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PREPARATION, PROPERTIES AND STRUCTURE OF STABLE IONIC DIALKYLBIS(2,2'-BIPYRIDINE)COBALT(III) TETRAALKYLALUMINATE AND RELATED COMPLEXES

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Summary

Two types of dialkylcobalt(III) complexes containing the 2,2'-bipyridine ligand have been isolated as products of the reactions of tris(2,4-pentanedionato)cobalt(III) (Co(acac)$_3$), 2,2'-bipyridine (bpy), and alkylaluminums in diethyl ether. When high Al/Co ratios (Al/Co > 7) were used, ionic complexes, dialkylbis(2,2'-bipyridine)cobalt(III) tetraalkylaluminates, [CoR$_2$(bpy)$_2$][AlR$_4$] (R = CH_3, C_2H_5) were obtained exclusively. Similar reactions at lower ratios (Al/Co = 1.5—2.0) gave neutral CoR$_2$(acac)(bpy) (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7). These compounds were characterized by IR and NMR spectroscopy as well as by elemental analysis and chemical reactions. Molecular structural analysis of the cationic dimethylcobalt compound confirmed the *cis* configuration. Stepwise formation of [CoR$_2$(bpy)$_2$][AlR$_4$] from Co(acac)$_3$ is postulated and the mechanism of the alkylation reaction is discussed.

Introduction

Much attention has been devoted to organocobalt chemistry, especially that related to the naturally occurring compound, vitamin B_{12} coenzyme. A number of alkylcobalt(III) complexes stabilized by macrocyclic ligands such as dimethylglyoximine and tetraphenylporphin have been reported [1]. However, only a few examples of alkylcobalt(III) complexes having other types of ligands than these macrocycles are known [2]. In the course of our investigations of various transition metal alkyl complexes, we have found that remarkably stable cationic dialkylcobalt complexes, [CoR$_2$(bpy)$_2$][AlR$_4$], are produced by the reaction of Co(acac)$_3$ with an excess of AlR$_3$ in the presence of bpy ligand *,

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* bpy = 2,2'-bipyridine.

TABLE 1

ANALYTICAL DATA FOR $[CoR_2(bpy)_2]X$

Compounds		Yield (%)	M.p. (dec.) (°C) [b]	Λ (Ω^{-1} cm^2)	Analyses (found (calcd.)) (%)		
					C	H	N
Ia	$[Co(CH_3)_2(bpy)_2][Al(CH_3)_4]$ [a]	82	130–135	21.3	61.8(63.9)	6.0(7.0)	12.1(11.5)
Ib	$[Co(C_2H_5)_2(bpy)_2][Al(C_2H_5)_4]$ [a]	73	120–123	35.0	68.3(67.1)	8.4(8.1)	9.9(9.8)
IV	$[Co(CH_3)_2(bpy)_2][Al(C_2H_5)_4]$		104–105		65.9(66.2)	8.2(7.8)	10.1(10.3)
IIa	$[Co(CH_3)_2(bpy)_2]Cl \cdot (CH_2Cl_2)$	20–50	[c]		52.3(52.9)	4.3(4.6)	11.6(10.7)
IIb	$[Co(C_2H_5)_2(bpy)_2]Cl \cdot (CH_2Cl_2)$	20–50	[c]		50.7(51.7)	4.8(4.9)	9.2(9.5)
IIIa	$[Co(CH_3)_2(bpy)_2][B(C_6H_5)_4] \cdot (H_2O)$	100	191–195		74.4(74.8)	5.9(6.0)	7.5(7.6)
IIIb	$[Co(C_2H_5)_2(bpy)_2][B(C_6H_5)_4] \cdot (H_2O)$	100	125–130	26.0	75.3(75.2)	5.7(6.3)	6.9(7.3)

[a] Good analytical values are not obtainable owing to the contamination with decomposed aluminum compounds. [b] Under nitrogen. [c] Gradually decomposed in a range of 100–190°C.

as we have already noted in a preliminary communication [3]. In this paper we report the details of the preparation, chemical properties, and structure of the cationic dialkylcobalt complexes,

Although cationic alkyltransition metal species with an aluminate anion as counter ion are often assumed to be formed in Ziegler type catalytic systems and their role in catalyses has been discussed [4], no study has been made of their properties by isolating the compounds from such reaction mixtures. We also found that employment of smaller ratios of AlR_3 to $Co(acac)_3$ in the reaction of $Co(acac)_3$, AlR_3, and bpy gives neutral dialkylcobalt(III) complexes which are formulated as $CoR_2(acac)(bpy)$ and which will be described here together.

