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Synthesis of a Dimethylcobalt(III) Complex Containing Di-2-pyridylamine Ligands and Catalytic Studies on Polymerization of Acrylonitrile

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A new dimethylcobalt(III) complex of di-2-pyridylamine (dpa), $[Co(dpa)_2(CH_3)_2]I$, was synthesized under an inert atmosphere by the reduction of $[Co(dpa)_2Cl_2]$ with $NaBH_4$, followed by oxidative addition reaction with CH_3I. Isolation of intermediate $[Co(dpa)_2(CH_3)Cl]I$ was achieved, and the mechanism for the formation of $[Co(dpa)_2(CH_3)_2]^+$ was proposed. Complex $[Co(dpa)_2(CH_3)_2]I$ produced methane and ethane by hydrolysis and thermolysis, respectively, but insertion of carbon monoxide between the Co–CH_3 bond did not occur. Reduction of $[Co(dpa)_2(CH_3)_2]I$ with $NaBH_4$ caused polymerization of acrylonitrile very effectively. The polymerization proceeded through a Ziegler–Natta type mechanism involving a low-valent cobalt alkyl presumably $[Co(dpa)_2R]$, as the actual catalytic species.

Introduction

Although the coordination of π-accepting ligands is not essential for stabilization of transition metal–carbon σ-bonds, most of the alkylcobalt complexes reported thus far are stabilized by the π-accepting ligands such as carbon monoxide, triaryl- or trialkylphosphines, cyclopentadienyl,[1-3] or tetradentate ligands with extensive π-conjugation.[4-7] Those containing bipyridine, o-phenanthroline, diiminosuccinonitrile, or Schiff bases have been also reported.[8-13]

We were interested in the preparation of alkylcobalt(III) complexes that contain poor π-accepting ligands and exhibit catalytic ability to polymerize olefins. For this purpose, flexible bidentate ligand di-2-pyridylamine (dpa) was utilized as the coordinating ligand.

The only alkylcobalt complex of pyridine derivatives reported to date is $(CH_3)_2Co(py)_2$.[14] Moreover, the only known cobalt(III) complex containing di-2-pyridylamine ligand has been $[Co(dpa)_3]^{3+}$, which was synthesized by the oxidation of $[Co(dpa)_3]^{2+}$.[15] In homogeneous catalysis, oxidative addition and reductive elimination reactions are frequently involved, and control of the coordination number by metal ions or/and ligands is important. The flexible bidentate di-2-pyridylamine was expected to control the coordination number of the metal ion without complete dissociation from the metal ion.

In this study, methylcobalt(III) complexes of di-2-pyridylamine, $[Co(dpa)_2(CH_3)_2]^+$ and $[Co(dpa)_2(CH_3)Cl]^+$, were prepared by a simple procedure; reduction of $[Co(dpa)_2Cl_2]$ followed by oxidative addition of alkyl halides. The alkylcobalt(III) complexes thus prepared exhibited excellent catalytic effects on the polymerization of acrylonitrile in the presence of $NaBH_4$.

Experimental Section

General Comments. All manipulations of oxygen- or water-sensitive materials were conducted by using standard Schlenk or vacuum line techniques. All solvents used in the syntheses were of reagent grade, dried over 5-Å molecular sieves, and degassed prior to use. Solvents used for spectra and conductivity measurements were purified according to the literature.[16]

Physical and Analytical Measurements. The conductivity measurements were performed by using an Industrial Instruments Model RC 216 B2 conductivity bridge. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Samples were prepared as either KBr pellets or hexachlorobutadiene mulls. ^1H NMR spectra were recorded on a Varian EM-360 60-MHz spectrometer. Ultraviolet and visible electronic absorption spectra were recorded on a Beckman Model 25 spectrophotometer. GC analyses were performed by using a Hewlett-Packard 5730A gas chromatograph equipped with a thermal conductance detector. The column used was 12 ft × $^1/_8$ in. stainless-steel Spherocarb 80/100. Column oven was maintained at 80 °C. Elemental analyses were performed by the Galbraith Laboratories, Inc. Knoxville, TN. Molecular weight of polyacrylonitrile was measured by using an Ubbelohode type capillary viscometer. Intrinsic viscosity was estimated by the measurement of viscosity of Me_2SO solutions of various concentrations of the polymer.

