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NMR STUDIES OF DYNAMIC BEHAVIOR OF DIALKYL(ACETYLACETONATO)BIS(TERTIARY PHOSPHINE)COBALT(III) AND RELATED COMPLEXES IN SOLUTION

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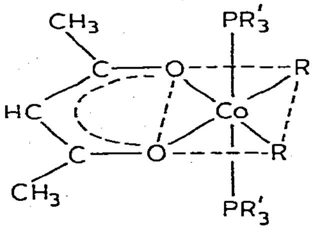
Summary

The ^1H, ^{31}P and ^{13}C NMR spectra of *cis*-dialkyl(acetylacetonato)bis(tertiary phosphine)cobalt(III) complexes were obtained in several solvents. These complexes have an octahedral configuration with *trans* tertiary phosphine ligands. The coordinated tertiary phosphine ligands are partly dissociated in solution. One of the phosphine ligands in $CoR_2(acac)(PR_3')_2$ can be readily displaced with pyridine bases to give pyridine-coordinated complexes. From observation of the ^1H and ^{31}P NMR spectra several kinetic and thermodynamic data for exchange reactions and displacement reactions of tertiary phosphines were obtained.

Introduction

In previous papers we have reported the preparation and a brief description of NMR spectra of a series of *cis*-dialkyl(acetylacetonato)bis(tertiary phosphine)cobalt(III) complexes (I—IV).

$Co(acac)_3 + AlR_2(OEt) + PR'_3$



(I) R = Me, $PR'_3 = PEt_3$
(IIa) R = Me, $PR'_3 = PPhMe_2$
(IIb) R = Et, $PR'_3 = PPhMe_2$
(IIc) R = n-Pr, $PR'_3 = PPhMe_2$
(IId) R = i-Bu, $PR'_3 = PPhMe_2$
(III) R = Me, $PR'_3 = PPh_2Me$
(IV) R = Me, $PR'_3 = P(n\text{-}Bu)_3$

Since most of these alkylcobalt complexes are thermally stable, insensitive to air, and soluble in many organic solvents, they provide a rather rare opportunity, among usually unstable alkyltransition metal complexes, for studying the behavior of these complexes in solution. Information regarding the partial dissociation of these coordinatively saturated complexes in solution, which would provide a vacant site in a decomposition pathway, is desirable for understanding the mechanism of thermolysis of these alkyltransition metal complexes. This subject will be discussed in a later paper [1c]. The importance of partial dissociation of the ligand from a coordinatively saturated complex, which provides a coordination site for a substrate to be activated, has been demonstrated in various transition metal-catalyzed reactions of olefins [2,3].

Results and discussion

General

The NMR spectra of the dialkylcobalt complexes I—IV are compatible with the octahedral structure with two cobalt-bonded alkyl groups and an acetylacetonato ligand coplanar with cobalt which also is coordinated with two tertiary phosphine ligands in mutually *trans* positions. Figure 1 shows representative spectra of $Co(CH_3)_2(acac)(PPhMe_2)_2$ (IIa) in toluene at two temperatures. The methyl groups bonded to cobalt appear as a triplet below 35°C due to coupling with two phosphine ligands in *trans* positions (^3J(P—H) 8 Hz) at τ 10.16 ppm. The other complexes show similar ^3J(P—H) values of 4—8 Hz as observed in various methyltransition metal complexes having tertiary phosphines at *cis* positions from the methyl group [4]. With an increase in temperature the triplet collapses to a broad singlet indicating dissociation of the phosphine ligands from the complex. The methyl resonance of the $PPhMe_2$ ligands in IIa appears as a triplet by virtual coupling with two phosphorus nuclei in mutually *trans* positions with an apparent coupling constant of 3 Hz (half of the separation between outer lines of the triplet [5]), although the spectrum is somewhat obscured by the methyl resonance of the acetylacetonato ligand. The triplet also collapses to a singlet on raising the temperature. Similar changes of the NMR spectra of methyltransition metal complexes involving dissociation of tertiary phosphine ligands on variation of temperature have been observed [4d—4h].

Figure 2 shows the ^1H, ^{31}P and ^{13}C spectra of the ethyl complex IIb. The methyl-proton-resonance of the $PPhMe_2$ ligands appears as a triplet at a higher field than that of the corresponding methyl complex IIa and is clearly separated from the CH_3 resonance of the acetylacetonato ligand. The shift to higher field may be caused by an increase of the electron density on cobalt by substitution of the methyl groups by more electron-releasing ethyl groups. A similar shift was observed with the resonance of the acac ligand; the methyl resonance of the acac ligand in IIb is shifted to higher field than that of IIa but the effect is smaller than for the $PPhMe_2$ ligands which are directly bonded to cobalt. The ^1H resonance of the cobalt-bonded ethyl groups is observed as a somewhat broadened singlet. This is considered to be due to the coincidence of chemical shifts of the methyl and methylene protons in the ethyl groups. The splitting due to the phosphine ligands may be included in the width of the signal. In order to confirm the coincidence of the proton chemical shifts of the methyl and methylene groups, ^{13}C NMR of IIb in a mixture of C_6H_5Br and C_6D_6 was observed at −20°C and

