Ni—ema bond

Figure 1a shows the ^{13}C NMR spectrum of Ia in benzene at room temperature. The olefinic carbon signals of ema are considerably shifted upfield on complex formation and they appear in the region where olefinic carbon signals of usual π-type olefin-transition metal complexes appear [3—6]. In the ^1H-decoupled spectrum each of the α- and β-olefinic carbons gives rise to a double doublet due to coupling with two magnetically non-equivalent ^{31}P's, the signal of the β-carbon being stronger than that of the α-carbon due to the nuclear Overhauser effect on the β-carbon. The double doublet of the β-carbon further splits into a triplet due to coupling with the olefinic β-hydrogens as the doupling is removed. The α-CH_3 protons are coupled with one of ^{31}P of the two PPh_3 ligands to give a doublet in the $^{13}C\{^1H\}$-NMR spectrum. The signals of the ethoxycarbonyl group of ema in Ia—Ie show only a minor shift on complex formation.

Complexes Ib, Ic, and Ie give rise to ^{13}C NMR patterns similar to that of Ia. However, the ^{13}C NMR spectrum of Id, the complex having the least sterically demanding phosphine ligands, (Fig. 1d) is different from those of the other complexes having bulky phosphine ligands. No coupling between the carbons of the ema ligand and ^{31}P's of PMe_2Ph is observable at room temperature because of the dynamic exchange of the ema ligand of Id with free ema partly liberated in benzene (vide infra). Signals assignable to free ema cannot be observed since the amount is very small [1]. The ^{13}C NMR data are summarized in Table 1. These ^{13}C NMR data, together with the previously reported ^1H NMR data, are consistent with the square-planar configurations for these complexes. The X-ray crystallographic analysis of Ia in fact revealed the square planar configu-

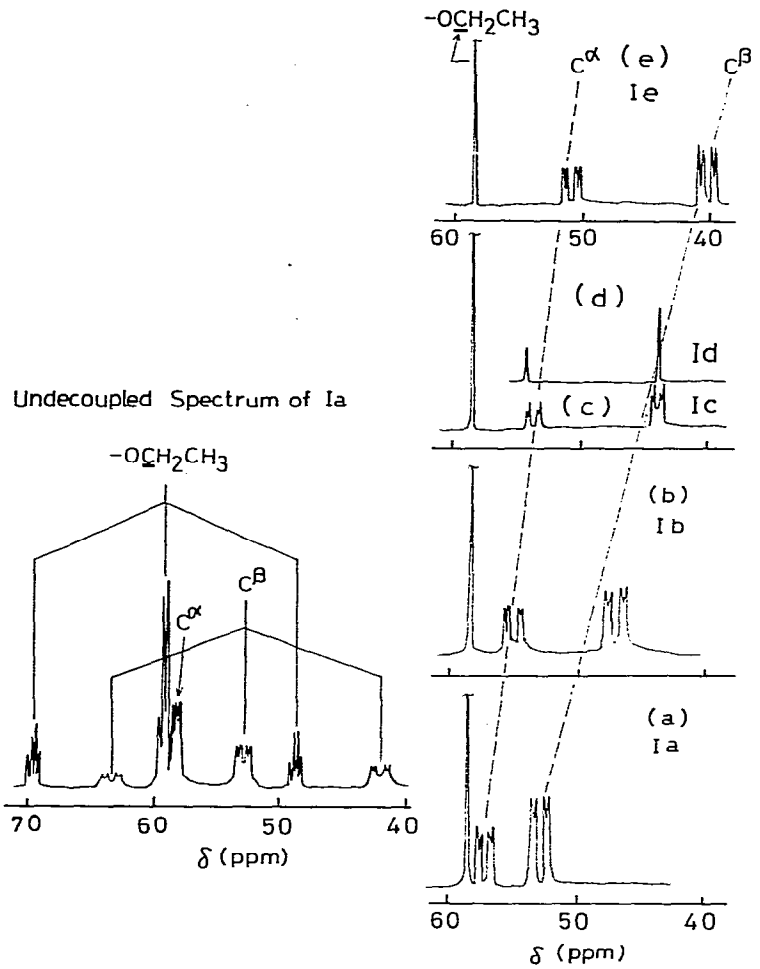


Fig. 1. $^{13}C\{^1H\}$ NMR spectra of the complexes Ia—Ie in C_6D_6 at room temperature. The undecoupled spectrum of Ia is shown at the left side of Fig. 1a.

ration [2] (Fig. 2) and it is reasonable to assume that complexes Ia—Ie have the same configuration also in solution.