Syntheses. All preparations were carried out under a nitrogen atmosphere.

$[Co(dpa)_2(CH_3)_2]I$. Method I. $[Co(dpa)_2Cl_2]\cdot CH_3OH$ was synthesized according to the method previously reported.[17] $[Co(dpa)_2Cl_2]\cdot CH_3OH$ (2×10^{-3} mol) was dissolved in degassed methanol (20 mL), and CH_3I (5×10^{-3} mol) was added to the solution. Then $NaBH_4$ (8.5×10^{-3} mol) was added slowly over a period of 30 min with stirring. The color of the mixture changed initially to dark brown, then to orange, and finally to red. The solution was stirred for additional 20 min and filtered. The filtrate was allowed to stand under a nitrogen atmosphere at room temperature for 2 days in the absence of light. The red crystals formed were filtered, washed with degassed methanol, and dried under vacuum. When excess $LiClO_4$ or NH_4PF_6, which was dissolved in degassed methanol, was added to the solution, the crystals of $[Co(dpa)_2(CH_3)_2]X$, where X = ClO_4^- or PF_6^-, were obtained; yield ~70%.

Method II. To a degassed methanol solution (50 mL) of $[Co(dpa)_2(CH_3)Cl]I\cdot 6CH_3OH$ (3.24×10^{-3} mol) was added CH_3I (3.34×10^{-3} mol), and then $NaBH_4$ (7.93×10^{-3} mol) was added

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over a period of 10 min with stirring. The solution was filtered, and the filtrate was allowed to stand under a nitrogen atmosphere at room temperature in the absence of light until red crystals formed. The crystals were filtered, washed with degassed methanol, and dried under vacuum; yield ~80%.

The red crystals synthesized by above methods contained methanol in the crystal lattice, which was verified by the ^1H NMR spectra. When dried under vacuum at ~80 °C, the crystals turned to powder.

$[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$. To a degassed methanol solution (20 mL) of $[Co(dpa)_2Cl_2] \cdot CH_3OH$ (1.3×10^{-3} mol) was added CH_3I (1.3×10^{-3} mol), and then $NaBH_4$ (3.3×10^{-3} mol) was added over a period of 30 min with stirring. The solution turned initially dark brown and then yellow. The solution was stirred for additional 30 min, and a methanol solution of KI (4.1×10^{-3} mol) was added. The solution was filtered, and the filtrate was kept at ~4 °C for 2 days under a nitrogen atmosphere in the absence of light. The yellow crystals formed were filtered, washed with methanol, and dried under nitrogen stream at room temperature; yield ~50%.

Thermal Decomposition of $[Co(dpa)_2(CH_3)_2]I$. A solid sample (0.1 g) was placed in a 10-mL round-bottomed flask and the outlet of the flask was plugged with glass wool. The flask was connected to the sampling loop of GC, and the whole system was evacuated. The flask was placed in an oil bath whose temperature was maintained at ~100 °C. The red sample turned black immediately upon heating. Gas product that was collected in the sampling loop was analyzed by GC.

Reaction of $[Co(dpa)_2(CH_3)_2]I$ with Water. The reaction flask was connected to the sampling loop of GC, and the whole system was evacuated. The compound dissolved in a minimum amount of degassed methanol was syringed into the reaction flask, and then degassed water was added. While vapor pressure of water and methanol was lowered by immersing the flask in an acetone–dry ice slush bath, gas collected in the sampling loop was analyzed by GC.