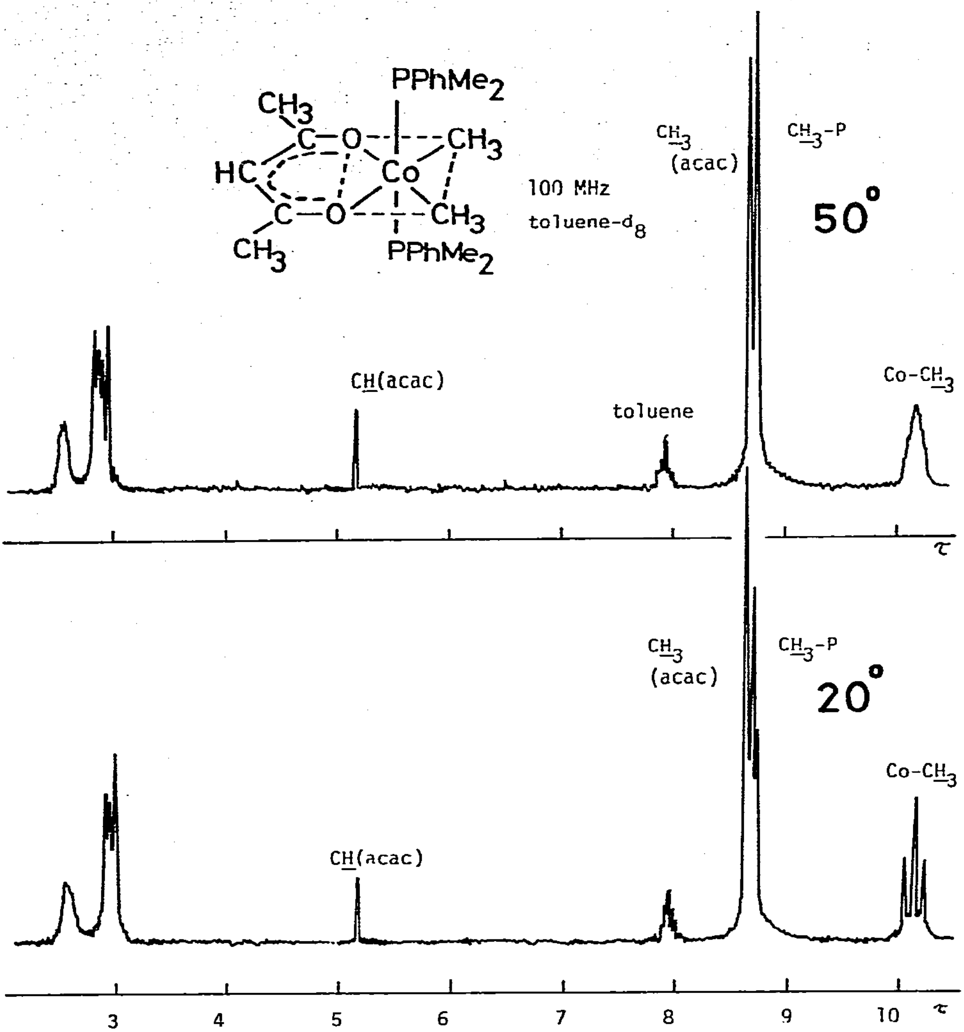


Fig. 1. ^{1}H NMR spectra of Co(CH$_3$)$_2$(acac)(PPhMe$_2$)$_2$ (IIa) in toluene at two temperature, 20 and 50°C.

compared with those of Co(CH$_3$)$_2$(acac)(PPhMe$_2$)$_2$ and Ni(C$_2$H$_5$)(acac)(PPh$_3$) [6]. The ^{13}C NMR spectrum of IIb shows that the methyl and methylene carbon signals of the ethyl groups appear separately at 16.3 and −4.3 ppm (referred to TMS, downfield positive), respectively. The methylene resonance is observed as a broad singlet at higher field than the methyl resonance because of the shielding effect of cobalt. The broadening may be caused by couplings with phosphorus nuclei and possibly with the Co nucleus ($I = 7/2$), which also could contribute to broadening of the spectrum though quadrupole relaxation. The assignments of other resonances are included in Fig. 2b and Table 1, which also includes the resonances of IIa and NiEt(acac)(PPh$_3$) [6]. The ^{13}C NMR signal of the methyl groups in PPhMe$_2$ ligands are observed as a triplet due to virtual coupling (apparent coupling constant 9.2 Hz). In order to further substantiate the assignments, an off-resonance spectrum of IIb was recorded (Fig. 2c). The

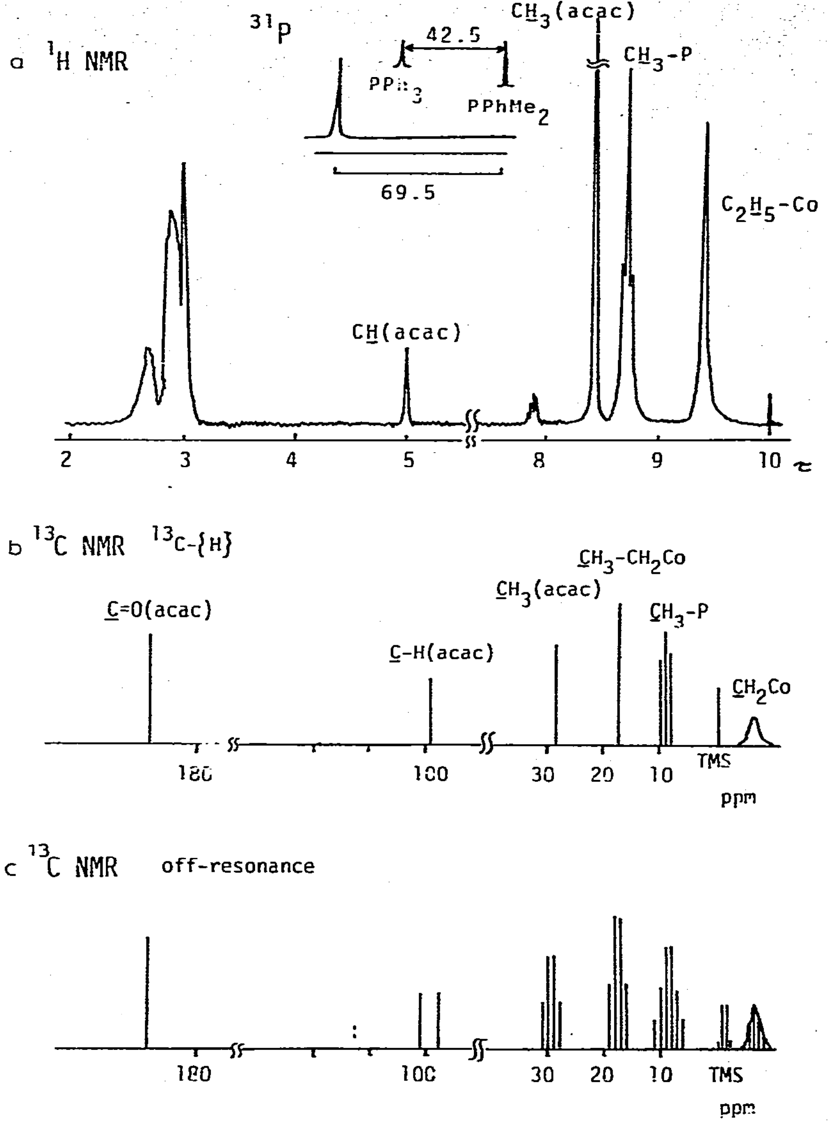


Fig. 2. ^{1}H, ^{31}P and ^{13}C spectra of ethylcobalt complex IIb in toluene a: ^{1}H (—20°C) and ^{31}P spectra (—70°C) (the chemical shifts of the reference PPh_3 and of the free $PPhMe_2$ ligand are indicated in the upper part of figure); b: ^{13}C—{^{1}H} spectrum (—20°C); c: ^{13}C off resonance.

peaks in Fig. 2c show the expected splittings or the absence of splitting. The singlet of the methyl group at 16.3 ppm splits to a quartet, whereas the broad singlet of the cobalt-bonded methylene group at —4.3 ppm splits to a complex multiplet. The complex splitting may be due to couplings with protons and phosphorus. The multiplet may also contain the contribution of a coupling with Co ($I = 7/2$) and may be effected by the quadrupole relaxation. These results reveal that the somewhat broad singlet of the cobalt-bonded ethyl groups in the ^{1}H NMR spectrum of IIb is clearly due to the very small difference between the chemical shifts of the methyl and methylene groups. It is also noted that the