Results and discussion

Preparation and spectroscopic properties of cationic dialkylcobalt(III) complexes

Reaction of $Co(acac)_3$ with an excess of $AlR_3(Al/Co > 7)$ in the presence of bpy in diethyl ether gave red cationic dialkylcobalt(III) complexes.

$$\underset{1\ :\ 3.4\ :\ \text{ca. }8}{Co(acac)_3 + bpy + AlR_3} \xrightarrow[\text{in } Et_2O]{\text{r.t.}} \underset{(Ia,\ R = CH_3;\ Ib,\ R = C_2H_5)}{[CoR_2(bpy)_2][AlR_4]} \tag{1}$$

Table 1 summarizes analytical data, decomposition points, and equivalent electric conductivities of Ia, Ib, and related complexes. These cationic dialkylcobalt(III) complexes are quite stable at room temperature under nitrogen and in dry air. Their thermal decomposition starts at temperatures higher than 100°C, evolving alkane and alkene (For $R = CH_3$ (d.p. = 140—142°C): CH_4 (46%), H_2 (trace); For $R = C_2H_5$ (d.p. = 106—109°C): C_2H_4 (33%), C_2H_6 (46%), H_2 (trace), the yields being based on the total molar amount of alkyl group.) The large electric conducitivities of Ia and Ib strongly support their ionic structures. IR and NMR spectral data of the complexes are given in Tabel 2. The IR spectra of Ia and Ib show strong ν(C—H) bands at 2800—2950 cm^{-1}, characteristic bands of AlR_4^- at 680 cm^{-1} and 630 cm^{-1} [5] and several bands assignable to coordinated bpy ligands. The IR spectrum of complex Ia shows two weak bands at 540 cm^{-1} and 330 cm^{-1} which disappear on thermolysis and might be assigned to ν(Co—C).

Methyl and methylene protons of $[AlEt_4]^-$ in Ib appear in its ^1H NMR spectrum as characteristic multiplets due to coupling with the Al nucleus ($I = 5/2$) [6]. On the other hand, the methyl and methylene protons of the ethyl groups bonded to cobalt are observed as a triplet and a couple of quartets, respectively. The appearance of the $Co—\underline{CH_2}—CH_3$ signal as a couple of quartets indicates that the ethyl groups are bonded to an asymmetric central cobalt atom [7], hence a *cis* configuration for Ib is suggested. The complex pattern of the coordinated bpy signals of Ib also supports the *cis* configuration. Thus the NMR spectrum of Ib shows two different types of pyridyl rings, one type being mutually *trans* and the other *trans* to the ethyl groups:

