

MECHANISMS OF THERMAL DECOMPOSITION OF DIALKYLCOBALT(III)
 COMPLEXES

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Summary

The thermal stability of a series of $\text{CoR}_2(\text{acac})(\text{PPhMe}_2)_2$ complexes decreases in the order: $\text{CH}_3 > \text{C}_2\text{H}_5 > \text{C}_3\text{H}_7 > \text{C}_4\text{H}_9$. Thermal decomposition of the alkylcobalt complex in toluene solution is first order with respect to the complex and activation energies for pyrolysis of the ethyl and propyl cobalt complexes are 30.6 and 25.5 kcal/mol, respectively. Addition of free PPhMe_2 to the solution of the ethyl cobalt complex strongly inhibits its thermal decomposition and the apparent activation energy increases with increasing the concentration of added PPhMe_2 approaching its limiting value of ca. 35 kcal/mol. Comparison of the relative rates of thermolysis of $\text{Co}(\text{C}_2\text{H}_5)_2(\text{acac})(\text{PPhMe}_2)_2$ and $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ revealed the presence of a considerable isotope effect ($k_{\text{H}}/k_{\text{D}} = 2.30 \pm 0.05$). The slow thermolysis of the ethyl- d_3 complex below 5° in benzene or toluene, and the thermolysis at room temperature in pyridine as well as rapid thermolysis of the solid sample, predominantly liberate

$\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 , the β -elimination products, whereas the H-D scrambling occurs above room temperature in benzene. On the basis of these results and NMR data on dynamic behavior of the complexes, a mechanism accounting for the thermolysis is proposed.

It involves non-rate-determining dissociation of the tertiary phosphine to accommodate a site for hydrogen abstraction, a rate-determining process where the cobalt-carbon bond is loosened and β -hydrogen is abstracted, and the ensuing process where the scrambling takes place depending on thermolysis conditions.

Introduction

The problem concerning the stability of metal-to-carbon σ -bond in organotransition metal compounds represents one of the central themes in organotransition metal chemistry [1]. After some period when the transition metal-to-carbon bond was regarded intrinsically weak, the utility of stabilizing ligands such as cyclopentadienyl, carbon monoxide, tertiary phosphines and bidentate organic nitrogen bases has been recognized with the resultant rapid increase in the successful isolation of a number of alkyltransition metal complexes. The role of the stabilizing ligand has been accounted for in terms of the ligand field theory by Chatt and Shaw who proposed that the presence of the stabilizing ligand causes the increase of the energy gap required for an electronic promotion from a filled d-orbital to an anti-bonding M-C orbital or from a bonding M-C orbital to an unoccupied d-orbital [2a]. Later, a theory which stresses the importance of a low energy thermolysis pathway, particularly the β -elimination, has been proposed [2b-2d] and it paved a route to successful isolation of many " γ -elimination stabilized" alkyl transition metal complexes [2b,f]. However, the variety of isolated alkyltransition metal complexes is still not enough to allow one for advancing a general

theory concerning the nature of the transition metal-to-carbon bond and the discussion to explain why some alkyltransition metal complexes are stable while others are not still remains somewhat conjectural. More extensive quantitative data are clearly required. Recent thermochemical studies have provided considerable information concerning the M-C bond strength revealing that the transition metal-carbon bonds in some complexes are as strong as in organometallic compounds of main group elements [3]. Reports of kinetic studies on thermolysis of alkyltransition metal complexes are still scarce, being restricted to stable alkylplatinum complexes [4]. The detailed kinetic studies are expected to provide important information supplementing the thermochemical data concerning the stability of alkyltransition metal complexes and their decomposition pathways. As extension of our previous efforts on kinetic studies concerning the thermolysis of alkyl-nickel and copper complexes [5], we have studied the kinetics of thermolysis of recently isolated cis-dialkyl(acetylacetonato)bis(tertiary phosphine)cobalt(III) and their analogous complexes[6].*

The kinetic study using these alkylcobalt complexes has the following advantages. (1) A series of alkylcobalt complexes containing a variety of ligands can be easily prepared and the effects of the cobalt-bonded alkyl group and the ligands on the thermal stability of the complexes can be examined. (2) Most of the complexes are thermally stable at room temperature, insensitive to air and soluble in ordinary solvents, thus making the handling and kinetic measurements very easy. (3) They are diamagnetic and amenable to NMR study concerning the ligand dissociation which is temperature dependent. (4) Deuterium labeling of the ethyl

* In this paper the same numbering as used in the previous papers [7] is employed.

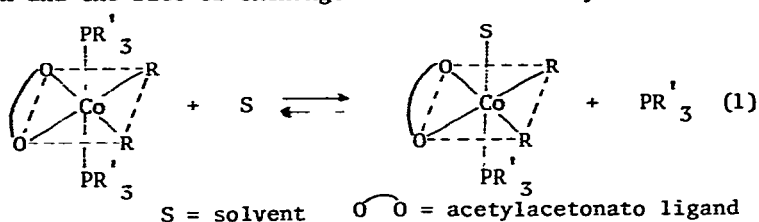
groups is feasible thus making the study of the fate of the deuterated ethyl groups and the isotope effect in the thermolysis accessible.

Results

Properties of cis-dialkyl(acetylacetonato)bis(tertiary phosphine) cobalt(III) and related cobalt(III) complexes

Preparations, chemical properties and dynamic behavior of the title complexes have been reported separately [7] and we describe here only their properties pertinent to the discussion of thermolysis mechanism, as well as the preparation of specifically deuterated diethylcobalt complex.

NMR studies of $\text{CoR}_2(\text{acac})(\text{PR}'_3)_2$ type complexes established their structures in solution as shown below. The coordinated tertiary phosphine ligands are partly released in solution and an exchange between the liberated and the coordinated phosphines takes place, slowly at low temperature and rapidly at higher temperature. The degree of dissociation and the rate of exchange can be observed by means of

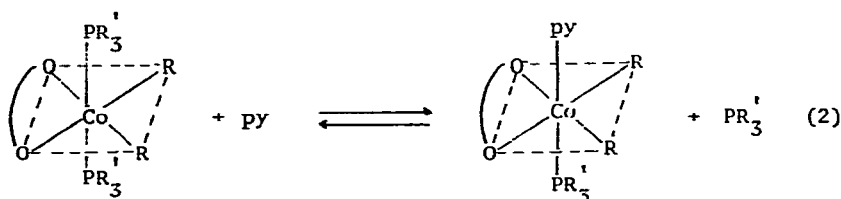


^{31}P and ^1H NMR spectroscopy. The exchange of the acetylacetonato ligand was not observed. The exchange of the tertiary phosphine ligands in the dimethylcobalt complexes can be monitored by following the ^1H NMR spectral change of the triplet of the cobalt-bonded methyl groups, which are coupled with two phosphorus nuclei in the tertiary phosphine ligands coordinated with cobalt at low temperatures, coalescing to a singlet at higher temperatures. Addition of a tertiary phosphine to the system

caused the appearance of the triplet methyl signal even at high temperatures where otherwise the singlet was observed.