TABLE 1

^{13}C CHEMICAL SHIFTS (δ, ppm) OF $CoR_2(acac)(PPhMe_2)_2$ (II) AND NiEt(acac)(PPh_3)

	$Co(C_2H_5)_2(acac)(PPhMe_2)_2$ [a]	$Co(CH_3)_2(acac)(PPhMe_2)_2$ [a]	$Ni(C_2H_5)(acac)(PPh_3)$ [b]
C=O(acac)	186.4	186.4	186.3
C—H(acac)	98.8	98.9	99.9
—CH_3(acac)	28.0	27.8	27.4
—R(Co—R) (CH_3)	16.3		26.8
(CH_2)	—4.3	[c]	13.9
—CH_3($PPhMe_2$)	9.3 t [d]	8.7 t [d]	6.8

[a] In C_6H_5Br/C_6D_6, at —20° C. TMS standard. [b] Ref. 6b. [c] No signal was observed because of broadening due to quadrupole relaxation by cobalt and coupling with tertiary phosphine ligands and possibly cobalt metal ($I = 7/2$). [d] t, triplet, other signals are all singlets.

methylene signal in the ^{13}C NMR spectrum of IIb appears at a considerably higher field than that in $Ni(C_2H_5)(acac)(PPh_3)$, presumably reflecting higher electron density on cobalt in IIb owing to the coordination of more-electron-releasing $PPhMe_2$ ligands in IIb than in $Ni(C_2H_5)(acac)(PPh_3)_2$ having more electron-accepting ligand, PPh_3.

Figure 2 also includes the ^{31}P—{H} NMR of IIb at —70° C. The spectrum shows a somewhat broadened singlet of the coordinated phosphine ligand suggesting that minor dissociation of the phosphine ligand and exchange of the liberated phosphine with the coordinated one is taking place at the temperature.

The ^1H NMR spectrum of the propyl complex IIc also shows the cobalt-bonded methylene resonance at higher field (τ 9.64 ppm) than the β-methylene and γ-methyl groups which are observed at τ 8.84 ppm as a singlet.

For further examining the effect of the tertiary phosphine ligands on the shape of the ^1H NMR signal of the cobalt-bonded ethyl groups, the ^1H NMR spectrum of a specifically deuterated complex $Co(CH_2CD_3)(acac)(PPhMe_2)_2$ [1a,c] was observed. It clearly shows a triplet (^3J(P—H) 10 Hz) at —20° C in toluene due to coupling with two phosphorus nuclei. The somewhat broad singlet observed in the ^1H NMR spectrum of the non-deuterated ethyl groups may have arisen as the overlap of the triplet with the resonances of the methyl and methylene groups, the chemical shifts of which are very close to each other but not exactly coincidental.

Dissociation of tertiary phosphine ligands from the alkylcobalt complexes

As demonstrated by the change of the ^1H NMR spectrum on variation of temperature as shown in Fig. 1, the coordinated tertiary phosphine ligands are liberated into solution as expressed by eq. 1.

$$CoR_2(acac)(PR_3')_2 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoR_2(acac)(PR_3') \cdot S + PR_3' \qquad (1)$$

S = solvent

The collapse of the triplet NMR signal of the cobalt bonded-methyl groups on temperature increase to a singlet and reappearance of the triplet on addition of an excess amount of the phosphine ligands support the assumption of the equilibrium. The coalescence temperature of the methyl complexes having different phosphine ligands (complexes I, IIa, and IV) decreases in the order of $PPhMe_2$ (35°C) > PEt_3 (10°C) > P-n-Bu_3 (5°C). The order suggests that the dissociation takes place more easily when the complex contains more basic ligands.

The presence of the equilibrium as represented by eq. 1 can be observed more directly by means of ^{31}P NMR spectroscopy. Figure 3 shows the ^{31}P NMR spectra of the PEt_3-coordinated complex I observed in CH_2Cl_2 at various temperatures in the presence and absence of PEt_3. In the absence of PEt_3, a somewhat broad singlet of the coordinated PEt_3 ligands is observed at 26 ppm downfield from the external reference of triphenylphosphine (in toluene) at —80°C. On raising the temperature the singlet becomes broader and shifts to higher field simultaneously. The broadness of the singlet at —80°C suggests that the complex is slightly dissociated even at —80°C and a slow exchange reaction between the

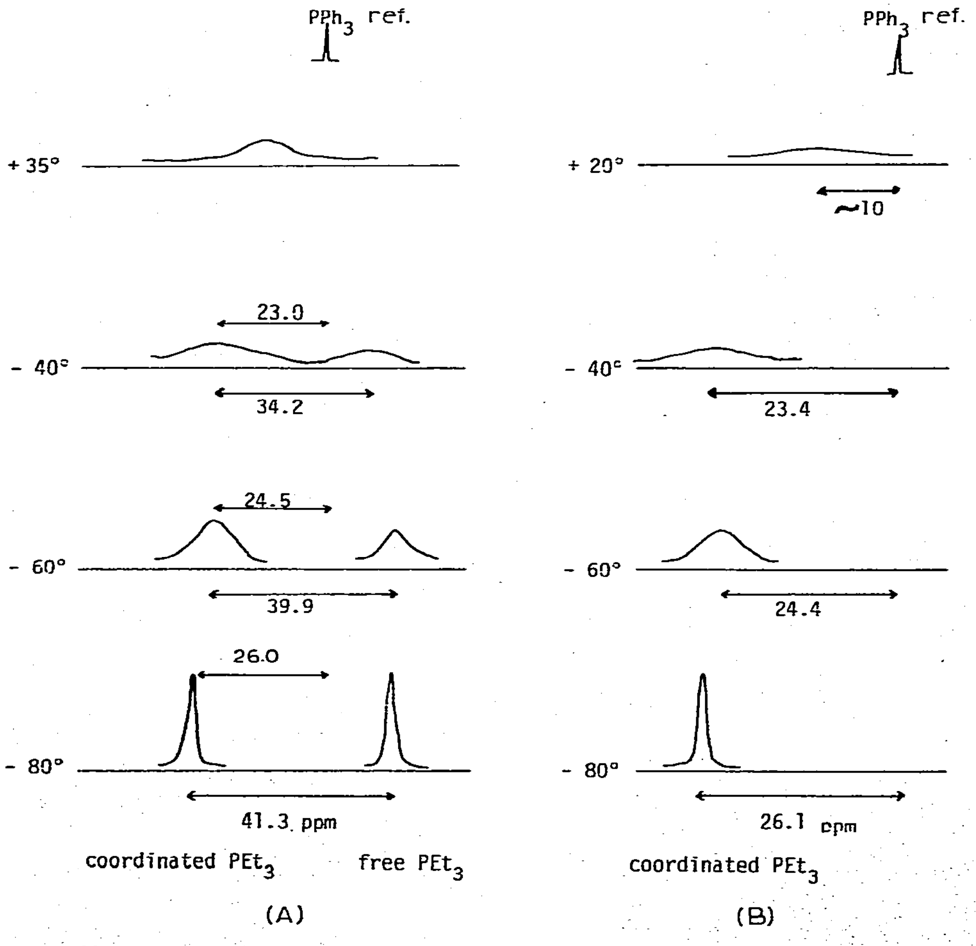


Fig. 3. ^{31}P NMR spectra of $Co(CH_3)_2(acac)(PEt_3)_2$ in the presence (A) and absence (B) of PEt_3 in CH_2Cl_2.

