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STUDY OF ORGANOCOBALT AND IRON COMPLEXES WITH TERTIARY PHOSPHINE LIGANDS

A Thesis Presented to Tokyo Institute of Technology

by

Takao Ikariya

January 1976

PREFACE

The studies presented in this thesis have been carried out under the direction of Prof. Akio Yamamoto at the Research Laboratory of Resources Utilization, Inorganic Chemistry Division, Tokyo Institute of Technology, during the year of 1973-1976.

The thesis concerns with the isolation of new types of organocobalt and -iron complexes, NMR studies of these complexes in solution and discussions on the mechanism of thermolysis of the alkylcobalt and iron complexes. The auther hopes that the present studies will provide some basic information regarding stability and activation of organotransition metal complexes which are regared as models of active species of catalysts in various transition metal-promoted catalytic reactions.

The author especially expresses his deep gratitude to Prof. Akio Yamamoto for continuing guidance and helpful discussion throughout the course of the study. He wishes to thank Prof. Sakuji Ikeda and Akio Yamamoto for giving him the opportunity of starting the attractive study in the field of organotransition metal chemistry. His grateful thanks are also due to Dr. Takashi Ito and Dr. Takakazu Yamamoto for helpful advice and instructive discussions to his research. The author must thank Prof. Akio Yamamoto for correcting his poor English sentences.

Acknowledgment is made for assistance given by Mr. Toyoji Saito through his ever-reliable microanalysis of unstable compounds, Mr. Yoshiyuki Nakamura for his skillful measurement of NMR spectra, Mr. Haruyoshi Sakurai for measurement of mass spectra, all menber in Yamamoto laboratory for their continued encouragement to him, and

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Finally, the author is grateful to his parents for their constant encouragement.

Takao Ikariya

January 1976

CONTENTS

General Introduction--- 1

Chapter I Preparation and Properties of cis-Dialkylcobalt Complexes, $R_2Co(acac)(PR'_3)_2$ --------------------------------- 4

Summary

Introduction

Results and discussion

References

Chapter II Preparation and Properties of Methylbis[1,2-bis(diphenylphosphino)ethane]cobalt(I) ---------------------------------- 25

Summary

Introduction

Results and discussion

References

Chapter III Preparation and Properties of Methyliron Complexes with Tertiary Phosphine Ligands and Their Decomposition Pathways through The Formation of Carbenoid Intermediates ---- 41

Summary

Introduction

Results and discussion

Referenes

Chapter IV NMR Studies of Dynamic Behabior of Dialkylcobalt(III) in Solution -- 66

Introduction

Results and discussion

References

Chapter V Mechanism of Thermal Decomposition of Dialkycobalt(III) Complexes ---- 96

Introduction

Results

Discussion

References

Chapter VI Olefin-Coordinated Iron(0) Complexes with Dimethylphenylphosphin Ligands ---- 132

Summary

Introduction

Results and discussion

References

Conclusion ---- 143

GENERAL INTRODUCTION

Since the discovery of " ferrocen" and "Ziegler-catalyst" the chemistry of organotranstion metal complexes has developed in a tremendous rate. Beside the versatile features of the organotransition metal complexes which merit the academic study in their own right, the chemistry of transition metal complexes with metal-carbon bonds invites the intensive studies for the following reasons. (1) Species with transition metal-carbon bonds have been considered as active intermediates in various catalytic reatctions involving olefins such as isomerization, hydrogenation, hydroformylation, polymerization, and oligomerization as well as in oxidation of olefins by Wacker process and study of complexes having transition metal-carbon bonds is of fundamental importance in understanding the mechanisms of these catalytic reactions. (2) Organotransition metal compounds are also considered as reaction intermediates in various metal-promoted organic sytheses. Attention of organic chemists has been recently attracted to the development of new techniques using transition metals and their derivatives which enable, in many cases, the synthese of organic compounds in very specific manners and under mild conditions. Acquisition of further information concernig the properties of organotransition metal complexes will trigger more useful and elegant applications in organic synthese. (3) During the development of the chemistry of organotransition metal compounds the discovery that a naturally occurring molecule, vitamin B_{12} coenzyme contains a carbon-cobalt bond stimulated the further rise of interest among the organotransition metal chemists. The effort unveiling the properties of the naturally occurring coenzyme has been greatly aided by the information concerning the properties of relatively stable model species with transition metal-carbon bond.

Clearly, the investigation of the isolated alkyltransition metal compounds will provide information in understanding mechanisms of various important reactions promoted by transition metals. The further systematic study on stability of metal-carbon bond and its activation will be a subject of essential importance.

The prime purpose of the present study is the preparation of new alkyltransition metal complexes and study of the properties of these complexes. In general the metal-cabon bond can be formed by several reaction: (1) Treatment of metal salts with alkylating reagents such as Grignard or alkyllithium and alkylaluminum compounds, (2) oxidative addition to low valent transition metal compounds, (3) insertion reactions of olefins into metal hydrogen bonds. As many of the reports from our laboratory shows, employment of the preparative route using transition metal acetylacetonate and organoaluninum compounds in combination with stabilizing ligands such as tertiary phosphines has proved quite useful in isolating novel alkyltransition metal complexes and their derivatives.

Although most of transition metal alkyls are very unstable, employment of stabilizing ligands such as cyclopentadienyl, carbon monoxide, tertiary phosphine, and organic nitrogen bases leads in many cases to successful isolation of alkyltransition metal compounds. The rolé of the stabilizing ligands has been accounted for in terms of a ligand theory as proposed by Chatt and Shaw or by a theory stressing the importance of the blocking ability of the ligand hindering the low energy β-elimination pathway as proposed by Wilkinson. However, these theories are not quite equivocal and the variety of the isolated alkyltransition metal complexes is still not enough to allow one for advancing a general theory concernig the nature of the transition metal-carbon bond. More extensive quantitative data for the stability of these species are clearly required.

This thesis is divided into six chapters, which consist of the follwing contents. Chapter I and II deal with the preparative methods of new types of dialkylcobalt(III) complexes, $CoR_2(acac)(PR'_3)_2$, and a methylcobalt(I) complex, $CoCH_3(dpe)_2$, respectively. Their properties including the reaction with carbon monoxide are described. In chapter III the preparative methods of new methyliron complexes, $Fe(CH_3)_2(dpe)_2$ and $Fe(CH_3)(acac)_2(PPhMe_2)$ are reported and their decomposition pathways involving the formation of carbenoid intermediates are discussed. Chapter IV is concerned with NMR studies of dialkylcobalt(III) complexes including the dynamic behavior of these complexes in solution such as tertiary phosphine ligand dissociation, exchange reaction, and replacement of tertiary phosphine ligands with organic nitrogen bases. In chapter V the thermal decomposition of dialkylcobalt(III) complexes and the H-D scrambling reaction of the ethyl groups in a specifically deuterated ethylcobalt complex, $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$, are investigated in detail. On the bases of the kinetic and NMR results a reaction mechanism accounting for relevant features of the thermolysis and the scrambling reaction is proposed. Chapter VI deals with the preparative method of ethylene-iron(0) complex, $Fe(CH_2{=}CH_2)(PPhMe_2)_4$, and olefin-coordinated iron(0) complexes formed by the reaction of the ethylene-iron(0) complex with several olefins.

Chapter I PREPARATION AND PROPERTIES OF CIS-DIALKYLCOBALT COMPLEXES, $R_2Co(acac)(PR'_3)_2$

SUMMARY

Treatment of Co(acac)$_3$ and tertiary phosphine with AlR$_2$(OEt) in ether under nitrogen gives remarkably stable trivalent cobalt complexes, CoR$_2$(acac)(PR'$_3$)$_2$ [R=Me, Et, n-Pr, iso-Bu, PR'$_3$=PEt$_3$, P(n-Bu)$_3$, PPhMe$_2$, PPh$_2$Me; acac=acetylacetonato]. ^{1}H, ^{31}P and ^{13}C NMR spectra show that these complexes have an octahedral configuration with two tertiary phosphine ligands in axial positions. Pyridine replaces a part of the phosphine ligands to give a pyridine-coordinated complex, Co(CH$_3$)$_2$(acac)(PEt$_3$)(Py), whereas a bidentate ligand 2,2'-bipyridine replaces two tertiary phosphines to yield the bipyridine-coordinated complexes, CoR$_2$(acac)(bipy). The isolated complexes readily react with carbon monoxide to yield the dialkyl ketone and a univalent carbonyl complex with an acetylacetonato ligand, Co(acac)(CO)$_2$(PR'$_3$).

INTRODUCTION

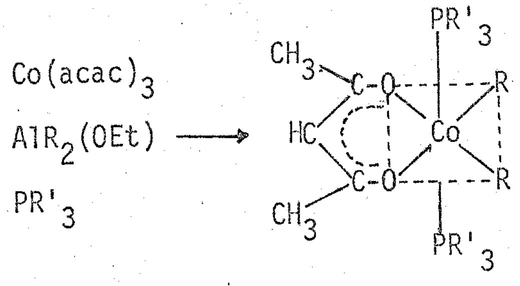
Much effort has been paid for preparation and study of organocobalt complexes containing a macrocyclic ligand, partly because of the importance of this class of compounds in relation to the naturally occurring organocobalt complex, vitamine B$_{12}$ coenzyme, and partly because of the belief that the macrocyclic ring contributes to stabilization of cobalt-carbon bond. The number of organocobalt(III) compounds of this type thus far prepared now exceeds a thousand[1]. In contrast, only little is known of other types of organocobalt complexes [2-5].

As part of our project to study the properties of transition metal alkyls and hydrides we have previously studied the reaction system consisting of cobalt acetylacetonate, alkylaluminum compounds and triphenylphosphine [6,7] or diphenylphosphinoethane [8] and obtained some univalent cobalt hydride and methyl complexes. This type of reactions is considered to proceed through exchange of the acetylacetonato ligands in the cobalt acetylacetonate with the alkyl groups of the alkylaluminum compounds with formation of an intermediate alkylcobalt complex having the acetylacetonato ligand. Such intermediate alkylation products have been in fact isolated in the reactions of nickel [9] and iron [7] acetylacetonates with alkylaluminum compounds in the presence of suitable tertiary phosphine ligands. Examination of the similar reaction system containing cobalt acetylacetonate, dialkylaluminum monoethoxide and other tertiary phosphines than triphenylphosphine and diphenylphosphinoethane has led to isolation of a variety of new dialkylcobalt(III) complexes containing an acetylacetonato and two tertiary phosphine ligands. These trivalent dialkylcobalt complexes proved to be remarkably insensitive to air, thermally considerably stable and quite amenable to NMR study. We have previously reported the preparation and properties of $CoR_2(acac)(PR'_3)_2$ in a preliminary form [10]. In this and following papers we describe in detail the preparation and properties of these dialkylcobalt complexes. A similar dimethylcobalt complex with trimethylphosphines and an acetylacetonato ligand has been recently prepared by the reaction of trimethyltris(trimethylphosphine)cobalt(III) with acetylacetone, but isolation of the complex in a pure form has failed due to the "instability" of the complex [5].

Insertion of carbon monoxide into Co-C bond constitutes one of the most important key steps in hydroformylation reaction of olefins catalyzed by cobalt carbonyl but very few model studies using an isolated alkylcobalt complex have been made. No example of CO insertion into alkylcobalt complexes with macrocyclic ligands has been reported [1,11]. The present complexes readily undergo the CO insertion reaction and provide some information concerning the reaction path of CO insertion into an alkylcobalt complex.

Results and discussion

The reaction of cobalt acetylacetonate and dialkylaluminum monoethoixde in the presence of suitable tertiary phosphine ligands, when conducted under appropriate control of the reaction temperature (see Experimental Section), gives dialkylcobalt(III) complexes containing two teriary phosphines and an acetylacetonato ligand as shown below.



I PR'_3 = PEt_3 R = Me

II PR'_3 = $PPhMe_2$

II_a R =Me , II_b = Et

II_c R =n-Pr, II_d = iso-Bu

III PR'_3 = PPh_2Me R = Me

IV PR'_3 = $P(n\text{-}Bu)_3$

These complexes are remarkably insensitive to air, soluble in almost any organic solvents and can be obtained as orange to yellow prisms. Table 1 summarizes the analytical data, yields and physical properties of the isolated complexes. Most of the complexes except for the isobutylcobalt complex, (II_d) are thermally stable and can be handled at room temperature. The melting point (with decomposition) of a series of dialkyl-(acetylacetonato)cobalt (III) with dimethylphenylphosphines (II_a-II_d) decreases with increase of the alkyl chain length. Attempts to obtain a series of dialkyl (acetylacetonato)cobalt complexes having other tertiary phosphine ligands than $PPhMe_2$ have so far been unsuccessful. The reaction of $Co(acac)_3$ with $Al(n\text{-}Pr)_2(OEt)$ and $Al(iso\text{-}Bu)_2(OEt)$ in the presence of diphenylmethylphosphine or dimethylphenylphosphine afforded only the known hydridocobalt(I) complex $CoH(PPh_2Me)_4$ (VII_a) [12] and $CoH(PPhMe_2)_4$, respectively. Apparently small differences in the electronic and steric factors in the tertiary phosphine ligand employed greatly influence the reactivity and stability of the alkylcobalt complex formed as we observed in the preparation of tertiary phosphine-coordinated alkylnickel complexes [12]. When the complexes having various tertiary phosphine ligands are compared, their melting point (with decomposition) are observed to decrease as $PPhMe_2 > PPh_2Me > PEt_3 > P(n\text{-}Bu)_3$.

It may be expected that further alkylation of $R_2Co(acac)(PR'_3)_2$ with alkylaluminum compounds followed by reduction via splitting of alkyl-cobalt bonds may afford a univalent alkylcobalt complex as we have previously obtained $CH_3Co(PPh_3)_3$ and $CH_3Co(PPh_3)_2$

Table I Analytical data for cis-dialkylcobalt complexes

	Compound	Yield	Color	M.p.(dec.)°C	Anal. (%) (calcd) C	H	N	IR (cm^{-1}) Co-C	CH_3
I	$(CH_3)_2Co(acac)(PEt_3)_2$	60 %	orange-yellow	78 ~ 81	54.1 (53.8)	11.0 (10.1)		573	2775 2840
IIa	$(CH_3)_2Co(acac)(PPhMe_2)_2$	70 %	"	116~119	59.2 (59.5)	8.1 (7.5)		580	2770 2870
IIb	$(C_2H_5)_2Co(acac)(PPhMe_2)_2$	65 %	yellow	67 ~ 68	60.7 (60.9)	7.9 (7.9)		578	2820
IIc	$(C_3H_7)_2Co(acac)(PPhMe_2)_2$	35 %	"	49 ~ 50	61.9 (62.3)	8.5 (8.3)		570	2800
IId	$(iso\text{-}Bu)_2Co(acac)(PPhMe_2)_2$	—	yellow green	unstable [b]	— —	—		574	2790 2845
III	$(CH_3)_2Co(acac)(PPh_2Me)_2$	90 %	orange-red	89 ~ 92	67.7 (67.4)	6.7 (6.6)		585	2775 2860
IV	$(CH_3)_2Co(acac)[P(n\text{-}Bu)_3]_2$	54 %	yellow	64 ~ 69	62.3 (62.2)	12.3 (12.2)		579	2865 2845
Va	$(CH_3)_2Co(acac)(PEt_3)(Py)$	32 %	"	100~105	55.8 (56.1)	8.9 (8.6)	3.7 (3.6)	580	2775 2850
Vb	$(CH_3)_2Co(acac)(PEt_3)(\gamma\text{-}Pi)$	40 %	"	100~101	57.3 (57.5)	8.7 (8.8)	3.6 (3.5)	580	2775 2850
VIa	$(CH_3)_2Co(acac)(bipy)$	35 %	red-purple	139~140 [a]	58.4 (59.3)	6.6 (6.1)	8.0 (8.1)	595	2770 2840
VIb	$(C_2H_5)_2Co(acac)(bipy)$	71 %	green	125~126 [a]	60.9 (61.3)	6.8 (6.7)	7.2 (7.5)	585	2840
VIc	$(C_3H_7)_2Co(acac)(bipy)$	41 %	"	45 ~ 47	63.6 (63.0)	7.0 (7.3)	6.1 (7.0)	550	2835

a At this temperature range the complex decomposes without melting.

b Microanalysis of IId was not feasible due to its instability.

from the reaction system of Co(acac)$_3$, AlMe$_2$(OEt) and PPh$_3$ [7]. Attempts of isolating such a methylcobalt(I) complex with other tertiary phosphines than PPh$_3$ have so far been unsuccessful. We have previously obtained a dinitrogen-coordinated complex, CoH(N$_2$)(PPh$_3$)$_3$ from a similar reaction system by carrying out the reaction under dinitrogen. In none of the present reaction systems formation of a dinitrogen-coordinated complex was observed.

These dialkyl(acetylacetonato)cobalt complexes were characterized on the basis of elemental analysis, IR and NMR spectroscopy and chemical properties. ^{1}H and ^{31}P NMR spectra of (I)-(IV) support the formulation of the complexes having octahedral configurations with two cobalt-bonded alkyl groups and an acetylacetonato ligand coplanar with cobalt which are coordinated with two tertiary phosphine ligands in the axial positions. Table 2 summarizes the ^{1}H NMR data for CoR$_2$(acac)(PR'$_3$)$_2$.

The two methyl groups in acac ligand in these complexes are magnetically equivalent in various solvents and appear as a singlet over a wide temperature range (-78° to +20°). The methyl resonance in PPhMe$_2$ in (II) shows characteristic triplet due to the virtual coupling with two phosphorus nuclei in mutually trans positions. The two methyl groups bonded to cobalt in (I), (II$_a$), (III) and (IV) are magnetically equivalent and appear as a triplet at low temperatures by coupling with two phosphine ligands and as a singlet at higher temperatures, where the phosphine ligands are partly dissociated and exchanging rapidly with each other.

^{1}H NMR spectrum of the ethyl groups in (II$_b$) shows a singlet in

Table 2 ^{1}H-NMR Data for $CoR_2(acac)(PR'_3)_2$

						acac	
	R	PR_3'	temp.	Co-R(τ)$^{a,b)}$	PR_3' (τ)	CH_3	CH (τ)
I	Me	PEt_3	-20	9.92(t, 6H)	8.9(qui, 18H) 8.4(m, 12H)	8.21(s, 6H)	4.93(s, 1H)
			0	9.98(s, 6H)	8.9(t, 〃) 8.4(q, 〃)	8.23(s, 6H)	4.91(s, 1H)
IIa	Me	$PPhMe_2$	20	10.1(t, 6H)	8.68(t, 12H)	8.64(s, 6H)	5.16(s, 1H)
			50	10.1(br.s, 6H)	8.68(s, 〃)	8.64(s, 6H)	5.16(s, 1H)
IIb	Et	〃	-20	9.44(s, 10H)	8.73(t, 〃)	8.44(s, 6H)	4.98(s, 1H)
IIc	n-Pr	〃	-40	8.84(s, 10H); 9.64(m, 4H)	8.76(t, 〃)	8.40(s, 6H)	4.94(s, 1H)
III	Me	PPh_2Me	20	9.74(s, 6H)	9.15(s, 6H)	8.60(s, 6H)	5.12(s, 1H)
IV	Me	$P(n\text{-}Bu)_3$	-30	9.88(t, 6H)	8.3 ~ 9.1(m, 18H)	8.15(s, 6H)	4.88(s, 1H)
			20	10.1(s, 6H)	〃	8.20(s, 6H)	4.85(s, 1H)

a) All the NMR spectra were observed in toluene-d_8. For avoiding the overlap of the TMS signal with that of cobalt bonded methyl group, no internal TMS was used. Instead, the light toluene impurity was used as the internal standard and the signals are referred to TMS based on the signal.

b) Abbreviation: s, singlet; d. doublet; t, triplet; q, quartet; qui, quintet; br.s, broad singlet; m, multiplet.

toluene and acetone due to the accidental coincidence of the chemical shifts of the methyl and methylene groups [14]. ^{1}H NMR spectrum of n-propyl groups in (II$_c$) shows a singlet due to β and γ-protons of n-propyl groups at τ =8.84 and a broad multiplet due to α-methylene protons of them at τ=9.64. $^{31}P-\{^{1}H\}$ NMR spectra of these complexes show a singlet for (I-IV) at low temperatures suggesting that two phosphorus nuclei are magnetically equivalent. At higher temperatures the partial dissociation and exchange of the tertiary phosphine ligands are observed.

IR spectra of these complexes show the characteristic aliphatic ν (C-H) bands due to the alkyl groups bonded to cobalt at 2770 - 2870 cm^{-1} in addition to bands due to tertiary phosphines and acetylacetonato ligand and show ν(Co-C) bands at 570 - 585 cm^{-1}.

Reactions of $CoR_2(acac)(PR'_3)_2$

When the ethyl complex (II$_b$) was decomposed in the solid state ethane and ethylene were liberated in a 1/1 ratio with a trace amount of n-butane. The thermolysis at 30° in a solution liberated ethane and ethylene in 1/1.3 to 1/2 ratio. Acidolysis of (II$_b$) with concentrated H_2SO_4 liberated ethane and ethylene in a 3/1 ratio. (II$_b$) reacts with methyl iodide to produce methane, ethane and ethylene and a trace amount of propane.

Displacement of the tertiary phosphine ligands in $CoR_2(acac)(PR'_3)_2$ with pyridine bases.

One of the two tertiary phosphine ligands in (I) can be readily displaced with pyridine to give a pyridine-coordinated complex, $Co(CH_3)_2(acac)(PEt_3)(Py)$, which was isolated from this system. Similar replacement took place with γ-picoline, but not with α and β-picolines.

$$\mathrm{Co(CH_3)_2(acac)(PEt_3)_2 + Py \longrightarrow \underset{(V_a)}{Co(CH_3)_2(acac)(PEt_3)(Py)} + PEt_3}$$

$$\mathrm{Co(CH_3)_2(acac)(PEt_3)_2 + \gamma\text{-}Pi \longrightarrow \underset{(V_b)}{Co(CH_3)_2(acac)(PEt_3)(\gamma\text{-}Pi)} + PEt_3}$$

γ-Pi = γ-picoline

The replacement of the tertiary phosphine ligand in (I) with pyridine is also observed by NMR spectroscopy. ^1H NMR spectrum of (I) in pyridine shows a doublet for the two cobalt-bonded methyl groups coupled with one phosphorus nucleus and a multiplet due to the free triethylphosphine ligand which is dissociated from complex (I).

A bidentate ligand, 2,2'-bipyridine, replaces two tertiary phosphine ligands to yield 2,2'-bipyridine-coordinated complexes, CoR_2(acac)(bipy) (VI_a - VI_d), which were isolated from the reaction of (II_a - II_d) in ether with 2,2'-bipyridine. Complex (IV_b), (IV_c) and (IV_d) are green at a low temperature (-10°) when prepared but turn to blue violet irreversibly at room temperature. This color change from green to blue violet might be due to a cis-trans configurational change between stereochemical isomers.

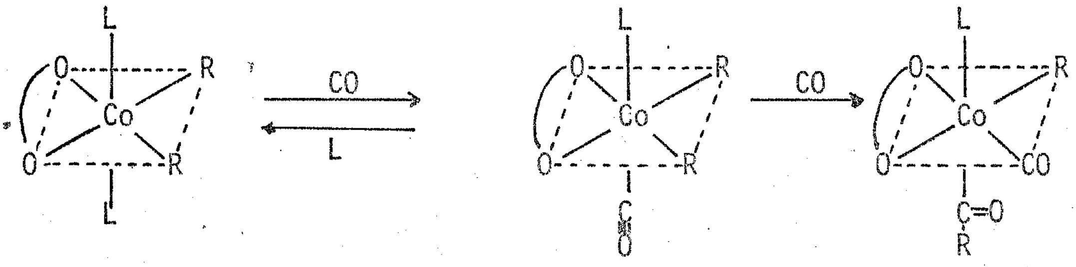
Although complex (II_d) is too unstable to handle at room temperature, (VI_d) is fairly stable. Thus employment of organic nitrogen bases such as pyridine and 2,2'-bipyridine enhances the stabilities of these complexes and makes the isolation of unstable complexes such as isobutyl complex easier. Table 1 includes the analytical data of these base-coordinated complexes.

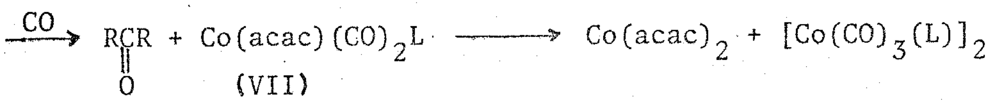
Similar displacement of tertiary phosphines in complex (I) with a bidentate tertiary phosphine, diphenylphosphinoethane, failed.

CO insertion into alkylcobalt bonds

In contrast to the reluctance of alkylcobalt complexes having macrocyclic ligands toward CO insertion into Co-C bond [11], the isolated dialkylcobalt(III) complexes(I-IV)undergo very facile CO insertion. Contact of toluene or ether solutions of(I-IV)with carbon monoxide at normal pressure causes a very facile reaction even at -50° and gives 1 mol equiv. of dialkylketone per cobalt and an isolable acetylacetonatocobalt(I) complex with a composition of $Co(acac)(CO)_2$-(PPh_2Me) (VII). Attempts to recrystallize the acetylacetonatocobalt(I) complex(VII)from acetone caused the disproportionation and recovery of a mixture of $Co(acac)_2$ and a binuclear cobalt complex having CO and PPh_2Me ligands without the acetylacetonato ligand, $[Co(CO)_3(PPh_2Me)]_2$. The similar binuclear cobalt carbonyl complexes $[Co(CO)_3P(n\text{-}Bu)_3]_2$ [15] and $[Co(CO)_3(PPh_3)]_2$ [16] have been prepared and the former was characterized by X-ray analysis.

Under similar reaction conditions the bipy-coordinated dimethylcobalt complex(VI_a) or $CH_3Co(dipy)_2$[17] did not react with carbon monoxide. These results together with the NMR information [8] that the coordinated tertiary phosphine ligands are exchanging considerably fast even at low temperatures suggest that a dissociation of a ligand at a cis position from the alkyl group may be required to accomodate a CO ligand which may be inserted into a Co-C bond (or mechanistically speaking the alkyl group may migrate to the CO ligand) to form an acyl-alkylcobalt complex, which gives the ketone and cobalt(I) complex(VII) on reductive elimination of the alkyl and acyl groups:





$$\xrightarrow{CO} R\underset{\underset{O}{\|}}{C}R + Co(acac)(CO)_2L \longrightarrow Co(acac)_2 + [Co(CO)_3(L)]_2$$

(VII)

In order to test the validity of this mechanism carbon monoxide was allowed to contact with a mixture of the ethyl complex (II_b) and the propyl complex (II_c) in toluene at -50° in a closed system and the ketone formed was examined. Gas chromatographic analysis indicated that only diethyl ketone was formed and neither di-n-propyl ketone nor ethyl n-propyl ketone was detected. The result suggests that the ethylcobalt complex (II_b) is much more susceptible to CO insertion to afford a propionyl ethyl complex which liberates diethyl ketone by reductive elimination and that no intermolecular reaction is taking place.