TABLE 2

^{1}H-NMR AND IR SPECTRA OF $[CoR_2(bpy)_2]X$

Compounds			Temp. (°C)	Solvent	Chemical shift[a]					IR spectra (cm^{-1})[c]		
	R	X			CoR_2		AlR_4		Others (aromatic)	ν(C—H) in CoR	ν(C—H) in AlR_4	
Ia	CH_3	$Al(CH_3)_4$	−50	CD_2Cl_2	CH_3	0.60 (6 H, s)	CH_3	−1.3 (12 H, m)	7.2—8.7 (16 H, c)	[b]	2900s	680s
			r.t.	$(CD_3)_2CO$	CH_3	0.74 (6 H, s)	CH_3	−0.9 (12 H, m)	7.2—8.8 (16 H, c)		2800(sh)	
Ib	C_2H_5	$Al(C_2H_5)_4$	−50	CD_2Cl_2	CH_3	0.07 (6 H, t(8))	CH_3	−0.6 (8 H, m)	7.0—8.6 (16 H, c)	[b]	2920(sh)	630s
					CH_2	1.59 (2 H, q(8))	CH_3	0.9 (12 H, m)			2880(sh)	
						1.74 (2 H, q(8))					2840s	
			−50	$(CD_3)_2CO$	CH_3	0.01 (6 H, t(8))	CH_2	−0.5 (8 H, m)	7.3—8.8 (16 H, c)		2775(sh)	
					CH_2	1.61 (2 H, q(8))	CH_3	1.0 (12 H, m)				
						1.82 (2 H, q(8))						
IIa	CH_3	Cl	r.t.	D_2O	CH_3	0.03 (6 H, s)			6.9—8.2 (16 H, c)	2930m		
			r.t.	CD_3OD	CH_3	0.78 (6 H, s)			7.4—8.9 (16 H, c)	2860m		
										2790w		
IIb	C_2H_5	Cl	r.t.	D_2O	CH_3	−0.46 (6 H, t(8))			6.9—9.2 (16 H, c)	2930m		
					CH_2	1.17 (2 H, q(8))				2870m		
						1.35 (2 H, q(8))				2790w		
			r.t.	CH_3OD	CH_3	−0.05 (6 H, t(8))			6.8—8.5 (16 H, c)			
						1.57 (2 H, q(8))						
					CH_2	1.72 (2 H, q(8))						
IIIa	CH_3	$B(C_6H_5)_4$	r.t.	$(CD_3)_2CO$	CH_3	0.76 (6 H, s)			6.7—8.6 (36 H, c)	2930 w		
										2830w		
IIIb	C_2H_5	$B(C_6H_5)_4$	r.t.	$(CD_3)_2CO$	CH_3	0.01 (6 H, t (8))			6.7—8.6 (36 H, c)	2930w		
						1.66 (2 H, q(8))				2830w		
					CH_2	1.84 (2 H, q(8))						
IV	CH_3	$Al(C_2H_5)_4$	r.t.	$(CD_3)_2CO$	CH_3	0.74 (6 H, s)	CH_2	−0.45 (8 H, m)	7.2—8.6 (16 H, c)	[b]	2920(sh)	600s
							CH_3	1.0 (12 H, m)			2880(sh)	
											2840s	
											2775(sh)	

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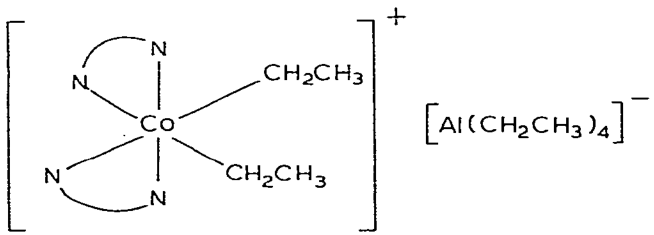
[a] Abbreviations: s, singlet; t, triplet; q, quartet; c, complexed peak; m, multiplet for ^{1}H NMR. The numbers in parentheses indicate coupling constants in Hz. Chemical shifts are referred to internal TMS. For IIa and IIb, the observed chemical shift (δ 5.35 ppm) of the CH_2Cl_2 as a solvent of crystallization was assumed. [b] Peaks of ν(C—H) of CoR were obscured by the large peaks of alkyl aluminate. [c] KBr disc. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.



where $\widehat{N\;N}$ represents 2,2′-bipyridine ligand. The ^{1}H NMR spectrum of 2,2′-bipyridine ligand of the methyl analogue, Ia, is explained similarly.

Chemical properties of dialkylbis(2,2′-bipyridine)cobalt(III) aluminate

The inertness of Ia and Ib toward water is noteworthy. This is surprising if one thinks of the extreme sensitivity of other non-transition metal salts with tetraalkyl aluminate anion. Strong acids such as concentrated sulfuric acid, however, cleave the alkyl—cobalt and —aluminum bonds to liberate alkane. The amounts of the alkanes released provided further support for the proposed structures with a total of six alkyl groups.

$$[CoR_2(bpy)_2][AlR_4] + H_2SO_4 \rightarrow 6\ RH \qquad (3)$$

On the other hand, dry hydrogen chloride reacts only with the aluminate anion to release four equivalents of alkane in diethyl ether, but Co—R bonds remain intact giving red cationic complexes of $[CoR_2(bpy)_2]Cl$.