coordinated and liberated phosphine ligands is taking place. In the presence of about an equimolar amount of the added phosphine, two broad singlets of an area ratio of 2 : 1 are observed at 26 and —15.3 ppm referred to the external standard of triphenylphosphine; the former signal is due to the coordinated PEt_3 and the chemical shift of the latter is the same with that of free PEt_3. On raising the temperature, the two resonances approach each other with simultaneous broadening. A visual inspection of the shapes of the resonances in the presence and absence of PEt_3 suggests that addition of triethylphosphine to the system does not markedly affect the exchange rate between the coordinated and free ligands.

Approximate rate constants for the liberation of the coordinated $PPhMe_2$ from IIa or IIb in the absence of $PPhMe_2$ were estimated by measuring the half widths of the ^{31}P NMR signals; the rate constant for IIa and IIb were estimated as 10 ± 3 kcal/mol and 8 ± 3 kcal/mol, respectively.

From observation of the ^{31}P mean chemical shift value of the exchange system in the absence of a phosphine one can estimate the equilibrium constant K for eq. 1 if each chemical shift value of $CoR_2(acac)(PR_3')_2$ and $CoR_2(acac)(PR_3')_2 \cdot S$ is known. Thus we estimated the equilibrium constants for equilibrium 2 at various temperatures and obtained thermodynamic parameters (see Experimental for details and required assumptions).

$$CoEt_2(acac)(PPhMe_2)_2 + S \rightleftharpoons CoEt_2(acac)(PPhMe_2) \cdot S + PPhMe_2 \qquad (2)$$

Table 2 shows the equilibrium constants K evaluated at various temperatures and thermodynamic parameters for equilibrium 2. An illustration of the degree of dissociation of IIb in toluene is given by the following; with a K value of 9.6×10^{-4} at 15°C and at a concentration of 0.10 M 24 ± 2% of IIb is dissociated.

Displacement of the tertiary phosphine ligands by pyridine bases from the alkylcobalt complexes

As we have previously observed [1], the tertiary phosphine ligands in the alkylcobalt complexes I—IV can be displaced readily by pyridine and its analogs.

TABLE 2

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE REACTION:

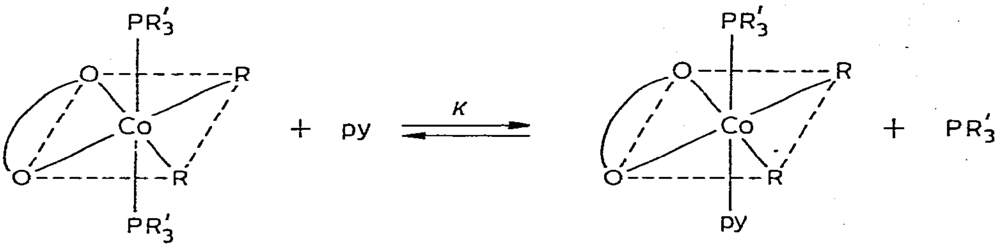
$$CoEt_2(acac)(PPhMe_2)_2 + \text{toluene} \overset{K}{\rightleftharpoons} CoEt_2(acac)(PPhMe_2) \cdot S + PPhMe_2$$

Temperature (°C)	$10^3/T$	$10^4\ K$ [a]
—72	4.98	0.46
—54	4.57	1.02
—48	4.44	1.25
—35	4.20	1.99

K_{288}	$\Delta H°$ (kcal/mol)	$\Delta G°$ (kcal/mol)	$\Delta S°$ (e.u.)
9.6×10^{-4}	4.2 ± 0.3	4.0 ± 0.2	0 ± 2

[a] Solvent, toluene; [IIb], 0.10 mol/l.

More basic tertiary phosphines such as PEt_3 and P-n-Bu_3 can be displaced more readily by pyridine bases such as pyridine (py), γ-picoline (γ-pic) and 2,2′-bipyridine (bipy). Alkylcobalt complexes containing less basic phosphines such as $PPhMe_2$ are less prone to such facile displacement. In the cases of trialkylphosphine-coordinated alkylcobalt complexes part or all of the tertiary phosphines are displaced by pyridines and alkylcobalt complexes containing pyridine bases such as $CoMe_2(acac)(PEt_3)(py)$ (Va), $CoMe_2(acac)(PEt_3)(\gamma\text{-pic})$ (Vb), and $CoMe_2(acac)(bipy)$ (VI) were actually isolated. Failure to isolate α- and β-picoline-coordinated complexes indicate that steric effects are important equilibrium 3.



(3)

The above equilibrium can be conveniently monitored by means of ^1H and ^{31}P NMR spectroscopy. On displacement of one of the two tertiary phosphines by pyridine part of the triplet ^1H NMR signal of the cobalt-bonded methyl groups is converted to a doublet, depending on the temperature and the kind of tertiary phosphine. Figure 4A demonstrates the typical change of the cobalt-bonded methyl resonance observed in pyridine at various temperatures. It can be seen that the doublet due to cobalt-bonded methyl groups in $CoMe_2(acac)(PPhMe_2)(py)$ increases in its integrated peak area in proportion to the corresponding decrease of the triplet due to $CoMe_2(acac)(PPhMe_2)_2$ on raising the temperature. A similar spectral change can be seen in Fig. 4B and 4C which illustrate the change of the cobalt-bonded alkyl resonances of $CoEt_2(acac)(PPhMe_2)_2$ (IIb) and Co-n-$Pr_2(acac)(PPhMe_2)_2$ (IIc) in pyridine on raising the temperature. The signal of the ethyl groups of IIb appears as a singlet at −35° C in pyridine as well as in toluene, but a broad singlet which may be assigned to the methyl groups of the ethyl groups in $CoEt_2(acac)(PPhMe_2)(py)$ (IIb′) develops on increasing the temperature to −20° C. The signal of the methylene protons in IIb is observed at τ 8.7 ppm, being obscured on the slope of the methyl resonance of $PPhMe_2$. Further increase of the temperature causes overlapping of the broad methyl and ethyl singlets due to complex IIb to a broad singlet at −5° C. Finally at 10° C the ethyl signal of IIb completely vanishes and a triplet at τ 9.2 ppm (^3J(P—H) 7 Hz) which may be due to the methyl protons of the ethyl groups in $CoEt_2(acac)(PPhMe_2)(py)$ (IIb′) dominates (not shown in Fig. 4B). The signal of n-propyl groups of IIc are observed at τ ca. 8.5—9.3 ppm, being overlapped with $PPhMe_2$ ligands. The methyl resonances of the acac ligand of IIc in pyridine appear as two singlets at τ 8.42 and 8.54 ppm. The singlet at τ 8.42 ppm which may be assigned to the methyl groups of the acac ligand in Co-n-$Pr_2(acac)(PPhMe_2)(py)$ (IIc′) develops on increasing the temperature (Fig. 4C). The spectral change is intriguing in several aspects: (1) It suggests the presence of the equilibrium as shown in eq. 3; (2) since the chemical shift difference between the methyl and methylene groups reflects the electronegativity of the entity bonded with the