Reaction of $[Co(dpa)_2(CH_3)_2]I$ with Carbon Monoxide. The complex (1.5×10^{-3} mol) was dissolved in methanol (20 mL), and carbon monoxide gas was bubbled through the solution for 1 h. The solution was stirred under a carbon monoxide pressure of 2 atm for 24 h. Ethyl ether was added dropwise until the solution became turbid. The precipitates were filtered and dried under carbon monoxide.

Effects of Several Systems on the Polymerization of Acrylonitrile. (i) A pulverized sample or a methanol (5 mL) solution of $[Co(dpa)_2(CH_3)_2]I$ (1.9×10^{-4} mol) was added to acrylonitrile (20 mL) with stirring. No polymerization reaction was observed for several months even when the reaction temperature was elevated to 80–90 °C. However, when $NaBH_4$ (5.2×10^{-4} mol) was added to the above mixture at room temperature over a 10-min period with stirring, the solution vigorously generated gas and heat, and the whole mixture became a lump of yellow solid within 20 min. (ii) The same experimental procedures as (i) were applied to $[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$. $[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$ did not cause polymerization of acrylonitrile even at ~80 °C, but it produced a yellow solid at room temperature exothermically when $NaBH_4$ was added. (iii) To a mixture of acrylonitrile (20 mL) and methanol (5 mL) was added $NaBH_4$ (8.9×10^{-3} mol). The solution generated heat, and yellow viscous liquid was formed in 1 h. However, in the absence of methanol, a viscous liquid was not produced. (iv) $[Co(dpa)_2Cl_2] \cdot CH_3OH$ (3.6×10^{-3} mol) was dissolved in methanol (10 mL) and added to acrylonitrile (20 mL). Polymerization was not observed even at an elevated temperature (~60 °C). Even the addition of large excess $NaBH_4$ (1.5×10^{-2} mol) did not lead to the formation of a lump of solid or a viscous liquid.

Results and Discussion

Synthesis and Characterization of the Methylcobalt(III) Complexes $[Co(dpa)_2(CH_3)_2]I$ and $[Co(dpa)_2(CH_3)Cl]I$. The most general method for the synthesis of alkylcobalt(III) complexes is to employ the corresponding cobalt(I) complexes. In particular, cobalt(I) complexes stabilized by conjugate tetradentate ligands having nitrogen or nitrogen and oxygen donor atoms behave as powerful nucleophiles toward alkyl halides and undergo oxidative addition reactions.[18,19] Dimethylcobalt(III) complexes containing bipyridine or *o*-phenanthroline were also prepared by the reaction of cobalt(I) complexes with alkyl halide.[9]

Table I. Analyses, Conductance, and Electronic Absorption Data for $[Co(dpa)_2(CH_3)_2]I$ and $[Co(dpa)_2(CH_3)Cl]I \bullet 6CH_3OH$

	$[Co(dpa)_2(CH_3)_2]I$	$[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$
elemental anal.	C, H, N, Co	C, H, N, Co
calcd	47.33, 4.33, 15.05, 10.56	42.06, 5.84, 10.90, 7.64
found	47.12, 4.31, 14.81, 10.47	40.47, 5.37, 10.93, 7.61
conductance, Λ_M[a]	85	87
electronic spectra, 0.1 μm^{-1} (ϵ)[b]	22.2 (39), 34.2 (31 300), 40.5 (42 700), 45.2 (42 000)	27.8 (620), 38.3 (910)

[a] Ω^{-1} mol^{-1} cm^2 in methanol. [b] Solvent used were acetonitrile for $[Co(dpa)_2(CH_3)_2]I$ and methanol for $[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$.