Salomon and Kochi [4] and Tolman et al. [5] reported similar upfield shifts of olefinic carbons on coordination of olefins to $Cu^IO_3SCF_3$ and bis(*o*-tolyl-phosphite)nickel(0), respectively, and concluded that the magnitude of the upfield shift reflects the degree of metal→olefin back-bonding. In the case of the present Ni—ema complexes plots of the chemical shifts of the α- and β-carbons against pK_a of the conjugate acid of PR_3 [7] afford two straight lines (Fig. 3).

The greater upfield shift of olefinic carbons in complexes having phosphines with the greater basicity is in agreement with our previous observation on the upfield shifts in the proton signals of the olefinic carbons influences by the basic phosphines [1]. The result is in line with the conclusion of Salomon and Kochi and of Tolman et al., namely the coordination of the more basic phosphine

TABLE 1

^{13}C NMR DATA OF Ia–Ie [a]

(i) Chemical Shift (δ, ppm from TMS)

Compound	pK_a [7] of PR_3	Cone angle [9] (°)	C=O	O–$\underline{C}H_2$	C^{α} [b]	$\Delta\delta(C^{\alpha})$ [c]	C^{β} [b]	$\Delta\delta(C^{\beta})$ [c]	α-$\underline{C}H_3$	$OCH_2\underline{C}H_3$
Ia	3.0	145	174.5	58.7	57.6	79.8	53.1	71.5	19.9	14.7
Ib	4.9	140	174.6	58.5	55.1	82.3	47.8	76.8	20.6	14.8
Ic	6.8	136	175.0	58.5	53.4	84.0	43.1	81.5	20.8	15.0
Id	6.2	122	174.5	58.4	54.4	83.0	43.0	81.6	20.5	15.0
Ie	8.6	132	174.9	58.4	50.9	86.5	40.2	84.4	20.6	14.1
ema			166.7	60.4	136.4		124.6		18.4	14.4

(ii) Coupling constant (Hz)

Compound	$J(C^{\alpha}, {}^{31}P)$ [d]	$J(C^{\beta}, {}^{31}P)$ [d]	$J(C^{\beta}, H)$	$J(\alpha\text{-}\underline{C}H_3, {}^{31}P)$	$J(\alpha\text{-}\underline{C}H_3, H)$
Ia	12.7	16.9	153.5	3.5	125.7
Ib	14.3	17.6	150.0	3.8	125.7
Ic	14.6	18.3	150.1	[e]	[e]
Id	—	—	151.5	—	125.5
Ie	14.7	19.1	152.2	3.3	122.4
ema			157.4		126.4

[a] In C_6D_6 at room temperature. [b] C^{α} = olefinic α-carbon, C^{β} = olefinic β-carbon. [c] Upfield shift of the olefinic carbon. [d] Only the larger coupling constant for the double doublet is given. The smaller coupling constant is of the range of 3 to 5 Hz and cannot be obtained with enough accuracy. [e] The value was not obtainable due to overlapping of the α-CH_3 signal with CH_2CH_3 signals of PEt_2Ph.