For further examination of the reactivity of the possible intermediate, acylcobalt complex, the methylcobalt complex (II_a) was treated with carbon monoxide in the presence of ethyl iodide. Acetone was formed as the sole ketone and no methyl ethyl ketone was detected. The result suggests that the reductive elimination of the acetyl and methyl groups is taking place rapidly prior to the attack of ethyl iodide to the acetyl group. Attempts to isolate the intermediate product containing the alkyl and acyl groups have been so far unsuccessful. We have recently observe a facile CO insertion into methylcobalt(I) complex with 1,2-bis-(diphenylphosphino)ethane(dpe) ligands to give acetylcobalt complex with the dpe ligands [8]. Klein [5] has observed the formation of acetone and an acetylcobalt(I) complex in the reaction of trimethyltris (trimethylphosphine)cobalt with carbon monoxide.

Reaction with Hg^{2+}

Methyl vitamin B_{12} has been shown to methylate Hg(II) ions in a simple acid-base reaction which may be one of the ways in which methylmercury is produced in living systems.

Complex (II_a) also reacted with $Hg(OAc)_2$ to produce dimethyl-mercury (II), which was detected by NMR spectroscopy. ^1H NMR spectrum of the reaction mixture of (II_a) and $Hg(OAc)_2$ in toluene-d_8 shows the mercury-bonded two methyl groups as a singlet (^2J(HgCH)=102Hz) at $\tau = 9.90$ [19].

$$Co(CH_3)_2(acac)(PPhMe_2)_2 + Hg(OAc)_2 \longrightarrow (CH_3)_2Hg$$

Similar methyl transfer reaction took place in the reaction of $CuI(PPh_3)_3$ and $Co(CH_3)_2(acac)(PEt_3)_2$ (I) in ether. When the ether solution of $CuI(PPh_3)_3$ and (I) was warmed to 30 to 35°, methane and ethane were evolved with deposition of metalic copper. This result suggests that following reaction took place [20].

$$Co(CH_3)_2(acac)(PEt_3)_2 + 2CuI(PPh_3)_2 \longrightarrow [2CuCH_3(PPh_3)_3]$$
$$\longrightarrow Cu^{\circ} + CH_4 + C_2H_6$$

Experimental

Materials and General Procedures.

All preparations and recrystallizations were carried out under deoxygenated nitrogen, argon, or *in vacuo.* Solvents were dried by usual methods, distilled and stored under netrogen or argon. Cobalt tris(acetylacetonate) and dialkylaluminum monoethoxides were prepared by usual methods.

Triethylphosphine and tri-n-butylphosphine were used as purchased, dimethylphenylphosphine [21] and diphenylmethylphosphine [22] were prepared as described in the literature. For each complex isolated, the absence of aluminum component was confirmed by the Aluminon method after decomposition of the complexes. Analytical data of the alkyl complexes are summarized in Table 1. IR spectra of the complexes were recorded on Hitachi Model EPI-3G as KBr discs and NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer. The microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2.

1. Preparation of $CoR_2(acac)(PR'_3)_2$.

a) $Co(CH_3)_2(acac)(PEt_3)_2$ (I)

To a mixture of $Co(acac)_3$ (1.00 g, 0.0028 mol) and triethylphosphine (1.5 ml, 0.01 mol) in ether dimethylaluminum monoethoxide (3 ml) was added at room temperature. The reaction mixture was warmed to 40 - 45° for a few minutes. At the temperature the reaction mixture suddenly changes from a green to a deep yellow solution with boiling of the solvent. As soon as the change to deep yellow set in 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 to greenish yellow crystals, which were filtered and washed with ether and n-hexane three or four times. The yellow crystals thus obtained were recrystallized from ether to give yellow prisms, (yield, 60 %) (I). Complex(I) is insensitive to air and moisture, thermally stable at room temperature, and decomposes at 78 - 81° liberating methane and ethane. (I) is soluble in almost any organic solvents such as alcohol, n-hexane, toluene, benzene, and ether. Acidolysis of (I) evolved methane. On iodolysis in benzene ethane (73 %) and methane (5 %) were liberated. Attempts to isolate the higher homologues of $CoR_2(acac)(PEt_3)_2$ or a univalent methyl cobalt complex failed.

b) $CoR_2(acac)(PPhMe_2)_2$ (II_a - II_d) (R = Me, Et, n-Pr, iso-Bu)

$Co(CH_3)_2(acac)(PPhMe_2)_2$ (II_a) and $Co(C_2H_5)_2(acac)(PPhMe_2)_2$ (II_b) were prepared similarly to (I) descrobed above (a).

n-Propyl complex (II_c) was obtained by the reaction of $Co(acac)_3$ (1.00g, 2.8 mmol), $PPhMe_2$ (1.5 ml, 10 mmol) and $AlPr_2(OEt)$ in ether at room temperature for 20 min. At the temperature when it changed to a deep yellow solution, it was cooled to 0° and stirred until reaction was complete. After evaporation of the solvent to one-fourth of its volume followed by addition of acetone (2.5 ml) the mixture was stirred at -78° until the yellow crystalline powder was deposited. The yellow precipitate was filtered and washed several times with ether, acetone and n-hexane and recrystallized from ether at low temperature, (yield, 35 %).

The isobutyl complex (II_d) was prepared similarly to (II_c).

However, isolation of the pure complex was difficult, and care must be taken to avoid decomposition of the complex by carefully controlling the reaction temperature and time. (II_d) was obtained as yellow to green crystals, sensitive to air and thermally unstable. It decomposed in ether solution turning from green to deep red even at 0°.

c) $CoH(PPhMe_2)_4$ (VII_b)

When the reaction mixture of $Co(acac)_3$, $PPhMe_2$ and $Al(iso\text{-}Bu)_2(OEt)$ was stirred for ca. 1h.at room temperature, a deep red solution was obtained. On cooling the red solution to -78° red crystals were deposited. The complex thus obtained is sensitive to air but thermally stable at room temperature under nitrogen. Its IR spectrum shows a characteristic ν (Co-H) at 1880 cm^{-1} and other bands due to the coordinated $PPhMe_2$ ligands, suggesting it to be the cobalt hydride complex, $CoH(PPhMe_2)_4$ (VII_b) (yields, 40 %) (Anal. Found C, 62.7; H, 7.9, Calcd. for $CoH(PPhMe_2)_4$ C, 62.8; H, 7.4).

d) $Co(CH_3)_2(acac)(PPh_2Me)_2$ (III)

Complex (III) was prepared similarly to (I) or (II_a) as described above. (III) is soluble in toluene and CH_2Cl_2 but much less soluble in ether and n-hexane.

e) $CoH(PPh_2Me)_4$

Using $AlPr_2(OEt)$ the reaction of $Co(acac)_3$ and PPh_2Me in ether at room temperature was carried out. The reaction mixture changed from a green suspension to a deep yellow solution at 40°. After concentration of the solvent by evaporation and addition of acetone to the residue with stirring at -78° red crystals were deposited, which were filtered and washed with ether and dried *in vacuo* (yield, 15 %). The red complex thus obtained is thermally stable and insensitive to air. Its IR spectrum shows the characteristic ν(Co-H) band at 1955 cm^{-1}, and other bands due to the coordinated PPh_2Me ligands but no band assignable to the acac ligand, suggesting it to be the known complex, $CoH(PPh_2Me)_4$ [12].

f) $Co(CH_3)_2(acac)[P(n\text{-}Bu)_3]_2$ (IV)

Complex (IV) was prepared similarly to (I) or (II_a) or (III) as described above, (yield, 54 %).

2. Reaction of $CoR_2(acac)(PR'_3)_2$

a) Ligand exchange reaction with pyridine

Pyridine (2 ml) was added to complex (I) (0.1 g) by a trap-to-trap distillation using a vacuum line and the reaction mixture was stirred at room temperature for 1 h. After concentration of the pyridine solution n-hexane was added to the residue to give a pyridine-coordinated complex as yellow crystals on cooling the mixture. The complex was recrystallized from n-hexane, (yield, 32 %). The IR spectrum of the yellow complex (V_a) shows peaks due to the coordinated pyridine in addition to the coordinated triethylphosphine and acetylacetonato ligands. The ligand exchange reaction of (I) with γ-picoline was carried out similarly to yield a yellow crystalline complex, $Co(CH_3)_2(acac)(PEt_3)$(r-picoline)(V_b) The corresponding α-and β-picoline-coordinated complexes were not obtained.

b-i) Reaction of (I) with 2,2'-bipyridine

Ether was added to a solid mixture of complex (I) (0.1 g) and 2,2'-bipyridine (0.033 g) at -5°. The temperature was gradually raised to 0° and the solution was stirred tor 2h. After color change of the solution to dark yellow the solution was further stirred at room temperature until red to purple micro-crystalline powder were deposited. The complex was filtered, washed repeatedly at low temperature with ether and n-hexane and dried in vacuum, (yield, 40 %).

b-ii) Reaction of $CoR_2(acac)(PPhMe_2)_2$ (R = Me, Et, n-Pr, iso-Bu) with 2,2'-bipyridine

These reaction were carried out similarly to the reaction of (I) with 2,2'-bipyridine described above (b-i) except that the reactions of the ethyl, n-propyl and iso-butyl complexes were carried out at lower temperature (-10°). On addition of ether to the solid mixture of (II) and bipyridine the color of the reaction system changed from yellow to deep green and a microcrystalline precipitate was deposited. When there was no precipitate deposited, concentration of the solution by evaporation and addition of n-hexane were necessary to induce the deposit of the green precipitate. The precipitate was washed with n-hexane and dried in vacuo. IR spectra of these green complexes were similar to that of $Co(CH_3)_2$-(acac)(bipy). The analytical values of the methyl, ethyl and n-propyl complexes (VI_a - VI_c) are given in Table I. The characterization of the isobutyl complex was made on the basis of its IR spectrum which is similar to that (VI_c).

c) Reaction of $CoR_2(acac)(PR'_3)_2$ with carbon monoxide

The reactions were carried out similarly for all the complexes with a composition of $CoR_2(acac)(PR'_3)_2$. The dialkyl(acetylacetonato)-complex was dissolved in 2 ml of toluene and brought in contact at -70° with carbon monoxide of an atmospheric pressure in a closed system. With the raise of the temperature the color of the solution changed from yellow to red. The amount of ketones formed in the reaction solutions were determined by VPC. Following are the yields of the ketones; acetone from (I), 83 %; from (II_a), 84 %, from (III), 91 %. diethyl ketone from (II_b), 78 %; di-n-propyl ketone from (II_c), 70 %. The cobalt carbonyl compounds with a formula of $Co(acac)(CO)_2(PR'_3)$ may be recovered from the reaction system. As an illustrative example we describe the reaction of (III) with carbon monoxide. The reaction was carried out at room temperature in ether, in which the product was less soluble and deposited as a red microcrystalline powder. The powder was filtered off, washed with ether and acetone cooled to -10° and dried in vacuo;yield, 65 %.; (Anal. Found; C, 57.0; H, 4.8. $Co(acac)(CO)_2(PPh_2Me)$ (VIII) calcd.; C,57.9; H, 4.8 %). IR(KBr): $\nu(C\equiv O)$, 1965, 1955 and 1940 cm^{-1}, (acac), 1584, 1510, 1400, 1265, and 765 cm^{-1}.

When complex (VIII) was dissolved in acetone at room temperature disproportionation occurred to produce a red complex $[Co(CO)_3(PPh_2Me)]_2$ (IX) and $Co(acac)_2$ which was characterized by the measurement of IR spectrum. IR(KBr); (acac)(max) 1605, 1520, 1400, 1025, 935, and 770 cm^{-1}. (IX)was characterized on the basis of elemental analysis and IR spectrum which indicates the presence of CO and PPh_2Me ligand and absence of the acac ligand. (Anal. Found; C, 55.6; H, 4.1. $[Co(CO)_3(PPh_2Me)]_2$ (IX) calcd.; C, 56.0; H, 3.8 %). IR(KBr): $\nu(C\equiv O)$, 1940 cm^{-1} (v.s.); (PPh_2Me) (max), 3045, 1470, 1435, 1000, 890, 885, 750, 735, and 695 cm^{-1}.

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Chapter II PREPARATION AND PROPERTIES OF METHYLBIS(DIPHENYLPHOSPHINOETHANE)COBALT(I)

SUMMARY

Reaction of cobalt(III) acetylacetonate with dimethylaluminum monoethoxide in the presence of 1,2-bis(diphenylphosphino)ethane (dpe) gives a methylbis[1,2-bis(diphenylphosphino)ethane]cobalt(I), $CoCH_3(dpe)_2$ (I), which was characterized by elemental analysis, chemical reactions, IR and NMR spectra. The cobalt-carbon bond in (I) is cleaved by a protic acid with liberation of methane. Co(I) acetylide, $RC{\equiv}CCo(dpe)_2$ (R = Me, Ph) (VII)was obtained by the reaction of (I) with $RC{\equiv}CH$. Insertion reaction of carbon monoxide into the cobalt-carbon bond under mild conditions gave an acetylcobalt complex, $Co(COCH_3)(CO)_2(dpe)\cdot\frac{1}{2}(Et_2O)$ (IV). The reaction of (I) with D_2 liberated CH_3D as a sole gaseous product and afforded $CoD(dpe)_2$ (III).

INTRODUCTION

A great number of trivalent alkylcobalt complexes with macrocyclic ligands have been synthesized and extensively studied [1], but only a few univalent alkylcobalt complexes are known [2]. In relation to the industrially important hydroformylation process of olefins using a cobalt complex more knowledge about the properties of a univalent alkylcobalt complexes is required for understanding the reaction mechanism and designing a new catalytic process. We have previously studied the reaction of cobalt tris acetylacetonate, diethylaluminum monoethoxide and diphenylphosphinoethane (dpe) and obtained $CoH(dpe)_2$ and $Co(dpe)_2$ [3]. Since the dpe ligand is known as a useful stabilizing ligand of nickel [4] and iron alkyls [5], we have reexamined the alkylation reaction of cobalt acetylacetonate in the presence of dpe using dimethylaluminum monoethoxide and obtained a new thermally stable methylcobalt complex, $CoCH_3(dpe)_2$ (I). This complex readily reacts with carbon monoxide, dihydrogen and active hydrogen compounds. We report here the preparation and properties of the new methylcobalt(I) complex.

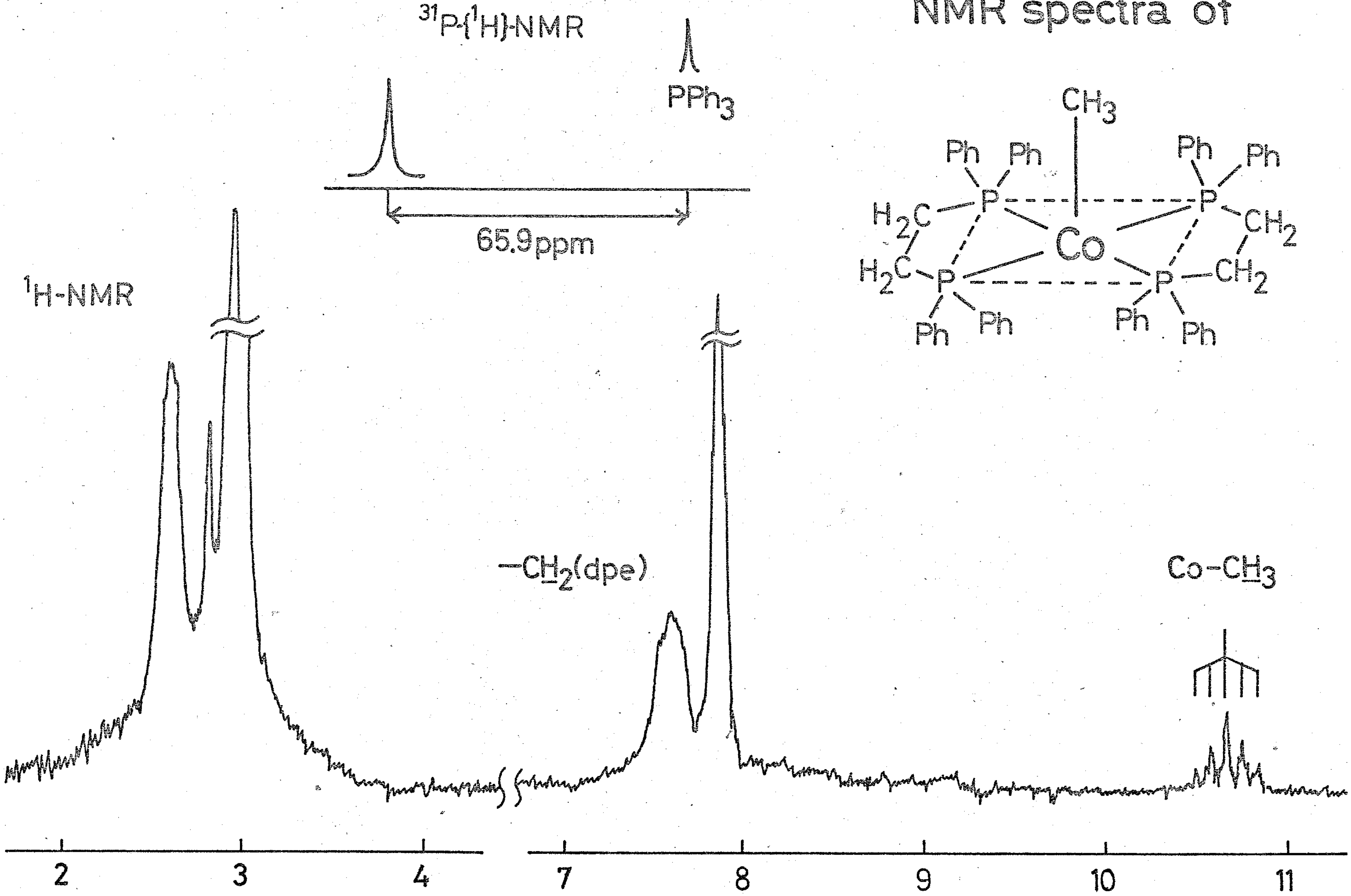
RESULTS AND DISCUSSION

The reaction of $Co(acac)_3$, $Al(CH_3)_2(OEt)$ and dpe in diethyl ether at room temperature gives $CoCH_3(dpe)_2$ (I) as red prisms. Attempts to prepare similar alkylcobalt complexes using $AlEt_3$, $AlEt_2(OEt)$, $Al(n\text{-}Pr)_3$ and $Al(iso\text{-}Bu)_3$ resulted in recovery of the knwon cobalt hydride complex, $CoH(dpe)_2$. Being prompted by isolation of intermediate dialkylcobalt(III) complexes having both acetylacetonato and tertiary phosphine ligands with a composition of $CoR_2(acac)(PR_3')_2$ [6] from the reaction mixture of $Co(acac)_3$, $AlR_2(OEt)$ and PR'_3, we tried to isolate a similar methylcobalt complex with the acetylacetonato and dpe ligands but the attempts have been so far unsuccessful.

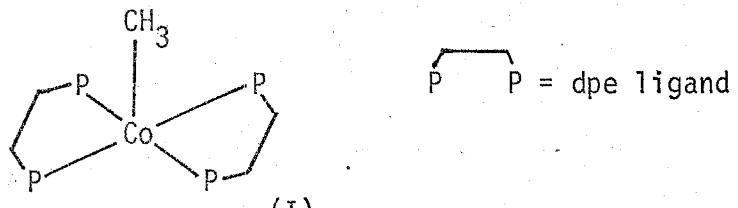
(I) is soluble in ether, toluene, benzene and pyridine, and can be recrystallized from ether. Although sensitive to oxygen and moisture, (I) is thermally very stable and decomposed at 194 - 195° in the solid state with liberation of methane and a trace of ethane.

IR spectrum of (I) shows the aliphatic ν(C-H) bands of the methyl group bonded to cobalt at 2870 and 2800 cm^{-1} and the presence of dpe ligands. ^1H NMR spectrum of (I) in toluene at 20° shows a quintet due to the methyl group bonded to cobalt at τ10.3 ($^3J(P\text{-}H)$ = 9 Hz, 3H) and the broad peak due to the methylene groups in the dpe ligands at τ 7.6 (8H) and the complex multiplet due to the phenyl groups in the dpe

NMR spectra of



ligands at τ 2.6 to τ 3 (40H). Proton decoupled ^{31}P NMR spectrum of (I) in toluene shows a singlet due to the four phosphorus nuclei in the dpe ligands at 65.9 ppm downfield from external triphenylphosphine reference. Fig. 1 shows the NMR spectra of (I) in toluene at 20°. These NMR data suggest that complex (I) has a square pyramidal geometry in solution at room temperature with a cobalt bonded methyl group.



(I)

Similar NMR data of a methylcobalt complex were observed with $CoCH_3[P(OCH_3)_3]_4$ and an analogous hydrido cobalt complexes [2b], which showed the fluxional behavior in solution. Acidolysis of (I) with H_2SO_4 liberated one equivalent of methane for the calculated value.

In contrast to triphenylphosphine [2c], the bidentate ligand, dpe, has a large stabilizing effect on the thermal stability of methylcobalt complex. This enhancement of stability is presumably due to the chelate effect of the dpe ligands. A similar chelate effect on the stability of alkyltransition metal complex was observed with 2,2'-bipyridine-coordinated complexes [7].

2. Reactions of (I)

2-1) Reactions with D_2 or H_2

The reaction of (I) with dihydrogen in a toluene solution at room temperature under atmospheric pressure quantitatively produced a deep red complex, $CoH(dpe)_2$ (II) and liberated methane. The similar reaction of (I) with D_2 released CH_3D as the sole gaseous product and produced a deep red complex, $CoD(dpe)_2$ (III).

$$Co(CH_3)(dpe)_2 + H_2 \longrightarrow CoH(dpe)_2 + CH_4$$

$$Co(CH_3)(dpe)_2 + D_2 \longrightarrow CoD(dpe)_2 + CH_3D$$

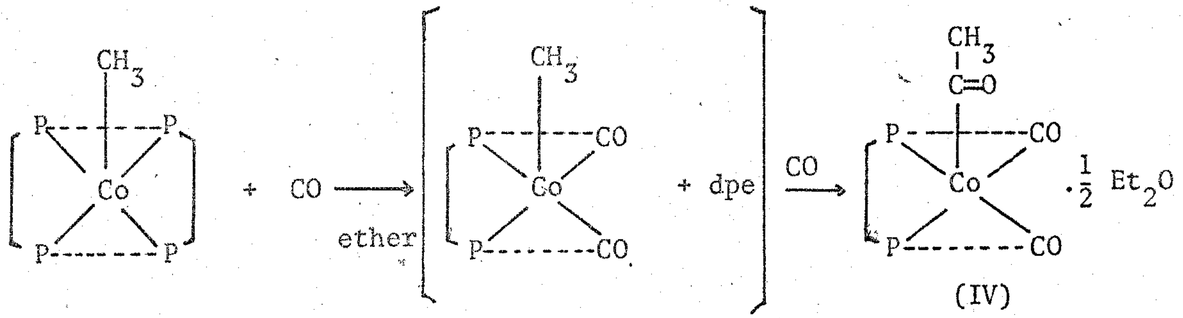
IR spectrum of (III) showed a ν(Co-D) band at 1355 cm^{-1} in comparison with the ν(Co-H) band of (II) at 1884, the ν(Co-H)/ν(Co-D) ratio being 1.4. The hydrogenation reaction of alkyltransition metal complexes is of interest in relation to the catalytic olefin hydrogenation or hydroformylation reaction. The facile hydrogenation observed here is one of a few examples of hydrogenolysis of isolated alkyltransition metal complexes so far reported [5,8,9].

2-2) Reaction with carbon monoxide

Reports of isolation of an acylcobalt complex from the reaction of an isotated alkylcobalt complex with carbon monoxide are still scarce [10], although reports that reactions of cobalt carbonyl with alkyl halides to give acylcobalt complexes have been made [11, 12, 13]. Carbon monoxide is readily inserted into cobalt-carbon bond in (I) under mild conditions. Contact of (I) with carbon monoxide under atmospheric pressure at room temperature in toluene solution gives a CO-coordinated acetylcobalt complex with a dpe ligand, $Co(COCH_3)(CO)_2(dpe)\cdot\frac{1}{2}Et_2O$ (IV). A part of the dpe ligands was recovered from the solution. IR spectrum of (IV) shows ν(C≡O) bands due to terminal carbonyl ligands bonded to cobalt at 1970, 1960 (sh) and 1910 cm^{-1} and a ν(C=O) band due to an acetyl group at 1640 cm^{-1} along with the aliphatic ν(C-H) band of the methyl group in the acetyl group at 2840 cm^{-1}. ^1H NMR spectrum of (IV) shows a singlet due to the methyl protons of acetyl group at τ 7.62 (s. 3H) and a doublet due to the methylene protons in the dpe ligand at

τ 7.66 (d, J(P-H) = 16Hz, 4H) and a complex multiplet due to the phenyl groups of dpe at τ 2.2 - 2.7 (20H) in addition to a quartet (^{3}J(H-H) = 7Hz, 2H) and a triplet (^{3}J(H-H) = 7Hz, 3H) due to the ethyl groups in ether at τ 6.46 and τ 8.54. No acetone was detected from the resultant solution. In relation to the hydroformylation reaction attempts to induce (IV) to react with hydrogen at atmospheric pressure or high pressures were unsuccessful. (IV) reacted with methyl iodide to give acetone, which was detected by gas chromatography.

These results suggest that the insertion reaction of carbon monoxide into cobalt-carbon bond is preceded by partial displacement of the dpe ligand from (I) by carbon monoxide.



In contrast to the reaction of the methyl cobalt complex with carbon monoxide, which afforded the insertion product the hydrido cobalt complex (II) reacted with carbon monoxide to give hydrido carbonyl complex, CoH(CO)$_2$(dpe) (V) as yellow crystals, which was characterized by elemental analysis and IR spectrum.