Di-2-pyridylamine is not as a strong ligand as *o*-phenanthroline or bipyridine, but the difference is not very large. The *Dq* value of $[Ni(dpa)_3]^{2+}$ is 1120 cm^{-1} [20,21] while it is 1270 cm^{-1} for $[Ni(o\text{-}phen)_3]^{2+}$.[22] The *Dq* value of $[Fe(dpa)_3]^{2+}$ is 1200 cm^{-1} [23] while it is 1310 cm^{-1} for $[Fe(o\text{-}phen)_3]^{2+}$.[24] The most significant difference between di-2-pyridylamine and bipyridine or *o*-phenanthroline is that the latter is planar or very nearly so in its complexes whereas the former is not. Moreover, the latter acts as a good π-accepting ligand whereas the former does not.[25–27]

Octahedral $[Co(dpa)_2Cl_2] \cdot CH_3OH$ has been synthesized, and its conversion to tetrahedral species in various solvents except alcohol has been observed in our laboratory.[17]

The octahedral dimethylcobalt(III) complex $[Co(dpa)_2(CH_3)_2]I$ was synthesized by the addition of CH_3I and $NaBH_4$ to a degassed methanol solution of $[Co(dpa)_2Cl_2] \cdot CH_3OH$. The mole ratio used was $Co^{II}:CH_3I:NaBH_4 = 1:2.5:4$. When $LiClO_4$ or NH_4PF_6 was added to the solution, $[Co(dpa)_2(CH_3)_2]X$ ($X = ClO_4^-$ or PF_6^-) was produced. When the ratio of $CH_3I:Co^{II}$ was less than 2, a mixture of the monomethyl complex $[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$ and the dimethyl complex $[Co(dpa)_2(CH_3)_2]I$ was obtained. Pure $[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$ was synthesized with the mole ratio $[Co(dpa)_2Cl_2] \cdot CH_3OH:CH_3I:NaBH_4 = 1:1:2$. Monomethyl complex thus prepared reacted with $NaBH_4$ and CH_3I, resulting in the dimethyl complex $[Co(dpa)_2(CH_3)_2]I$. This indicates that the monomethyl species $[Co(dpa)_2(CH_3)Cl]^+$ is an intermediate during the formation of the dimethyl complex $[Co(dpa)_2(CH_3)_2]^+$.

Elemental analyses and conductance data as well as the electronic spectra are summarized in Table I.

$[Co(dpa)_2(CH_3)_2]I$ is red and reasonably stable in solid state or in solution toward air and light at room temperature. $[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$ is yellow and ex-

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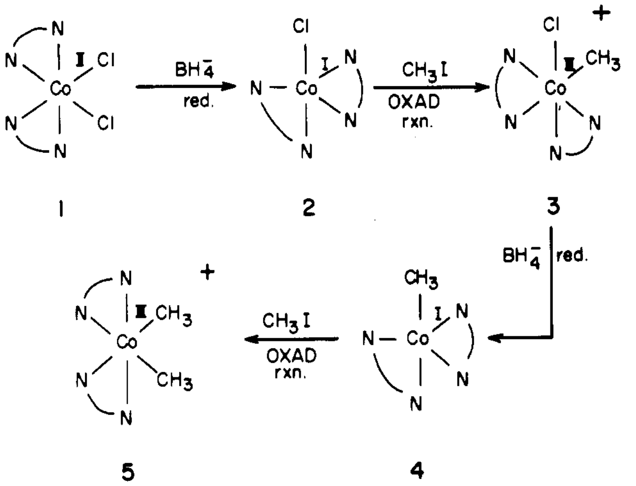
Table II. ^{1}H NMR Data for Methylcobalt(III) Complexes