The coalescence temperatures, observed in the absence of the added phosphine, of the dimethylcobalt complexes coordinated with various tertiary phosphine ligands decreased in the order of $\text{PPhMe}_2 > \text{PEt}_3 > \text{P(n-Bu)}_3$. The rates of the exchange reactions of the PPhMe_2 ligands coordinated with the methyl and ethyl complexes can be roughly estimated by observing the variable temperature ^{31}P NMR. The activation energy for the ligand exchange of the methyl complex was evaluated higher (10 ± 3 kcal/mol) than that of the ethyl complex (8 ± 3 kcal/mol). These effects of the alkyl groups and tertiary phosphine ligands suggest that the more basic the cobalt complex or the tertiary phosphine is, the coordinated tertiary phosphine ligands tend to be liberated to the greater extent into solution.

The phosphine ligand(s) in the methylcobalt complexes can be readily displaced with pyridine bases to give pyridine base-coordinated complexes $\text{CoR}_2(\text{acac})(\text{PEt}_3)(\text{py})$ and $\text{CoR}_2(\text{acac})(\text{bipy})$, where py is pyridine or β -picoline and bipy is 2,2'-bipyridine.



The equilibrium and exchange can be monitored by observing the ^1H NMR signal of the cobalt-bonded methyl groups to coalesce from a doublet at lower temperature to a singlet at higher temperature.

The IR spectra of the isolated dialkylcobalt complexes show a sharp medium band in the range between 550 and 595 cm^{-1} which disappear on heating the solid sample. We tentatively assign the band to the $\nu(\text{Co-C})$ vibration. Table 1 shows the $\nu(\text{Co-C})$ band and decomposition

Table 1 IR DATA AND DECOMPOSITION POINT OF $\text{CoR}_2(\text{acac})\text{L}_2$

Complex ^{a)}	R	L	pKa of L	$\nu_{\text{Co-C}}$ (cm^{-1})	d.p. ($^{\circ}\text{C}$)
I	CH_3	2 PEt_3	8.69	573	78-81
IV	CH_3	2 $\text{P}(\text{n-Bu})_3$	8.43	578	64-81
IIa	CH_3	2 PPhMe_2	6.50	580	116-119
IIb	C_2H_5	"	"	578	67-68
IIc	C_3H_7	"	"	570	49-50
IId	C_4H_9	"	"	574	unstable at r.t.
III	CH_3	2 PPh_2Me	4.61	585	89-92
Va	CH_3	PEt_3 , py	8.69, 5.19	580	100-105
VIa	CH_3	bipy		595	139-140
VIb	C_2H_5	"		585	125-126
VIc	C_3H_7	"		550	45-47

a) See the preceding paper [7] for numbering.

temperatures together with pKa values of the conjugated acids of the tertiary phosphine ligands. With increase of the alkyl chain length the decomposition temperature of the alkylcobalt complex having PPhMe_2 and bipy ligands falls in the order of $\text{CH}_3 > \text{C}_2\text{H}_5 > \text{n-C}_3\text{H}_7 > \text{iso-C}_4\text{H}_9$. A similar trend of decrease of the decomposition temperature with increase of the alkyl chain length was observed in thermolysis of $\text{NiR}_2(\text{bipy})$ [5a], $\text{FeR}_2(\text{bipy})_2$ [10], $\text{CrRCl}_2(\text{THF})_3$ [8] and $\text{CrRCl}_2(\text{py})_3$ [9] but not in $\text{CuR}(\text{PPh}_3)_2$ [5b]. The decomposition points of the methyl complexes having trialkylphosphines were similar but substitution of one of the alkyl groups by phenyl group seems to enhance the decomposition point. However, further phenyl substitution causes the fall of the decomposition temperature, presumably due to the steric effect.

In the series of bipy-containing dialkyl complexes the decrease of the $\nu(\text{Co-C})$ band with increase in the alkyl chain length is noted. A similar but less definite trend is observable in the PPhMe_2 -coordinated complexes.

Replacement of the tertiary phosphine ligand(s) with pyridine(s) causes enhancement of the decomposition temperature of the methylcobalt complex with simultaneous increase of the $\nu(\text{Co-C})$ frequency. The pyridine ligands may not be acting as simple electron donors but the contribution of back-donation from cobalt to the coordinated pyridine may be significant for stabilization of the alkyl-cobalt(III) bonds. The previous NMR study [7b] has shown that pyridine replaces trialkylphosphines more easily from $\text{CoMe}_2(\text{acac})(\text{PR}'_3)_2$ than dimethylphenylphosphine from $\text{CoR}_2(\text{acac})(\text{PPhMe}_2)_2$.

Analysis of thermolysis products of $\text{CoR}_2(\text{acac})(\text{PR}'_3)_2$ in the solid state and in solutions.

Table 2 shows the thermolysis products of various dialkyl(acetylacetonato)cobalt complexes coordinated with PPhMe_2 in the solid state and in CH_2Cl_2 and toluene solutions. The thermolysis conditions do not markedly affect the compositions of thermolysis products; thermolysis of the dimethylcobalt complex gives the coupling product of the methyl groups whereas dialkylcobalt complexes of longer alkyl chains give the disproportionation products of the alkyl groups in a 1/1 ratio. The results are similar to but somewhat different from the thermolysis of dialkyl(bipyridyl)nickel which produced coupling products from methyl and ethyl complexes whereas the disproportionation products from n-propyl and isobutyl complexes [5a]. We have also observed that thermolysis of diethylbis(bipyridyl)iron(II) afforded ethane and ethylene and dimethylbis(bipyridyl)iron(II) gave mainly methane [10].

These results are not compatible with a free radical mechanism but suggest an intramolecular process.