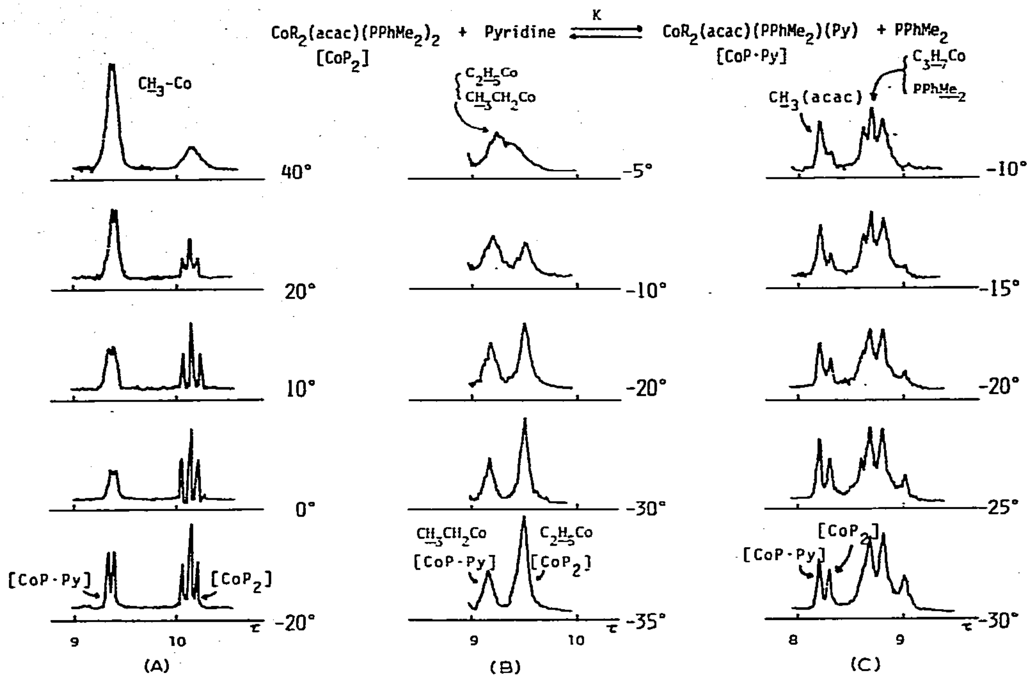


Fig. 4. ^{1}H NMR spectra of $CoR_2(acac)(PPhMe_2)_2$ in pyridine. A: $Co(CH_3)_2(acac)(PPhMe_2)_2$, B: $Co(C_2H_5)_2(acac)(PPhMe_2)_2$; C: $Co(C_3H_7)(acac)(PPhMe_2)_2$.

ethyl group [7], the separation of the methyl (τ 9.2 ppm) and methylene (τ 8.7 ppm) resonances in IIb′ from the singlet ethyl signal in IIb on displacement of one of the $PPhMe_2$ ligand in IIb by pyridine suggests that the electronegativity of the entity bonded with the ethyl groups was increased by coordination with pyridine. This fact implies that pyridine is in fact playing the role of a π-acid as compared with $PPhMe_2$ in eq. 3 (vide infra); (3) as the difference between Fig. 4A, 4B and 4C shows, the cobalt-bonded alkyl groups exert a marked effect on the equilibria of pyridine displacement reactions. Displacement by pyridine is much more favored in the propylcobalt complex than in the methylcobalt complex.

From the peak areas of the cobalt-bonded alkyl groups or the CH_3(acac) groups in $CoR_2(acac)(PPhMe_2)_2$ and $CoR_2(acac)(PPhMe_2)(py)$ as shown in Fig. 4 we have calculated the equilibrium constants:

$$K = \frac{[CoR_2(acac)(PPhMe_2)(py)][PPhMe_2]}{[CoR_2(acac)(PPhMe_2)_2][py]}$$

for a series of dialkylcobalt complexes and plotted the ln K values vs. the reciprocal temperatures in Fig. 5. The equilibrium constants and thermodynamic parameters are summarized in Table 3. It can be seen from Table 3 that increase in the alkyl chain length makes the enthalpy change for the displacement of $PPhMe_2$ by pyridine in eq. 3 more favorable but the effect is compensated by the entropy change. For illustration of the degree of dissociation of IIb in pyridine the K value of 0.018 at 15° C as derived by extrapolation of the K values at lower temperatures with the concentration of 0.11 M means that 70 ± 2% of

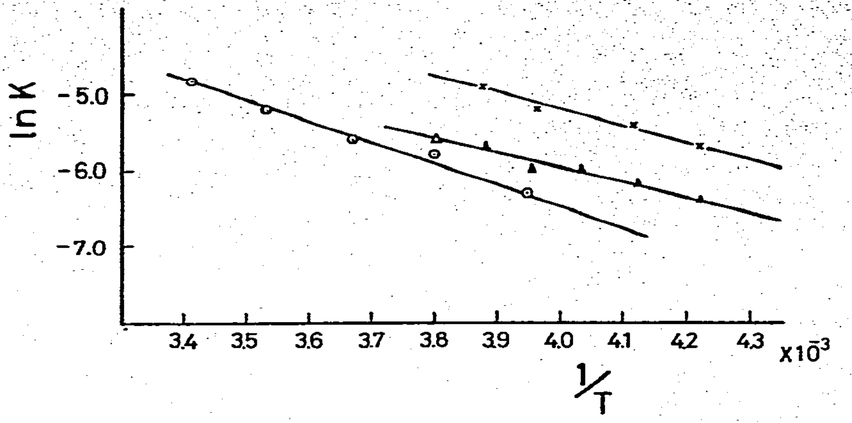


Fig. 5. ln K vs. $1/T$ for the equilibria of pyridine displacement as shown in eq. 3. ○: $Co(CH_3)_2(acac)(PPhMe_2)_2$; X: $Co(C_2H_5)(acac)(PPhMe_2)_2$; △: $Co(C_3H_7)_2(acac)(PPhMe_2)_2$.