complex[a]	solv	δ(Co–CH_3)	ref
$[Co(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH$	$Me_2SO\text{-}d_6$	1.96	this study
$[Co(dpa)_2(CH_3)_2]I$	$Me_2SO\text{-}d_6$	1.04	this study
$[Co(bpy)_2(CH_3)_2](ClO_4)_2$	$CDCl_3$	0.8	9
$[Co(TIM)(CH_3)Br]BPh_4$	$Me_2SO\text{-}d_6$	1.14	18
$[Co(TIM)(CH_3)Cl]BPh_4$	$Me_2SO\text{-}d_6$	1.17	19
$[Co(TIM)(CH_3)_2]ClO_4 \cdot H_2O$	$CH_3CN\text{-}d_3$	0.35	30
$[Co(TIM)(CH_3)_2]BPh_4$	$Me_2SO\text{-}d_6$	0.36	18
$[Co(CR)(CH_3)Br]PF_6$	$Me_2SO\text{-}d_6$	0.53	18
$[Co(CR)(CH_3)_2]BPh_4$	$Me_2SO\text{-}d_6$	0.18	18

[a] CH_3 and X or two CH_3's are cis to each other in dpa and bpy complexes whereas they are trans in the TIM and CR systems.

Scheme I



tremely sensitive to air either in solid state or in solution. The methanol solutions of the compounds form yellow precipitates of AgI immediately upon the addition of $AgNO_3$.

Electronic spectra of $[Co(dpa)_2(CH_3)_2]^+$ and $[Co(dpa)_2(CH_3)Cl]^+$ show broad bands around 450 and 360 nm, respectively, which indicate that the complexes have a cis configuration. *cis-* and *trans-*$[Co^{III}L_4Z_2]^{x+}$ species are readily distinguished on the basis of intensity and band position. Cis complexes are acentric and almost invariably exhibit more intense transitions than the trans ones. In addition, provided that L and Z differ sufficiently in ligand field strength, the $^1T_{1g}$ state is split in the trans complex but is rarely split in the cis complex.[15,28,29] Molecular models also indicate that the trans cations involve severe steric hinderance between the hydrogen atoms in the 6-positions of the di-2-pyridylamine ligand and should be much less stable than the cis isomers.

^{1}H NMR spectra of dimethyl- and monomethylcobalt(III) complexes show proton peaks of Co–CH_3 at δ 1.04 and 1.96, respectively, which appear at a higher field than those of the methyl groups in common organic compounds. The proton peak of Co–CH_3 for the dimethyl complex appears at a higher field than for the monomethyl complex. This is observed for other Co(III) complexes (Table II) and can be explained by the stronger σ-donating character of CH_3^- than Cl^-. The fact that proton peak of Co–CH_3 in $[Co(dpa)_2(CH_3)_2]^+$ appears at a lower field than that in $[Co(bpy)_2(CH_3)_2]^+$ indicates that dipyridylamine is a less electron-donating ligand than bipyridine.

Scheme II

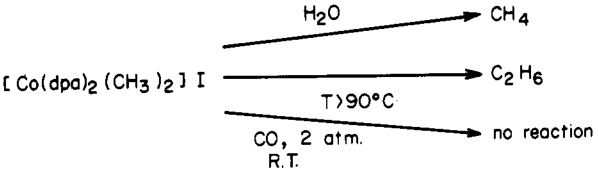


Table III. Catalytic Ability of Various Systems in Polymerization of Acrylonitrile[a]

$$\text{(i)}\ [Co^{III}(dpa)_2(CH_3)_2]I\ (\text{in MeOH}) \xrightarrow{AN} \text{no};\quad \xrightarrow{AN\ +\ NaBH_4} \text{yes}$$

$$[Co^{III}(dpa)_2(CH_3)_2]I\ (\text{solid}) \xrightarrow{AN\ +\ NaBH_4} \text{yes}$$

$$\text{(ii)}\ [Co^{III}(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH\ (\text{in MeOH}) \xrightarrow{AN} \text{no};\quad \xrightarrow{AN\ +\ NaBH_4} \text{yes}$$

$$[Co^{III}(dpa)_2(CH_3)Cl]I \cdot 6CH_3OH\ (\text{solid}) \xrightarrow{AN\ +\ NaBH_4} \text{yes}$$

$$\text{(iii)}\ NaBH_4 + MeOH \xrightarrow{AN} \text{no}^{b}$$

$$NaBH_4 \xrightarrow{AN} \text{no}$$

$$\text{(iv)}\ [Co^{II}(dpa)_2Cl_2] \cdot CH_3OH\ (\text{in MeOH}) \xrightarrow{AN} \text{no};\quad \xrightarrow{AN\ +\ NaBH_4} \text{no}$$

$$[Co^{II}(dpa)_2Cl_2] \cdot CH_3OH\ (\text{solid}) \xrightarrow{AN\ +\ NaBH_4} \text{no}$$