Table 2. THE PRODUCTS OF THERMOLYSIS OF $\text{CoR}_2(\text{acac})(\text{pph}(\text{C}_2)_2)^{\text{a)}$

Decomp. Products ^{b)}	Co-CH ₃	Co-C ₂ H ₅	Co-C ₃ H ₇	Co-C ₄ H ₉
I				
R(-H)	0	46	47	50
R(+H)	0	54	53	50
R-R	100	trace	0	0
II				
R(-H)	0	45	48	45
R(+H)	5	55	52	55
R-R	95	0	0	0
(solvent)	CH ₂ Cl ₂	toluene	toluene	toluene

a), Decomposition temperature in the solid state, Co-Me, 116-119°; Co-Ft, 67-68°; Co-Pr, 49-50°; Co-Bu, unstable at room temperature. Figures in the table denotes the percentage of the evolved gas.

b), R(-H), alkene; R(+H), alkane; R-R, coupling product (alkane)

I: in the solid state

II: in solution

Thermolysis of $\text{Co}(\text{C}_2\text{H}_5)_2(\text{acac})(\text{PPhMe}_2)_2$ was carried out in C_6D_6 and ethane and ethylene evolved were examined. The result indicated that there was no detuerium incorporation into ethane excluding the hydrogen abstraction from the solvent in the thermolysis experiment.

In order to obtain further information concerning the thermolysis mechanism we have prepared a specifically deuterated ethyl complex, $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ (see Experimental for preparation) and its thermolysis product was examined. Table 3 summarizes the product distribution of the evolved gases from $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ (VII)

Table 3 THE COMPOSITIONS(%) OF DEUTERATED ETHYLENES AND ETHANES EVOLVED DURING THE HEAT TREATMENT OF $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ (VII)

Run	conditions	C_2HD_3	$\text{C}_2\text{H}_2\text{D}_2^{1)}$	$\text{C}_2\text{H}_3\text{D}$	$\text{C}_2\text{H}_2\text{D}_4$	$\text{C}_2\text{H}_3\text{D}_3$
1	a	12	79	9	75	25
2	b	13	76	11	73	27
3	c	-	100 ²⁾	-	100	-
4	d	-	100 ³⁾	-	100	-

- a, Kept at 28° for 1 day in benzene
 b, Kept at 42° for 2 days in benzene
 c, Kept below 5° for a few days in toluene
 d, Thermolyzed at 70° in the solid state

1), $\text{C}_2\text{H}_2\text{D}_2 = \text{asym-}\text{C}_2\text{H}_2\text{D}_2 + \text{cis-}\text{C}_2\text{H}_2\text{D}_2 + \text{trans-}\text{C}_2\text{H}_2\text{D}_2$

2), Consisted of only asym- $\text{C}_2\text{H}_2\text{D}_2$.

3), Consisted mainly of asym- $\text{C}_2\text{H}_2\text{D}_2$ and a trace amount of cis- and trans- $\text{C}_2\text{H}_2\text{D}_2$

thermolized under various conditions. It is seen that the thermolysis is accompanied by H-D scrambling under certain conditions (vide infra) but slow thermolysis in toluene below 5° gave cleanly $\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 in a 1/1 ratio without contamination by cis- and trans-CHD=CHD. Rapid thermolysis of the solid sample at 70° also gave $\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 predominantly with trace amounts of cis- and trans-CHD=CHD. These results clearly demonstrate the occurrence of the β -elimination process as the principal thermolysis pathway.

Kinetics

The kinetics of thermolysis of $\text{CoR}_2(\text{acac})(\text{PPhMe}_2)_2$ in toluene solution was studied by measuring the volume of gases evolved at a fixed temperature. The kinetic study of the thermolysis of solid samples was not feasible because they melted with decomposition over narrow temperature ranges. In thermolysis of alkyl complexes in solution the reaction followed first-order kinetics.

$$-d[\text{CoR}_2(\text{acac})(\text{PPhMe}_2)_2]/dt = k[\text{CoR}_2(\text{acac})(\text{PPhMe}_2)_2]$$

The decomposition temperature of the methyl complex (II_a) was too high for this type of kinetic measurement in solution. The first-order rate constants of thermolysis of the ethyl and n-propyl complexes at various temperatures are shown in Table 4.

The isobutylcobalt complex was too unstable for the kinetic measurement.

From the Arrhenius plot of $\ln k$ vs $1/T$ the activation energy for the splitting of $\text{C}_2\text{H}_5\text{-Co}$ bonds was estimated as 30.6 kcal/mol, and that for $\text{Co}(\text{C}_3\text{H}_7)_2(\text{acac})(\text{PPhMe}_2)_2$ as 25.5 kcal/mol, each with an estimated uncertainty of 0.5 kcal/mol.

The addition of dimethylphenylphosphine to the solution of (II_b) in toluene strongly inhibits its thermal decomposition, although decomposition still follows the first-order kinetics. The apparent

Table 4. THE FIRST-ORDER RATE CONSTANTS OF THERMALYSIS

OF $\text{Co}(\text{C}_2\text{H}_5)_2(\text{acac})(\text{PPhMe}_2)_2$ AND $\text{Co}(\text{C}_3\text{H}_7)_2(\text{acac})(\text{PPhMe}_2)_2$

Complex	solvent	conc. of PPhMe_2	$10^4 k$ (temp.)
$\text{Co-C}_2\text{H}_5$ (II _b)	toluene	0	7.6 17.7 33.0 73.5 (10.8°) (15.0°) (20.3°) (24.0°)
$\text{Co-C}_2\text{H}_5$ (II _b)	toluene	0.03 M	5.9 8.8. 18.6 28.5 (17.7°) (21.0°) (24.1°) (25.9°)
$\text{Co-C}_2\text{H}_5$ (II _b)	toluene	0.70 M	0.34 0.69 1.76 3.15 (25.3°) (28.7°) (33.3°) (36.4°)
$\text{Co-C}_3\text{H}_7$ (II _c)	toluene	0	0.72 0.98 1.96 3.60 (-9.5°) (-7.3°) (-4.0°) (0°)
$\text{Co-C}_2\text{H}_5$ (II _b)	pyridine	0	1.75 2.79 4.13 6.81 (28.0°) (30.9°) (34.0°) (37.2°)

activation energy for thermolysis of (II_b) in the presence of PPhMe₂ (0.03 M) was found to be 33.7 kcal/mol and in the presence of PPhMe₂ (0.70 M) 34.7 kcal/mol. Thus the apparent activation energy increased with increasing the concentration of added PPhMe₂ approaching its limiting value of ca. 35 kcal/mol. Table 5 summarizes the Eyring parameters for thermolysis of the ethyl and propyl complexes in toluene and pyridine in the presence and absence of the added PPhMe₂.