2-3) Reactions with olefins.

Complex (I) initiates the polymerization of acrylonitrile at low temperature. When the reaction of (I) with acrylonitrile was carried out under carefully controlled conditions, a yellow complex was obtained accompanied by some polymer of acrylonitrile and the liberated dpe ligand. Thus obtained yellow complex (VI) has a methyl group and coordinated-acrylonitrile. IR spectrum of (VI) shows a characteristic $(C\equiv N)$ bands due to the coordinated acrylonitrile at 2175 and 2170 cm^{-1} and aliphatic ν(C-H) bands at 2880, 2875, and 2830 cm^{-1} in addition to the very weak band due to the polymer of acrylonitrile.

Acidolysis and thermolysis of (VI) liberated small amounts of methane and free acrylonitrile. Formation of a similar olefin-coordinated transition metal alkyl to (VI) was observed in the nickel alkyl complex which was formed by the reaction of $NiEt_2$(bipy) and acrylonitrile at -78° [14]. These olefin-coordinated alkyl complexes may be regarded as models of active intermediates in the coordination polymerization by transition metal catalysts. Complex (I) also initiates the polymerization of styrene, whereas hydrido complex (II) did not react with such vinyl compounds.

2-4) Reactions with RC≡CH and other active hydrogen compounds

Corresponding to the hydrolysis of (I) with H_2SO_4 and HCl, which quantitatively released methane, the cleavage of cobalt-carbon bond occurred by the reaction of (I) with active hydrogen compounds such as RC≡CH (R = Me, Ph) producing cobalt(I) acetylides, $RC\equiv CCo(dpe)_2$ (VII) and liberating methane quantitatively.

$$CoCH_3(dpe)_2 + RC\equiv CH \longrightarrow RC\equiv CCo(dpe)_2 + CH_4$$

(VII_a) : R = Me

(VII_b) : R = Ph

(VII_a) and (VII_b) are stable in air, soluble in common organic solvents and can be recrystallized from toluene as red and brown crystalline complexes. IR spectra of (VII_a) and (VII_b) show the characteristic $\nu(C\equiv C)$ bands at 2100 cm^{-1} and 2070 cm^{-1}. Table 1 shows the analytical data for the isolated dpe-coordinated cobalt(I) complexes (I) - (VII).

The reactions of (I) with other types of active hydrogen compounds such as acetaldehyde and nitromethane also liberated methane. (I) reacted with acetaldehyde in toluene for a few days releasing methane and carbon monoxide. From the resultant solution a yellow complex was obtained. Its IR spectrum shows the $\nu(C\equiv O)$ bands at 1965 cm^{-1} and 1910 cm^{-1}. These results suggest the reaction proceeds through oxidative addition of acetaldehyde to cobalt followed by decarbonylation. Since the carbonyl complex thus obtained is very sensitive to air and is contaminated with some polymers of acetaldehyde, its compositon could not be determined.

(I) reacted with nitromethane releasing methane. But the product has not been characterized.

Experimental

General

All procedures were carried out under a nitrogen or argon atmosphere. Solvents were dried by usual methods, distilled and stored under nitrogen.

The isolated complexes were characterized by chemcial reactions such as pyrolysis and hydrolysis, elemental analysis and IR and NMR spectroscopy. IR spectra were recorded on a Hitachi model EPI-3G using KBr discs prepared under nitrogen and NMR spectra were recorded with a Japan-Electron Optics Lab. JNM-PS-100 spectrometer. Analysis of gases was carried out by mass spectrometry and gas chromatography after collecting gases using a Toepler pump. The microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. For the isolated complex, the absence of aluminum compounds was confirmed by Aluminon test after decomposition of the complexes.

1. Preparation and properties of $CoCH_3(dpe)_2$ (I)

Cobalt(III) acetylacetonate (2.0 g, 5.6 mmol) and dpe (4.5 g, 11.3 mmol) were suspended in 20 ml of diethylether and 8 ml of dimethylaluminum monoethoxide was added to the suspension at 20°. Sometimes heating the reaction mixture to 30° for a short period was effective to accelerate the reaction. The color of the reaction mixture changed from green to deep yellow and then a deep red solution was obtained. A red powder was deposited on cooling the deep red solution. The precipitate was filtered, washed several times with ether and n-hexane and recrystallized from ether to give deep red prisms, which were dried *in vacuo* at room temperature. Yield, 82 %.

(I) is soluble in toluene, benzene, ether, and pyridine and thermally stable in the solid state but sensitive to air and moisture. Hydrolysis of (I) with H_2SO_4 released 92 % of methane for (I). (I) was decomposed by heating under vacuum at 194 - 195° and melted at 200 - 203°, releasing methane and a trace amount of ethane. IR(KBr): ν(C-H)(CH_3-Co), 2870 and 2800 cm^{-1}; dpe(max), 1580, 1475, 1425, 1085, 735, and 695 cm^{-1}. ^1H NMR (20°, toluene-d_8) τ 10.3 (quintet, J(P-H) = 9Hz, 3H), τ 7.6 (broad multiplet, 8H) τ 2.6 - 3 (complex multiplet, 20H), ^{31}P- H -NMR (20°, toluene) 65.9 ppm (s) (downfield from external triphenylphosphine).

Attempts to obtain the intermediate reaction alkylation product containing the methyl, acetylacetonato and dpe ligands such as $Co(CH_3)_2$-(acac)(dpe) has so far been unsuccessful.

When $AlEt_3$, $AlEt_2(OEt)$, $Al(n\text{-}Pr)_3$, or $Al(iso\text{-}Bu)_3$ was used instead of $AlMe_2(OEt)$, the known complex $CoH(dpe)_2$ (II) was obtained. The IR spectrum of (II) shows a characteristic ν(Co-H) band at 1884 cm^{-1} in addition to the bands due to dpe ligands.

2. Reactions of (I)

1) With H_2 or D_2

Contact of (I) (0.25 g, 0.29 mmol) with D_2 in toluene under atmospheric pressure at room temperature caused the color change to give a red solution and then the red crystalline complex was deposited. At the same time CH_3D evolved. Thus obtained red complex (III) was washed with ether and n-hexane, and dried in vacuo. Yield, 90 %. IR(KBr): ν(Co-D), 1355 cm^{-1}, dpe(max), 3040, 1575, 1480, 1440, 1090, 740, and 695 cm^{-1}.

The reaction of (I) with H_2 was carried out similarly to the reaction with D_2.

2) with CO

A solution of (I) (0.32 g, 0.37 mmol) in toluene was allowed to contact with CO under an atmospheric pressure at room temperature in a closed system. The reaction mixture was stirred for 2 h. to give a yellow solution. Free dpe was recovered on cooling the resultant yellow solution. After evaporation of the solvent the yellow residue was extracted with ether and the yellow prisms obtained from the extract was purified by repeated recrystallization with ether. In the reaction mixture niether acetone nor α-diketone was detected. Yield, 62 %.
IR(KBr): ν(C≡O), 1970, 1960 (sh), and 1910 cm^{-1}; ν(C=O) of CH_3COCo, 1640 cm^{-1}; ν (C-H) of the acetyl group, 2840 cm^{-1}; dpe(max), 3050, 1585, 1480, 1435, 1100, 1067, 750, and 698 cm^{-1}. ^1H NMR (CD_2Cl_2) τ 7.62 (s, 3H), τ 7.66 (d, J(P-H) = 7Hz, 3H), τ 2.2 - 3 (20H), τ 6.46 (quart. J(H-H) = 7Hz, 2H), τ 8.54 (t, J(H-H) = 7Hz, 3H).

When the similar reaction of complex (II), $CoH(dpe)_2$ (0.09 g, 0.1 mmol) with carbon monoxide was carried out under the same conditions, the color of the reaction mixture changed from red to yellow. On cooling the solution a yellow crsytalline complex deposited, which was purified by recrystallization from ether and characterized as (V) by elemental analysis and IR spectrum. Yield, 67 %.

IR(KBr): ν(Co-H), 1884 cm^{-1}; ν(C≡O), 1978 and 1917 cm^{-1}; dpe(max), 1585, 1482, 1438, 1092, 740, and 698 cm^{-1}.

3) with olefins

Acrylonitrile (1 - 2 ml) was transferred into a Schlenk tube containing complex (I) (0.1 g) by trap-to-trap distillation in vacuum. At -15° - -5° the reaction mixture was stirred for 2h. to cause the color change from deep red to yellow. When the color changed to yellow, the reaction system was cooled to -78° to precipitate a yellow complex. The precipitate was freed from acrylonitrile by evaporation. If the yellow solution was further stirred the polymerization of acrylonitrile took place.

The yellow precipitate (VI) thus obtained was washed with ether and n-hexane and dried in vacuo. Its unequivocal characterization was not possible because of the contamination of the product with some polymers of acrylonitrile but the composition is close to $Co(CH_3)(CH_2{=}CHCN)(dpe)_2$ on the basis of elemental analysis and some chemical reactions and IR spectroscopy. On acidolysis of (VI) methane and acrylonitrile were released. On pyrolysis at 130 - 135° the yellow solid changed to deep red and above 150° it decomposed releasing methane and acrylonitrile. (VI) reacted with methyl iodide to produce methane and a trace amount of ethane. The gaseous products evolved in these reactions were identified by gas chromatography. (Found; C, 74.8; H, 6.1; N, 3.4. $C_{56}H_{54}NCo$ calcd.; C, 82.7; H, 5.9, N, 1.5 %)

IR(KBr); $\nu(C{\equiv}N)$, 2175 and 2170 cm^{-1}; $\nu(C\text{-}H)$, 2880, 2875, and 2830 cm^{-1}; dpe(max), 1585, 1482, 1435, 1097, and 699 cm^{-1}. Complex (II) did not react with acrylonitrile even if it was allowed to contact with acrylonitrile for a week.

4) with RC≡CH

To a toluene solution of (I) (0.25 g, 0.25 mmol) PhC≡CH (100μl) was added by a trap-to-trap distillation and the reaction mixture was stirred for 5 h. at room temperature. The color of the reaction mixture changed from deep red to brown evolving a quantitative amount of methane

(100 %) for (I) and a brown powder was obtained from the solution. Recrystallization from a toluene-n-hexane mixture gave brown crystals (VII_b). Yield, 70 %. IR(KBr): ν(C≡C), 2095 cm^{-1}, ν(C-H) 2875 and 2825 cm^{-1}; dpe(max), 3045, 1585, 1480, 1430, 1095, 735, and 695 cm^{-1}.

A similar experiment with $CH_3C{\equiv}CH$ gave $Co(C{\equiv}CCH_3)(dpe)_2$ (VII_a) in a 80 % yield.

The reaction of (I) with acetaldehyde at room temperature gave a pale red solution evolving a gas consisted of 26 % of methane and 74 % carbon monoxide as determined by mass spectrometry. From the pale red solution air sensitive yellow crystals were deposited, which were purified by repeated recrystallization. The IR spectrum of the complex shows the characteristic ν(C≡O) bands at 1965 and 1910 cm^{-1} suggesting that it is the carbonyl complex with dpe ligands.

Table I Analytical data for dpe-coordinated Co(I) complexes

Complex		color	d.p.	anal.(%)	(calcd.)
$Co(CH_3)(dpe)_2$	(I)	deep red	194-195	72.5(73.1)	6.0(5.9)
$CoD(dpe)_2$	(III)	red	265-270	72.6(72.9)	5.8(5.6)
$Co(COCH_3)(CO)_2(dpe)\cdot\frac{1}{2}Et_2O$	(IV)	yellow	120-121	64.8(65.4)	5.4(5.9)
$CoH(CO)_2(dpe)$	(V)	yellow	- -	65.9(65.4)	5.0(4.9)
$Co(C\equiv CCH_3)(dpe)_2$	(VII_a)	red	188-	74.0(73.8)	6.2(5.7)
$Co(C\equiv CPh)(dpe)_2$	(VII_b)	brown	187-	74.7(75.3)	5.8(5.6)

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Chapter III PREPARATION AND PROPERTIES OF METHYLIRON COMPLEXES WITH TERTIARY PHOSPHINE LIGANDS AND THEIR DECOMPOSITION PATHWAYS THROUGH THE FORMATION OF CARBENOID INTERMEDIATES

SUMMARY

Reaction of $Fe(acac)_3$, $AlMe_2(OEt)$ and 1,2-bis(diphenylphosphino)-ethane (dpe) gives a new dimethyliron complex, $Fe(CH_3)_2(dpe)_2$ (I). Complex (I) is unstable in solution and gives a methyliron complex containing an orthometallated ring, $Fe(CH_3)(dpe)\{Ph_2PCH_2CH_2PPh(o\text{-}C_6H_4)\}$ (II) with liberation of methane. On thermal decomposition and treatment with CH_2Cl_2 (I) liberates ethylene, the formation of which suggests the intermediacy of carbenoid complexes. Reactions of (I) toward H_2 or D_2, carbon dioxide, phenylacetylene yield $FeH_2(dpe)_2$ (III) or $FeD_2(dpe)_2$ (VI), $Fe(OOCCH_3)(CO_2)_m(Py)_n$ (VII) and $FeH(C{\equiv}CPh)(dpe)_2$ (VIII), respectively. [illegible] yield acetone.

(I) initiates the polymerization of acrylonitrile. Employment of $PPhMe_2$ instead of dpe in the reaction of $Fe(acac)_3$ and $AlMe_2(OEt)$ gave a new methylbis(acetylacetonato)iron(III) complex, $Fe(CH_3)(acac)_2)(PPhMe_2)$ (V). (I) and (V) react with carbon monoxide to yield acetone.

Introduction

Many alkyliron complexes having cyclopentadienyl or carbonyl ligands are known [1], but much less is known about alkyliron complexes having other ligands. We have previously observed a pronounced stabilization effect of 2,2'-bipyridine [2] and a somewhat weaker stabilizing effect of triphenylphosphine [3] and prepared various alkyltransition metal complexes having these ligands. A bidentate ditertiary phosphine ligand, 1,2-bis(diphenylphosphino)ethane (dpe) often serves as an excellent stabilizing ligand of alkyl- and hydrido-transition metal complexes and some stable alkylnickel [4,5] and -cobalt

[6] and hydrido-cobalt [7] complexes have been isolated. We now describe the preparation of dimethylbis[1,2-bis(diphenylphosphino)-ethane]iron(II), $Fe(CH_3)_2(dpe)_2$ (I), by reaction of iron(III) acetylacetonate, dimethylaluminum monoethoxide and dpe. Hata et al. previously reported the preparation of an ethylene-coordinated iron(0) complex, $Fe(CH_2=CH_2)(dpe)_2$ by the reaction of $Fe(acac)_3$, $AlEt_2OEt$ and dpe [8]. The ethylene-iron complex is considered to be derived through formation of an ethyliron intermediate obtained by alkylation with $AlEt_2OEt$. The dimethyliron complex (I) is thermally stable and decomposes on pyrolysis at elevated temperatures and on reaction with dichloroalkanes at room temperature forming ethylene in addition to methane and ethane. The decomposition pathway presumably involves the formation of carbenoid intermediates as we reported in a preliminary form [9]. This paper also describes other chemical properties of (I) such as the reactions with H_2 and D_2, phenylacetylene, carbon monoxide and carbon dioxide.

In attempts to examine the stabilizing effect of other tertiary phosphines we have isolated another methyliron complex, methylbis-(acetylacetonato)(dimethylphenylphosphine)iron(III), $FeCH_3(acac)_2$-$(PPhMe_2)$ in the reaction of $Fe(acac)_3$, $AlMe_2(OEt)$ and $PPhMe_2$. This complex may be regarded as the intermediate alkylation product of $Fe(acac)_3$ with alkylaluminum compounds. Similar transition metal complexes containing the alkyl, acetylacetonato and tertiary phosphine ligands have been prepared in reaction systems using $Fe(acac)_3$ [3], $Co(acac)_3$ [3, 10] and $Ni(acac)_2$ [11].

Result and discussion

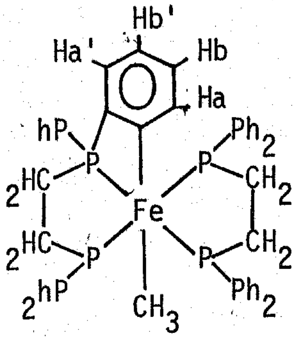
1. Preparation and properties of methyliron complexes

The dimethyliron complex (I) was prepared as orange crystals by the reaction of Fe(acac)$_3$, dpe and dimethylaluminum monoethoxide or trimethylaluminum in ether at -30° to 0° under nitrogen.

$$\underset{}{Fe(acac)_3} + \underset{(AlMe_3)}{AlMe_2(OEt)} + dpe \longrightarrow \underset{(1)}{Fe(CH_3)_2(dpe)_2}$$

Since the complex is insoluble in any common organic solvents and decomposed in others such as pyridine and CH_2Cl_2, recrystallization and NMR measurement were not feasible, but elemental analysis and chemical characterization of (I) supported its formulation as $Fe(CH_3)_2(dpe)_2$. Complex (I) is stable in air for 10 - 15 min. and decomposes slowly releasing CH_4 and C_2H_6. Acidolysis with concentrated H_2SO_4 released 1.8 mol of CH_4 per Fe. Iodolysis in benzene liberated methane and ethane in a 1/2.5 ratio and yielded FeI_2(dpe). Complex (I) is stable in the solid state under nitrogen at room temperature and decomposes at 130 - 135° releasing methane, ethane and ethylene in a ratio of 75/20/5, the amount of the gas liberated accounting for 75 % of the methyl groups bonded to iron on assumption that the hydrocarbon source is the methyl group (vide infra).

In attempts to recrystallize the complex (I) from toluene, methane was liberated and a yellow to orange solution was obtained. On cooling it to -70° orange crystals were deposited. IR spectrum of (II) shows new bands at 1555 cm^{-1} and 730 cm^{-1}, which were absent in the original complex (I). The new band appeared at 1555 cm^{-1} may be assigned to the metallated phenylring vibration stretching, and the intense band at 730 cm^{-1} to the C-H out-of-plane deformation of an ortho-disubstituted benzene ring. The recovered dpe ligand after acidolysis of (II) with D_2SO_4 were found to have C-D bond in the dpe ligand as revealed by the mass spectroscopic examination of water produced on oxidative degradation of the dpe ligand with CuO. Evidence supporting the orthometallated structure as shown below was also obtained by examination of the NMR spectrum of (II) in CD_2Cl_2. The NMR spectrum of (II) at -20° shows a broad peak due to the methyl group bonded to iron at τ 10.8 (3H), two sets of broad peaks due to the methylene groups of the dpe ligand at τ 7.8 (4H) and 8.2 (4H), the broad peaks due to H_b and H_b' protons in the above structure at 4.16 (2H), the broad peaks due to H_a and H_a' protons at 3.62 (2H), and two sets of complex multiplet at τ2.5 - 3.4 due to the phenyl protons, H_a, H_a', H_b, and H_b' protons excluded. Acidolysis of (II) gave methane.



(II)

There are many examples of orthometallation involving the loss of hydrogen from an aromatic ring of a ligand with the concomitant formation of a metal-carbon bond as reviewed recently [12], and the similar orthometallated reactions promoted by recrystallization of alkyl complexes have been demonstrated by Keim and Kaesz et al. in an alkylrhodium [13], and an alkylmanganese complex [14], and by Hata et al. in an ethylene-iron complex producing $HFe(dpe)(C_6H_4PPhCH_2CH_2PPh_2)$ [8]. However, no precedent of this type of complex having alkyl group and an orthometallated ring has been reported.

In contrast to the methyliron complex the similar reaction of $Fe(acac)_3$ with $AlEt_2(OEt)$ instead of $AlMe_2(OEt)$ in the presence of dpe in ether gives the ethylene-coordinated complex, $Fe(CH_2=CH_2)(dpe)_2$ [8]. Alkylation with $Al(n\text{-}Pr)_3$ and $Al(i\text{-}Bu)_3$, on the other hand, afforded the known hydride, $FeH_2(dpe)_2$ (III) [15], which on recrystallization from benzene was recovered as $FeH_2(dpe)_2 \cdot C_6H_6$ (IV) [8]. These results suggest that higher alkyl homologs of $FeR_2(dpe)_2$ are less stable than (I) and prone to decompose <u>via</u> β-elimination process affording (III). The reaction under similar conditions using $AlEt_3$ instead of $AlEt_2(OEt)$ also gave the dihydride complex (III), but the ethylene-complex was obtained only when the reaction was conducted by carefully controling the reaction temperature and the product was contaminated with (III). The variation of reduction product depending upon the use of either $AlEt_2(OEt)$ or $AlEt_3$ implies that the decomposition pathway of an ethyliron complex which is formed as an intermediate alkylation product may be influenced by the kind of the ethylating agents which exist in some excess in the reaction system. We have previously observed that alkyltransition metal complex once isolated are susceptable for further attack by alkylaluminum compounds [16].

The intermediate alkylation product of $Fe(acac)_3$ with $AlMe_2(OEt)$ was isolated as $FeCH_3(acac)_2(PPhMe_2)$ (V) when dimethylphenylphosphine was employed. (V) is thermally stable at room temperature under nitrogen but sensitive to air. It is soluble in ether and other organic solvents and can be recrystallized as red crystals from ether. Paramagnetism of (V) precludes the NMR measurement, but its IR spectrum indicates the presence of the acac and $PPhMe_2$ ligands and of an iron-bonded methyl group as observed in the ν(C-H) bands at 2900 and 2850 cm^{-1}. Complex (V) decomposes with melting at 55 - 58° evolving methane, ethane and ethylene in a ratio of 75/14/11, the total amount of the gas accounting for 100 % of the iron-bonded methyl group on the assumption that the $PPhMe_2$ ligand is not thermolyzed at the temperature to produce these hydrocarbons (vide infra). Acidolysis of (V) released 0.92 mol of methane per Fe. Attempts to prepare a methyliron complex containing no acetylacetonato ligand by further methylation of (V) did not lead to any isolable product.

The reaction of (I) with dihydrogen in a toluene suspension at room temperature liberates methane to produce $FeH_2(dpe)_2$ from the resultant solution. The similar reaction of (I) with D_2 released CH_3D as the sole gaseous product and gave $FeD_2(dpe)_2$, which on recrystallization from benzene afforded yellow crystals of composition, $FeD_2(dpe)_2 \cdot C_6H_6$ (V)

$$Fe(CH_3)_2(dpe)_2 + H_2 \longrightarrow CH_4 + \underset{(III)}{FeH_2(dpe)_2} \xrightarrow{C_6H_6} \underset{(IV)}{FeH_2(dpe)_2 \cdot C_6H_6}$$

$$Fe(CH_3)_2(dpe)_2 + D_2 \longrightarrow CH_3D + FeD_2(dpe)_2 \xrightarrow{C_6H_6} FeD_2(dpe)_2 \cdot C_6H_6$$

The IR spectrum of the iron dideuteride complex (IV) showed a ν(Fe-D) band at 1330 cm^{-1} in comparison with ν(Fe-H) band of (IV) at 1840 cm^{-1}, the ν(Fe-H)/ν(Fe-D) ratio being 1.4. The presence of the single ν(Fe-H) or ν(Fe-D) band suggests the trans-configuration for the dihydride and dideuteride complexes [15]. Similar hydrogenolysis of other methyl-transition metal complexes such as $CoCH_3(dpe)_2$ [6], and $RhCH_3(PPh_3)_3$ [13] under mild conditions to afford the deuteride complexes are known.

Complex (IV) showed a peculiar photochemical behavior in sunlight; the color of the solid complex changed from yellow to red without evolution of hydrogen upon irradiation with sunlight. The IR spectrum of the red complex shows a new ν(Fe-H) band at 1890 cm^{-1} and a new band at 728 cm^{-1} due to the ortho metallated species. On recrystallization of the red complex from benzene (IV) was recovered.

The interconversion suggests either an isomerization between trans and cis configurations or hydrogen transfer involving the orthometallation. The hydrogen transfer from the dpe ligand to a transition metal hydride has precedents in $Ru(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) [17] and $Fe(C_2H_4)(dpe)_2$ [8]. In the latter case the hydrogen transfer took place on irradiating the iron complex. The IR band at 728 cm^{-1} appeared on UV irradiation of the solid complex was interpreted as indication of the occurrence of the orthometallation, together with other supporting NMR evidence. The appearance of the IR band at 728 cm^{-1} on irradiation of the present complex is in line with the behavior of $Fe(C_2H_4)(dpe)_2$ and may be taken as an indication of the intramolecular hydrogen transfer as shown below.

$$FeH_2(dpe)_2 \cdot C_6H_6 \underset{C_6H_6\text{(in solution)}}{\overset{h\nu\text{ (solid)}}{\rightleftarrows}} FeH_3(C_6H_4PPhCH_2CH_2PPh_2)(dpe) \cdot C_6H_6$$

A similar hydrogen transfer involving the orthometallation has been observed on UV irradiation of $FeH_2N_2(PPh_2Et)_3$ [18].

In view of the recent growing interest on reactions of carbon dioxide with transition metal complexes having metal-carbon [19] and metal-hydrogen [20] bonds, (I) was treated with CO_2 in pyridine. A very air-sensitive and thermally unstable yellow solid was obtained which was proved to be an iron(II) acetate containing pyridine and some coordinated CO_2. The dpe ligands in (I) were completely displaced by pyridine and went into the pyridine solution. We tentatively formulate the complex as $Fe(OOCCH_3)_2(CO_2)_m(py)_n$ (VII). The IR spectrum of (VII) shows the ν(OCO) bands of the acetato groups at 1610 and 1380 cm^{-1} and bands due to the coordinated CO_2 at 2650, 1670, 1420, 1340,and 850 cm^{-1} [19] in addition to bands associated with the coordinated pyridine ligands. The formation of the iron acetate complex (VII) by CO_2 insertion into $Fe-CH_3$ bands has been supported by comparison of the IR spectrum of (VII) with that of a complex obtained by the reaction of iron(II) acetate with CO_2 in pyridine. A similar CO_2 insertion into Fe-H bond to give a formate complex has been recently reported [21].

Phenylacetylene having an acidic hydrogen reacts with (I) evolving methane and small amounts of ethane and ethylene to produce a crystalline hydridoiron(II) acetylide, $FeH(C\equiv CPh)(dpe)_2$ (VIII), which was characterized on the basis of elemental analysis and IR spectrum showing a ν(Fe-H) band at 1850, ν(C≡C) at 2035 and ν(Fe-C) at 560 cm^{-1}. The hydridoacetylido complex (VIII) is considered to be formed by oxidative addition of PhC≡CH to an intermediate which was formed during dissolution (I) in toluene. Similar oxidative addition reactions of mono-substituted acetylenes with several transition metal complexes have been observed [22].