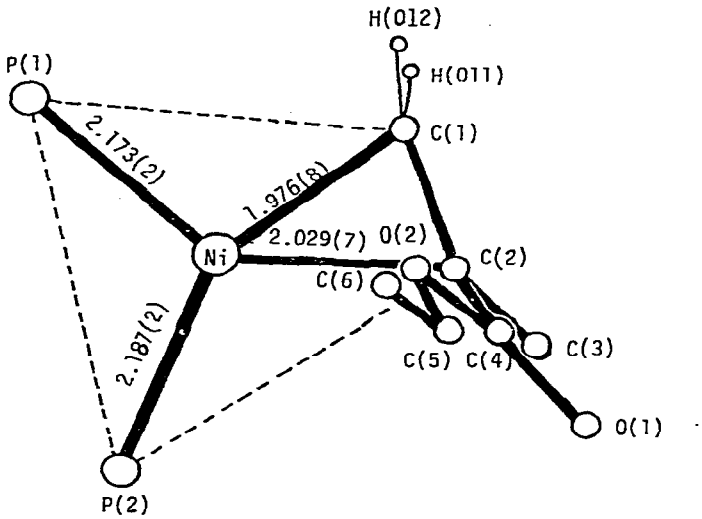


Fig. 2. The equatorial plane of Ni(ema)$(PPh_3)_2$ (Ia). Bond distances (Å) with their e.s.d.'s in parentheses are given. C(1) and C(2) represent C^{β} and C^{α}, respectively.

ligand enhances the Ni→ema back-bonding, thus increasing the shielding of the olefinic carbons.

It is seen from Fig, 3 that the ^{13}C chemical shift of the β-carbon of the coordinated ema is more strongly influenced by the phosphine basicity than that of the α-carbon. The effect may be accounted for in terms of Ni→ema back bonding since the β-carbon of ema in the uncoordinated state has less electron density than the α-carbon by the effect of the electron-withdrawing ethoxycarbonyl group and the back donation of electron density from nickel

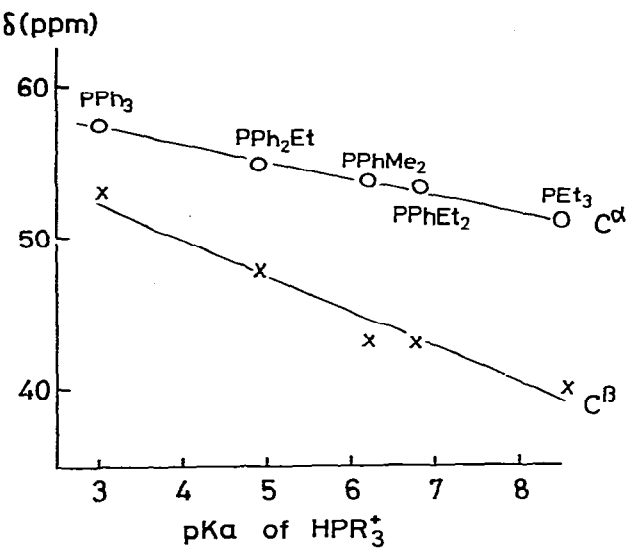


Fig. 3. Plots of the ^{13}C chemical shifts of the olefinic α- and β-carbons against pK_a of $[HPR_3]^+$.

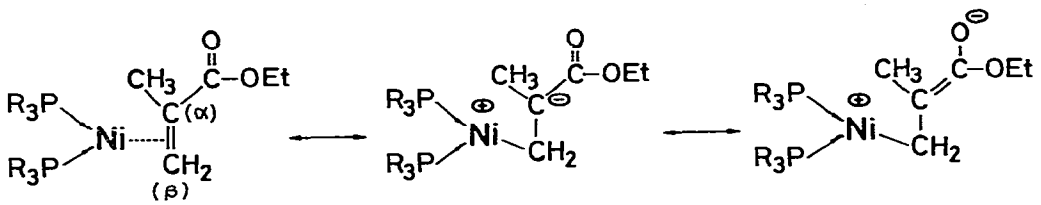


Fig. 4. Valence bond representation of the Ni—ema bond.

to the double bond would increase the electron density at the β-carbon to a relatively greater extent than at the α-carbon.

It is tempting to explain the results in terms of the resonance structures shown in Fig. 4, where greater interaction between Ni and the β-carbon is considered. The X-ray analysis of Ia (Fig. 2) in fact shows a somewhat shorter bond length for Ni—C^{β} than for Ni—C^{α}. However, it may be premature to advance discussion before information on the molecular structures of the series of the ema-coordinated complexes is available since the small difference between the Ni—C^{α} and Ni—C^{β} bond lengths may arise from steric reasons.