Table 5 ACTIVATION ENERGIES AND KINETIC PARAMETERS FOR THERMOLYSIS OF COBALT ALKYL

Complex	Solvent	PPhMe ₂	E _a (kcal/mol)	ΔH [‡] (kcal/mol)	ΔS [‡] (e.u.)	ΔG [‡] (kcal/mol)
Co-C ₂ H ₅ (II _b)	toluene	0	30.6	30.0	31.6	20.6
Co-C ₂ H ₅ (II _b)	"	0.03 M	33.7	33.1	39.9	21.2
Co-C ₂ H ₅ (II _b)	"	0.70 M	34.7	34.1	36.2	23.3
Co-C ₃ H ₇ (II _c)	"	0	25.5	24.9	16.8	20.3
Co-C ₂ H ₅ (II _b)	pyridine	0	27.4	26.8	13.6	22.7

Further kinetic studies were made to examine various factors influencing the thermolysis process. Fig. 1 illustrates the linear dependence of the reciprocal of the first order rate constant of thermolysis of CoEt₂(acac)(PPhMe₂)₂ at 15° on the concentration of added PPhMe₂. Addition of trialkylphosphines to the toluene solution of CoEt₂(acac)(PPhMe₂) causes weaker inhibition effect than that of PPhMe₂.

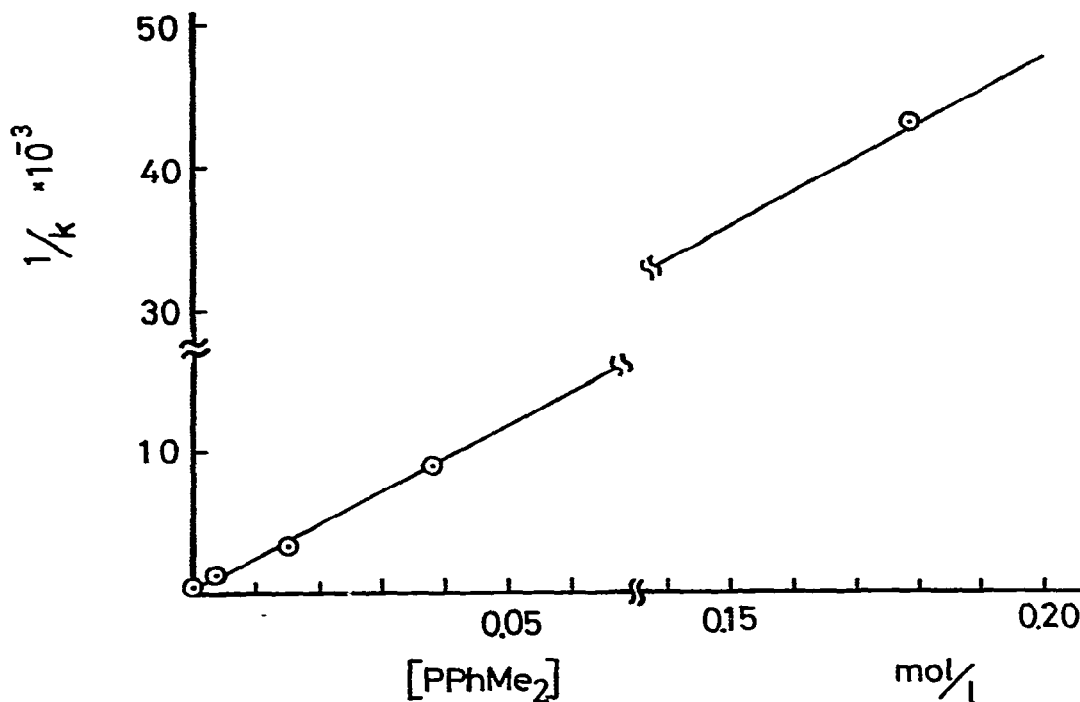


Fig. 1 The dependence of $1/k$ on the concentration of added PPhMe_2 ,
 $[\text{Iib}] = 0.03 \text{ mol/l}$

Table 6 compares the thermolysis rate constants of $\text{CoEt}_2(\text{acac})(\text{PPhMe}_2)_2$ (0.18 M) at 16.0° in the presence of 0.17 M each of various phosphines.

Table 6 Effect of Addition of Tertiary Phosphines on Thermolysis Rate Constants of $\text{CoEt}_2(\text{acac})(\text{PPhMe}_2)_2$

PR_3	PEt_3	$\text{P}(\text{n-Bu})_3$	PPhMe_2	PPh_2Me	PPh_2Et
pKa	8.69	8.43	6.50	4.61	2.62
$10^3 k$	1.7	1.5	0.02	0.20	0.26

The fact that the less basic phosphine such as PPhMe_2 has higher inhibition effect than the more basic trialkylphosphines suggests that the inhibition effect is associated with coordination of the added phosphine to shift

Eq. (1) to the left, the fact in line with NMR evidence [7b]. The less marked inhibition effect of diphenylalkylphosphines than that of PPhMe_2 may be due to the steric effects of the former ligands which are in somewhat less favorable situation than PPhMe_2 for coordination to cobalt [11].

The kind of solvent used for the thermolysis experiment also has a considerable effect on the thermolysis rate. The first order rate constant of thermolysis of (II_b) observed at 15.0° in various solvents decreased in the order: acetone (relative rate constant = 1.6) > toluene (1) > N,N-dimethylformamide (0.44) > pyridine (0.17). The smaller thermolysis rate of (II_b) in pyridine than in toluene is in contrast with the smaller activation energy of thermolysis (27.4 kcal/mol) in pyridine than in toluene. In this case, however, the contribution of the entropy factor is greater (see Table 5).

Comparison of the relative rates of thermolysis of $\text{Co}(\text{C}_2\text{H}_5)_2(\text{acac})\text{-}(\text{PPhMe}_2)_2$ and $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ (isotopic purity 84 %) revealed the presence of a considerable isotope effect ($k_{\text{H}}/k_{\text{D}} = 2.30 \pm 0.05$) indicating the involvement of β -elimination process in the rate-determining step of thermolysis.