Complex (I) reacted with carbon monoxide under mild conditions to produce acetone and an iron carbonyl complex containing dpe ligand with a composition of $Fe(CO)_2(dpe)_2$. Since the reaction of (I) with carbon monoxide proceeds with partial decomposition of (I), the yields of acetone and the iron carbonyl complex were low. On the other hand, a similar reaction of (V) with carbon monoxide gave quantitatively one equivalent of acetone per two iron atoms accompanied by formation of $Fe(acac)_2$. We have previously observed a disproportionation of $FeEt(acac)(PPh_3)_3$ in acetone or tetrahydrofuran affording $Fe(acac)_2$ [3] and quantitative formation of 1 mol equivalent of ketone from 1 mol of $CoR_2(acac)L_2$ (L = tertiary phosphines) and carbon monoxide [10]. A further example of CO insertion into transition metal-alkyl bond producing ketone is provided by the reaction of $NiMe(acac)(PPh_3)_2$ or $NiEt(acac)(PPh_3)$ with carbon monoxide to give acetone or diethyl ketone and $Ni(acac)_2$ [23]. The present reaction probably follows the similar pattern as shown below.

$$\underset{(V)}{FeMe(acac)_2(PPhMe_2)} + CO \longrightarrow FeMe(acac)_2(CO) + PPhMe_2$$

$$FeMe(acac)_2(CO) \longrightarrow Fe(COMe)(acac)_2$$

$$Fe(COMe)(acac)_2 + \begin{array}{l} FeMe(acac)_2(CO) \\ \text{or } FeMe(acac)_2(PPhMe_2) \end{array} \longrightarrow 2Fe(acac)_2 + Me_2CO + CO \text{ or } PPhMe_2$$

An acyliron complex related to the proposed intermediate in the present reaction has been obtained in the reaction of η^5-$C_5H_5Fe(CO)_2R$ and a tertiary phosphine [24]. Kinetic study of the CO insertion was not feasible in the present case since the reaction proceeded too fast even at low temperature.

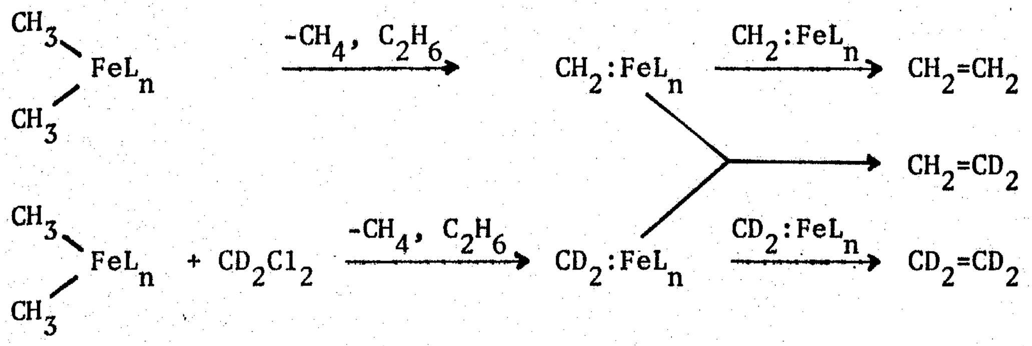
2. On thermal stability of the methyliron complex (I) and its decomposition pathways.

The dimethyliron complex (I) having the bidentate dpe ligands exhibits a pronounced thermal stability compared with the corresponding iron complex having triphenylphosphine ligands[3]. The much higher stability of methylbis(acetylacetonato)iron complex (V) having $PPhMe_2$ ligand than ethyl(acetylacetonato)iron complex having PPh_3 ligand [3] is also noted. The role of ligands such as tertiary phosphine, cyclopentadienyl, and CO for stabilization of a metal-carbon bond has been accounted for by Wilkinson [25] and other workers [26, 27] as a blocking agent to hinder the β-elimination to take place.

We have observed ourselves the effect of addition of tertiary phosphine ligands to hinder the occurrence of the β-elimination in $Co(C_2H_5)_2$-(acac)$(PPhMe_2)_2$ in solution [28]. However, the same reasoning cannot be applied to the discussion on the stability of methyl-transition metal complexes. Evidence supporting the occurrence of α-elimination from the methyl-transition metal complex is still scarce [29] but its importance is accquiring a growing attention in connection with olefin metathesis catalysts using transition metal halides and alkylating agents [30]. We present below some evidence supporting the α-elimination taking place. If the α-elimination process provides a low-energy pathway for decomposition of methyl-transition metal complexes the tertiary phosphine ligands may be regarded, at least partly, as playing the role of blocking agents to prevent the α-elimination. The enhanced thermal stability of the hexa-coordinated dimethyliron complex coordinated with the bidentate dpe ligands compared with the PPh_3-coordinated methyliron complex may be accounted for as such. The $PPhMe_2$ ligand in the hexa-coordinated complex $FeCH_3(acac)_2(PPhMe_2)$ may also play the role as the blocking agent, but other factors such as electronic influence of the ligands and the oxidation state of the iron complex may be also important.

Thermolysis of the solid sample of (I) liberates methane, ethane and ethylene (vide supra). Formation of methane may be accounted for by hydrogen abstraction by the methyl group in the process of homolysis of $Fe-CH_3$ bonds from the ligand (vide supra) or from the other methyl group and the formation of ethane may be explained as coupling of two methyl groups. By the term homolysis, however, we do not intend to suggest the formation of free methyl radicals, since some evidence against the free radical formation in the reductive elimination of dialkyl transition metal complexes are known [2]. The formation of ethylene may be accounted for either by decomposition of the dpe ligands or by coupling of a carbenoid species formed by an α-elimination of the methyl complex. Since the formation of ethylene was also observed in thermolysis of $Fe(CH_3)(acac)_2(PPhMe_2)$, which contains no dpe ligand and is decomposed at relatively low temperature (55 - 58°) and no gas was detected on thermolysis of $Ni(dpe)_2$ [31] at 240 - 245°, we regard the iron-bonded methyl group as the source of ethylene. The insolubility of (I) in organic solvents precluded the kinetic study to decide whether the α-elimination is a unimolecular or bimolecular process. The following study, however, concerning the decomposition of (I) in dichloroalkanes lends support to the assumption of a bimolecular process involving coupling of intermediate iron-carbenoid species.

When (I) was treated with CH_2Cl_2 at 20° the gas evolved contained a larger amount of ethylene and a lesser amount of methane than in thermolysis of (I) as shown in Table I. In order to confirm the source of ethylene (I) was treated with deuterated dichloromethane. The gas liberated on treatment of (I) with CD_2Cl_2 of 99 % isotopic purity consisted of CH_4, C_2H_6, C_2H_4, $CH_2{=}CD_2$, and $CD_2{=}CD_2$ in a ratio of 50/25/8/14/4 as confirmed by IR and mass spectroscopy. The amount of the evolved gas with correction for the part of the deuterated ethylene components accounts for ca. 90 % of the fate of the methyl groups in (I). From the reaction mixture an off-white powder of composition $FeCl_2$(dpe) was recovered. The absence of deuterated methane in the gaseous product produced on treatment of (I) with CD_2Cl_2 excludes the dichloromethane as the hydrogen source for giving methane, indicating that this is not a radical process. The formation of C_2D_4 in the reaction suggest an intermediacy of a carbenoid species formed by Cl_2-abstraction by the iron complex. Similar dehalogenation from gem-dihalides by transition metal complexes to produce olefins are known [32]. The exclusive formation of $CH_2{=}CD_2$ and the absence of other deuterated ethylenes and ethanes suggests the formation of a carbenoid species, $[CH_2{:}Fe]$, produced by the α-elimination from the iron methyl group and its self-coupling and cross-coupling with another carbenoid species, $[CD_2{:}Fe]$, formed by dehalogenation of CD_2Cl_2.



The insertion of the carbenoid entity into the Fe-CH_3 bond followed by β-elimination to afford $CH_2=CD_2$ seems unlikely because such a reaction would accompany the formation of a deuterated ethane which was not detected.

The nature of the "carbenoid" species assumed as the intermediate may be very different from that of a "free" carbene, since addition of olefins such as styrene, hexene-1 and cyclohexene to the reaction system of (I) with CH_2Cl_2 did not appreciably alter the gas composition nor the total amount of the gas produced as shown in Table I.

Complex (I) does not react with CCl_4 but attacks other dichloroalkanes and acts as a Cl_2-abstracting agent. Treatment of (I) with $ClCD_2CD_2Cl$ liberated CH_4, C_2H_6, C_2D_4 and $C_3H_3D_3$ in a ratio of 44/35/12/9 but no C_2H_4 was detected. The reactions of (I) with CH_3CHCl_2 and CH_3ClCH_2Cl produced mainly methane and minor amounts of C_2H_6 and C_3H_6.

Table 1

Run	Complex	Solvent	Temp.(day)	Composition of the evolved gas		
				CH_4	C_2H_6	C_2H_4 (%)
1	$Fe(CH_3)_2(dpe)_2$		130-135°	75	20	5
2	"	CH_2Cl_2	20° (1.5 days)	55	15	30
3	"	"	" (1 day)	50	24	26
4	"	" + styrene	" "	51	21	28
5	"	" + 1-hexene	" "	57	16	29
6	"	" + 	" "	55	16	27
7	"	CCl_4	" "	0	0	0
8	$Fe(CH_2{=}CH_2)(dpe)_2$	CH_2Cl_2	" "			100
9	$FeCH_3(acac)_2(PPhMe_2)$	-	55-58°	75	14	11
10	$Ni(CH_3)_2(dpe)$	-	130-131°	30.	57	13
11	$Ni(dpe)_2$	-	235-240°	0	0	0

Experimental

All manipulations were carried out under an atmosphere of oxgen-free nitrogen. Solvents were dried in usual manner, distilled and stored under nitrogen or argon. IR spectra were recorded on a Hitachi EPI-G3 spectrometer using KBr pellets prepared under an inert atmosphere. Microanalyses were carried out by Mr. T. Saito of our Research Laboratory. Geses evolved during the preparation of complexes and their chemical reactions were analysed by gas chromatography and/or mass spectrometry after collecting the gas by a Toepler pump, by which means the volume of the gas was also measured. Deuterated ethylenes were examined by observing the IR spectra of gas samples introduced into a gas cell of 4 cm path. This method proved useful in checking the presence of partially deuterated ethylenes [33].

Tris(acetylacetonato)iron, 1,2-bis(diphenylphosphino)ethane, (dpe) [ ], and dimethylphenylphosphine [34] were prepared according to the literature. The several chlorinated compounds were used as purchased from Tokyo Kasei Ltd. after dehydration. CD_2Cl_2 and CD_2ClCD_2Cl were used as purchased from Stohler Isotope Chemicals without further purification.

1. Preparation of $Fe(CH_3)_2(dpe)_2$ (I)

To an etheral suspension of $Fe(acac)_3$ (1 g, 2.8 mmol) and 2 molar equivalents of dpe (2.25 g), 6 molar equivalents of dimethylaluminum monoethoxide or trimethylaluminum were added at -30° with stirring. The temperature was gradually raised to 0° to give an orange to red microcrystalline powder deposited. The reddish orange crystals were filtered off and washed with ether and n-hexane several times below 0°, and dried in vacuo. Yield, 70 %. (Found; C, 73.8; H, 6.4. $C_{54}H_{54}FeP_4$ calcd.; C, 73.5; H, 6.1 %. IR(KBr): ν(C-H) of Fe-CH_3, 2905 and 2850 cm^{-1}, dpe(max); 3030, 1585, 1483, 1430, 1090, 875, 819, 745, and 700 cm^{-1}.

2. Preparation of $Fe(CH_3)(dpe)(Ph_2PCH_2CH_2PPh(C_6H_4))$ (II)

Complex (I) (1 g) was dissolved in toluene (10 ml) by warming slightly. The yellow to orange filtrate was separated by filtration, concentrated by evaporation, and cooled to -78° to produce orange crystals, which were washed with n-hexane at room temperature and dried in vacuo. Yield, 10 %. (Found: C, 72.9; H, 5.7. $C_{53}H_{50}FeP_4$ calcd., C, 73.5; H, 5.8.) d.p.: 160 - 170°. IR(KBr): new peaks which are not observed in (I), 1555 and 730 cm^{-1}. NMR (CD_2Cl_2, -20°) τ 10.8 (br, Fe-$C\underline{H}_3$, 3H),

τ 7.8 and 8.2 (br, dpe, 8H), τ 4.1 (br, 2H), τ 3.62 (br, 2H) (ortho-metalated phenyl group in dpe ligand), τ 2.5 - 3.4 (complex multiplet, 35H). Acidolysis of (II) with H_2SO_4 released methane. After acidolysis of (II) with D_2SO_4 the dpe ligand liberated was recovered by extraction with ether. The dpe thus obtained was oxidatively degradated with CuO to give carbon dioxide and water and the deuterium content in the water was determined by mass spectroscopy. The deuterium content in the water was 1.9 % compared with the calculated value of 3.2 % on the assumption that one phenyl group contains a deuterium per two dpe ligands.

3. Preparation of $FeH_2(dpe)_2$ (III) and $FeH_2(dpe)_2 \cdot C_6H_6$ (IV)

The similar reaction of $Fe(acac)_3$, dpe, and $AlEt_3$ or $Al(n\text{-}Pr)_3$ or $Al(iso\text{-}Bu)_3$ in ether under nitrogen at -5 to 0° gave yellow crystals which were separated by filtration and washed with ether and n-hexane. The yellow compound was recrystallized from benzene-n-hexane to give pure yellow crystals, $FeH_2(dpe)_2\ C_6H_6$ (IV), which were dried in vacuo. (Found: C, 75.0; H, 6.4. $C_{58}H_{56}FeP_4$ calcd.: C, 74.7; H, 6.0 %) IR(KBr): ν(Fe-H), 1840 cm^{-1}; dpe(max), 3030, 1585, 1478, 1430, 1095, 870, 809, 740, and 690 cm^{-1}.

4. Preparation of $Fe(CH_3)(acac)_2(PPhMe_2)$ (V)

To an etheral solution of $Fe(acac)_3$ (1.0 g, 2.8 mmol) and $PPhMe_2$ (1.4 ml, 11 mmol) dimethylaluminum monoethoxide (3 ml) was added at -30 to -40° under nitrogen. The reaction mixture turned to a deep red solution at -10° and on stirring the mixture for 2 h. at the temperature red crystals appeared.

The reaction mixture was cooled to -78° and red crystals deposited were filtered off, washed with ether and n-hexane at -78° and recrystallized from ether. Yield, 50 %. (II) is sensitive to air, thermally stable at room temperature under nitrogen and soluble in ether. (Found: C, 55.4; H, 7.9. $C_{19}H_{28}O_4PFe$ calcd.: C, 56.0; H, 6.9 %.) IR(KBr): ν(C-H) of Fe-CH_3, 2900, 2850 cm^{-1}; ν(Fe-C), 550 cm^{-1}; $PPhMe_2$, 3050, 1435, 925, 895, 740, 690, and 580 cm^{-1}; acac, 1570, 1510, 1390, 1270, 1050, and 790 cm^{-1}.

5. Reaction of (I) with D_2 and preparation of $FeD_2(dpe)_2 \cdot C_6H_6$ (VI).

Complex (I) (0.30 g, 0.34 mmol) was suspended in 5 ml of toluene and brought in contact at -10° with D_2 of an atmospheric pressure in a closed system. With the raise of temperature the reaction mixture changed from the initial orange suspension to a deep yellow solution, which was stirred further 1 day at room temperature. The gas evolved during the reaction was confirmed to be CH_3D. The solution on recrystallization from benzene-n-hexane gave 0.3 g of yellow crystals of composition $FeD_2(dpe)_2 \cdot C_6H_6$ (VI). Yield, 90 %. (Found: C, 74.0; H, 5.8; $C_{58}H_{56}FeP_4$ calcd.: C, 74.7; H, 6.0 %.) IR(KBr): ν(Fe-D), 1330 cm^{-1}.

6. Reaction of (I) with carbon dioxide

A dry CO_2 stream was bubbled through a pyridine suspension containing (I) at -10°. After the gradual temperature raise to 0° the reaction mixture changed from the initial orange-red suspension to a yellow solution and a yellow precipitate was deposited from the solution. The yellow solid (VII) was separated by filtration from the yellow solution, washed n-hexane at -10 to 0° and dried *in vacuo* below 0°. From the solution dpe ligand was recovered. Because of the instability of the yellow complex micro-analysis was not successful. IR(KBr): ν(OCO) of CH_3COO groups, 1610 and 1385 cm^{-1}; CO_2 (coordinated), 2650, 1670, 1420, 1340, and 850 cm^{-1}; pyridine (max), 1600, 1485, 1445, 1325, 1215, 1040, 765, and 705 cm^{-1}.

Thermolysis of (VI) at 150° released CO_2 and pyridine and treatment of (VII) in benzene with dry HCl gas liberated CO_2 and pyridine and treatment of (VII) in benzene with dry HCl gas liberated CO_2 and acetic acid as detected by gas chromatography.

Complex (VII) was prepared via another route by the reaction of $Fe(CH_3COO)_2(py)_n$ and CO_2 in pyridine and was identified by comparison of the IR spectra.

7. Reaction of (I) with PhC≡CH

To complex (I) (0.20 g, 0.25 mmol) suspended in toluene (5 ml) was added phenylacetylene(0.1 ml) at -30° by means of a syringe. The reaction mixture was stirred at 0° for 20 min. and then further for 4 h.

at room temperature. The orange suspension turned to a brown solution evolving CH_4 (0.2 mmol) and small amounts of C_2H_4 and C_2H_6. The amount of gas formed accounted for about 40 % of the calculated value for (I). On addition of n-hexane to the brown solution and subsequent cooling brown crystals were deposited, which were washed with n-hexane after filtration and dried <u>in vacuo</u>. Yield, 45 %. (Found: C, 75.2; H, 5.8. $C_{60}H_{53}FeP_4$ calcd.: C, 75.5; H, 5.6 %.) IR(KBr): ν(C≡C), 2035 cm^{-1}, ν (Fe-H), 1850 cm^{-1}; ν(Fe-C), 560 cm^{-1}; dpe(max), 3050, 1480, 1435, 1090 and 690 cm^{-1}.

8. Reactions of (I) and (V) with carbon monoxide

a) A dry CO stream was bubbled through a toluene solution containing (I) (0.28 g, 0.32 mmol) at room temperature for 0.5 h. After bubbling of CO the system was closed under CO and was further stirred at room temperature for 1 day. The system changed from an orange suspension to a yellow solution. The amount of acetone formed in the reaction mixture was determined by VPC as 30 % per iron. An iron carbonyl compound was recovered from the resultant solution as yellow crystals. (Found: C, 70.8; H, 5.5. $C_{54}H_{48}O_2FeP_4$ calcd.: C, 71.4; H, 5.3 %). IR(KBr): ν(CO), 1985, 1915 (sh), 1895, and 1835 cm^{-1}; dpe, 3060, 1588, 1490, 1440, 1090, 740, and 698 cm^{-1}.

b) Complex (V) was dissolved in 2 ml of toluene and brought in contact with carbon monoxide of an atmospheric pressure at -70° in a closed system. At the temperature the color of the system changed from red to green. This color change took place reversibly. With rising the temperature the green solution changed to a brownish yellow solution. At room temperature the system was stirred for 3 h. The amount of acetone formed in the reaction solution was determined by VPC as 90 %. From the resultant solution an oragne to brown complex Fe(acac)$_2$ was obtained. Its IR spectrum shows the presence of only acetylacetonato ligands [3]. IR(KBr): acac(max), 1575, 1525, 1360, 1275, 1020, and 930 cm^{-1}.

9. Reactions of (I) with a few vinyl compounds.

Acrylonitrile (2 g) was distilled into a flask containing complex (I) (0.1 g) in vacuum. As soon as the temperature was raised to 0° polymerization of acrylonitrile took place suddenly and poly(acrylonitrile) was obtained in 80 % yield. No reaction of (I) with styrene was observed.

10. Thermolysis and CH_2Cl_2 treatment of (I)

On thermolysis of (I) (0.18 g, 0.21 mmol) in the solid state at 130 - 135° CH_4 (4.2 ml STP), C_2H_6 (1.3 ml) and C_2H_4 (0.3 ml) were evolved. The total amount of gas liberated was equivalent to 75 % of the methyl groups bonded to iron. Table 1 shows the composition of gases evolved on treatment of (I) with CH_2Cl_2. A typical procedure is described below. CH_2Cl_2 (1 ml) was added to complex (I) (0.15 g, 0.17 mmol) by a trap-to-trap distillation using a vacuum line and the reaction mixture was stirred at room temperature for 1 day. The initial orange suspension turned to a dark red solution and a white precipitate was deposited. The gas evolved in the process was examined by means of mass spectroscopy and VPC. Using CD_2Cl_2 (isotopic purity 99 %) a similar treatment of (I) (0.23 g, 0.27 mmol) was carried out under the same conditions and the gas composition was determined. CH_4, C_2H_6, $CH_2{=}CH_2$, $CH_2{=}CD_2$, $CD_2{=}CD_2$ in a ratio of 50/24/8/14/4 were produced.

Neither cis- or trans-CHD=CHD nor CH_3D or CD_2HCH_3 was detected. From the resultant solution free dpe ligand and an off-white compound with an approximate composition of $FeCl_2$(dpe) were recovered. (Found: C, 61.1; H, 5.2; Cl, 12.5. $C_{26}H_{24}Cl_2FeP_4$ calcd.: C, 59.51; H, 4.6; Cl 13.5 %.)

11. Treatment of (I) with several chlorinated compounds

Treatment of (I) with several chlorinated compounds such as CD_2ClCD_2Cl, CH_2ClCH_2Cl, $CH_3CHClCH_2Cl$, and CH_3CHCl_2 were carried out similarly to that of (I) with CH_2Cl_2 as described above.

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Chapter IV NMR STUDIES OF DYNAMIC BEHAVIOR OF DIALKYL-COBALT(III) COMPLEXES IN SOLUTION

Introduction

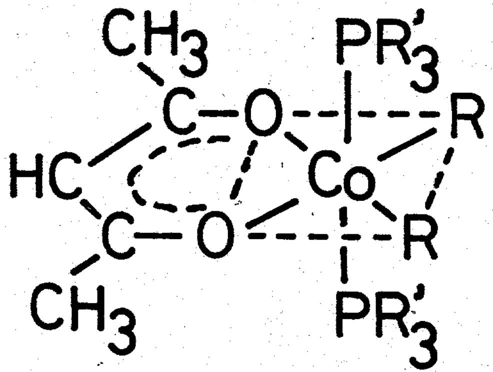
In the previous paper we have reported the preparation and a brief description of NMR spectra of a series of cis-dialkyl(acetylacetonato)-bis(tertiary phosphine)cobalt(III) complexes (I)-(IV) having the structure as shown below[1]. Since most of these alkylcobalt complexes are thermally stable, insensitive to air, and soluble in many organic solvents, they provide 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 accommodating a vacant site for a decomposition pathway is desirable for understanding the mechanism of thermolysis of these alkyltransition metal complexes as will be discussed in the ensuing paper. The importance of partial dissociation of the ligand from a coordinatively saturated complex providing 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

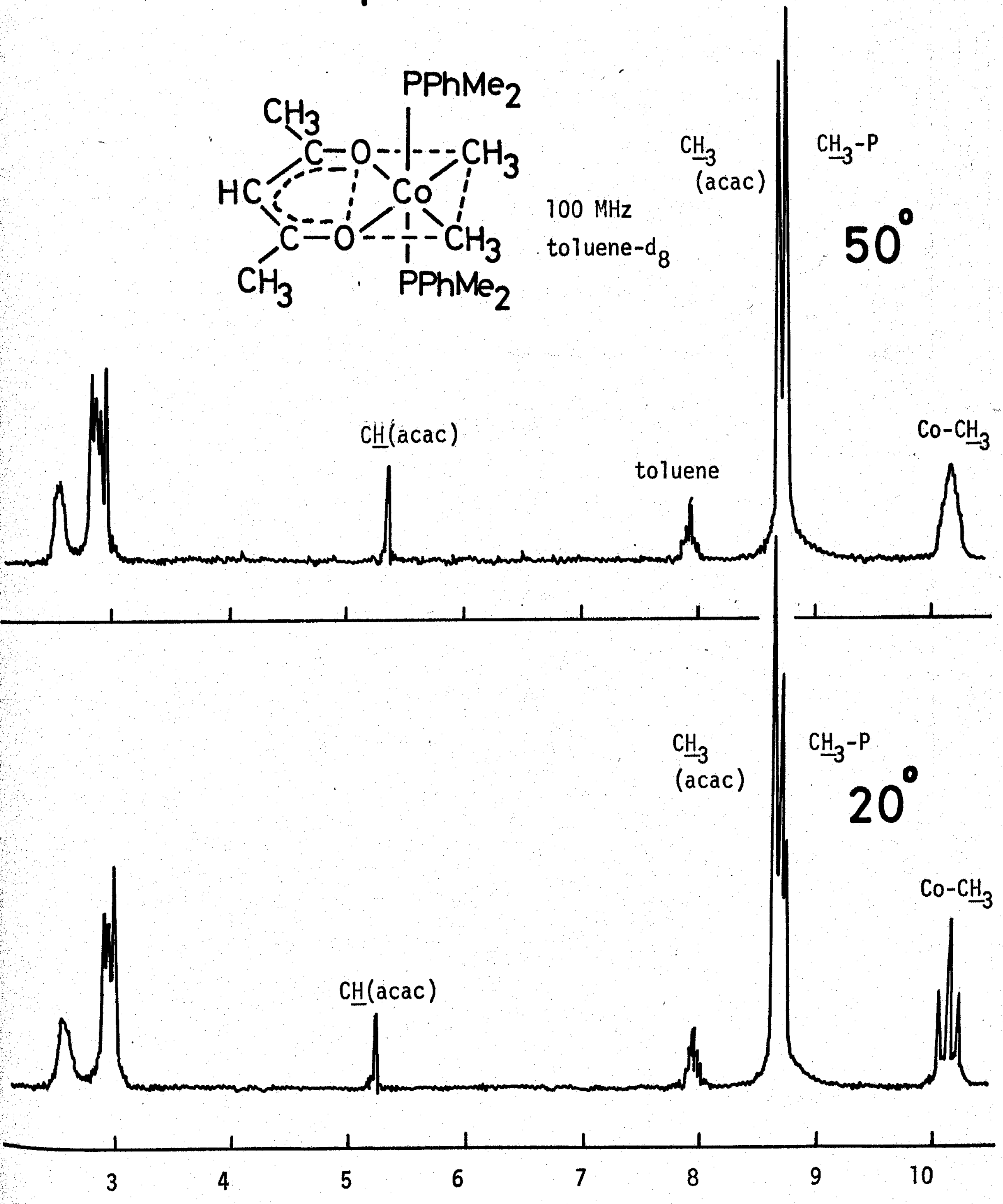
The NMR spectra of the dialkylcobalt complexes (I)-(IV) are compatible with the octahedral structure with two cobalt-bonded alkyl groups and an acetylacetonato ligand coplanar with cobalt which is coordinated with two tertiary phosphine ligands in the axial positions. Fig. 1 shows representative spectra of $Co(CH_3)_2(acac)(PPhMe_2)_2$ (II_a) in toluene at various temperatures. The methyl groups bonded with cobalt