IIb is dissociated in pyridine whereas the degrees of dissociation of IIa and IIc in pyridine at the same temperature are 45 ± 2% and 78 ± 2%, respectively.

We examined further the ^1H NMR spectra of the isolated alkylcobalt complexes containing pyridine bases in toluene and CD_2Cl_2. Table 4 summarizes the NMR data. The pyridine-coordinated complex Va and the γ-picoline-coordinated complex Vb show spectra which can be accounted for by assuming a configuration having the *cis*-dimethyl groups and an acetylacetonato ligand coplanar with cobalt. The PEt_3 and pyridine or γ-picoline groups are positioned *trans* to each other above and below this plane. The cobalt-bonded methyl groups give rise to a doublet due to coupling with a PEt_3 ligand and the methyl groups in the acetylacetonato ligand are equivalent *. It is to be noted that the α-protons in the co-

TABLE 3

THERMODYNAMIC PARAMETERS FOR

$$CoR_2(acac)(PPhMe_2)_2 + Pyridine \overset{K}{\rightleftharpoons} CoR_2(acac)(PPhMe_2)(py) + PPhMe_2$$

R	$10^3 K_{263}$	$\Delta H°$ (kcal/mol)	$\Delta G°$ (kcal/mol)	$\Delta S°$ (e.u.)
CH_3	4.5	5.5	2.8	10.3
C_2H_5	8.4	4.6	2.5	8.0
C_3H_7	4.0	4.1	2.9	4.6

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* In the foregoing discussion concerning the NMR spectra of the dialkyl(acetylacetonato)bis(tertiary phosphine)cobalt(III) complexes I—IV the structure of *cis*-dialkyl(acetylacetonato)-*trans*-bis(tertiary phosphine)cobalt has been assumed as a configuration compatible with the NMR spectra. A referee pointed out that a configuration of *trans*-dialkylbis-*cis*-(tertiary phosphine)cobalt also is compatible with the NMR spectra. However, the NMR spectra of the pyridine- and γ-picoline-coordinated complexes Va and Vb obtained by displacement of one tertiary phosphine ligand from I are consistent with the *cis*-dialkyl structure and not compatible with the *trans*-dialkyl structure. Furthermore, the NMR spectra of the pyridine- and γ-picoline-coordinated complexes Va and Vb are reverted to that of I by addition of excess PEt_3 without any appreciable change in the CH_3(acac) signal. Hence it seems more reasonable to assign the *cis*-dialkyl structure also to the starting bis(tertiary phosphine) complexes I—IV.

TABLE 4

^{1}H NMR DATA FOR THE BASE-COORDINATED COMPLEXES (For symbols a-d see structure VI)

Complex	Solvent ^{a}	Co—R	acac		Other
			CH_3	CH_2	
$Co(CH_3)_2(acac)(PEt_3)(py)$ (Va)	toluene	9.30(d, 6H)	8.18(s, 3H)	5.08(s, 1H)	py: 1.28(d, α-H, 2H) 3.20(t, γ-H, 1H) 3.44(t, β-H, 2H)
$Co(CH_3)_2(acac)(PEt_3)(\gamma\text{-pic})$ (Vb)	toluene	9.34(d, 6H)	8.18(s, 3H)	5.10(s, 1H)	py: 1.54(d, α-H, 2H) 3.72(d, β-H, 2H) 8.45(s, γ-CH_3, 3H)
$Co(CH_3)_2(acac)(bipy)$ (VIa)	CD_2Cl_2	9.60(s, 3H) ^{a} 8.55(s, 3H) ^{b}	8.15(s, 3H) ^{c} 8.31(s, 3H) ^{d}	4.90(s, 1H)	bipy: 1.48—2.85 (unresolved)
$Co(C_2H_5)_2(acac)(bipy)$ (VIb)	CD_2Cl_2	10.20(t, 3H) ^{a}, 8.85(q, 2H) ^{a}	8.15(s, 3H) ^{c}	4.90(s, 1H)	bipy: 1.60—2.85
		9.27(t, 3H) ^{b}, 7.55(q, 2H) ^{b}	8.37(s, 3H) ^{d}		(unresolved)

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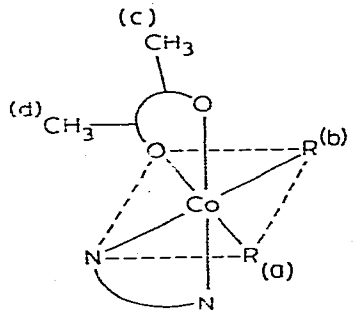
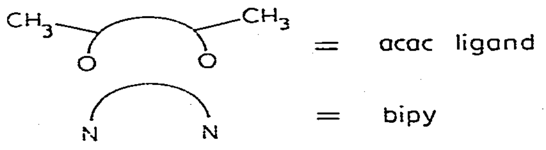
[a] For avoiding the overlap of the TMS signal with that of cobalt-bonded alkyl groups, no internal TMS was used. Instead, the light toluene or CH_2Cl_2 were used as the internal standard. Abbreviation: s, singlet; d, doublet; t, triplet; q, quartet.

ordinated pyridine and γ-picoline groups are very much deshielded.

In the bipyridine-coordinated dimethylcobalt complex both cobalt-bonded-CH_3 and acac-CH_3 groups are observed as non-equivalent singlets, supporting the *cis*-configuration VI shown below:



(VI)



(VIa) R = Me
(VIb) R = Et

The bipy-coordinated ethyl complex shows two sets of resonances due to the CH_3 and CH_2 groups bonded to cobalt as clearly separated triplets and quartets. The chemical shift differences between CH_3 and CH_2 groups in two sets are fairly large indicating the net electron-accepting property of the bipyridine ligand as a π-acid. Since the dimethylcobalt and diethylcobalt complexes show two methyl and two sets of ethyl resonances, a question remains concerning the assignments of these resonances in the configuration of VI. Although no direct evidence is available, it seems likely that the signal of the methyl groups in *trans* position from one of the oxygens of the acetylacetonato ligand will appear at the approximately same field as in the pyridine-coordinated complex Va in which the methyl groups are situated at *trans* positions from oxygen atoms of the acetylacetonato ligand. The other methyl resonance observed at considerably lower field in the spectrum of VIa is then ascribed to the methyl group in the *trans* position from the nitrogen of the bipyridine ligand. The two sets of the ethyl resonances are assigned in a similar manner. The assignment is consistent with our assumption of regarding pyridine analogs as π-acids. Extension of the similar argument leads to a tentative assignment of the lower field methyl signal of the acac ligand to $CH_3^{(c)}$ and the higher one to $CH_3^{(d)}$ as labelled in structure VI. Table 5 shows the chemical shift differences between resonances of the CH_3 and CH_2 groups in complexes IIb, IIb′ and VIb. The difference between $\tau(CH_3)$ and $\tau(CH_2)$ in the spectra of these complexes increases upon replacement of the phosphine ligands in IIb by pyridine or bipyridine. The latter exerts the more pronounced effect particularly when it is at the *trans* position to the ethyl group. This result suggests that the π-acidity of the ligands increases in the order of $PPhMe_2$ < pyridine < bipyridine (vide supra).