H-D Scrambling in the thermolysis of $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ (VII)

Although the deuterium labeled complex decomposes cleanly by β -elimination process evolving $\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 when the thermolysis was carried out slowly at low temperature (below 5°) or rapidly by heating the solid sample at 70° , considerable scrambling does occur when the complex is allowed to stand in benzene at somewhat higher temperature than 5° as shown in Table 3. Infrared spectroscopy has proved to be quite useful in analyzing various isotopic mixtures of deuterated ethylenes. Fig. 2 demonstrates some of the typical results. It is seen that absorption bands of each deuterated ethylene appear separately without

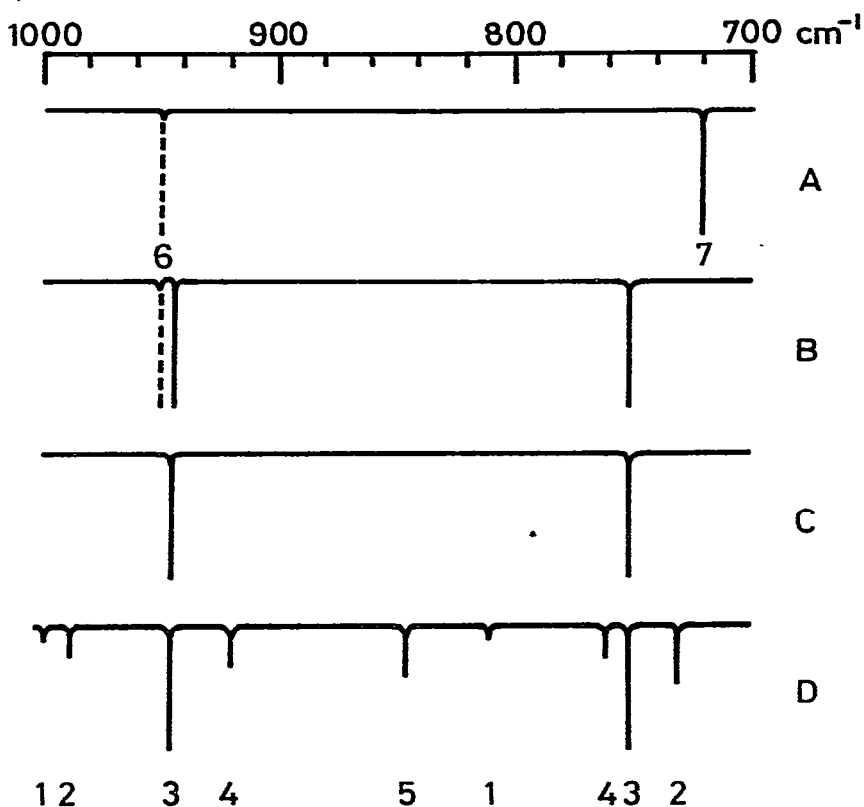


Fig. 2 IR spectra of deuterated ethylenes evolved on thermolysis of $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ (VII)

A: $\text{IIb} + \text{C}_2\text{D}_4$, at 28° , 1 day, B: $\text{IIb} + \text{asym-C}_2\text{H}_2\text{D}_2$ at 28° , 1 day, C: VII, at 5° , for a few days, D: VII, at 32° , 1 day, assignment of the peak: number 1, $\text{C}_2\text{H}_3\text{D}$; 2, $\text{trans-C}_2\text{H}_2\text{D}_2$; 3, $\text{asym-C}_2\text{H}_2\text{D}_2$; 4, C_2HD_3 ; 5, $\text{cis-C}_2\text{H}_2\text{D}_2$; 6, C_2H_4 ; 7, C_2D_4 .

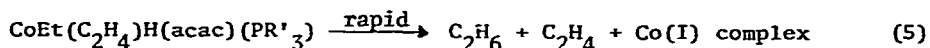
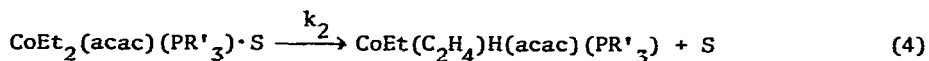
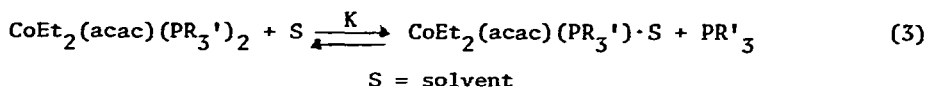
being masked by absorptions of deuterated ethanes owing to the small absorption coefficients of the ethanes in the region between 700 and 1000 cm^{-1} .

Following observations connected with the scrambling mechanism may be made. (i) Contact of non-deuterated diethylcobalt complex II_b

with deuterated ethylenes, C_2D_4 and $CH_2=CD_2$ at 28° caused no deuterium incorporation into the ethylene evolved. This observation indicates that the scrambling rate is much faster than the possible exchange of free ethylene with the cobalt-bonded ethyl groups which would liberate ethylene via β -elimination. (ii) The formation of a significant amount of C_2H_3D in the scrambling reaction suggests the simultaneous involvement of two ethyl groups in the scrambling process. β -Elimination and ethylene re-insertion involving a single CD_3CH_2-Co entity would not produce C_2H_3D . (iii) Quenching experiment by cooling and treating the reaction system with conc. H_2SO_4 after allowing the deuterated ethyl complex to stand at 28° in benzene for 1 day liberated mainly CH_3CD_3 and no $C_2H_2D_4$ was detected in the ethane evolved. The result suggests that the scrambling takes place only during the decomposition process and the remaining ethyl group undergoes no scrambling. The result is in contrast with the result of H-D scrambling in $Ni(CH_2CD_3)(acac)(PPh_3)$ in toluene and acetone where H-D scrambling occurred without appreciable thermolysis of the deuterated ethylnickel complexes [12].

Discussion

On the basis of these experimental results we propose the following mechanism for thermolysis of $CoEt_2(acac)(PR'_3)_2$ type complexes. The thermolysis mechanisms of propyl and butylcobalt complexes may be quite similar.