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



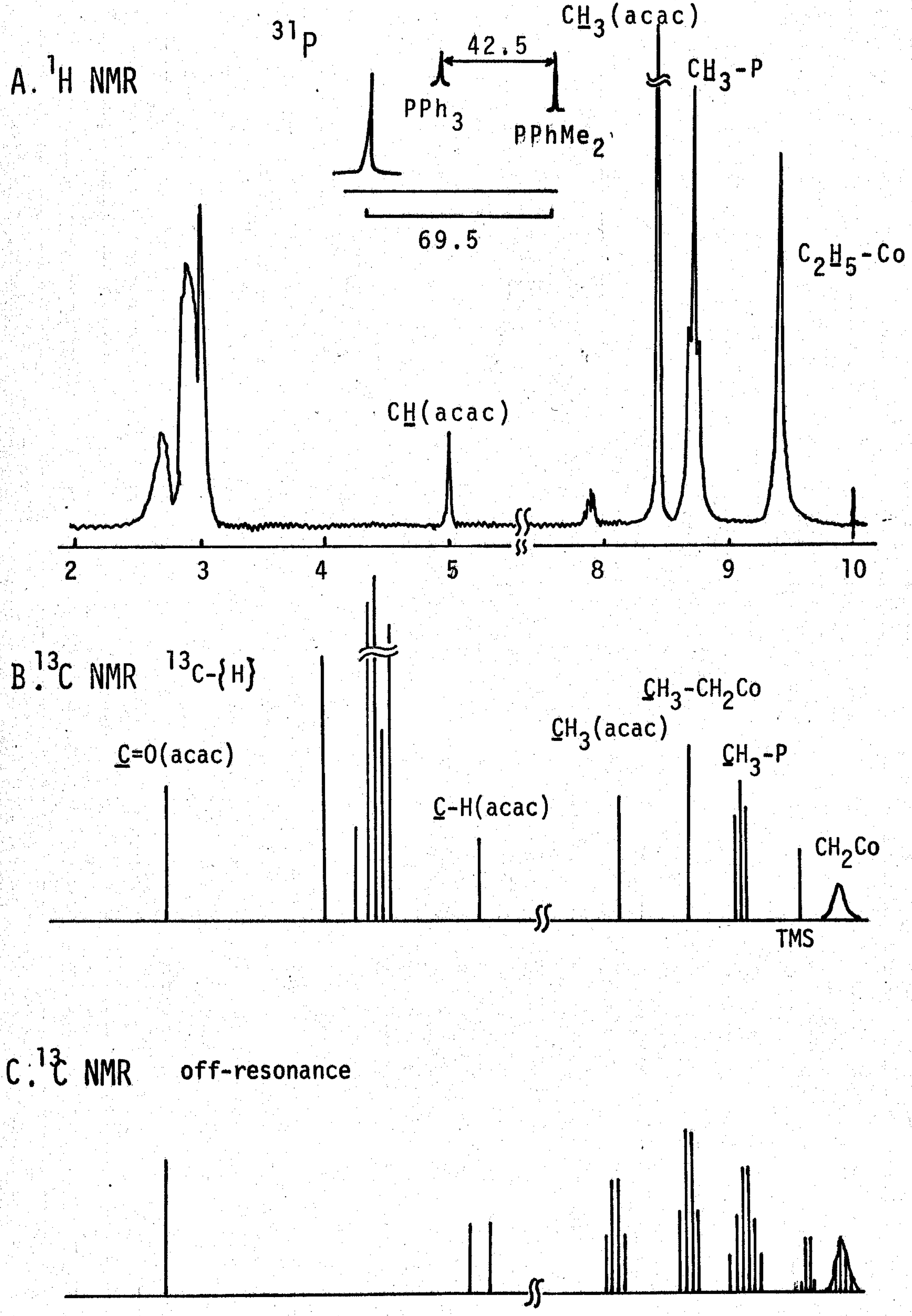
	R	PR'_3
I	= Me	= PEt_3
II_a	= Me	= $PPhMe_2$
II_b	= Et	= "
II_c	= n-Pr	= "
II_d	= i-Bu	= "
III	= Me	= PPh_2Me
IV	= Me	= $P(n\text{-}Bu)_3$

^{1}H-NMR spectra of



appear as a triplet below 35° due to coupling with two phosphine ligands in axial positions ($^3J(P-H) = 8Hz$) at τ 10.16. Other complexes (I)-(IV) show similar $^3J(P-H)$ values of 4-8 Hz as observed in various methyl-transition metal complexes having tertiary phosphines at <u>cis</u> positions from the methyl group. With temperature increase the triplet coalesces to a singlet indicating dissociation of the phosphine ligands from the complex. The methyl resonance of the $PPhMe_2$ ligands in (II_a) appears as a triplet ($J(P-H) = 3Hz$) by virtual coupling with two hosphorus nuclei in mutually <u>trans</u> positions, although the spectrum is somewhat obscured by the methyl resonance of the acetylacetonato ligand. The triplet also coalesces to a singlet on raising the temperature.

Fig. 2 shows the ^1H and ^{13}C spectra of the ethyl complex (II_b). The proton methyl resonance of the $PPhMe_2$ ligands appears as a triplet at a higher field than that of the corresponding methyl complex II_a clearly separated from the CH_3 resonance of the acetylacetonato ligand. The shift to the higher field may be caused by increase of the electron density on cobalt by substitution of the methyl groups by more electron releasing ethyl groups. A similar behaviour was observed with the resonance of acac ligand. The methyl resonance of the acac ligand is also shifted to a higher field than that of (II_a) but the effect is smaller than for the $PPhMe_2$ ligands which are directly bonded with 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 the chemical shifts of the methyl and methylene protons in the ethyl groups. The splitting due to the phosphine ligands may be included in the envelope of the signal. In order to confirm the


A. ^{1}H NMR
^{31}P
42.5
PPh$_3$
PPhMe$_2$
69.5
C$\underline{H}_3$(acac)
C$\underline{H}_3$-P
C$_2\underline{H}_5$-Co
C$\underline{H}$(acac)
2
3
4
5
8
9
10
B. ^{13}C NMR ^{13}C-{H}
$\underline{C}$=O(acac)
$\underline{C}$-H(acac)
$\underline{C}$H$_3$(acac)
$\underline{C}$H$_3$-CH$_2$Co
$\underline{C}$H$_3$-P
CH$_2$Co
TMS
C. ^{13}C NMR off-resonance

coincidence of the proton chemical shifts of the methyl and methylene groups ^{13}C NMR of (II_b) in a mixture of C_6H_5Br and C_6D_6 was observed at -20° and compared with those of $Co(CH_3)_2(acac)(PPhMe_2)_2$ and $Ni(C_2H_5)$-(acac)(PPh_3) [4]. The ^{13}C NMR spectrum of (II_b) 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 a higher field than the methyl resonance because of the shielding effect of cobalt. The broadening may be caused by coupling with phosphorus atoms and possibily with Co (I = 7/2) nucleus. The assignments of other resonances are included in Fig. 3b and Table 1, which also includes the resonances of II_a and NiEt(acac)(PPh_3) [4]. The ^{13}C NMR signal of the methyl groups in $PPhMe_2$ ligands are observed as a triplet due to the virtual coupling (J(P-C) = 9.2Hz). In order to further substantiate the assignments an off-resonance spectrum of (II_b) was recorded (Fig. 2c). The peaks in Fig. 2c show the expected splitting 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 coupling with Co (I = 7/2). These results reveal that the somewhat broad singlet of the cobalt-bonded ethyl groups in the ^{1}H NMR spectrum of (II_b) is clearly due to the very small difference between the chemical shifts of the methyl and methylene groups. It is also noted that the methylene signal in the ^{13}C NMR of II_b appears at a considerably higher field than that in $Ni(C_2H_5)$(acac)-

^{13}C Chemical Shifts of $CoR_2(acac)(PPhMe_2)_2$

	$Co(C_2H_5)_2(acac)(PPhMe_2)_2$ (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 26.8
-R (Co-R)	16.3 -4.3	(c)	13.9 6.8
$-CH_3$ ($PPhMe_2$)	9.3 (t)	8.7 (t)	

(a): in $C_6H_5Br-C_6D_6$, at -20° ; TMS standard. (b): reference (4). (c): No signal was observed because of broadening due to coupling with protons, ^{31}P, cobalt metal $(I=\frac{7}{2})$.

(PPh_3), presumably reflecting higher electron density on cobalt in (II_b) owing to the coordination of more electron releasing $PPhMe_2$ ligands in (II_b) than in $Ni(C_2H_5)(acac)(PPh_3)$ having more electron-attracting ligand, PPh_3.

The ^1H NMR spectrum of the propyl complex II_c also shows the cobalt-bonded methylene resonance at higher field (τ 9.64) than the β-methylene and γ-methyl groups which are observed at τ 8.84 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 $Co(CH_2CD_3)(acac)(PPhMe_2)_2$ [5] was observed. It clearly shows the triplet ($^3J(P\text{-}H)$ = 10Hz) at -20° in toluene due to the coupling with two phosphorus nuclei at axial positions. 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 each other but not completely coincide.

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) and they exchange each other.

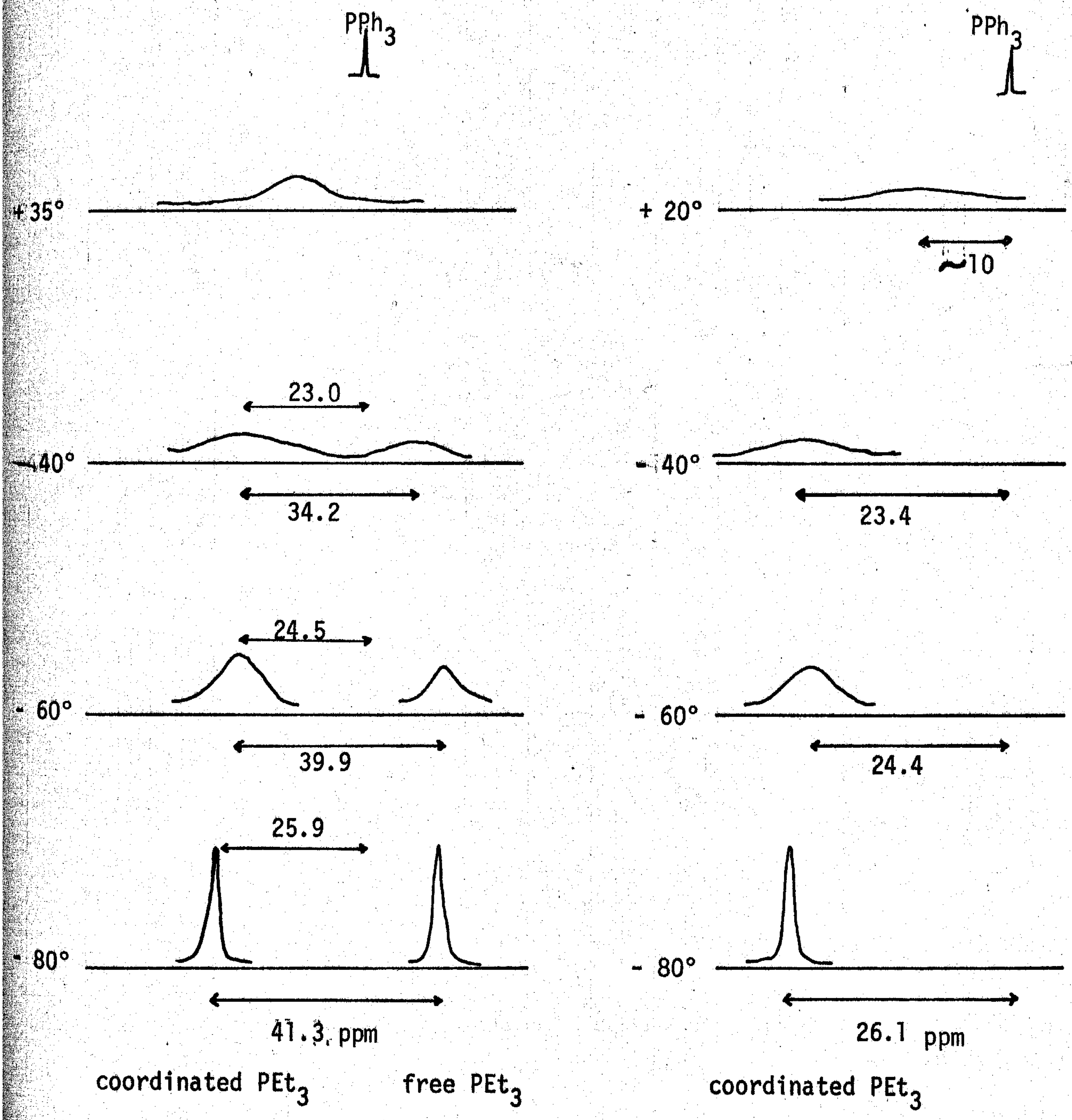
$$CoR_2(acac)(PR_3')_2 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoR_2(acac)(PR_3')\cdot S + PR_3' \qquad (1)$$

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), (II_a), and (IV)) decreases in the order of $PPhMe_2 > PEt_3 > P(n\text{-}Bu)_3$. 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. Fig. 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 added PEt_3. In the absence of the added PEt_3 a somewhat broad singlet of the coordinated PEt_3 ligands is observed at 26 ppm downfield from external reference of triphenylphosphine at -80°. On raising the temperature the singlet becomes broader and shifts to higher field simultaneously. The broadness of the singlet at -80° suggests that the complex is slightly dissociated even at -80° and a slow exchange reaction between the coordinated and liberated phosphine ligands are taking place. In the presence of the about equimolar amount of the added phosphine two broad singlets of about equal peak area are observed at 26 ppm and -15.4 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 two resonances approach each other with simultaneous broadening. A crude analysis of the shapes of the resonances in the presence and absence of the added

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



PEt_3 suggests that addition of triethylphosphine to the system does not markedly affect the exchange rate between the coordinated and free ligands.

In the presence of about equimolar amount of added triethylphosphine to the solution containing (II_a), broad ^{31}P NMR signals of the coordinated $PPhMe_2$ and free PEt_3 are observed at -70°. On raising the temperature to -40° they coalesce to a broad singlet indicating the exchange occurring between the coordinated $PPhMe_2$ and added PEt_3 ligands. Approximate rate constants for the liberation of the coordinated $PPhMe_2$ from (II_a) or (II_b) were estimated by measuring the half widths of the ^{31}P NMR signals and the rate constant for dissociation of $PPhMe_2$ at -40° thus estimated was $(2.6 \pm 0.2) \times 10^2$ sec^{-1}. The approximate activation energies of the ligand dissociation for (II_a) and (II_b) were estimated as 10 ± 3 kcal/mol and 8 ± 3 kcal/mol, respectively.

From observation of the mean chemical shift value of the exchanging system in the absence of an added phosphine one can estimate the equilibrium constant K for Eq. (1) if each chemical shift value of $CoR_2(acac)(PR_3')_2$ and $CoR_2(acac)(PR_3')\cdot S$ is known. Thus we estimated the equilibrium constants for the following equilibrium 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

Table 2 Equilibrium Constants and thermodynamic Parameters for the Reaction:

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

temp.	$10^3/T$	$10^4K^{a)}$
-72°	4.98	0.46
-54°	4.57	1.02
-48°	4.44	1.25
-35°	4.20	1.99

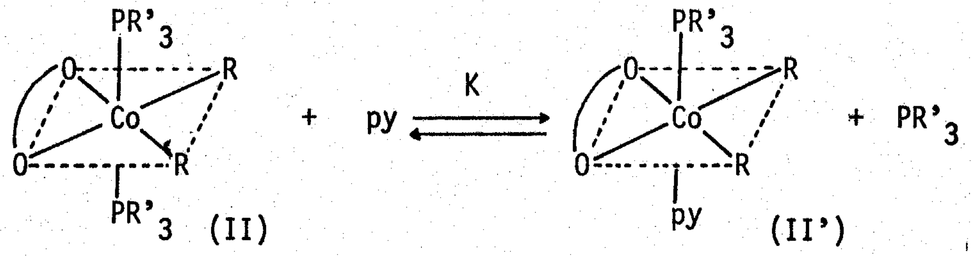
a): solvent = toluene , [IIb] = 0.10 mol/l

K_{288}	ΔH°(kcal/mol)	ΔG°(kcal/mol)	ΔS°(e.u.)
9.6×10^{-4}	4.2 ± 0.3	4.0 ± 0.2	0 ± 2

and thermodynamic parameters for the above equilibrium. For illustration of the degree of the dissociation of II_b in toluene the K value of 9.6×10^{-4} at 15° with the concentration of 0.10 M means that 24 ± 2 % of II_b is dissociated in toluene.

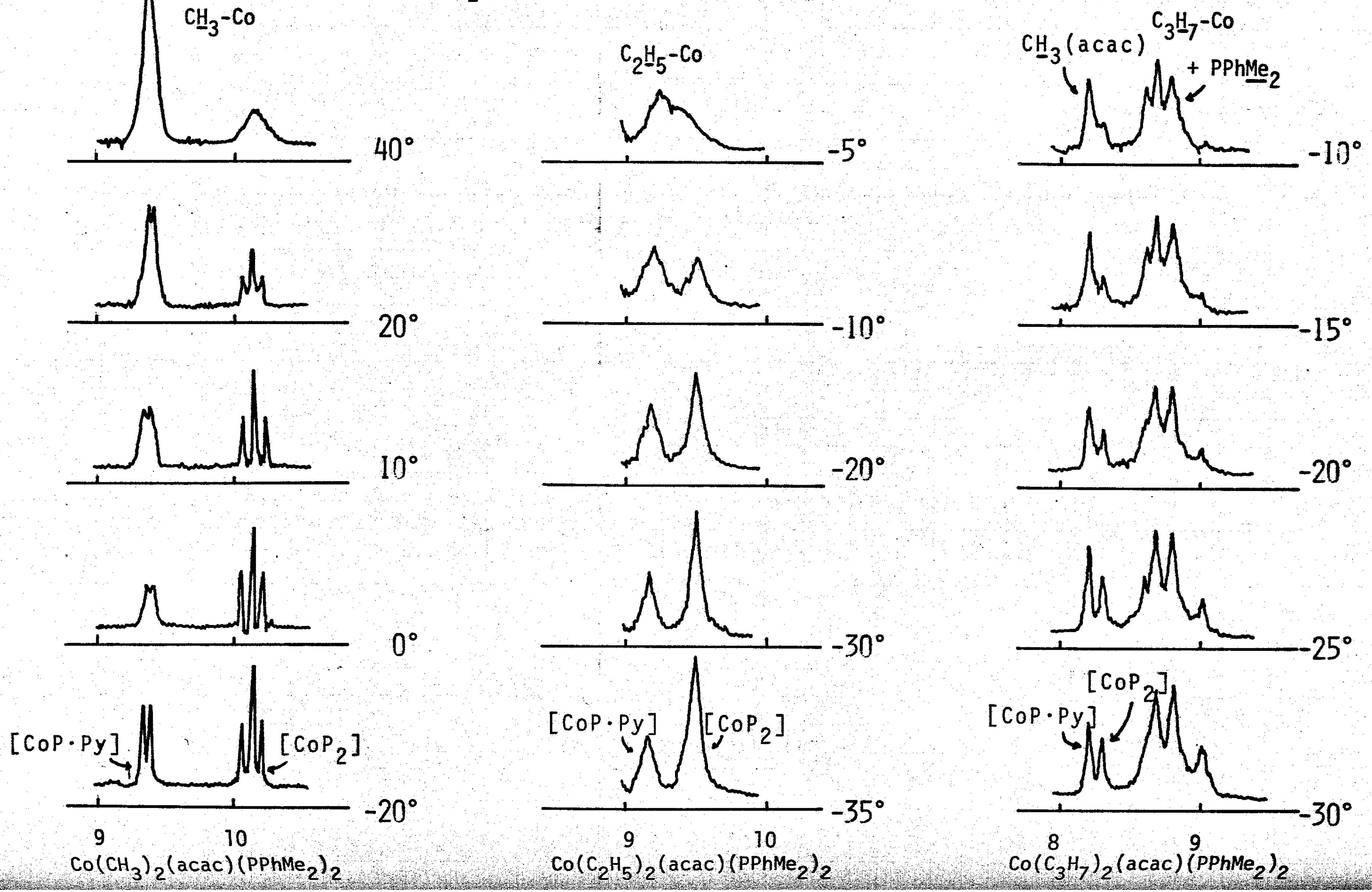
Displacement of the tertiary phosphine ligands by pyridine bases from the alkylcobalt complexes

As we have previously observed [1], the tertiary phosphine ligand(s) in the alkylcobalt complexes (I)-(IV) can be readily displaced by pyridine and its analogs. More basic tertiary phosphines such as PEt_3 and $P(n\text{-}Bu)_3$ can be displaced more readily by pyridine bases such as pyridine (py), γ-picoline (γ-pi) and 2,2'-bipyridine (bipy) than alkylcobalt complexes containing less basic phosphines such as $PPhMe_2$. In the cases of trialkylphosphine-coordinated alkylcobalt complexes a part or all of the tertiary phosphines are displaced by pyridines and the alkylcobalt complexes containing the pyridine bases such as $CoMe_2(acac)(PEt_3)(py)$ (V_a), $CoMe_2(acac)(PEt_3)(\gamma\text{-Pi})$ (V_b), and $CoMe_2(acac)(bipy)$ (VI) were actually isolated. Failure of isolation of α- and β-picoline-coordinated complexes may be an indication that a steric factor has a considerable contribution in the following equilibrium:



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 a 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 the tertiary phosphine. Fig. 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 the 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 resonance of $CoEt_2(acac)(PPhMe_2)_2$ (II_b) and $Co(n\text{-}Pr)_2(acac)(PPhMe_2)_2$ (II_c) in pyridine on raising the temperature. The signal of the ethyl groups of (II_b) appears as a singlet at -35° in pyridine as in toluene, but a broad singlet which may be assigned to the methyl groups of ethyl groups in $CoEt_2(acac)(PPhMe_2)$-(py) (II_b') develops on increasing the temperature to -20°. Further increase of the temperature causes overlapping of the broad singlet and the singlet due to the complex II_b to a broad singlet at -5°. Finally at 10° the ethyl signal of (II_b) completely vanishes and a triplet at τ 9.2 ($^3J(P\text{-}H)=7Hz$) which may be due to the methyl protons of ethyl groups in $CoEt_2(acac)(PPhMe_2)(py)(II_b')$ dominates. The signal of the methylene protons in (II_b) is observed at τ 8.7 being obscured on the slope of the methyl resonance of $PPhMe_2$. The signal of n-propyl groups of (II_c) are observed at τ ca. 8.5 - 9.3 being overlapped with $PPhMe_2$ ligands. The methyl resonances of acac ligand of (II_c) in pyridine appear as two singlets at τ 8.42 and τ 8.54. A singlet at τ 8.42 which may be assigned to the methyl groups of acac ligand in $Co(n\text{-}Pr)_2(acac)$-$(PPhMe_2)(py)(II'_c)$ develops on increasing the temperature (Fig. 4c).