$$\underset{(I)}{[CoR_2(bpy)_2][AlR_4]} + \underset{\text{excess}}{HCl} \rightarrow \underset{(II)}{[CoR_2(bpy)_2]Cl} + 4\ RH \qquad (4)$$

$$(\text{IIa},\ R = CH_3;\ \text{IIb},\ R = C_2H_5)$$

Complexes IIa and IIb were also obtained on slow crystallization of Ia and Ib from chlorinated solvents such as methylene chloride and chloroform, with abstraction of chlorine from the solvent, These cationic dialkylcobalt(III) chlorides were identified by spectroscopic and chemical analysis (Tables 1 and 2) as well as by comparison with the known iodide analogue $[CoR_2(bpy)_2]I$ previously reported by Mestroni et al. [2a].

The chloride complexes IIa and IIb are more stable than Ia and Ib in protic solvents such as H_2O and CH_3OH. Heating the D_2O solution of IIa and IIb for 4 h at 50°C caused only slight decomposition as proved by NMR spectroscopy. They are stable even in dilute (<1 N) aqueous solutions of HCl and H_2SO_4, but decompose in more concentrated acids. The low reactivity of the $[CoR_2(bpy)_2]^+$ cation toward H_2O and HCl may be due, at least partly, to the positive charge on cobalt, which prevents the attack of proton on the complex.

Although the Co—R bond is stable in protic solvents, the irradiation of IIa with ultraviolet light caused facile decomposition of IIa in water at 15°C, giving mainly methane. Homolytic fission of the Co—CH_3 bond by photolysis probably gives methyl radicals, which would be further converted into methane in H_2O. Similar homolytic fission has been observed in the photolysis of methylcobaloxime(III), which gives methane [8]. The cationic complexes IIa and IIb show poor reactivity toward H_2, CO and C_2H_4. The starting material was recovered after prolonged reactions at room temperature. Blocking the coordination sites in IIa and IIb by bpy probably serves to hinder the interaction of the substrates with cobalt.

The ionic complexes I and II underwent a facile metathesis reaction with sodium tetraphenylborate $Na[B(C_6H_5)_4]$ in moist acetone to give $[CoR_2(bpy)_2][B(C_6H_5)_4]H_2O$.

$$\left.\begin{array}{l} [CoR_2(bpy)_2][AlR_4] + Na[B(C_6H_5)_4] \\ \quad (I) \\ [CoR_2(bpy)_2]Cl + Na[B(C_6H_5)_4] \end{array}\right\} \rightarrow \underset{(III)}{[CoR_2(bpy)_2][B(C_6H_5)_4]\cdot H_2O} \qquad (5)$$

$$(II) \qquad \text{in acetone}/H_2O \qquad (IIIa,\ R = CH_3;\ IIIb,\ R = C_2H_5)$$

A metathesis of complex IIa with $Li[Al(C_2H_5)_4]$ also proceeds smoothly to give an ionic dimethylcobalt complex with the $[Al(C_2H_5)_4]^-$ anion [9a].

$$\underset{(IIa)}{[Co(CH_3)_2(bpy)_2]Cl} + Li[Al(C_2H_5)_4] \xrightarrow[\text{in THF-hexane}]{} \underset{(IV)}{[Co(CH_3)_2(bpy)_2][Al(C_2H_5)_4]} \qquad (6)$$

No exchange between the methyl groups bonded to cobalt and the ethyl groups in aluminate was confirmed by the ^1H NMR and IR spectroscopic analyses of IV showing only their characteristic signals of the dimethylcobalt cation and the tetraethyl aluminate anion.

Molecular structure of dialkylbis(2,2'-bipyridine)cobalt(III) aluminate

The molecular structure of IV obtained by the X-ray diffraction technique is illustrated in Fig. 1, together with relevant bond lengths. Detailed crystallographic