Dynamic behavior of the complexes in solutions studied by variable temperature ^1H NMR

Fig. 5 shows variable temperature ^1H NMR spectra of Id in the presence and absence of added ema. In the absence of added ema (Fig. 5a) the α-CH_3 protons of ema is coupled with ^{31}P of one of the PMe_2Ph ligands below —20°C to give rise to a doublet. In the ^{31}P-decoupled ^1H NMR spectrum of Id at —38°C the α-CH_3 signal appears as a singlet. The presence of the coupling between α-CH_3 and ^{31}P clearly indicates that both the ema and PMe_2Ph ligands are tightly bonded to Ni at the temperatures. On raising the temperature, the coupling between α-CH_3 protons and ^{31}P of PMe_2Ph disappears, probably due to exchange between the coordinated ema and free ema partly liberated from Id.

$$Ni(PMe_2Ph)_2(ema) + ema^* \rightarrow Ni(PMe_2Ph)_2(ema^*) + ema \qquad (2)$$

The exchange on the NMR time scale between the coordinated and free PMe_2Ph also explains the disappearance of the ^1H—^{31}P coupling. However, the partial liberation of PMe_2Ph from Id is not plausible since addition of an excess of ema to the solution of Id did not give any sign of formation of complex with 0 or 1 PMe_2Ph ligands, whereas addition of an excess of PMe_2Ph gave an ema-free complex, $Ni(PMe_2Ph)_n$ [1].

The exchange on the NMR time scale between the coordinated and free ema undoubtedly is taking place in the presence of excess ema. When ema is added to the toluene solution of Id (Fig. 5b), the olefinic proton signals of the coordinated ema are broadened. The olefinic proton signals of free ema also show broadening, supporting the occurrence of the exchange on the NMR time scale between the coordinated and free ema. The increase in the amount of ema added causes further broadening of the olefinic proton signals of the coordinated ema. In contrast, the broadness of the olefnic proton signals of free ema does not

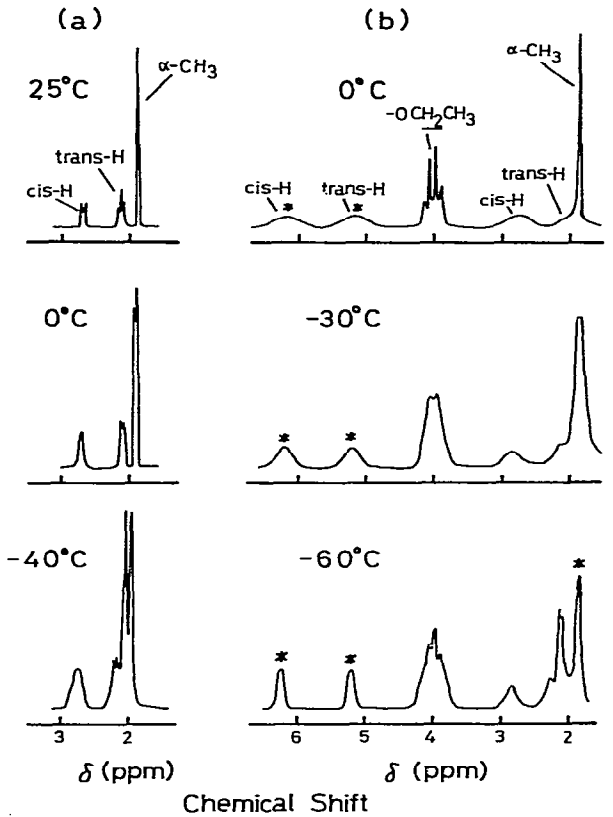


Fig. 5. Temperature variable ^{1}H NMR spectra of (a) Id and (b) a mixture of Id and ema in a 1/1 ratio. Solvent, toluene-d_8. The asterisks indicate the peaks due to the uncoordinated ema.

TABLE 2

RATE OF THE EXCHANGE REACTION [a]

$$Ni(ema)(PMe_2Ph)_2 + ema^{\star} \xrightarrow{R} Ni(ema^{\star})(PMe_2Ph)_2 + ema$$

Temp. (°C)	[ema] [b] (mol/l)	$1/\tau$ [d] (sec^{-1})	$R = [ema]/\tau$ (mol l^{-1} sec^{-1})	k_2K [e] (mol^{-1} l sec^{-1})
0	0.17	69	12	510 } 430 (average)
0	0.34	75	25	440 }
—29	0		0 [c]	
—29	0.085	43	3.6	250 } 230
—29	0.170	38	6.5	220 }
—29	0.340	38	13	220 }
—59	0.170	14	2.4	82 } 77
—59	0.340	12	4.1	71 }

E_a 3.2 kcal/mol, $\Delta H^{\neq}_{273}$ 2.7 kcal/mol
$\Delta G^{\neq}_{273}$ 12.7 kcal/mol, $\Delta S^{\neq}_{273}$ —37 e.u.