Fig.4 $\underset{[\mathrm{CoP_2}]}{\mathrm{CoR_2(acac)(PPhMe_2)_2}} + \text{Pyridine} \xrightleftharpoons{K} \underset{[\mathrm{CoP\cdot Py}]}{\mathrm{CoR_2(acac)(PPhMe_2)(Py)}} + \mathrm{PPhMe_2}$



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 electronegativety of the entity bonded with the ethyl group [6], appearance of the methyl and methylene resonances in (II_b') on displacement of one of the $PPhMe_2$ ligands in (II_b) by pyridine suggests that the electronegativity of the entity bonded with the ethyl was increased by coordination with pyridine. This fact implies that pyridine is in fact playing the role of π-acid 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 $CoR_2(acac)(PPhMe_2)_2$ and $CoR_2(acac)(PPhMe_2)(py)$ as shown in Fig. 4 we have calculated the equilibrium constants

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

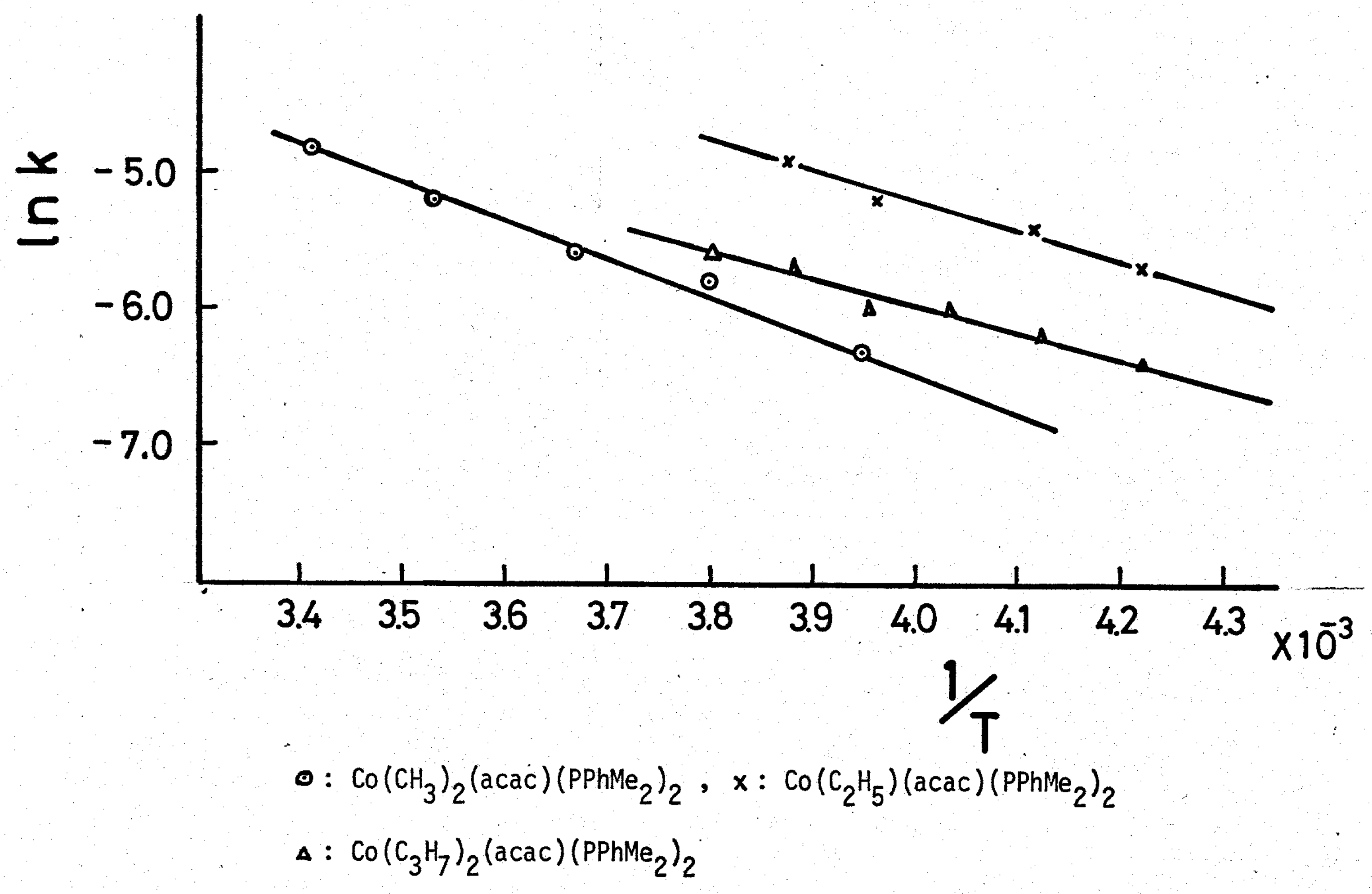
for a series of dialkylcobalt complexes and plotted the ln K values vs the reciprocal temperatures in Fig. 5. The equilibrium constants and thermodynamic parameters are summarized in Table 3. It can be seen from Table 3 that increase in the alkyl chain length makes the enthalpy change for Eq. (3) more favorable but the effect is compensated by the entropy change. For illustration of the degree of dissociation of (II_b) in pyridine the K value of 0.018 at 15° with the concentration of 0.11 M

Thermodynamic Parameters for

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

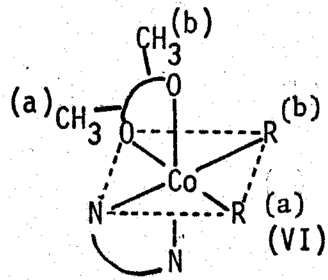
R	$10^3 K_{263}$	$\Delta H°$ (kcal/mol)	$\Delta G°$ (kcal/mol)	$\Delta S°$ (e.u.)
CH_3	4.5	5.5	2.8	10.3
C_2H_5	8.4	4.6	2.5	8.0
C_3H_7	4.0	4.1	2.9	4.6

Fig.5 $CoR_2(acac)(PPhMe_2)_2 + pyridine \overset{K}{\rightleftarrows} CoR_2(acac)(PPhMe_2)(py) + PPhMe_2$

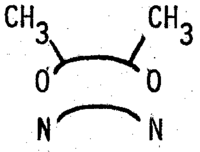


means that 70 ± 2 % of (II_b) is dissociated in pyridine whereas the degree of dissociation of (II_a) in pyridine at the same temperature is 45 ± 2 %.

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 (V_a) and γ-picoline-coordinated complex (V_b) show the spectra which can be accounted for by assuming the configuration having cis-dimethyl groups and an acetylacetonato ligand coplanar with cobalt coordinated with PEt_3 and pyridine or γ-picoline in axial positions. The cobalt-bonded methyl groups give rise to a doublet due to coupling with PEt_3 and the methyl groups in the acetylacetonato ligand are equivalent. It is noted that the α-protons in the coordinated pyridine and γ-picoline are very much deshielded. In the bipyridine-coordinated dimethylcobalt complex both cobalt-bonded and acac-CH_3 groups are observed as non-equivalent singlets, supporting the cis-configuration (VI) shown below;



(VI)



= acac ligand

= bipyridine

VIa , R= Me

VIb , R= Et

The bipy-coordinated ethyl complex shows two sets of resonances due to 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-attracting property of the bipyridine ligand as a π-acid. Since the dimethylcobalt and diethylcobalt complexes show two methyl and two sets of the ethyl

Table 4. ^{1}H NMR data for the base-coordinated complexes

complex	solvent	Co-R	acac		others
			CH_3	CH	
$Co(CH_3)_2(acac)(PEt_3)(py)$ (V_a)	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)
$Co(CH_3)_2(acac)(PEt_3)$(γ-pi) (V_b)	"	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)
$Co(CH_3)_2(acac)(bipy)$ (VI_a)	CD_2Cl_2	9.60(s,3H)^a 8.55(s,3H)^b	8.15(s,3H)^b 8.31(s,3H)^a	4.90(s,1H)	bipy: 1.48-2.85 (unresolved)
$Co(C_2H_5)_2(acac)(bipy)$ (VI_b)	"	10.20(t,3H)^a,8.85(q,2H)^a 9.27(t,3H)^b,7.55(q,2H)^b	8.15(s,3H)^b 8.37(s,3H)^a	4.90(s,1H)	bipy: 1.60-2.85 (unresolved)

For symbols a and b see the previous illustration of structure (VI)

For avoiding the overlap of the TMS signal with that of cobalt bonded alkyl groups, no interna TMS was used. Instead, the light toluene or CH_2Cl_2 were used as the internal standerd.

Abbreviation: s, singlet; d, doublet; t, triplet; q, quartet.

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 group in trans position from one of the oxygens of the acetylacetonato ligand will appear at approximately same field as in the pyridine-coördinated complex (V_a) 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 (VI_a) is then ascribed to the methyl group in trans position from the nitrogen of the bipyridine ligand. The two sets of ethyl resonances are assigned in a similar manner. The set of ethyl resonance at higher field is assigned to the ethyl group at trans position from one oxygen atom of the acac ligand and the other set at lower field to the ethyl group at trans position from the nitrogen atom of the bipyridine ligand. The assignment is consistent with our assumption of regarding pyridine analogs as π-acids. Extension of similar argument leads to a tentative assignment of the lower field methyl signal of the acac ligand to $CH_3^{(a)}$ and the higher one to $CH_3^{(b)}$ as labelled in the illustrated structure of (VI). Table 5 shows the chemical shift differences between resonances of the CH_3 and CH_2 groups in Complex II_b, II_b' and VI_b. The difference between $\tau(CH_3)$ and $\tau(CH_2)$ in the spectra of these complexes increases with increasing by replacement of the phosphine ligands in (II_b) by pyridine and bipyridine, the latter exerting the more pronounced effect particularly when it is at the trans position from the ethyl group. This result suggests that the π-acidity of the ligands increases in the order of $PPhMe_2 <$ pyridine $<$ bipyridine (vide supra).

Table 5 Chemical shift differences between $\tau(CH_3)$ and $\tau(CH_2)$

Complex	solvent	chemical shift		
		CH_2	CH_3	$\Delta(CH_3\text{-}CH_2)$
$Co(C_2H_5)_2(acac)(PPhMe_2)_2$ (II_b)	pyridine	9.50(s)	9.50(s)	~0
$Co(C_2H_5)_2(acac)(PPhMe_2)(py)$ (II_b')	"	8.70(m)	9.34(t)	0.64
$Co(C_2H_5)_2(acac)(bipy)$	CD_2Cl_2	8.85(q)	10.20(t)	1.35^a
(VI_b)		7.55(q)	9.27(t)	1.72^b

a and b For assignments see the illustration of the structure of (VI_b)

We consider next the exchange of the coordinated pyridine in $CoMe_2(acac)(PEt_3)(py)$ (V_a) with free pyridine. Table 6 shows the temperature dependence of the ^1H NMR spectrum of (V_a) in toluene. The spectrum at -40° shows the doublet at τ 9.26 which is assigned to the cobalt bonded methyl group coupled with PEt_3 ligand, and α-, β- and γ-protons of the coordinated pyridine at τ 1.22, 3.50 and 3.25 respectively. The fact that the α-protons appear at particularly low field is noticeable. On raising the temperature the doublet of cobalt-bonded methyl groups collapses to a singlet at 20° 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 each other. The result seems to indicate that exchange of the coordinated pyridine is also taking place.

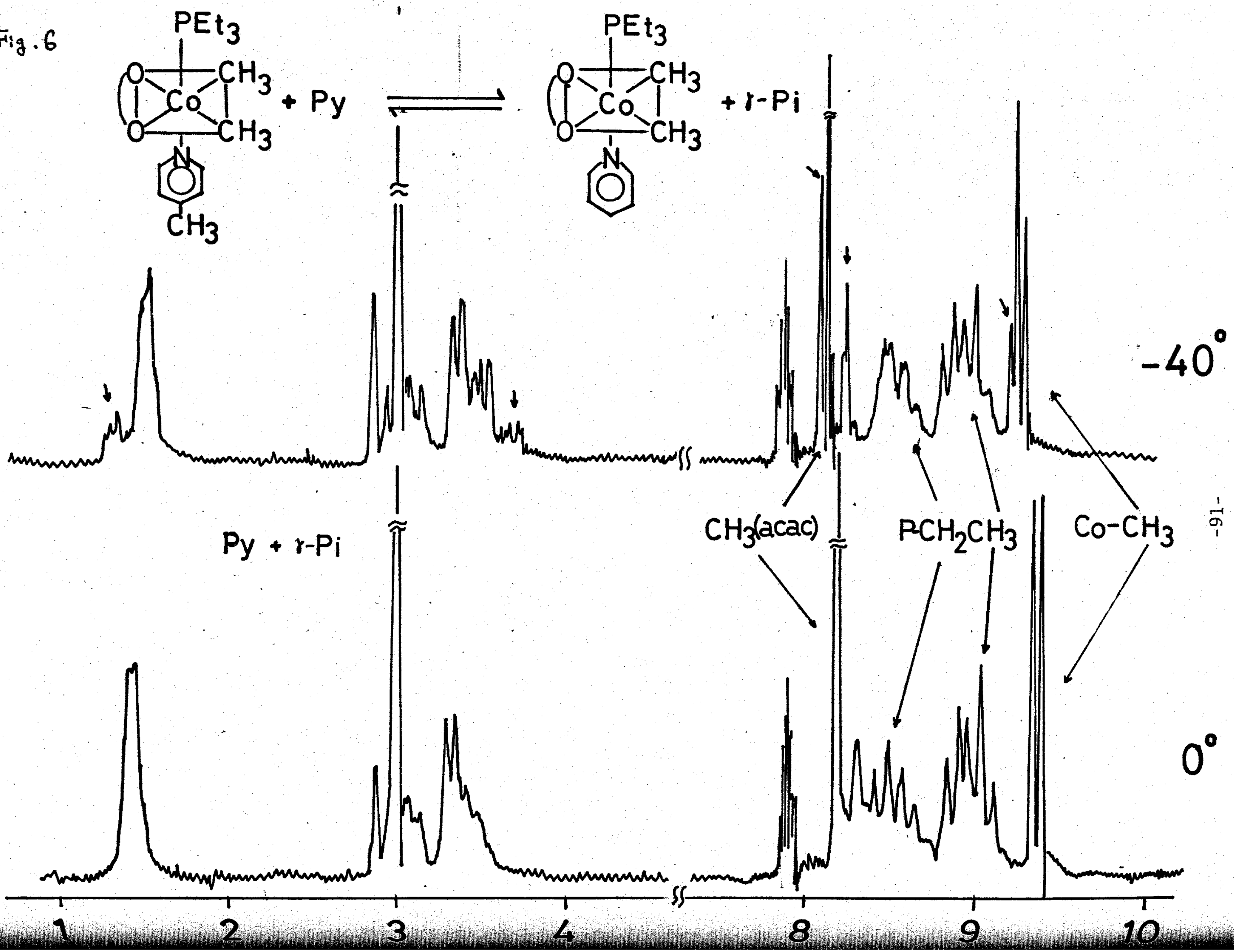
For further clarifying the exchange of the coordinated pyridine we examined the temperature change of the γ-picoline-coordinated complex (V_b) in toluene in the presence of an added excess amount of pyridine as shown in Fig. 6. The spectrum at -40° shows the peaks due to the coordinated γ-picoline as marked with small arrows in Fig. 6. On raising the temperature to 0° the peaks of the coordinated pyridine and γ-picoline coalesce indicating that the coordinated γ-picoline exchanges rapidly with pyridine at 0° where the exchange of the phosphine ligand is slow. On further increase of the temperature to 70° in pyridine the sharp singlet due to the cobalt-bonded methyl group in (I) starts again broadening. The effect may be accounted for by displacement of the remaining PE_3 by pyridine as shown in Eq.(4). Attempts to isolate a

Table 6 The temperature dependence of the chemical shifts of Co$(CH_3)_2$(acac)(PEt_3)(py) in toluene

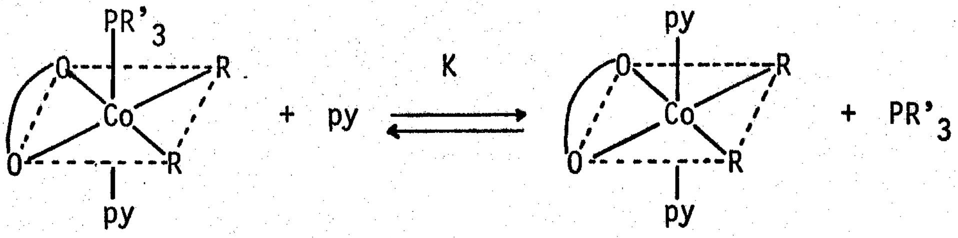
		acac		pyridine		
temp.	$C\underline{H}_3$-Co	CH_3(6H)	CH(1H)	α-H(2H)	β-H(2H)	γ-H(1H)
40°	9.47(s)	8.24(s)	5.08(s)	0.15(br)	3.26(t)	3.49(t)
20°	9.44(br.s)	8.23(s)	5.08(s)	0.70(br)	3.36(br.s)	
0°	9.36(d)	8.20(s)	5.08(s)	1.30(br)	3.38(br.m)	
-20°	9.30(d)	8.18(s)	5.08(s)	1.28(br.d)	3.49(t)	3.25(t)
-40°	9.26(d)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

Abbreviation: S, singlet; d, doublet; t,triplet; br.s, broad singlet; br.m; broad multiplet

Fig. 6


PEt3
CH3
Co
CH3
N
CH3
+ Py
PEt3
CH3
Co
CH3
N
+ γ-Pi
-40°
Py + γ-Pi
CH3(acac)
P-CH2CH3
Co-CH3
0°
1
2
3
4
8
9
10

bis-pyridine coordinated complex failed, but bipy-coordinated complex was readily obtained.



We have neglected so far the discussion concerning the exchange of the acetylacetonato ligand. The ^1H methyl peak of the acac ligand in every alkylcobalt complex (I)-(V) is observed as a sharp singlet, whose width does not vary on temperature change over a wide range (-78 to 20°). Although it is likely that the acac ligand is not exchanging on NMR time scale, the possibility that the methyl groups in the acac ligand is rapidly exchanging even at low temperatures can not 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, eleminates 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 [7]. It should be added further that the latter complexes undergo rapid disproportionation reaction giving $Ni(acac)_2$ and a PPh_3-coordinated Ni(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 the previous report and the pyridine base-coordinated complexes were prepared by the reaction of $CoR_2(acac)(PR_3')_2$ with the bases [1]. Deuterated solvents were used as purchased from Merck and Co., Inc. The 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 dialkyl cobalt complexes by a 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 $\pm$ 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 an internal protonic impurity in deuterated solvents. ^{31}P-NMR signals are referred to external triphenylphosphine (downfield positive).

In order to estimate the equilibrium constants and thermodynamic parameters for Eq. (2) from the ^{31}P NMR spectra the information about the ^{31}P limiting spectra of $CoEt_2(acac)(PPhMe_2)_2$ (II_b) and $CoEt_2(acac)(PPhMe_2)\cdot S$ is required. Although the ^{31}P NMR spectrum of (II_b) still shows some broadening enen at -78° 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 (II_b) 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 (II_b) in toluene, on the other hand, was not available and it was necessary to estimate 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 $CoEt_2(acac)(PPhMe_2)(toluene)$ will be ca. 10 ppm. Thus the limiting ^{31}P chemical shift of $CoEt_2(acac)(PPhMe_2)(toluene)$ was estimated as ca. 39 ppm. Using these estimated limiting chemical shift values for $CoEt_2(acac)(PPhMe_2)_2$ (29.0 ppm) and $CoEt_2(acac)(PPhMe_2)(toluene)$ (39 ppm) and that of free $PPhMe_2$ (-42.5 ppm) we can evaluate the degree of dissociation x for Eq. (2) from the observed chemical shift value f of an partially dissociated and exchanging system. The value of f can be expressed on these assumptions as

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

which leads to the equation

$$x = \frac{(58 - 2f)}{61.5}$$

The degree of dissociation was thus calculated with the equation.

Acknowledgment

The authors thank Mr. Y. Nakamura for 100 MHz ^1H, ^{31}P, ^{13}C NMR measurements.

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Chapter V MECHANISM OF THERMAL DECOMPOSITION OF DIALKYL-COBALT(III) COMPLEXES

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. 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 [1]. Later, a theory which stresses the importance of a low energy thermolysis pathway, particularly β-elimination has been proposed[2] and it paved a route to successful isolation of many "β-elimination stabilized" alkyl transition metal complexes [3]. 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-carbon bonds in some complexes are as strong as in organometallic compounds of main group elements.

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.

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

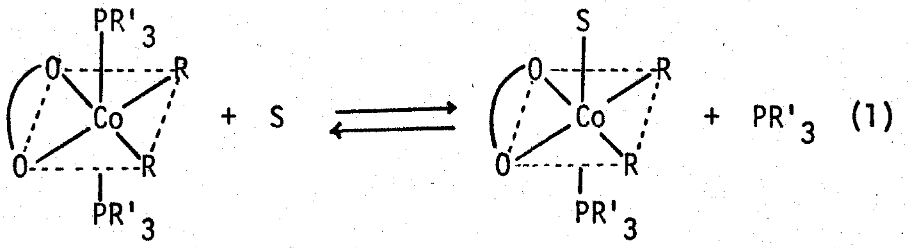
Preparation and some properties of the dialkylcobalt complexes have been previously reported in a preliminary form [6].

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 $CoR_2(acac)(PR'_3)_2$ 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

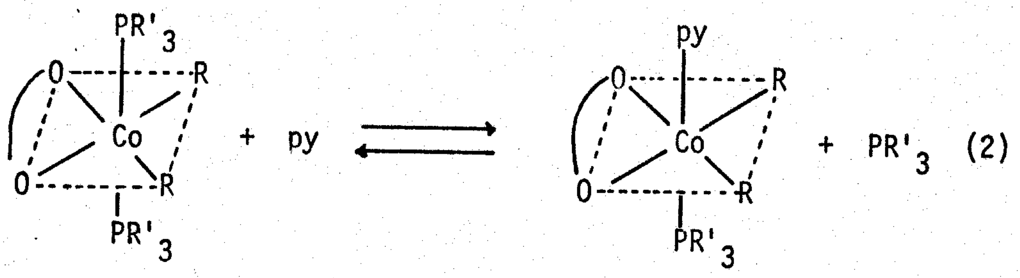


S = solvent

^{31}P and ^{1}H 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 ^{1}H 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 causes the shift of Eq. (1) to the left with the consequence that the triplet methyl signal can be observed in the presence of free tertiary phosphine even at high temperatures where otherwise the singlet is 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 $PPhMe_2 > PEt_3 > P(n\text{-}Bu)_3$. 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 $CoR_2(acac)(PEt_3)(py)$ and $CoR_2(acac)(bipy)$, where py is pyridine or 4-methylpyridine 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.

Relationship between the Co-C stretching vibrations and decomposition temperatures of the dialkylcobalt complexes.

The IR spectra of the isolated dialkylcobalt complexes show a 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 ν(Co-C) vibration. Table 1 shows the ν(Co-C) band and decomposition temperatures

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Insert here Table 1

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together with pKa values of the conjugated acids of the tertiary phosphine ligands. With increase of the alkylchain length the decomposition temperature of the alkylcobalt complex having $PPhMe_2$ and bipy ligands falls in the order of $CH_3 > C_2H_5 > n\text{-}C_3H_7 > iso\text{-}C_4H_9$ with simultaneous decrease of the ν(Co-C) frequency. A similar trend of decrease of the decomposition temperature with increase of the alkylchain length was observed in thermolysis of $NiR_2(bipy)$ [5a], $FeR_2(bipy)_2$ [5a], $CrRCl_2(THF)_3$ [8] and $CrRCl_2(py)_3$ [9] but not in $CuR(PPh_3)_2$ [5_b].

On the other hand, when compared among the methyl complexes having various tertiary phosphine ligands, increase of the ν(Co-C) frequency with the decrease of the basicity of the tertiary phosphine ligand is observed. The result suggests the strengthening of the Co-C bond by coordination of less basic ligands. However, the correlation between the basicity and the decomposition temperature is less clear. Substitution of one of the alkyl groups in trialkylphosphine ligands by the phenyl

Table 1. IR data and Decomposition point of $CoR_2(acac)L_2$

R	L	pKa of L	νCo-C (cm^{-1})	d.p.(°C)
CH_3	2 PEt_3	8.69	573	78-81
CH_3	2 $P(n\text{-}Bu)_3$	8.43	578	64-81
CH_3	2 $PPhMe_2$	6.50	580	116-119
C_2H_5	"	"	578	67-68
C_3H_7	"	"	570	49-50
C_4H_9	"	"	574	unstable at r.t.
CH_3	2 PPh_2Me	4.61	585	89-92
CH_3	PEt_3, py		580	100-105
CH_3	bipy		595	139-140
C_2H_5	"		585	125-126
C_3H_7	"		550	45-47

$CoR_2(acac)L_2$: L= py,pyridine; bipy,2,2'-bipyridine.

group seems to enhance the decomposition point but further phenyl substitution causes the fall of the decomposition temperature, presumably due to the steric effect.

Replacement of the tertiary phosphine ligand(s) with pyridines causes enhancement of the decomposition temperature of the methylcobalt complex with simultaneous increase of the ν(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. This assumption is in line with the NMR observation concerning Eq. (2) that pyridine replaces trialkylphosphines more easily from $CoR_2(acac)(PPhMe_2)_2$.

Analysis of thermolysis products of $CoR_2(acac)(PR'_3)_2$ 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

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Insert here Table 2

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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

Table 2. The products of thermolysis of $CoR_2(acac)(PPhMe_2)_2$

		$Co-CH_3$	$Co-C_2H_5$	$Co-C_3H_7$	$Co-C_4H_9$
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_2Cl_2	toluene	toluene	toluene

a, Decomposition temperature in the solid state, Co-Me, 116-119°; Co-Et, 67-68°; Co-Pr, 49-50°; Co-Bu, unstable at room temperature.

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

I: in the solid state

II: in solution

and ethyl complexes whereas the disproportionation products from n-propyl and isobutyl complexes. 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. For further substantiating the assumption the thermolysis of $Co(C_2H_5)_2(acac)(PPhMe_2)_2$ 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, $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ (see Experimental for preparation) and its thermolysis product was examined. Table 3 summarizes the product distribution of the evolved gases from $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ thermolyzed 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 $CH_2{=}CD_2$ 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 $CH_2{=}CD_2$ and CH_2DCD_3 predominantly with a trace amount of cis-and trans-CHD=CHD. These results clearly demonstrate the occurrence of β-elimination process as the principal thermolysis pathway.

Kinetics

The kinetics of thermolysis of $CoR_2(acac)(PPhMe_2)_2$ in toluene

Table 3 The composition of ethylene and ethane evolved during the heat treatment

Run	conditions	C_2HD_3	$C_2H_2D_2$1)	C_2H_3D	$C_2H_2D_4$	$C_2H_3D_3$
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, Treatmente of (V) at 28° for 1 day in benzene

b, Treatmente of (V) at 42° for 2 days in benzene

c, Treatmente of (V) below 5° for a few days in toluene

d, Thermolysis of (V) at 70° in the solid state

1), $C_2H_2D_2$ = asym-$C_2H_2D_2$ + cis-$C_2H_2D_2$ + trans-$C_2H_2D_2$

2), Consisted of only asym-$C_2H_2D_2$.

3), Consisted mainly of asym-$C_2H_2D_2$ and a trace amount of cis- and trans- $C_2H_2D_2$

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 as shown in Figure 1.

$$-d[CoR_2(acac)(PPhMe_2]/dt = k[CoR_2(acac)(PPhMe_2)_2]$$

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 temperature are shown in Table 4.