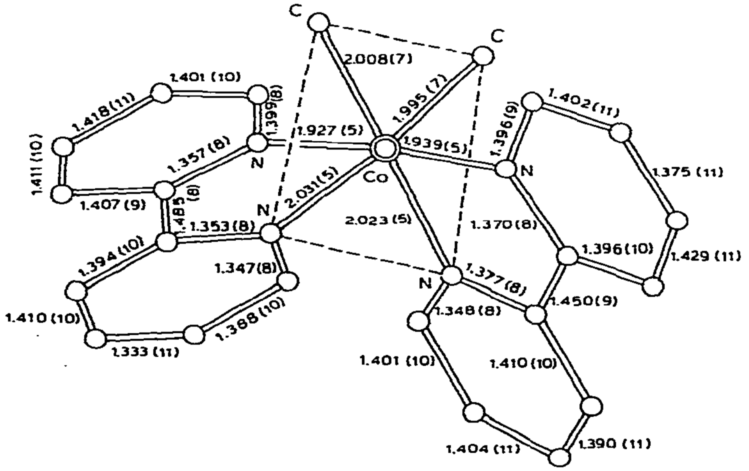
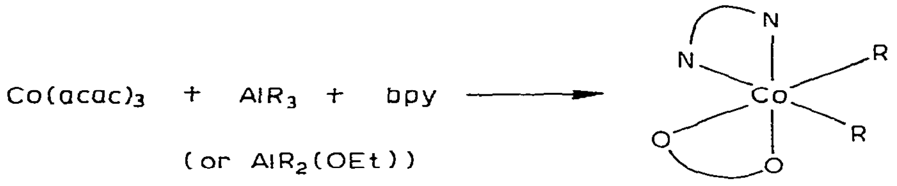


Fig. 1. Molecular structure of $[CoMe_2bpy_2]^+AlEt_4^-$.

data will be reported elsewhere [9b]. This molecular structure agrees with the *cis* structure which we proposed on the basis of the ^{1}H NMR spectroscopic studies. The geometry around Co(III) is almost octahedral and no covalent bond between cobalt and the aluminum moiety was observed, indicating an ionic structure in the crystal. Bond lengths of Co—CH_3 are 1.995 and 2.008 Å, which are comparable with the known bond lengths of 1.99—2.01 Å in alylcobalt(III) complexes with macrocyclic ligands [10]. Longer distances of Co—N bonds *trans* to the methyl group (2.031 Å and 2.023 Å) than those of Co—N bonds *trans* to nitrogen (1.927 and 1.939 Å) demonstrates the strong *trans* influence of the methyl groups as proposed in the literature [10].

Formation of neutral dialkyl(2,4-pentanedionato)(2,2'-bipyridine)cobalt(III)

In contrast to the formation of ionic aluminate complexes at higher Al/Co ratios from the system of $Co(acac)_3$, AlR_3 (or $AlR_2(OEt)$) and bpy, neutral dialkylcobalt complexes having both acac and bpy ligands, *cis*-$CoR_2(acac)(bpy)$, were obtained in good yields from the reaction mixtures at low Al/Co ratios:



(7)

(V)

Al/Co = 1.5 - 2.0

(Va, R = CH_3; Vb, R = C_2H_5;
Vc, R = n-C_3H_7; Vd, R = i-C_3H_7)
Yield 70 - 100 %

where O⌒O and N⌒N represent 2,4-pentanedionato and 2,2'-bipyridine ligand, respectively. The remarkable variation of the products obtained in the reaction of $Co(acac)_3$, AlR_3 and bpy depending on the amount of organoaluminum employed suggests the presence of a delicate balance among the chemical species formed under the preparative conditions. The dimethyl-, diethyl-, and di-n-propylcobalt complexes of type V (Va—Vc) have been prepared also by the ligand exchange reaction of $CoR_2(acac)(PR_3')_2$ with bpy [2h].

Process of the formation of the alkylcobalt complexes

Alkyl exchange reaction of transition metal salts with alkylating reagent in Ziegler type catalysis has been considered as an important fundamental step [11] and much effort has been devoted to the isolation of alkylmetal complexes from these catalyst systems and to clarify the process of the alkyl exchange reaction [12]. In the present system the alkylation of $Co(acac)_3$ with alkylaluminum compounds is summarized as:

$$\mathrm{Co(acac)_3 + bpy + AlR_3} \begin{cases} \xrightarrow{\mathrm{Al/Co\ =\ 1.5-2.0}} \mathrm{CoR_2(acac)(bpy)} \\ \qquad\qquad\qquad\quad (\mathrm{V}) \\ \xrightarrow{\mathrm{Al/Co\ >\ 7}} [\mathrm{CoR_2(bpy)_2}][\mathrm{AlR_4}] \\ \qquad\qquad\qquad\quad (\mathrm{I}) \end{cases} \tag{8}$$