We now consider the exchange of the coordinated pyridine in $CoMe_2(acac)(PEt_3)(py)$ (Va) with free pyridine. Table 6 shows the temperature dependence of the ^1H NMR spectrum of Va in toluene. The spectrum at −40° C shows a doublet at τ 9.26 ppm which is assigned to the cobalt-bonded methyl groups coupled with the PEt_3 ligand, and α-, β- and γ-protons of the coordinated pyridine at τ 1.22, 3.50 and 3.25 ppm, respectively. The fact that the α-protons ap-

TABLE 5

CHEMICAL SHIFT DIFFERENCES BETWEEN $\tau(CH_3)$ AND $\tau(CH_2)$

Complex	Solvent	Chemical shift		$\Delta(CH_3—CH_2)$
		CH_2	CH_3	
$Co(C_2H_5)_2(acac)(PPhMe_2)_2$ (IIb)	pyridine	9.50s	9.50s	~0
$Co(C_2H_5)_2(acac)(PPhMe_2)(py)$ (IIb′)	pyridine	8.70m	9.34t	0.64
$Co(C_2H_5)_2(acac)(bipy)$ (VIb)	CD_2Cl_2	8.85q 7.55q	10.20t 9.27t	1.35 [a] 1.75 [b]

[a], [b] For assignments, see structure formula of VI on foregoing page.

pear at a particularly low field is noticeable. On raising the temperature the doublet of the cobalt-bonded methyl groups collapses to a singlet at 20° C due to dissociation of PEt_3 as we already discussed. The signals of the coordinated pyridines show a peculiar behavior. The signal due to α-protons shifts markedly to lower field, whereas those due to β- and γ-protons shift slightly to opposite directions. The results seem to indicate that exchange of the coordinated pyridine also is taking place.

For further clarifying the exchange of the coordinated pyridine we examined the temperature change of the γ-picoline-coordinated complex Vb in toluene in the presence of an excess amount of pyridine as shown in Fig. 6. The spectrum at —40° C shows peaks due to the picoline-coordinated complex as marked with small arrows in Fig. 6. On raising the temperature to 0° C the peaks of the coordinated pyridine and γ-picoline groups coalesce indicating that the coordinated γ-picoline exchanges rapidly with pyridine at 0° C where the exchange of the phosphine ligand is slow. When the dimethylcobalt complex I having two PEt_3 ligands is dissolved in pyridine the proton NMR spectrum shows a doublet due to the cobalt-bonded methyl group coupled with one PEt_3 ligand —30° C indicating the presence of equilibrium 3. The doublet collapses to a singlet upon raising the temperature above 40° C and becomes a sharp singlet at τ 9.46 ppm at 60° C. On further increase of the temperature of the pyridine solution containing I to 70° C the singlet due to the cobalt-bonded methyl groups starts to

TABLE 6

THE TEMPERATURE DEPENDENCE OF THE CHEMICAL SHIFTS [a] OF $Co(CH_3)_2(acac)(PEt_3)(py)$ (Va) IN TOLUENE

Temperature (°C)	$C\underline{H}_3—Co$	acac		pyridine		
		CH_3(6H)	CH(1H)	α-H(2H)	β-H(2H)	γ-H(1H)
40	9.47s	8.24s	5.08s	0.15br	3.26t	3.49t
20	9.44br. s	8.23s	5.08s	0.70br	3.36br. s	
0	9.36d	8.20s	5.08s	1.30br	3.38br. m	
—20	9.30d	8.18s	5.08s	1.28br. d	3.49t	3.25t
—40	9.26d	8.16s	5.08s	1.22d	3.50t	3.25t

[a] Abbreviations: s, singlet; d, doublet; t, triplet; br. s, broad singlet; br. m, broad multiplet.

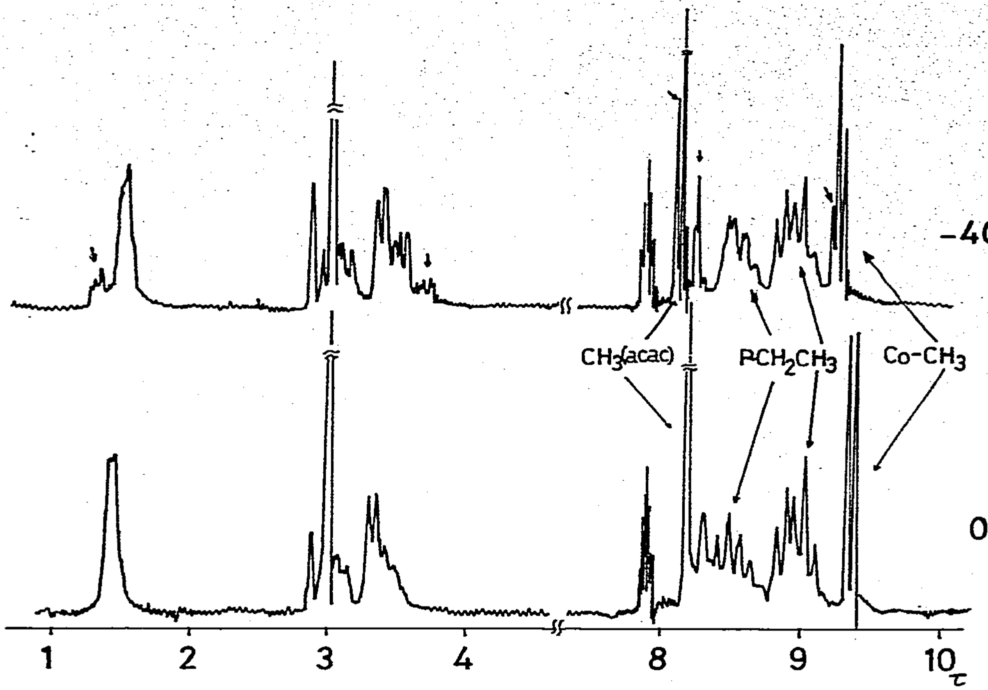
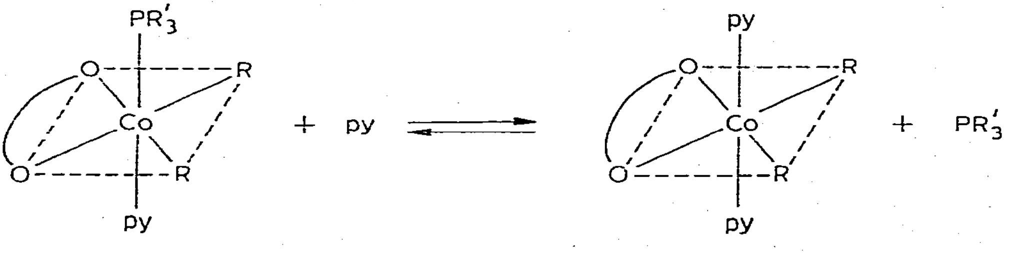