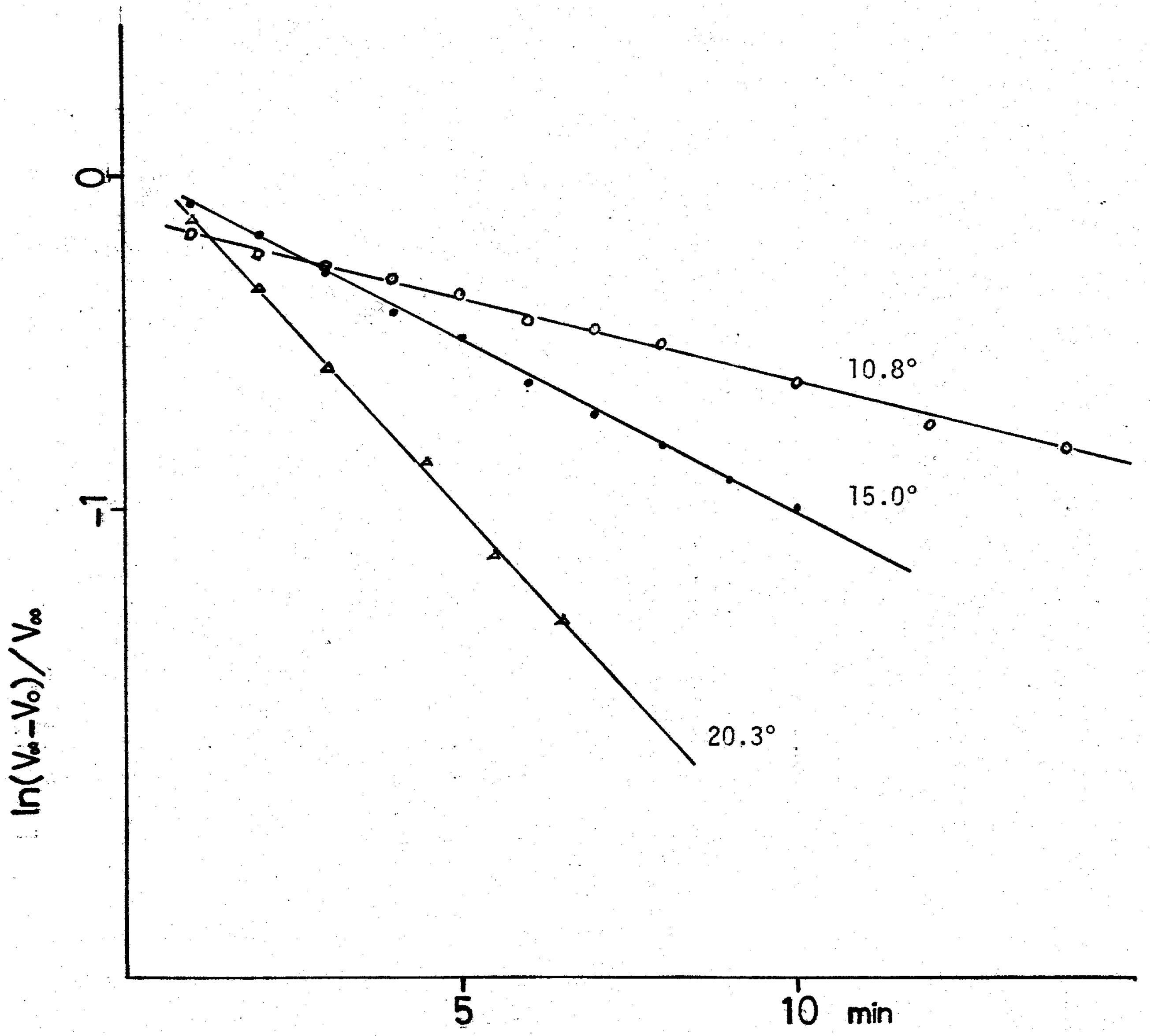
Insert here Table 4 and Fig.1

The diisobutyl cobalt complex was too unstable for the kinetic measurement.

From the Arrhenius plot of ln k vs 1/T as shown in Fig 2 the activation energy for the splitting of C_2H_5-Co bonds was estimated as 30.6 kcal/mol, and that for $Co(C_3H_7)_2(acac)(PPhMe_2)_2$ as 25.5 kcal/mol.

Insert here Fig. 2

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 activation energy for thermolysis of of (II_b) in the presence of $PPhMe_2$ (0.03 M) was found to be 33.7 kcal/mol and in the presence of $PPhMe_2$ (0.70 M) 34.7 kcal/mol.

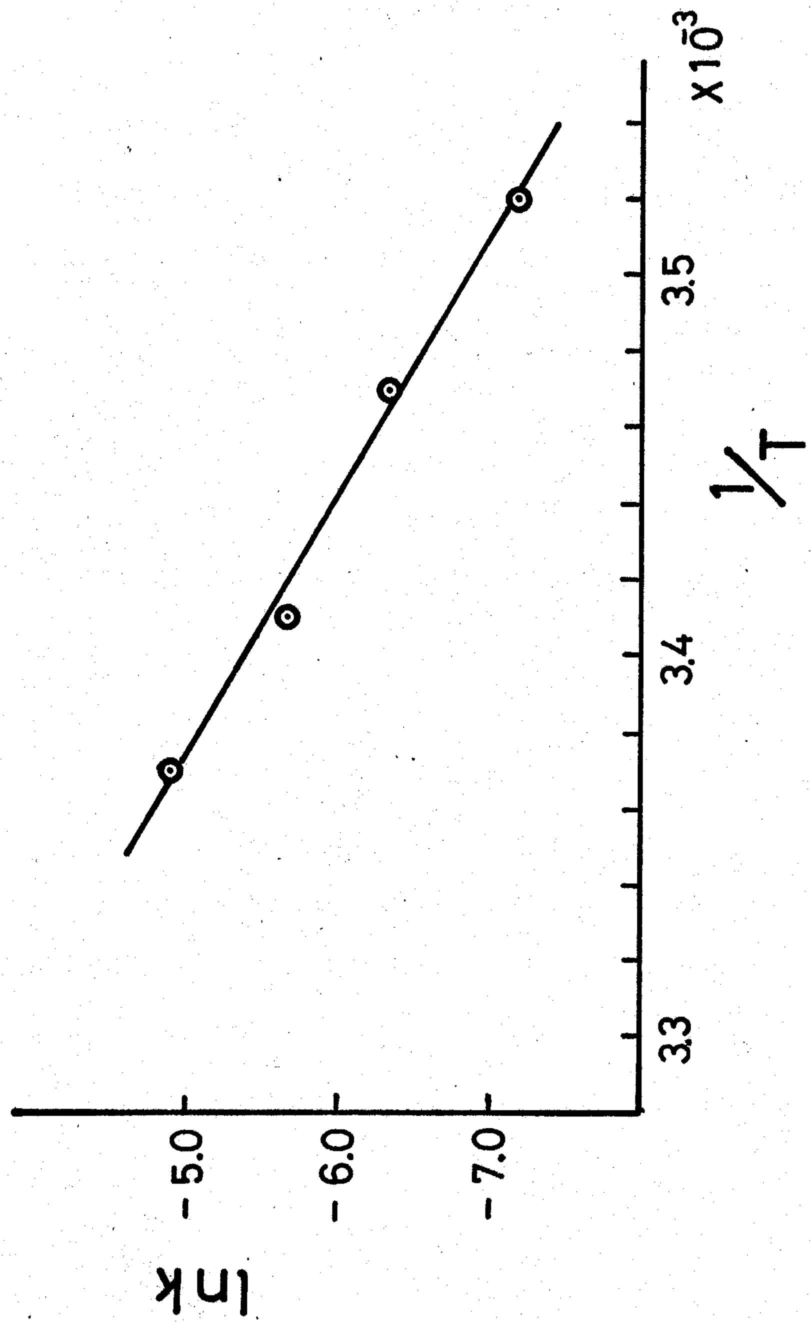


0
-1
ln(V∞-V₀)/V∞
5
10 min
10.8°
15.0°
20.3°

Table 4. The first-order rate constants of thermolysis of $Co(C_2H_5)_2(acac)(PPhMe_2)_2$ and $Co(C_3H_7)_2(acac)(PPhMe_2)_2$

Complex	solvent	conc. of $PPhMe_2$	$k\ 10^4$ (temp.)			
Co-C_2H_5 (II_b)	toluene	0	7.6	17.7	33.0	73.5
			(10.8°)	(15.0°)	(20.3°)	(24.0°)
Co-C_2H_5 (II_b)	toluene	0.03 M	5.9	8.8.	18.6	28.5
			(17.7°)	(21.0°)	(24.1°)	(25.9°)
Co-C_2H_5 (II_b)	toluene	0.70 M	0.34	0.69	1.76	3.15
			(25.3°)	(28.7°)	(33.3°)	(36.4°)
Co-C_3H_7 (II_c)	toluene	0	0.72	0.98	1.96	3.60
			(-9.5°)	(-7.3°)	(-4.0°)	(0°)
Co-C_2H_5 (II_b)	pyridine	0	1.75	2.79	4.13	6.81
			(28.0°)	(30.9°)	(34.0°)	(37.2°)

Fig.2 ln k vs 1/T



The apparent activation energy increased with increasing the concentration of added $PPhMe_2$ approaching its limiting value of ca. 35 kcal/mol. Table 5 summarizes the Eyring parameters for thermolysis of ethyl and propyl complexes in toluene and pyridine in the presence and absence of the added $PPhMe_2$.

Insert here Table 5

Further kinetic studies were made to examine various factors influencing the thermolysis process. Fig. 3 illustrates the linear dependence of the reciprocal of the first order rate constant of thermolysis of $CoEt_2(acac)(PPhMe_2)_2$ at 15° on the concentration of added $PPhMe_2$. Addition of trialkylphosphines to the toluene solution of $CoEt_2(acac)(PPhMe_2)_2$ causes weaker inhibition effect than that of $PPhMe_2$.

Insert here Fig. 3

Table 6 compares the thermolysis rate constansts of $CoEt_2(acac)(PPhMe_2)_2$ (0.18 M) at 16.0° in the presence of 0.17 M each of various phosphines.

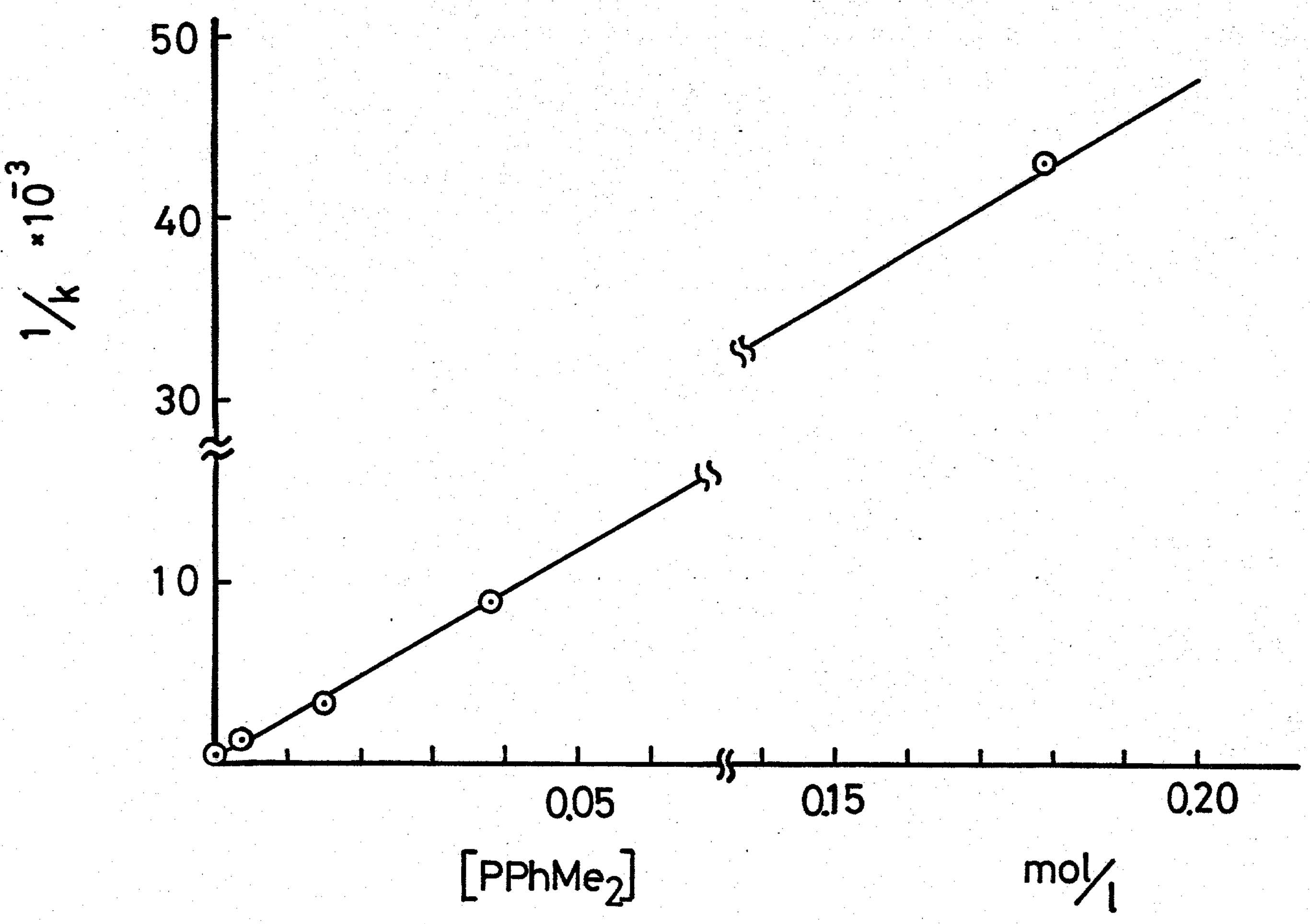
Table 6.

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

Table 5 Activation energies and kinetic parameters for thermolysis of cobalt alkyls

Complex	Solvent	$PPhMe_2$	Ea (kcal/mol)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (e.u.)	$\Delta G^\ddagger$ (kcal/mol)
Co-C_2H_5 (II_b)	toluene	0	30.6	30.0	31.6	20.6
Co-C_2H_5 (II_b)	"	0.03 M	33.7	33.1	39.9	21.2
Co-C_2H_5 (II_b)	"	0.70 M	34.7	34.1	36.2	23.3
Co-C_3H_7 (II_c)	"	0	25.5	24.9	16.8	20.3
Co-C_2H_5 (II_b)	pyridine	0	27.4	26.8	13.6	22.7

Fig. 33 The [illegible] dependence of 1/k on th conc. of added $PPhMe_2$



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 [8]. 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'-dimethyl formamide (0.44) > pyridine (0.17). Although the activation energy for thermolysis of (II_b) in pyridine was found to be smaller (27.4 kcal/mol) than in toluene reflecting the smaller entropy of activation in thermolysis in pyridine as shown in Table 4 (vide infra).

Comparison of the relative rates of thermolysis of $Co(C_2H_5)_2$-(acac)$(PPhMe_2)_2$ and $Co(CH_2CD_3)_2$(acac)$(PPhMe_2)_2$ (isotopic purity 84 %) revealed the presence of a considerable isotope effect (k_H/k_D = 2.30 ± 0.05) indicating the involvement of β-elimination process in the rate-determining step of thermolysis.

H-D Scrambling in the thermolysis of $Co(CH_2CD_3)_2$(acac)$(PPhMe_2)_2$ (V)

Although the deuterium labbled complex decomposes cleanly by β-elimination process evolving $CH_2{=}CD_2$ 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 then 5° as shown in Table 3. Infrared spectroscopy proves quite useful in analyzing various isotopic mixtures of dueterated ethylenes. Fig. 4 demonstrates some of the typical results. It is seen that absorption bands of each deuterated ethylene appear separately without being masked

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Insert here Fig. 4

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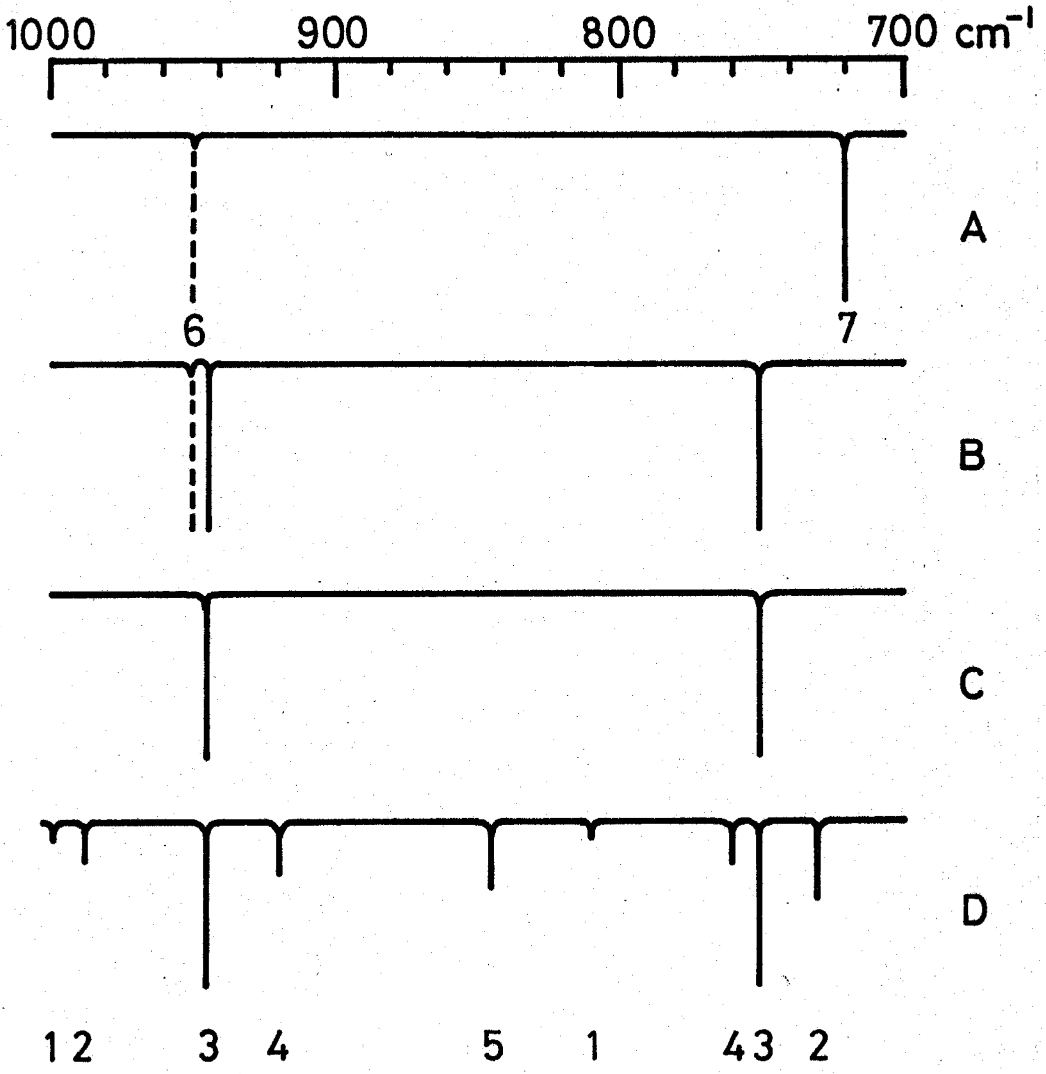
by absorptions of deuterated ethanes owing to the small absorption coefficients of the ehtanes in the region between 700 and 1000 cm^{-1}.

Following observations also give cludes concerning the scrambling mechanism. (i) Contact of non-deuterated diethylcobalt complex 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 ethyl groups by the process which would occur via β-elimination and exchange of the eliminated ethylene with the free ethylene. (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

Fig.4 IR spectra of $C_2H_4-D_n$

A) $II_b + C_2D_4$ at 28°, 1 day
B) $II_b +$ asym-$C_2H_2D_2$ at 28°, 1 day
C) V at 5° for a few days
D) V at 32°, 1 day



1, C_2H_3D; 2, trans-$C_2H_2D_2$; 3, asym-$C_2H_2D_2$;
4, C_2HD_3; 5, cis-$C_2H_2D_2$; 6, C_2H_4; 7, C_2D_4;

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 ethylnickl 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.

$$CoEt_2(acac)(PR_3')_2 + S \overset{K}{\rightleftharpoons} CoEt_2(acac)(PR_3')\cdot S + PR'_3 \qquad (3)$$

S = solvent

$$CoEt_2(acac)(PR'_3)\cdot S \xrightarrow{k_2} CoEt(C_2H_4)H(acac)(PR'_3) + S \qquad (4)$$

$$CoEt(C_2H_4)H(acac)(PR'_3) \xrightarrow{rapid} C_2H_6 + C_2H_4 + Co(I)\ complex \qquad (5)$$

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

$$[Et_2Co(III)]_{total} = [CoEt_2(acac)(PR'_3)\cdot S] + [CoEt_2(acac)(PR'_3)_2]$$

leads to the following rate expression,

$$-\frac{d}{dt}[Et_2Co(III)]_{total} = k_2[CoEt_2(acac)(PR'_3)\cdot S]$$

$$= k_2 \frac{[Et_2Co(III)]_{total}}{1 + \frac{[PR'_3]}{K[S]}}$$

$$= k[Et_2Co(III)]_{total}, \qquad (6)$$

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

We have followed the decrease of the total concentration of diethylcobalt(III) complex by following the volume of evolved ethane and ethylene, finding the thermolysis reaction is first order in $[Et_2Co(III)]_{total}$ 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. 3 is consistent with the proposed mechanism, since the reciprocal of Eq. (7) gives Eq. (8)

$$\frac{1}{k} = \frac{[PR'_3]}{k_2K[S]} + \frac{1}{k_2'} \quad , \qquad (8)$$

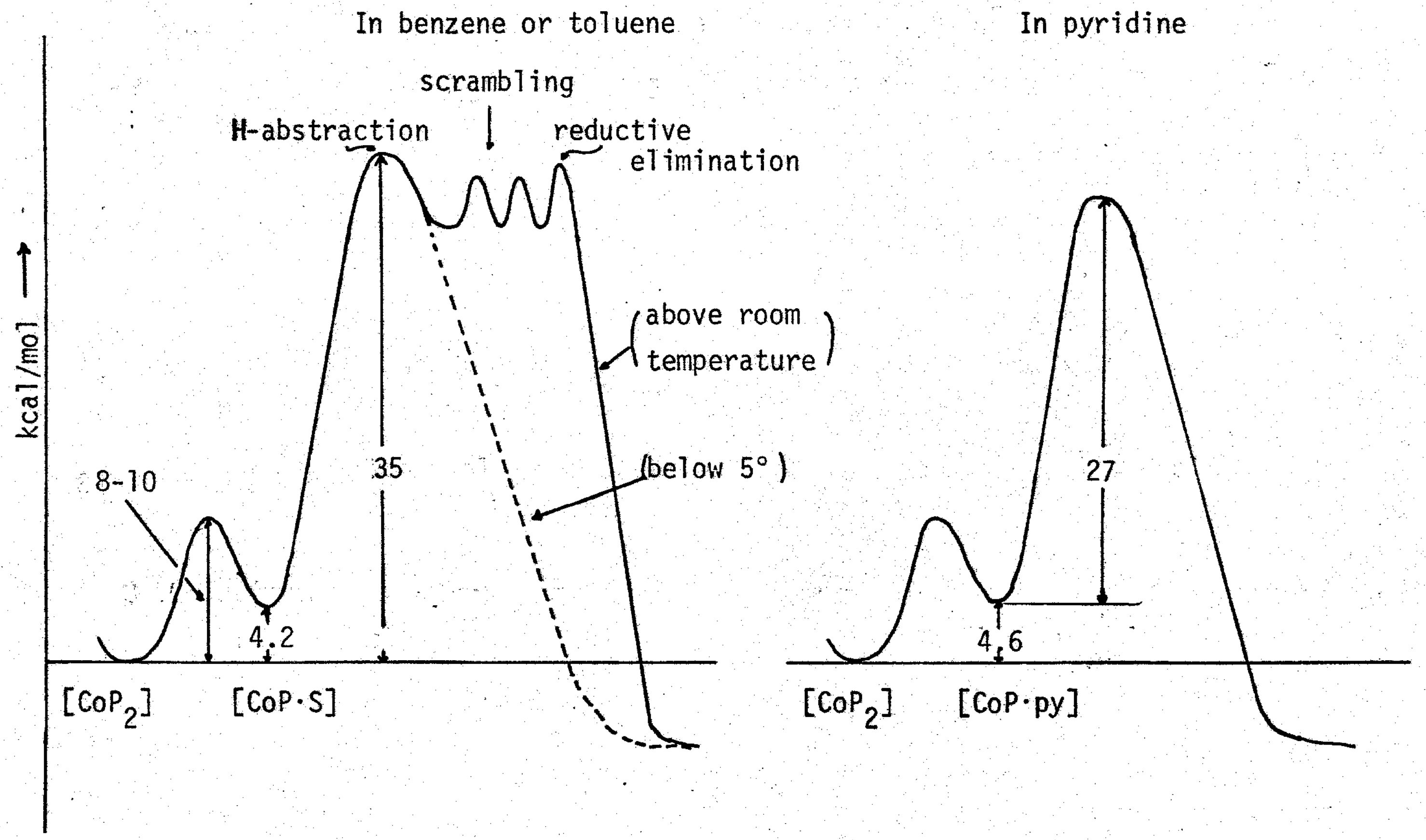
which represents the feature of Fig. 3, where the intercept corresponds to $1/k_2$ and the slope to $1/k_2K[S]$. The value of K at 15° obtained from the slope of the line in Fig. 3 using Eq. (8) was 0.0024. At the concentration of $[Co(III)]_{total} = 0.03$ M this value indicates that ca. 20 ± 3 % of $CoEt_2(acac)(PPhMe_2)_2$ 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 ± 2 in approximate agreement with the value obtained from analyzing Fig. 3. The $\Delta H°$ 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 ± 3 kcal/mol.

Observation of the occurrence of clear β-elimination process at 5° as substantiated by evolution of $CH_2{=}CD_2$ and CH_2DCD_3 from $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ and of the isotope effect in the thermolysis, k_H/k_D being 2.30 ± 0.05 at 15°, strongly suggests 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 $PtBu_2(PPh_3)_2$, 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 the scrambling processes [4_a]. Schwartz and coworkers recently reported the k_H/k_D value of 2.28 ± 0.20, which is close to the value obtained in the present study, for β-elimination of an alkyl-iridium(I) complexes [13].

As the schematical representation of the reaction profile Fig. 5 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 [8] are included in Fig. 5. 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 $CoR_2(acac)(PR_3')_2$ does <u>not</u> constitute the rate-determining step. 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 [4_a], the effect should be ascribed to the consequence of the shift of equilibrium represented by Eq. (1) to hinder the dissociation of $CoR_2(acac)(PR_3')_2$ as revealed by NMR examination of the equilibrium in the presence of the added phosphine ligands [8]. In the presence of excess added $PPhMe_2$ the overall activation energy for thermolysis increase to ca. 35 kcal/mol from the

Thermolysis reaction profile



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 (Ea = 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 merkedly 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) thus hindering 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 ligands to the alkylcobalt complex.