[a] Acrylonitrile is abbreviated to AN. [b] A viscous liquid is formed instead of solid polymer.

The mechanism for the formation of the complexes is proposed in Scheme I. In this scheme, the cobalt(II) complex $[Co(dpa)_2Cl_2]$ (**1**) is reduced by $NaBH_4$ to produce a five-coordinate cobalt(I) complex, $[Co(dpa)_2Cl]$ (**2**). The reduction of cobalt(II) complexes with $NaBH_4$, Na(Hg), or Zn to cobalt(I) complex have often been observed in other ligand systems.[9,12,31-33] The cobalt(I) complex thus formed, $[Co(dpa)_2Cl]$, behaves as a nucleophile toward CH_3I, undergoing oxidative addition reaction to yield the monomethylcobalt(III) complex $[Co(dpa)_2(CH_3)Cl]^+$ (**3**). The fact that the reactive cobalt(I) species is five-coordinate is substantiated by the isolation of the $[Co(dpa)_2(CH_3)Cl]^+$ complex. For the formation of $[Co(dpa)_2(CH_3)Cl]^+$, it is required that the cobalt(I) species retains one of the Cl^- ions in its coordination sphere during the reaction. $[Co(dpa)_2(CH_3)Cl]^+$ is reduced by $NaBH_4$ to form the five-coordinate cobalt(I) compound $[Co(dpa)_2(CH_3)]$ (**4**), which in turn undergoes oxidative addition reaction with CH_3I to produce the dimethylcobalt(III) complex $[Co(dpa)_2(CH_3)_2]^+$ (**5**).

Reactions of $[Co(dpa)_2(CH_3)_2]I$. The results of hydrolysis, thermal decomposition, and carbon monoxide insertion of the compound are summarized in Scheme II. The compound reacts with water, producing methane. The cleavage of a M–CH_3 bond by an acid to produce methane is well-documented. Thermolysis of the compound leading to ethane can be explained by reductive coupling.[34,35] Insertion of carbon monoxide to Co–C bond of the compound is not observed by the IR spectra. Coordination of carbon monoxide to the metal, which is essential for the

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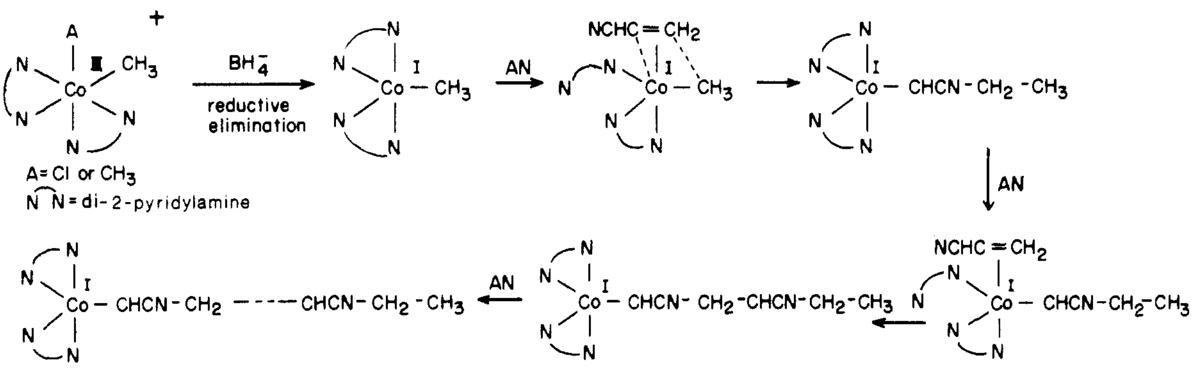
Scheme III