Assumption of the rate-determining step for Eq. (4) and of the condition,

$$[\text{Et}_2\text{Co(III)}]_{\text{total}} = [\text{CoEt}_2(\text{acac})(\text{PR}'_3)\cdot\text{S}] + [\text{CoEt}_2(\text{acac})(\text{PR}'_3)_2]$$

leads to the following rate expression,

$$\begin{aligned} -\frac{d}{dt} [\text{Et}_2\text{Co(III)}]_{\text{total}} &= k_2[\text{CoEt}_2(\text{acac})(\text{PR}'_3)\cdot\text{S}] \\ &= k_2 \frac{[\text{Et}_2\text{Co(III)}]_{\text{total}}}{1 + \frac{[\text{PR}'_3]}{K[\text{S}]}} \\ &= k[\text{Et}_2\text{Co(III)}]_{\text{total}} \end{aligned} \quad (6)$$

$$\text{where } k = \frac{k_2}{1 + \frac{[\text{PR}'_3]}{K[\text{S}]}} \quad (7)$$

We have followed the decrease of the total concentration of diethyl cobalt(III) complex by following the volume of evolved ethane and ethylene, finding the thermolysis reaction is first order in $[\text{Et}_2\text{Co(III)}]_{\text{total}}$ in agreement with Eq. (6).

The inhibition effect of the thermolysis of the diethylcobalt(III) complex by addition of the tertiary phosphine ligand as illustrated by Fig. 1 is consistent with the proposed mechanism, since the reciprocal of Eq. (7) gives Eq. (8)

$$\frac{1}{k} = \frac{[\text{PR}'_3]}{k_2 K[\text{S}]} + \frac{1}{k_2}, \quad (8)$$

which represents the feature of Fig. 1, where the intercept corresponds to $1/k_2$ and the slope to $1/k_2 K[\text{S}]$. Since the intercept derived by the graphical method is too small and entails a considerable error we assumed k in the absence of the added PR'_3 as k_2 and computed K at 15° from the slope of the line in Fig. 1 as 0.002 ± 0.001 . At the concentration of $[\text{Co(III)}]_{\text{total}} = 0.03 \text{ M}$ this value indicates that ca. $20 \pm 3 \%$ of $\text{CoEt}_2(\text{acac})(\text{PPhMe}_2)_2$ is dissociated liberating the tertiary phosphine

ligand. Estimation of the degree of dissociation for Eq. (1) by means of ^{31}P NMR spectroscopy gave the value of $24 \pm 2\%$ [7b] in approximate agreement with the value obtained from Fig. 1. The ΔH° value for Eq. (1) was estimated by NMR spectroscopy as 4.2 kcal/mol. The activation energy for the exchange of the tertiary phosphine ligands was evaluated also by NMR spectroscopy as 8 ± 5 kcal/mol.

Observation of the occurrence of the clear β -elimination process at 5° as substantiated by evolution of $\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 from $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ and the presence of the isotope effect in the thermolysis, $k_{\text{H}}/k_{\text{D}}$ being 2.30 ± 0.05 at 15° , strongly suggest that β -elimination is intimately associated with the rate-determining process. Conclusions of previous workers vary on this matter. Whitesides et al. observed no isotope effect in thermolysis of $\text{PtBu}_2(\text{PPh}_3)_2$, and its β -dideuterated analog, whose thermolysis is accompanied by H-D scrambling, and concluded that the dissociation of PPh_3 constitutes the rate-determining step followed by the scrambling processes [4a]. Schwartz and coworkers recently reported the $k_{\text{H}}/k_{\text{D}}$ value of 2.28 ± 0.20 , which is close to the value obtained in the present study, for β -elimination of an alkyliridium(I) complexes [13].

As the schematical representation of the reaction profile Fig. 3 accounts for various features of the thermolysis reactions observed in the present study. Some kinetic data obtained in the present study and the thermodynamic data for Eq. (1) evaluated by the NMR study [7b] are included in Fig. 3. A comprehensive study of these data provides several important conclusions regarding the thermolysis mechanism of the dialkylcobalt(III) complexes.

First, the dissociation of the tertiary phosphine ligand from $\text{CoR}_2(\text{acac})(\text{PR}'_3)_2$ does not constitute the rate-determining step.

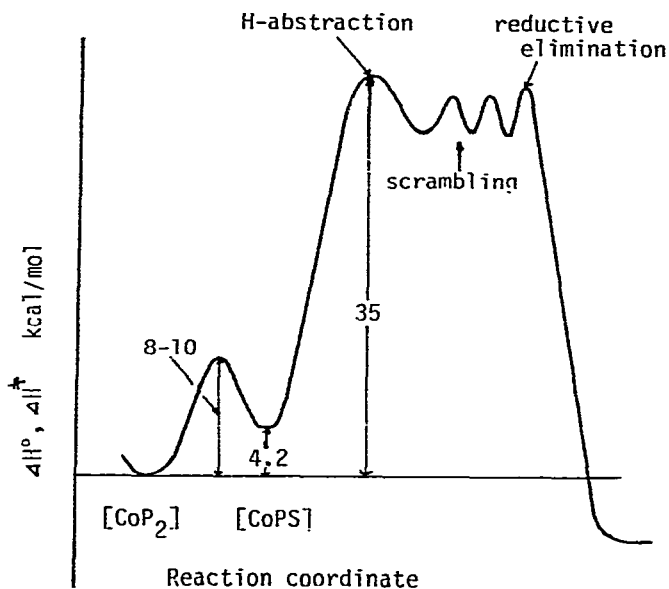


Fig. 3 Thermolysis reaction profile.

The value of the activation energy for dissociation of the tertiary phosphine ligand is much smaller than the overall activation energy for the thermolysis. Although addition of tertiary phosphine does suppress the thermolysis as observed by Whitesides [4a], the effect should be ascribed to the consequence of the shift of equilibrium represented by Eq. (1) to hinder the dissociation of $\text{CoR}_2(\text{acac})(\text{PR}'_3)_2$ as revealed by NMR examination of the equilibrium in the presence of the added phosphine ligands [7b]. In the presence of excess added PPhMe_2 the overall activation energy for thermolysis increase to ca. 35 kcal/mol from the value of 30.6 kcal/mol observed in the absence of the ligand. The increase is considered to reflect the

equilibrium shift to the undissociated side of Eq. (1). On the other hand, the thermolysis activation energy observed in pyridine was lower ($E_a = 27.4$ kcal/mol) than in toluene. The difference may be related with the shift of Eq. (2) to the right, if one assumes the pyridine coordination does not markedly affect the rate-determining process. The ΔH° value of 4.6 kcal/mol for Eq. (2) observed from NMR measurements roughly corresponds to the difference between the thermolysis activation energies in toluene and pyridine. It is also observed that the first-order rate constant for thermolysis in pyridine at 15° is smaller than in toluene. This is due to the smaller entropy of activation for thermolysis in pyridine than in toluene (Table 5). Presumably the system containing the alkylcobalt complex in pyridine may have already gained some entropy, liberating the PPhMe_2 ligand, than in toluene and the entropy gain required for reaching the activation state is less than that in toluene.