Fig. 6. ^{1}H NMR spectra of $Co(CH_3)_2(acac)(PEt_3)(\gamma\text{-pic})$ in toluene in the presence of pyridine. (Peaks with a small arrow are due to $Co(CH_3)_2(acac)(PEt_3)(\gamma\text{-pic})$).

broaden again. This change is reversible and the doublet is restored on lowering the temperature to 0° C. The reversible change between the doublet and the singlet can be accounted for by assuming the presence of equilibrium 4 in addition to equilibrium 3. The broadening of the singlet on increase of the tempera-



(4)

ture over 70° C may be associated with some configurational change of the bis-pyridine coordinated complex but the precise reason is not clear. Attempts to isolate a bis-pyridine-coordinated complex failed, but a bipy-coordinated complex VI was obtained readily.

We have neglected so far any discussion concerning the exchange of the acetylacetonato ligand. The ^{1}H methyl peak of the acac ligand in all alkylcobalt complexes I—V is observed as a sharp singlet, whose width does not vary over a wide temperature range (—78 to 20° C). Although it is not likely that the acac ligand is exchanging on NMR time scale, the possibility that the methyl groups in the acac ligand are rapidly exchanging even at low temperatures cannot be excluded.

The observation of the methyl groups in the acac ligand of VI as two sharp singlets, which do not coalesce on raising the temperature, eliminates the possibility that a rapid exchange reaction is taking place, at least in the case of the bipyridine-coordinated complexes, and the exchange of the acac ligand in I—V as we observed in the related alkyl(acetylacetonato)(triphenylphosphine)nickel(II) complexes is highly unlikely [6b,8]. It should be added further that the latter complexes undergo a rapid disproportionation reaction giving $Ni(acac)_2$ and a PPh_3-coordinated nickel(0) complex in pyridine presumably by a process involving the partial dissociation of the bidentate acac ligand to a unidentate form. On the other hand the present cobalt complexes have been found quite stable in pyridine and its analogs.

Experimental

Materials

$CoR_2(acac)(PR_3')_2$ was prepared according to our previous report [1b] and the pyridine base-coordinated complexes were prepared by the reaction of $CoR_2(acac)(PR_3')_2$ with the bases. Deuterated solvents were used after purification by usual methods.

Spectroscopic measurements

^1H NMR spectra were recorded on 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. The solvent was added to an NMR tube containing dialkylcobalt complexes by trap-to-trap distillation in vacuum, and the NMR tube was sealed. The temperature calibrations for the variable temperature spectra were obtained with ethylene glycol standards and are expected to be accurate to ±2°. ^1H and ^{13}C NMR chemical shifts are referred to internal TMS. When the signal of complexes are overlapped with TMS, ^1H NMR chemical shifts are referred to the internal protonic impurity in the deuterated solvents. ^{31}P NMR signals are referred to external triphenylphosphine in toluene (downfield positive).

In order to estimate the equilibrium constants and thermodynamic parameters for eq. 2 from the ^{31}P NMR spectra, information about the ^{31}P limiting spectra of $CoEt_2(acac)(PPhMe_2)_2$ (IIb) and $CoEt_2(acac)(PPhMe_2) \cdot S$ is required. If one assumes ^{31}P chemical shift values of α for the undissociated species $CoEt_2(acac)(PPhMe_2)_2$, β for the solvent-coordinated species $CoEt_2(acac)(PPhMe_2) \cdot S$ and γ for the liberated $PPhMe_2$ in the following equilibrium:

$$CoEt_2(acac)(PPhMe_2)_2 + S \rightleftharpoons CoEt_2(acac)(PPhMe_2) \cdot S + PPhMe_2 \qquad (2)$$

and the number of species: $1 - x$, x and x, respectively, the chemical shift value f of the partially dissociated and exchange system with a degree of dissociation x can be expressed as weighted mean of the chemical shifts α, β, and γ as:

$$f = \frac{2\,\alpha(1-x) + \beta x + \gamma x}{2(1-x) + x + x}$$

where the number of the undissociated species is doubled since it contains two phosphorus atoms. The limiting chemical shift values α, β, and γ were estimated as follows:

α: although the ^{31}P NMR spectrum of IIb still shows some broadening even at $-78°$C and the limiting ^{31}P NMR spectrum for $CoEt_2(acac)(PPhMe_2)_2$ was not observable, we can safely assume that the limiting spectrum of IIb is in the range between 28.5 and 29.0 downfield from the external PPh_3 reference, judging from the way of convergence of the spectrum as lowering the temperature.

The chemical shift of the dissociated species of IIb in toluene was not available and it was necessary to estimate it indirectly from the ^{31}P chemical shift difference of $CoMe_2(acac)(PEt_3)_2$ and $CoMe_2(acac)(PEt_3)(py)$ which showed ^{31}P signals of both undissociated and dissociated species at 27 and 38.4 ppm, the difference being 11.4 ppm. On the assumption that the ^{31}P chemical shift difference between the undissociated and dissociated species will be largest on replacement of the phosphine by pyridine, we assessed that the ^{31}P chemical shift difference between $CoEt_2(acac)(PPhMe_2)_2$ and $CoEt_2(acac)(PPhMe_2)\cdot$(toluene) will be ca. 10 ppm. Thus the limiting ^{31}P chemical shift (β) of $CoEt_2(acac)(PPhMe_2)$-(toluene) was estimated as ca. 39 ppm. Using these estimated limiting chemical shift values for $CoEt_2(acac)(PPhMe_2)_2$ (α, 29.0 ppm), $CoEt_2(acac)(PPhMe_2)$-(toluene) (β, 39 ppm), and free $PPhMe_2$ (γ, -42.5 ppm), the value of f may be expressed as:

$$f = \frac{2(1-x)(29.0) + 39x - 42.5\,x}{2(1-x) + x + x}$$

which leads to the equation

$$x = (58 - 2f)/61.5$$

The degree of dissociation was calculated with this equation.

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