The second important conclusion we draw is that the thermolysis processes such as β-elimination ensue the metal-to-carbon activation and that β-elimination is not the prerequisite for the thermolysis to take place. 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 higher homologs of the dialkylcobalt complex than the ethyl complex. (The dimethylcobalt complexes decompose via reductive elimination process). However, we regard the β-elimination as the consequence of thermal activation of metal-alkyl bond and the hydrogen abstraction from the β-carbon takes place immediately after the alkylcobalt complex reached the activated state. 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 α-elimination, reductive elimination, β-elimination etc. Our previous observation of lower activation energy for thermolysis of $CH_3Cu(PPh_3)_2$ 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 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 $Co(CH_2CD_3)_2(acac)$-$(PPhMe_2)_2$ (V) 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 (V) below 5° in benzene or toluene, and the thermolysis at room temperature in pyridine as well as and the rapid thermolysis of the solid sample liberate $CH_2=CD_2$, the β-elimination product, predominantly, whereas the H-D scrambling occurred above room temperature in benzene or toluene solution. Analysis of the deuterated ethylenes produced by thermolysis of (V) also reveals some interesting features of the scrambling process accompanying the thermolysis. Since examination of the remaining complex (V), which liberated some amount of scrambled ethylenes and ethanes, revealed that the remaining ethyl groups were intact and not subjected to the H-D scrambling, the scrambling process chould be situated after the transition state. The fact that C_2H_3D and C_2D_3H were formed in comparable amounts can not be explained by 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 system.

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 is connected with electronic factors. The theory stressing the importance of electronic promotion [1, 5a] may be valid for accounting 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 thermal process, but nevertheless they may have some important bearing on the theory to explain the thermal stability.

The diethylcobalt complex (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) [5_a]. 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-G3 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.

Synthesis

cis-Dialkyl(acetylacetonato)bis(tertiary phosphine)cobalt(III) (I) - IV) were prepared according to the method described in previous report [6].

Di(ethyl-2,2,2-d_3)(acetylacetonato)bis(dimethylphenylphosphine)cobalt(III) (V)

Complex (V) was prepared by the reaction of cobalt tris(acetylacetonate), $Al(CH_2CD_3)_2(OEt)$ and dimethylphenylphosphine. The deuterated diethylaluminum monoethoxide was prepared by the following route:

$$CD_3COOD \xrightarrow{LiAlH_4} CD_3CH_2OH \xrightarrow{PBr_3} CD_3CH_2Br \xrightarrow{Mg} CD_3CH_2MgBr$$

$$\xrightarrow{AlCl_3} Al(CH_2CD_3)_3 \xrightarrow{CH_3CH_2OH} Al(CH_2CD_3)_2(OEt).$$

The isotopic purity of $Al(CH_2CD_3)_2(OEt)$ was determined by NMR spectroscopy to be 99 %.

To a mixture of $Co(acac)_3$ (1.00 g; 2.8 mmol) and dimethylphenylphosphine (1.5 ml; 10 mmol) in ether $Al(CH_2CD_3)_2(OEt)$ (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 (V), 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 $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ by ^1H NMR spectroscopy was not feasible because of the coincidence of the methylene and methyl resonances of cobalt-bonded ethyl groups. 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°, $CD_3CH_2COCH_2CD_3$ formed in the reaction was separated and the isotopic purity of $CD_3CH_2COCH_2CD_3$ was determined to be 95 % by NMR spectroscopy.

Analysis of gaseous thermolysis products of $CoR_2(acac)(PR'_3)_2$

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 General methods.

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 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. 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. Typical data obtained are plotted in Fig. 2.

H-D scrambling reaction of (V) in benzene

The scrambling reaction of (V) 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° 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°, 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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Chapter VI OLEFIN-COORDINATED IRON(0) COMPLEXES WITH DIMETHYLPHENYLPHOSPHINE LIGANDS

SUMMARY

Reaction of $Fe(acac)_3$, $AlEt_2(OEt)$ and dimethylphenylphosphine ($PPhMe_2$) gives a new air-sensitive ethylene-coordinated complex, $Fe(CH_2{=}CH_2)(PPhMe_2)_4$ (I).

(I) reacts with a few olefins such as butadiene, propylene, styrene, alkyl methacrylate to produce olefin-coordinated complexes, $Fe(olefin)(PPhMe_2)_3$ or 4.

Introduction

Information concerning the interaction of olefins with transition metals in vital in understanding the mechanisms of olefin catalyses. Many studies have been made in this line [1], and a variety of olefin-coordinated transition metal complexes have been isolated and characterized [2]. However, rather limited and sporadic studies have be made concerning the olefin-coordinated iron(0) complexes, most of which contain carbonyl and cyclopentadienyl ligands and there has been reported, to our knowledge, only one ethylene-coordinated iron complex without these ligands [3].

In the course of our study for preparation of alkyliron complexes by the reaction of iron acetylacetonate, organoaluminum compounds and tertiary phosphine ligands we have isolated a new, ethylene-coordinated complex, $Fe(CH_2{=}CH_2)(PPhMe_2)_4$ (I). This complex proved to be very reactive toward other olefin and to provide a convenient starting material for preparing various olefin-coordinated iron(0) complexes by displacement of the coordinated ethylene with other olefins. We now describe the preparation and properties of (I) and other olefin-coordinated complexes derived from it.

Results and discussion

The ethylene-coordinated iron complex (I) was prepared by the reaction of Fe(acac)$_3$, PPhMe$_2$ and dimethylaluminum monoethoxide in ether at -10° under nitrogen.

$$\mathrm{Fe(acac)_3 + PPhMe_2 + AlEt_2(OEt) \longrightarrow \underset{(I)}{Fe(CH_2{=}CH_2)(PPhMe_2)_4}}$$

Probably complex (I) was formed through an intermediate ethyliron complex which on splitting of the ethyl-iron bond may produce ethane and ethylene, the latter of which coordinated with a zerovalent iron complex giving (I). It is known that the similar reaction of Fe(acac)$_3$, AlEt$_2$(OEt), and 1,2-bis(diphenylphosphino)ethane (dpe) gives Fe(CH$_2$=CH$_2$)(dpe)$_2$ [3].

(I) is sensitive to air and moisture but thermally stable at room temperature under nitrogen. (I) is soluble in ether, toluene, and acetone at low temperature, and can be recrystallized from ether to give yellow crystals, In solution (I) is unstable and decomposes evolving ethylene even at 0°. Thermolysis of (I) at ca. 50° released 100% of ethylene per Fe. Acidolysis of (I) with concentrated H_2SO_4 released ethylene and ethane in a 1/1 molar ratio, the latter presumably being formed by the reaction of the evolved ethylene with H_2SO_4. The amount of the gas liberated accounted for 81% of the ethylene coordinated with iron. IR spectrum of (I) shows a ν(C-H) band due to the ethylene coordinated with iron at 3015 cm^{-1} and ν(C=C) band of the coordinated ethylene at 1475 cm^{-1}. The frequency of ν(C=C) at 1475 cm^{-1} is smaller than those of other transition metal-ethylene complexes. The previously observed ν(C=C) bands of ethylene-coordinated complexes are 1487 cm^{-1} for nickel [2e], 1526 cm^{-1} for platinum [4], and 1524 cm^{-1} for rhodium [5]. ^{1}H NMR spectrum of (I) at -30° shows a broad peak due to the ethylene coordinated with iron at τ7.5 (4H). The known $Fe(CH_2=CH_2)(CO)_4$ complex shows the ethylene signal at τ7.5 and a ν(C=C) band at 1510 cm^{-1} [6]. Observation of the lower ν(C=C) band at 1475 cm^{-1} for (I) than that of $Fe(CH_2=CH_2)(CO)_4$ suggests that the $PPhMe_2$-coordinated complex has a higher basicity and hence the ability for greater back donation than the CO-containing complex.

Complex (I) reacts with several olefins to give the olefin-coordinated complexes liberating ethylene. Table 1 summarizes the IR data of olefin-coordinated complexes comparing with those of the known olefin-iron carbonyls. The frequencies of the ν(C=C) bands of the isolated olefin-iron complexes with $PPhMe_2$ ligands are lower than those of the olefin-iron carbonyls. In contrast to the $Fe(CH_2=CH_2)(dpe)_2$ complex (I) shows considersble reactivities toward some olefins and is suitable as a starting material for preparing the olefin-coordinated iron(0) complexes containing tertiary phosphine. The reactions of (I) with several olefins are descrived below.

a) Formation of a butadiene-coordinated complex

Complex (I) reacted with butadiene at room temperature to give a yellow complex, $Fe(C_4H_6)(PPhMe_2)_3$ (II). Complex (II) is more stable than the starting ethylene complex (I). IR spectrum of (II) shows a ν(C=C)band of the butadiene coordinated with iron at 1470 cm^{-1}. The ^1H NMR spectrum of (II) shows two peaks of equal intensities at τ5.6(m,2H) and τ9.5(d,2H). By comparison with other butadiene complexes of established structure such as $Fe(C_4H_6)(CO)_3$ [7] the multiplet at τ5.6 has been assigned to the two equivalent protons on central carbon atoms and the doublet at τ9.5 is assigned to the two of four terminal protons. Other two terminal protons seem to be overlapped with methyl protons of $PPhMe_2$ ligands as judged by comparison of the peak areas of the methyl protons with other signals.

b) Formation of a styrene-coordinated complex

Complex (I) reacted with styrene to give a deep brown complex, which was recrystallized from styrene as brown crystals of a composition $Fe(CH_2{=}CHC_6H_5)(PPhMe_2)_4$ (III). No polymer was formed. Complex (III) is sensitive to air but thermally stable under nitrogen at room temperature. Because of its instability in solution and low solubility in common organic solvents the measurement of NMR spectrum of (III) was unsuccessful. IR spectrum of (III) shows a characteristic band due to the phenyl group of styrene coordinated with iron at 1595 cm^{-1} and a $\nu(C{=}C)$ band due to the vinylic entity in styrene bonded to iron at 1470 cm^{-1} as shown in Table 1.

c) Reaction of (I) with acrylonitrile (AN)

Complex (I) initiates the polymerization of acrylonitrile(AN). The reaction system of AN and (I) changed the color from initial yellow to red and then polymerization occurred suddenly even at -40°. When the reaction of (I) with AN was conducted below -30° and free AN was removed before the start of polymerization a red complex which is contaminated with a small amount of polyacrylonitrile was obtained. The IR spectrum of the red complex shows the characteristic $\nu(C{\equiv}N)$ band of AN coordinated with iron through the double bond at 2150 cm^{-1} in addition to bands due to the polymer of AN. The unequivocal characterization of this complex could not be performed because of contamination with acrylonitrile polymers.

d) Reactions of (I) with other olefins such as alkyl methacrylate and propylene

Ethyl methacrylate (EMA) and methyl methacrylate (MMA) reacted with complex(I) releasing ethylene to give red crystalline complexes. these complexes are soluble in several solvents and the MMA complex melts at room temperature. The instability of the alkyl methacrylate complexes hindered further characterization.

Propylene reacted with (I) to give a yellow complex, which can be recrystallized from n-hexane as yellow crystals. This complex is very sensitive to air and melts at room temperature. Because of its instability its complete characterization could not be performed. Thermolysis of the propylene-coordinated complex liberates propylene. Analogy with the parent ethylene complex suggests the composition of $Fe(C_3H_6)(PPhMe_2)_4$.

Expermental

All reactions were carried out under nitrogen atmosphere. Solvents and olefins were purified by usual methods and stored under nitrogen before use. Liquid olefins were introduced by a trap-to-trap distillation in a vaccum line into a reaction tube containing the ethylene complex (I). Gaseous olefins were broughtin contact with ether solution of (I)

Analysis of gases produced during the reaction was carried out by mass spectrometry and gas chromatography after collecting the gas using a Toepler pump, by which the volume of the gas was measured. IR and NMR spectra were measured by a Hitachi-EPI-3G spectrometer and a JEOL JNM-PS-100 spectrometer. The microanalysis of carbon, hydrogen, and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2.

Preparation of (ethylene)tetrakis(dimethylphenylphosphine)iron(0) (I)

To a solution of $Fe(acac)_3$(1.0g, 0.0028 mol) and dimethylphenylphosphine (2ml, 0.013 mol) in ether diethylaluminum monoethoxide with gradual raise of temperature to -10°. When the color of the reaction mixture changed from red to deep yellow at the temperature, the solution was cooled to -78° to precipitate the yellow compound which was separated by filtration and washed with ether, acetone, and n-hexane The yellow compound thus obtained was recrystallized from ether to give yellow crystals. Yield, 20 %. Complex (I) is very sensitive to air but thermally stable at room temperature. It decomposes at 40-50° liberating 100% of ethylene calculated for (I). Acidolysis of (I) with concentrated H_2SO_4 evolved ethylene and ethane in a 1/1 ratio. The microanalysis of (I) was not feasible due to its instability. IR(KBr): ν(C=C), 1475 cm^{-1}; ν(C-H) of the coordinated ethylene, 3015 cm^{-1}; $PPhMe_2$ (max), 3050, 2985, 2910, 1490, 1438, 930, 890, 740, and 700 cm^{-1}. NMR($C_6D_5CD_3$ at -30°) : τ7.5(m. 4H, CH_2=CH_2) (Found: Fe,8.2; $C_{36}H_{50}FeP_4$ calcd., Fe,8.8%)

a) <u>Reaction of (I) with butadiene</u>

Butadiene was brought in contact with complex (I) (0,09 g, 0.14 mmol) in ether (2 ml) in a closed system for 5h. at -10° with stirring to give a yellow solution. The yellow solution was further stirred at room temperature for 5 h. In the gas phase ethylene was recovered. After evaporation of solvent the residue was extracted with n-hexane. On cooling the n-hexane extract to -70° a yellow compound was obtained. It was recrystallized from ether-n-hexane system as yellow crystals which were separated, washed with n-hexane, and dried *in vacuo*. Yield, 45%. (Found: C,63.8: H,8.0. $C_{28}H_{39}FeP_3$ calcd.; C, 64.2: H, 7.5%) IR(KBr): ν(C=C) of the coordinated butadiene 1470 cm^{-1};$PPhMe_2$, 3042, 2960, 2900, 1585, 1435, 1190, 930, 900, 885, 740, and 695 cm^{-1}. NMR(CD_3COCD_3): C_4H_6 coordinated with iron, τ5.6(m,2H), τ9.5 (d, 2H).

b) <u>Reaction of (I) with styrene</u>

Styrene was condensed into a Schlenk tube containing complex (I) in ether solution by a trap-to-trap distillation. The reaction mixture was stirred at -30° till the color changed from yellow to deep brown. The system was further stirred at room temperature for 1 h. Cooling the solution caused precipitation of a deep brown compound which was separated by filtration. The brown compound thus obtained was recrystallized from styrene as deep brown crystals (III). Yield, 40%. Complex (III) is sensitive to air but thermally stable at room temprerature. (Found: C, 69.8; H, 7.7. $C_{40}H_{52}FeP_4$ calcd.: C, 67.4; H, 7.3 %). IR(KBr) : ν(C=C) of the coordinated styrene, 1470 cm^{-1}.

c) Reaction of (I) with acrylonitrile

Acrylonitrile (AN) was condensed into a Schlenk tube containing a solid sample of (I) by a trap-to-trap distillation. When the color of the reaction mixture changed from yellow to red at -40--30° the system was rapidly cooled to -70° and the free AN was evaporated to give the red complex. The red complex thus obtained was washed with n-hexane and dried *in vacuo*. IR spectrum of the red complex shows the characteristic ν(C≡N) band due to the AN coordinated to iron at 2150 cm^{-1} in addition to the bands due to polymers of AN.

d) Reactions of (I) with other olefins such as alkyl methacrylates and propylene.

The reactions of (I) with alkyl methacrylates were carried out in a similar manner to the reaction with styrene. Since the red complexes thus obtained melt at room temperature, the complete characterization could not be performed.

The reaction of (I) with propylene was carried out in a similar manner as described above and yellow air-sensitive crystals which melt at room temperature were obtained. Because of its instability sufficient characterization could not be performed. It decomposes in solution liberating propylene.

Table 1 IR data of olefin-coordinated iron(0) complexes

	ν(C=C) or ν(C=N)		
$Fe(C_2H_4)(PPhMe_2)_4$	ν(C=C) 1475	1510	$Fe(C_2H_4)(CO)_4$
$Fe(C_4H_6)(PPhMe_2)_3$.	ν(C=C) 1470	1487 1480	$Fe(C_4H_6)(CO)_3$
$Fe(C_3H_6)(PPhMe_2)_4$	ν(C=C) -	1493	$Fe(C_3H_6)(CO)_4Fe(CO)_5$
$Fe(CH_2CHC_6H_5)(PPhMe_2)_4$	ν(C=C) 1470	1505	$Fe(CH_2CHC_6H_5)(CO)_4$
$Fe(CH_2CHCN)(PPhMe_2)_n$	ν(C=N) 2150	2210	$Fe(CH_2CHCN)(CO)_4$

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CONCLUSION

This thesis is concerning with the synthesis of new types of organo-cobalt and -iron complexes in Chapter I,II,III,and VI, their properties in solution in Chapter IV and a thermolysis mechanism of the alyklcobalt complexes in Chapter V.

Most of the organotransition metal complexes reported in this thesis have been prepared by treatment of organoaluminum compounds in combination with transition metal acetylacetonates in the presence of stabilizing ligands such as tertiary phosphines and 2,2'-bipyridine. The number of new complexes prepared in the present study exceeds 35.

Chapter I: The reaction of $Co(acac)_3$ and some tertiary phosphines with $AlR_2(OEt)$ gave remarkably stable trivalent cobalt alkyls, $CoR_2(acac)(PR'_3)_2$ (A, B, C, and D)[R=Me, Et, n-Pr, iso-Bu; PR'_3=PEt_3,$P(n\text{-}Bu)_3$, $PPhMe_2$, PPh_2Me; acac= acetylacetonato]. These complexes are considered as the reaction intermediates in the reaction of $Co(acac)_3$ with $AlR_2(OEt)$ in the presence of stabilizing ligands to low valent alkyl complexes. These complexes proved to be quite suitable as model compounds for studying the properties of alk alkylcobalt complexes for the following reasons. (1) Most of them are the thermally stable at room temperature, insensitive to air and soluble in ordinary solvents. (2) They are diamagnetic and amenable to NMR study concerning the ligand exchange reactions. (3) A series of alyklcobalt complexes containing a variety of ligands can be easily prepared. The pyridine base-coordinated complexes, $CoR_2(acac)(PR'_3)(py)$ (E) and $CoR_2(acac)(bipy)$ (F) were prepared by the replacement of tertiary phosphine ligands with the organic nitrogen bases such as pyridine(py) and 2,2'-bipyridine (bipy). The isolated complexes readily reacted with CO to yield the dialkyl ketons and a carbonyl complex, $Co(acac)(CO)_2(PR'_3)$ (G).

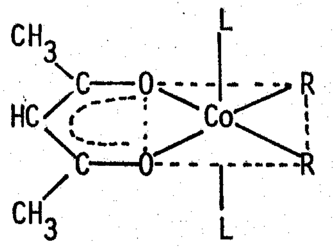
Chapter II: The reaction of $Co(acac)_3$ and $AlMe_2(OEt)$ in the presence of 1,2-(diphenylphosphino)ethane (dpe) ligand instead of monodentate tertiary phosphines(PR'_3) gave a univalent methylcobalt complex, $Co(CH_3)(dpe)_2$ (H). In this case alkylcobalt complex containing the acetylacetonato ligand was not obtained. This complex reacts with CO and H_2 or D_2 to give CO insertion product, $Co(COCH_3)(CO)_2(dpe) \cdot 1/2(Et_2O)$ (I) and a hydride, $CoH(dpe)_2$ (J) or $CoD(dpe)_2$ (K), respectively. Complex (H) reacts with RC≡CH to give a cobalt(I) acetylide, $RC{\equiv}CCo(dpe)_2$ (L) (R=Me,Ph), and reacts with acrylonitrile to give a new type of olefin-coordinated methylcobalt complex, $CoCH_3(CH_2{=}CHCN)(dpe)_2$ (M).

Chapter III : The reaction of $Fe(acac)_3$ with $AlMe_2(OEt)$ in the presence of dpe and $PPhMe_2$ give new methyliron complexes, $Fe(CH_3)_2(dpe)_2$ (N) and $Fe(CH_3)(acac)_2(PPhMe_2)$ (O), respectively. Complex (N) is thermally stable but insoluble in any organic solvents. On recrystallization of (N) from toluene a new type of orthometallated methyliron(II) complex, $Fe(CH_3)(C_6H_4PPhCH_2CH_2PPh_2)(dpe)$ (P), which is the first example of the orthometallated complex containing an alkyl ligand, was obtained. Complex (N) and (O) react with CO to yield acetone. Complex(N) reacts with D_2, PhC≡CH and CO_2 to give $FeD_2(dpe)_2$ (Q), $FeH(C{\equiv}CPh)(dpe)_2$ (R) and $Fe(O_2CCH_3)(CO_2)_m(py)_n$ (S), respectively. Thermal decomposition of (N) and (O) and treatment of (N) with CH_2Cl_2 liberated ethylene, the formation of which suggests the intermediacy of a carbenoid complex involved in decomposition of the methyliron complex. Treatment of (N) with CD_2Cl_2 released C_2H_4, $CD_2{=}CH_2$, C_2D_4, C_2H_6, and CH_4 in a ratio of 8/14/4/24/50/. These results also suggest the formation of $Fe{:}CH_2$ and $Fe{:}CD_2$ type intermediates and their coupling

reactions

reactions taking place. This behavior is considered as one example of α- elimination of methyl group bonded to metal.

Chapter IV : The NMR studies of complex (A)-(F) led to the following results. (I) These complexes have an octahedral configuration as shown below.



L= PR'$_3$, pyridine

(2) The coordinated tertiary phosphine ligands are partly released in solution and an exchange reaction between the liberated and the coordinated phosphines takes place.

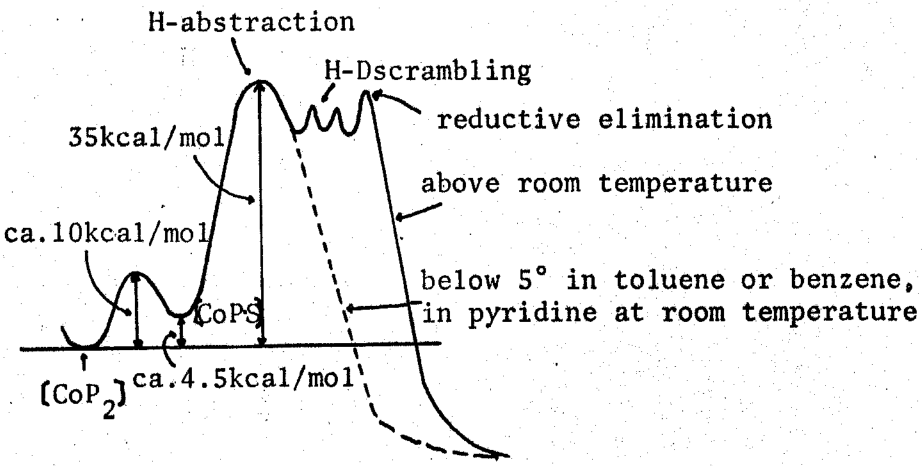
$$CoR_2(acac)(PR'_3)_2 + S \xrightleftharpoons{K_1} CoR_2(acac)(PR'_3)\cdot S + PR'_3$$

From observation of ^{31}P NMR spectra several kinetic and thermodynamic data for exchange reactions of tertiary phosphines were obtained. (3) It was found that one of the phosphine ligands in $CoR_2(acac)(PR'_3)_2$ can be readily displaced with pyridine bases to give pyridine-coordinated complexes(E) .

$$CoR_2(acac)(PR'_3)_2 + py \xrightleftharpoons{K_2} CoR_2(acac)(PR'_3)(py) + PR'_3$$

The equilibrium constants K_2 of the above equilibrium were measured by means of ^{1}H NMR spectroscopy and the thermodynamic parameters were estimated by studying the temperature dependence of K_2. The increase in alkyl chain length makes the enthalpy change for the equilibrium more favorable but the effect is compensated by the entropy change. These NMR studies suggest the ligand dissociation and exchange reaction taking place more easily when the complexes become more basic by coordination of more basic ligands or by bonding of cobalt with alkyl groups of longer chain length.

Chapter V : The thermal stability of a series of (C) decreases in the order: $CH_3 > C_2H_5 > C_3H_7 > C_4H_9$. Thermal decomposition of (C) in toluene solution is first order with respect to (C) and activation energies for pyrolysis of ethylcobalt and propylcobalt complexes are 30.6 and 25.5 kcal/mol, respectively. Addition of free $PPhMe_2$ to the solution of the ethylcobalt complex strongly inhibits its thermal decomposition and the 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 $Co(C_2H_5)_2(acac)(PPhMe_2)_2$ and $Co(CH_2CD_3)_2$-$(acac)(PPhMe_2)_2$ (T) revealed the presence of a considerable isotope effect ($k_H/k_D = 2.30 \pm 0.05$) indicating the involvement of β-elimination process in the rate determining step of thermolysis. The analysis of thermolysis product of (T) revealed the following features. (1) The slow thermolysis of (T) below 5° in benzene or toluene as well as the thermolysis at room temperature in pyridine and the rapid thermolysis of the solid sample predominantly liberate $CH_2=CD_2$ and CH_2DCD_3, the β-elimination products, whereas the H-D scrambling occurred above room temperature in benzene solution. (2) The fact that C_2H_3D and C_2D_3H were formed in comparable amounts with each other suggests that the β-elimination process is taking place with the simultaneous participation of two ethyl groups in the H-D scrambling process with a negligible isotope effect. (3) The remaining ethyl groups after treatment of (T) above room temperature in benzene were not subjected to the H-D scrambling. Although we did not measure the activation energy for the scrambling, these suggest the activated state for scrambling reaction is close to the highest activation state. The following reaction profile was proposed to described the decomposition pathways of thermolysis.



Chapter VI: The ethylene-coordinated iron complex, $Fe(CH_2=CH_2)(PPhMe_2)_4$ (U), was prepared by the reaction of $Fe(acac)_3$, $AlEt_2(OEt)$ and $PPhMe_2$. Complex (U) is sensitive to air but has good reactivities toward several olefins. Complex (U) reacts with butadiene, styrene, to give $Fe(C_4H_6)(PPhMe_2)_3$ (V) and $Fe(CH_2=CHC_6H_5)(PPhMe_2)_4$ (W), respectively. Complex (U) also reacts with other olefins such as alkyl methacrylate, acrylonitrile and propylene to produce the olefin-coordinated complexes.