Formation of V in the presence of lesser amounts of the aluminum compound suggests that the simple exchange reaction of 2,4-pentanedionato ligands with the alkyl groups in trialkylaluminum takes place. Similar alkylmetal complexes with 2,4-pentanedionato ligand have been isolated in reactions of iron [2g], cobalt [2h] and nickel [13] 2,4-pentanedionates with alkylaluminum compounds in the presence of suitable tertiary phosphine ligands. Further alkylation of V will lead to the formation of trialkylcobalt(III) species. Indeed, an analogue of Va, $\mathrm{Co(CH_3)_2(acac)[P(CH_3)_2(C_6H_5)]_2}$, was found to be further alkylated by methyllithium to give the trimethylcobalt(III) compound $\mathrm{Co(CH_3)_3[P(CH_3)_2(C_6H_5)]_3}$, which is easily converted back to $\mathrm{Co(CH_3)_2(acac)[P(CH_3)_2(C_6H_5)]_2}$ by the reaction with 2,4-pentanedione [14].

$$\begin{tikzcd} \mathrm{Co(acac)_3 + L + AlR_2OEt} \arrow[r] & \mathrm{Co(CH_3)_2(acac)L_2} \arrow[d, shift right, "\begin{matrix}+\mathrm{MeLi}\\ +\mathrm{L}\end{matrix}"'] \\ \mathrm{L = P(CH_3)_2(C_6H_5)} & mer\text{-}\mathrm{Co(CH_3)_3L_3} \arrow[u, shift right, "\begin{matrix}+\mathrm{Hacac}\\ -\mathrm{L}\end{matrix}"'] \end{tikzcd} \tag{9}$$

Formation of a trimethylcobalt(III) complex containing the trimethylphosphine ligand also was reported by Klein et al. [2d]. Formation of a similar trialkylcobalt(III) complex, $\mathrm{CoR_3(bpy)}_n$, also is expected in the present reaction system between $\mathrm{Co(acac)_3}$ and $\mathrm{AlR_3}$ in the presence of bpy. However, the supposed $\mathrm{CoR_3}$ intermediate seems to be unstable. The monoalkylcobalt complex may be formed through the decomposition of the supposed $\mathrm{CoR_3}$ species when a moderate amount of organoaluminum (Al/Co = ca. 4) is used *. In the presence of a large excess of $\mathrm{AlR_3}$, on the other hand, one of the three R groups in the $\mathrm{CoR_3}$ species may shift to $\mathrm{AlR_3}$, giving a stable cationic dialkylcobalt complex with tetraalkylaluminate. Migration of an alkyl group R from a transition metal to aluminum is known [15].

$$\begin{tikzcd} \mathrm{Co(acac)_3 + bpy + AlR_3} \arrow[r] & \mathrm{CoR_2(acac)(bpy)} \arrow[d, "+\mathrm{AlR_3}"] & \\ & \mathrm{CoR_3(bpy)}_n \arrow[r, "\ell", "\begin{matrix}-\mathrm{RH},\ -\mathrm{R(-H)}\\ \mathrm{etc.}\end{matrix}"'] \arrow[d, "+\mathrm{AlR_3}"] & \mathrm{CoR(bpy)_2} \\ & [\mathrm{CoR_2(bpy)_2}][\mathrm{AlR_4}] & \end{tikzcd}$$

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* At first the complex was reported [2e] to have two R groups ($\mathrm{CoR_2(bpy)_2}$), but later it was found to have one R group [11d].

A dark blue compound (presumably $CoR(bpy)_2$) was formed by dissolving complex Ia or Ib in donor solvents such as THF and acetone (see Experimental). The liberation of trialkylalyminum from Ia or Ib by complexing with the donor solvent and the successive reductive elimination of the resulting trialkylcobalt species may lead to the monoalkylcobalt complex.

$$\begin{array}{c} [CoR_2(bpy)_2][AlR_4] \xrightarrow[\text{solvent}]{} [CoR_3(bpy)_n] + (\text{solvent})AlR_3 \\ \Big\downarrow {\scriptstyle -RH,\ -R(-H)\ \text{etc.}} \\ CoR(bpy)_2\ (\text{blue complex}) \end{array} \tag{10}$$

Complex formation of trialkylaluminums with Lewis bases is well known [16] and the facile liberation of the aluminum component from alkyl/copper/aluminum complexes in a relatively basic solvent has been also reported [17].