[a] The concentration of Id is 0.170 mol l^{-1}. Solvent, toluene-d_8. [b] The concentration of ema added to the solution. [c] In the absence of ema added the ema ligand is tightly bonded to Ni at —29°C. [d] τ, life time of free ema. [e] $k_2K = R/([ema][Id]) = (1/\tau)(1/0.170)$.

depend on the amount of ema added when the temperature is fixed, indicating that the life-time of ema in the uncoordinated state is independent of the amount of free ema and, therefore, the rate of exchange is proportional to the amount of free ema.

We estimated the rate of exchange by the shape analysis of the olefinic protons of free ema [8]. Table 2 summarizes the concentration of ema added to the solution, the life-time of the ema ligand in the uncoordinated state, τ, and the rate of exchange R at the fixed concentration of Id computed from τ (R = [ema]/τ). It is seen from Table 2 that the exchange rate R linearly increases with increase in [ema]. This fact can be taken as an indication that the exchange proceeds by an S_N2 mechanism (Fig. 6).

Under a condition, K[ema] = (k_1/k_{-1})[ema] $\ll$ 1, the mechanism leads to the rate equation (3):

$$R = -d[Id]/dt = -d[ema]/dt = k_2K[Id][ema] \quad (3)$$

If the exchange proceeds through an S_N1 mechanism, R does not depend on [ema]. The validity of the assumption, K[ema] $\ll$ 1, is supported by the absence of a peak assignable to the intermediate II as well as by the fact that the peak area of the *cis*-olefnic proton of free ema to that of coordinated ema is equal to the ratio of [ema added] to [Id]. Activation parameters for the exchange reaction calculated from the temperature dependence of k_2K are given in Table 2. The large negative value of $\Delta S^{\neq}$ is consistent with the S_N2 mechanism.

In the case of other Ni-ema complexes, Ia, Ib, Ic, and Ie, the exchange scarcely occurs even at 50°C. Addition of free ema did not cause the exchange, either. Since PMe_2Ph and PEt_2Ph have similar basicities, the difference in the dynamic behavior of the complex can be ascribed mainly to steric rather than electronic effects. The difficulty in forming the doubly ema-coordinated intermediate II with the complexes other than Id accounts for the difference, cf. the cone angles of the tertiary phosphines ($\theta(PMe_2Ph)$ 127° < $\theta(PEt_3)$ 132° < $\theta(PEt_2Ph)$ 136° < $\phi(PEtPh_2)$ 141° < $\theta(PPh_3)$ 145° [9]). The structure analysis of Ia by the X-ray crystallography revealed that coordination of one more ema to Ia is difficult.

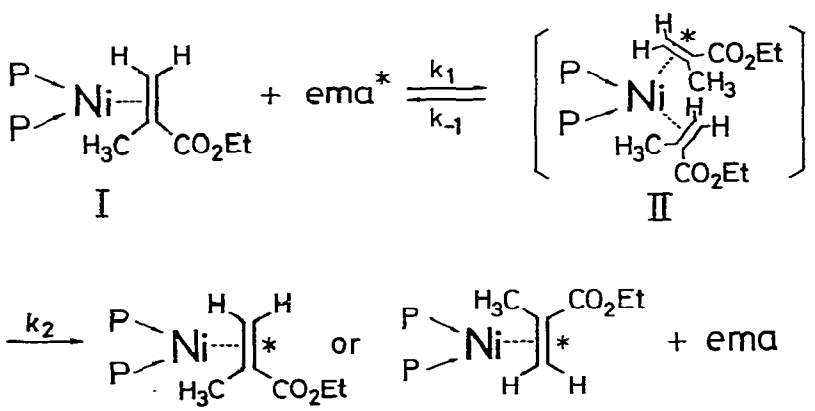


Fig. 6. S_N2 mechanism for the exchange between the coordinated ema and free ema.