The effects of addition of various tertiary phosphines on the thermolysis (Table 6) may be also accounted for by assuming the shift of Eq. (1) to hinder the thermolysis. Less pronounced inhibition effects of thermolysis by more basic trialkylphosphine than less basic PPhMe_2 may be due to smaller shift of Eq. (1) to the left. The smaller inhibition effects of diphenylalkylphosphines may be due to the less favorable situation in coordination of these bulky ligand to the alkylcobalt complex.

Secondly, we regard the β -elimination not as the prerequisite for the thermolysis to take place but as the consequence of the thermal activation of the metal-alkyl bonds. As the presence of the considerable isotope effect shows, the activation state for thermolysis is associated with the β -elimination process for the thermolysis of the ethyl complex. However, this does not necessarily require the β -elimination process as the prerequisite for the thermolysis. As the X-ray structural analysis on a related ethyl(acetyl-

acetonato)(triphenylphosphine)nickel(II) showed [15], the ethyl group is bonded to nickel in a normal manner in the solid state. The fact suggests that the direct interaction of the metal d-orbital with the β -hydrogen may be too weak for initiating the hydrogen abstraction in the ground state, but loosening of the metal-carbon bond may facilitate the enhanced interaction between the hydrogen and the metal for allowing the β -elimination process to proceed. The view regarding the loosening of the metal-carbon bond as the prerequisite for the thermolysis for the present type of complexes allows us to compare comprehensively the mode of thermolysis of the series of alkyl complexes including the dimethyl complex which thermolyzed evolving ethane. An alkyltransition metal complex may be thermally activated with the loosening of the metal-to-alkyl bond and it may be decomposed via one of the available pathways among β -elimination, reductive elimination, α -elimination etc. Our previous observation of lower activation energy for thermolysis of $\text{CH}_3\text{Cu}(\text{PPh}_3)_2$ than that for its higher homologs [5_b] revealed that β -elimination does not necessarily provide the lowest energy thermolysis pathway of alkyltransition metal complexes. The thermal decomposition of diethyl(bipyridyl)nickel(II) liberating butane and of dipropyl- and dibutyl-(bipyridyl)nickel(II) liberating 1/1 molar ratio of alkanes and alkenes [5_a] illustrates the delicate feature of the thermolysis pathways but nevertheless indicates that the β -elimination is not always the lowest energy pathway.

Thirdly, the analysis of thermolysis product of $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})-(\text{PPhMe}_2)_2$ (VII) reveals that there are some alternative pathways after the activation state as reflected by the evidence showing that thermolysis pathways depend on experimental conditions in such ways that slow thermolysis of (VII) below 5° in benzene or toluene, and the thermolysis at room temperature in pyridine as well as the rapid thermolysis of the solid sample liberate $\text{CH}_2=\text{CD}_2$, the β -elimination product, predominantly, whereas the H-D scrambling occurred above room temperature in benzene

or toluene solution. Since examination of the remaining complex (VII) after liberation of some amounts of scrambled ethylenes and ethanes, revealed that the remaining ethyl groups were intact and not subjected to the H-D scrambling, the scrambling process should be situated after the rate-determining step as shown in Fig. 3. Under the conditions where the scrambling takes place, the diethyl complex may undergo the transition state involving loosening of the cobalt-carbon bond and the hydrogen abstraction, but the subsequent scrambling may take place at the considerably "activated state" where the abstracted hydrogen may interact further with the coordinated ethylene moiety thus produced to regenerate the activated ethyl group from which a hydrogen may be again abstracted. Repeating of such processes will cause the scrambling. Eventually the abstracted hydrogen may combine with another ethyl group to liberate ethane in a process formally similar to reductive elimination as depicted as the last peak in Fig. 3 which is lower than the highest peak of the rate-determining process. The fact that C_2H_3D and C_2D_3H were formed in comparable amounts can not be explained by a simple β -elimination process taking place with involvement of only one of the two ethyl groups, but rather simultaneous participation of two ethyl groups in the H-D scrambling process with minor isotope effect. Although we did not attempt to measure the activation energy for the scrambling, the process is certainly accelerated by applying heat to the solution containing VII.

Exclusion of the β -elimination process as the prerequisite for thermolysis, at least in the present case, requires other reasoning than " β -elimination stabilization" for explaining the stability of M-C bond. We consider that the reason for stability should be sought in the intrinsic bond strength rather than circumstantial effect as β -elimination, and its stability may be connected more

closely with electronic factors. The theory stressing the importance of electronic promotion [1, 5a] may be valid for accounting for photochemical reactions but has some drawbacks in explaining thermal reactions. The energetic considerations [1, 5a] should be understood at most as the first approximation related with the thermal process, but nevertheless they may have some important bearing on the theory to explain the thermal stability.

The diethylcobalt (II_b) had a higher activation energy than the dipropylcobalt complex (II_c). Unfortunately the kinetics of thermolysis of the methyl and isobutyl complexes could not be investigated by the technique used in the present study, but we observed the decomposition point of the dialkyl complexes decreases in the order: Me > Et > n-Pr > iso-Bu. Although it is not justified to correlate a decomposition point with an activation energy for thermolysis, as we experienced in thermolysis of alkylcopper complexes [5b], it seems to be safe to extrapolate the trend observed between the ethyl and propyl complexes to the methyl and isobutyl complexes and to assume the order of the activation energy decreasing as follows, Me > Et > n-Pr > iso-Bu, the same order as Yamamoto et al. observed in $NiR_2(bipy)$ [5a]. The present complexes and $NiR_2(bipy)$ have some similarities in that both are diamagnetic and have spin-paired filled d-orbitals and vacant upper lying d-orbitals. The previous argument by Yamamoto et al. taking into consideration of the energy difference between the vacant d-orbital and bonding metal-to-carbon orbitals appears to have more relevance to the present case as a very approximate measure to correlate with stability of alkyltransition metal complexes than arguments based on propensity to β -elimination of alkyl transition metal complexes.