Experimental

All preparations were carried out under purified inert gas (N_2 or Ar) or in vacuo. Solvents were purified by usual methods and stored under nitrogen before use. Tris(acetylacetonato)cobalt(III) (Tokyo Kasei Co., Ltd.) was used after recrystallization from benzene. Trialkylaluminums were obtained from Ethyl Coorporation Co., Ltd. and were used without further purification. Dialkylaluminum monoethoxides were prepared by the reaction of corresponding trialkylaluminum with equivalent amounts of ethyl alcohol. $LiAlEt_4$ was prepared by the reaction of $AlEt_3$ with Li metal [18]. ^1H NMR and IR spectra were recorded on JEOL-PS 100 and Hitachi Model EPS-3T or EPI-G3 spectrometers, respectively. Microanalyses were performed by Mr. Saito with a Yanagimoto CHN Autocorder Type MT-2. Electric conductivities were measured with a Yanagimoto Model MY-7 Conductivity Outfit. Gases evolved were analyzed by gas chromatography after collecting them by using a Toepler pump by which the volumes of the gases were measured.

Preparation of $[Co(CH_3)_2(bpy)_2][Al(CH_3)_4]$*, Ia, and* $[Co(C_2H_5)_2(bpy)_2]$*-*$[Al(C_2H_5)_4]$*, Ib*

Trimethylaluminum (3.8 g, 53 mmol) was added to a suspension of $Co(acac)_3$ (2.4 g, 6.7 mmol) and bpy (3.6 g, 23 mmol) in diethyl ether (60 ml) at − 60°C. The reaction mixture was warmed slowly to room temperature, giving a brown homogeneous solution. Precipitation of a deep red solid (powder) started after the solution had been stirred at room temperature for 1 h. After 10 h, the deep red solid which precipitated was separated by filtration, washed with hexane more than 5 times and dried in vacuo to yield 2.7 g of Ia (76%).

Complex Ib (2.8 g, 45%) was prepared similarly from $Co(acac)_3$ (2.4 g, 6.7 mmol), bpy (3.6 g, 23 mmol), and $Al(C_2H_5)_3$ (5.8 g, 51 mmol);

Acidolysis of Ia (0.157 mmol) with conc. H_2SO_4 gave CH_4 (0.856 mmol, 91%) and trace amounts of C_2H_4 and C_2H_6. Acidolysis of Ib (0.103 mmol) with conc. H_2SO_4 gave C_2H_4 and C_2H_6 in a ratio of ca. 1/3. The total amount of gas evolved was 0.612 mmol (99%).

Thermolysis of Ia (59.8 mg, 0.123 mmol) at 180°C gave CH_4 (0.340 mmol) and a trace of hydrogen. Complex Ib (72.4 mg, 0.127 mmol) afforded C_2H_4

(0.249 mmol), C_2H_6 (0.353 mmol) and a trace of hydrogen on thermolysis at 180°C.

When complex Ib was dissolved in THF, the color of the solution gradually changed from red to dark blue accompanied by evolution of ethylene and ethane in a few hours. Dark blue crystals were formed on cooling and were separated by filtration. The IR spectrum of the resulting complex showed ν(C—H) bands at 2840 and 2900 cm^{-1} (w), probably due to Co—CH_3, and several bands for coordinated bpy. No bands attributable to the aluminate moiety were observed. Acidolysis of the resulting complex (45.3 mg) by conc. sulfuric acid gave ethane (0.051 mmol). Complex Ia gave a similar color change. These compounds are tentatively assigned as $CoR(bpy)_2$ by comparing their spectral data with those of the monoalkylcobalt complexes previously reported *.