TABLE 3

^{31}P NMR DATA OF THE COMPLEXES [a]

Compound	Chemical shift [b]		$J(P_A, P_B)$ (Hz)	$\delta_A - \delta_B$
	δ_A	δ_B		
Ia	42.08	36.26	34.5	5.82
Ib	36.22	29.73	36.1	6.49
Id [c]	8.26	0.96	41.5	7.30
Ie	28.68	19.72	37.1	8.96

[a] In toluene. At room temperature except for Id. [b] Ppm from external PPh_3 (downfield positive). [c] At −40°C.

When PMe_2Ph is added to a toluene solution of Id at −30°C in a 1/1 ratio, the ^{1}H NMR spectrum shows that about one third of the ema is liberated by the ligand exchange reaction:

$$Id + PMe_2Ph \rightarrow Ni(PMe_2Ph)_n + ema \quad (4)$$

On raising the temperature of the toluene solution of Id and PMe_2Ph, the olefinic proton signals of both the coordinated and free ema become broad due to the exchange between the coordinated and free ema.

^{31}P NMR

When the exchange between the coordinated ema and free ema is frozen out,

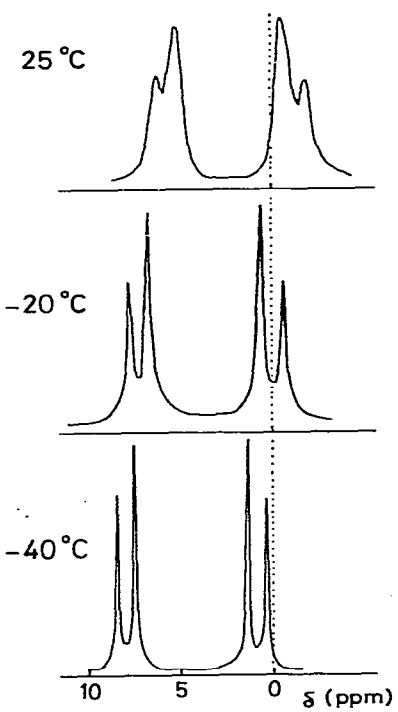


Fig. 7. Temperature variable ^{31}P NMR of Id in a mixture of toluene and toluene-d_8.

the Ni-ema complexes give rise to two doublets in ^{31}P NMR spectra as the two phosphine ligands occupy magnetically non-equivalent positions in the square planar complexes. At the present stage it is not clear which position is referred to the higher or lower magnetic field. Table 3 summarizes the ^{31}P NMR data of the complexes.

The signals of Ia, Ib, and Ie are sharp enough over a temperature range from —50 to 60°C indicating that there is neither rapid dissociation of the ligands nor rotation of the ema ligand around the Ni-ema axis. Addition of ema to toluene solutions of these complexes causes slight broadening of the signals. In contrast to the ^{31}P NMR spectra of these complexes, the spectrum of Id, depends on the temperature due to the exchange reaction on the NMR time scale (Fig. 7). In accord with the results obtained from the variable temperature ^{1}H NMR study, the ^{31}P NMR spectrum of Id shows two doublets below —30°C and the signal becomes broad on raising the temperature due to the dynamic exchange shown in Fig. 6. Addition of ema also causes broadening of the signal.

There is a trend that the difference in the chemical shifts of the two ^{31}P nuclei, $\delta_A - \delta_B$, increases with increase in the basicity of the phosphine ligand.

Experimental

The Ni-ema complexes, Ia, Ib, Id, and Ie, were prepared as reported in a previous paper [1]. Complex Ic was prepared analogously. Deuterated solvents were used as purchased from Merck and Co., Inc. The samples for NMR studies were prepared under an atmosphere of nitrogen. The ^{1}H NMR spectra were recorded on a Japan Electron Optics Laboratory PS-100 spectrometer. The ^{13}C and ^{31}P NMR spectra were obtained with the same spectrometer in the pulsed Fourier transform mode. Chemical shifts are referred to internal TMS in ^{1}H and ^{31}C NMR and to external PPh_3 in ^{31}P NMR.

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