Experimental

General procedures

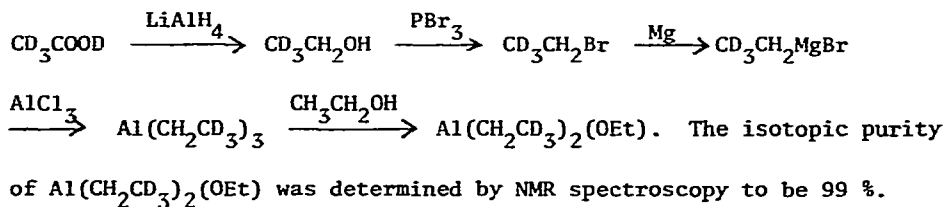
All synthetic experiments were carried out under deoxygenated argon or nitrogen atmosphere, or in vacuum. Solvents were dried by usual procedures, distilled and stored under argon or nitrogen. ^1H NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer. IR spectra of the solid samples were recorded on a Hitachi Model EPI-G5 using KBr discs prepared under nitrogen. Analysis of gas, evolved in thermolysis of the complexes and in H-D scrambling reactions, was carried out by means of mass spectrometry and gas chromatography. Identification of the deuterated gaseous products evolved during the H-D scrambling was carried out by IR spectroscopy, after collecting the gas into a gas cell.

Synthesiscis-Dialkyl(acetylacetonato)bis(tertiary phosphine)cobalt(III) (I - IV)

were prepared according to the method described in the previous report [7a]. Other pyridine- and bipy-coordinated complexes were prepared by exchange reactions [7a].

Di(ethyl-2,2,2-d₃)(acetylacetonato)bis(dimethylphenylphosphine)cobalt(III) (VII)

Complex (VII) was prepared by the reaction of cobalt tris(acetylacetonate), $\text{Al}(\text{CH}_2\text{CD}_3)_2(\text{OEt})$ and dimethylphenylphosphine. The deuterated diethyl-aluminum monoethoxide was prepared by the following route:



To a mixture of $\text{Co}(\text{acac})_3$ (1.00 g; 2.8 mmol) and Me_2PhP (1.5 ml; 10 mmol) in ether (10 ml) $\text{Al}(\text{CH}_2\text{CD}_3)_2(\text{OEt})$ (2 ml) was added at room temperature. The reaction mixture was warmed to 30° for a few

minutes. At the temperature the reaction mixture suddenly changes from a green suspension to a deep yellow solution. As soon as the change to deep yellow started, the system was rapidly cooled to 0° and was stirred at the temperature until the reaction was complete. Then it was cooled to -78° to precipitate the yellow crystals, which were filtered and washed with ether. The yellow crystals thus obtained were recrystallized immediately from ether to give yellow prisms (VII), yield, 60 %.

IR(KBr): ν (C-H), 2840 cm^{-1} ; ν (C-D), 2190, 2160, 2095 and 2050 cm^{-1} ; ν (Co-C). 578 cm^{-1} ; (acac), 1585, 1515, 1395, 1260 cm^{-1} .

Determination of the isotopic purity of $\text{Co}(\text{CH}_2\text{CD}_3)_2(\text{acac})(\text{PPhMe}_2)_2$ by ^1H NMR spectroscopy was not feasible because of the coincidence of the methylene and methyl resonances of cobalt-bonded ethyl groups [7a]. Therefore the isotopic purity was examined by converting the ethyl groups to diethylketone by reaction of the diethyl complex with carbon monoxide. The diethylcobalt complex in CD_3COCD_3 was allowed to contact with carbon monoxide at -40°, $\text{CD}_3\text{CH}_2\text{COCH}_2\text{CD}_3$ formed in the reaction was separated and the isotopic purity of $\text{CD}_3\text{CH}_2\text{COCH}_2\text{CD}_3$ employed for the scrambling experiment was determined to be 95 % and that for the study of the isotopic effect 84 % by NMR spectroscopy.

Analysis of gaseous thermolysis products of $\text{CoR}_2(\text{acac})(\text{PR}'_3)_2$

A Schlenk tube containing ca. 0.1 g of an alkylcobalt complex in the solid state or its solution was heated in an oil bath.

Evolved gas was collected using a Toepler pump, by which the volume of the gas was measured, and analyzed by VPC and mass spectrometry. Table 2 shows the compositions of gaseous products evolved on thermolysis of these complexes in the solid state and in solutions.

Kinetic Studies.

A sample of 0.10 - 0.15 g was weighed in air and placed in a Schlenk tube having a side arm, connected with a reservoir for the solvent, and

a jacket to circulate water of a constant temperature kept with a precision within $\pm 0.5^\circ\text{C}$ around the Schlenk tube. The tube was connected to a vacuum line equipped with a mercury manometer and was evacuated. The solvent was poured by rotating the side arm connected with the solvent reservoir and the sample was quickly dissolved in the solvent by stirring it with a magnetic stirrer. The rate constant for thermal decomposition of the complex was obtained by measuring the volume of the gas evolved at the temperature on the assumption that the total amount of the gas evolved corresponds to the total amount of the dialkylcobalt(III) complex. It was confirmed in most cases that the composition of the gas evolved on thermolysis did not vary. In the thermolysis of the propyl complex the amount of the solvent was restricted to minimum to avoid dissolution of the evolved gas into the solvent over the permissible extent for the kinetic measurement.

H-D scrambling reaction of (VII) in benzene

The scrambling reaction of (VII) in benzene was carried out by the following procedure.

To a sample of 0.1 - 0.15 g benzene (1 ml) was added at $-30 - 40^\circ$ and the system was evacuated. The Schlenk tube containing the sample was immersed in a water bath maintained at a constant temperature. At the end of the reaction the Schlenk tube was cooled to $-30 - 40^\circ$, and the gas evolved during the reaction was collected using the Toepler pump for analysis by mass spectrometry. The deuterated ethylenes were identified by means of IR spectroscopy using a gas cell. In the IR range of 1000 to 700 cm^{-1} the absorption bands of deuterated ethylenes were observed clearly separated without disturbance by bands of deuterated ethanes because of the very small absorption coefficients of the ethanes in the region [14].

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