Reaction of Ia and Ib with dry hydrogen chloride

Addition of dry HCl (1.8 mmol) to Ia (70.8 mg, 0.145 mmol) in diethyl ether gave methane (0.542 mmol, 93% based on eq. 3) and IIa (68 mg). ν(C—H) for Co—CH_3 = 2930, 2860 and 2780 cm^{-1}. Complex Ib (81.0 mg, 0.141 mmol) reacted with dry HCl (2.0 mmol) giving ethane (0.628 mmol, 110%) and IIb similarly. A trace amount of hydrogen was also evolved in these reactions.

Conversion of Ia and Ib into $[Co(CH_3)_2(bpy)_2]Cl$, IIa and $[Co(C_2H_5)_2(bpy)_2]Cl$, IIb in chlorinated solvents

The complex Ia was dissolved in a mixture of CH_2Cl_2 (ca. 10 ml/g of the complex Ia) and hexane and the solution was allowed to stand at room temperature. After 3—5 days, the needles of IIa which had precipitated were collected by filtration and recrystallized from CH_2Cl_2 (yield 20—50%). The IR spectrum of IIa showed absorption bands of CH_2Cl_2 which is included into the crystals at 1420, 1240, 890 and 730 cm^{-1}. Crystallization from $CHCl_3$ also gave IIa having $CHCl_3$ as solvent of crystallization. Extensive washing of the solvated complexes with hexane gave non-solvated complexes.

Metathesis reactions of Ia, Ib, IIa, and IIb with $Na[B(C_6H_5)_4]$

Complex Ia (0.30 g) was mixed with $Na[B(C_6H_5)_4]$ (0.73 g) in acetone (15 ml) at —78°C to give a red homogeneous solution. The solution was poured into a large excess of water to cause the instant precipitation of IIIa (in quantitative yield) which was collected by filtration and dried in vacuo. Metathesis reaction of Ib (0.19 g) with $Na[B(C_6H_5)_4]$ (0.93 g) was performed similarly.

Addition of an aqueous solution of $Na[B(C_6H_5)_4]$ (0.177 g) to an aqueous solution of IIa (0.2049 mg) caused instantaneous precipitation of a red complex formulated as $[Co(CH_3)_2(bpy)_2][B(C_6H_5)_4]H_2O$. The complex was filtered, washed with distilled water until no chloride ion was detected in the filtrate by a test with a $AgNO_3$ solution, and dried in vacuo. Reaction of IIb with $Na[BC_6H_5)_4]$ was carried out similarly.

Reaction of IIa with $LiAlEt_4$

On mixing the complex IIa (0.9 g) and $LiAlEt_4$ (0.35 g) in THF (10 ml), a homogeneous red solution was obtained. n-Hexane (30 ml) was added to the red solution giving red needles of IV in a few hours. Isolation was carried

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* See footnote on p. 354.

out at low temperature (ca. —30°C). Thermolysis of IV (0.097 mmol) at 150°C gave methane (0.110 mmol), ethane (0.142 mmol) and ethylene (0.095 mmol). Trace amounts of C_3H_6, C_3H_8 and n-C_4H_8 were also detected.

Photolysis of IIa by ultraviolet light

An aqueous solution (5 ml) of IIa (0.16 mmol) was irradiated with a 100W super high-pressure mercury lamp at 15°C for 2 h, giving mainly methane (0.02 mmol) accompanied by a trace of ethane. Further irradiation for a day led to complete decomposition of IIa.

Preparation of [Co(C_2H_5)$_2$(acac)(bpy)] Vb

Al$(C_2H_5)_3$ (1.4 ml, 10 mmol) was added to a mixture of Co(acac)$_3$ (2.4 g, 6.7 mmol) and bpy (3.6 g, 23 mmol) suspended in 40 ml of diethyl ether at —78°C. The reaction mixture was warmed to room temperature and stirring of the reaction mixture for 1 h gave a dark brown homogeneous solution. Further stirring at room temperature for 2 h afforded a dark green solid which was separated by filtration and washed with hexane thoroughly to give Vb quantitatively. Complex Va was prepared similarly. The complexes Va, Vb, Vc, and Vd also were prepared analogously by the reaction of Co(acac)$_3$ with AlR$_2$(OEt) in the presence of bpy in diethyl ether (Al/Co = 1.5—2.0).

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