carbonyl insertion reaction, may not occur because the electron density on cobalt(III) is insufficient for the π-back-bonding to carbon monoxide. Alternatively, carbon monoxide pressure (2 atm) used in this research may be too low to promote the coordination of carbon monoxide to cobalt(III) ion. Several other alkylcobalt(III) complexes which contain chelate ligands such as DMG, salene, or corrinoid were reported to resist insertion of carbon monoxide also.[36]

Catalytic Effects of $[Co(dpa)_2(CH_3)_2]I$ on the Polymerization of Acrylonitrile. Results of polymerization of acrylonitrile catalyzed by various systems are summarized in Table III. Addition of pulverized samples or methanol solutions of $[Co(dpa)_2(CH_3)_2]I$ or $[Co(dpa)_2(CH_3)Cl]I{\cdot}6CH_3OH$ to acrylonitrile did not produce polyacrylonitrile at either room temperature or above 80 °C. However, acrylonitrile polymerized to a lump of yellow solid when $NaBH_4$ was also added, producing a large amount of heat. This polymerization reaction proceeded in the air as well as under a nitrogen atmosphere. The yellow solid thus formed turns red above 100 °C, softens at 130 °C, and becomes black above 220 °C. The yellow solid is soluble in Me_2SO and DMF. Infrared spectrum (KBr pellet, $\nu_{CH} = {\sim}3000$ and $\nu_{CN} = 2250$ cm^{-1}) and ^1H NMR spectrum (α-H, δ 3.20, β-H, δ 1.92 in Me_2SO-d_6) indicate that the yellow solid is polyacrylonitrile, which is a linear paraffin with nitrile groups on alternate carbon atoms. The average molecular weight of the polyacrylonitrile was estimated as 4.4×10^4 by the measurement of intrinsic viscosity in Me_2SO.[37]

When $NaBH_4$ was added to acrylonitrile in the presence of methanol, a viscous liquid was obtained. However, in the absence of methanol, it was not formed. It is well-known that reaction of $NaBH_4$ with methanol produces $NaB(OCH_3)_4$, which decomposes to sodium methoxide and methyl borate.[38] Thus, the formation of a viscous liquid can be explained by the oligomerization of acrylonitrile catalyzed by methoxide anion. Therefore, the formation of polyacrylonitrile by the system of $[Co(dpa)_2(CH_3)_2]I$ and $NaBH_4$ in the absence of methanol indicates that the catalytic species for the polymerization is not $NaBH_4$, but a low-valent cobalt complex formed by reduction of $[Co(dpa)_2(CH_3)_2]I$ with $NaBH_4$. Moreover, the fact that $[Co(dpa)_2Cl_2]{\cdot}CH_3OH$ did not lead to polymerization of acrylonitrile forming a lump of solid or viscous liquid even in the presence of $NaBH_4$ and methanol[39] indicates that the alkyl group is essential for the catalysis. Therefore, the actual catalytic species must be a low-valent cobalt alkyl such as cobalt(I) methyl.

Table IV. Polymerization Rate of Acrylonitrile by the Catalytic Mixture of $[Co(dpa)_2(CH_3)_2]I$ and $NaBH_4$

amount of $[Co(dpa)_2(CH_3)_2]I$, 10^{-4} mol	amount of $NaBH_4$, 10^{-4} mol	time required for the polymerization of 20 mL of AN,[a] h
0.4	1.0	>>72
0.6	1.6	24
1.2	3.3	1
1.9	5.0	1/3
0.7	5.3	24
1.2	5.3	1
2.0	5.3	1/3

[a] Reactions were carried out with 20 mL (~0.3 mol) of neat acrylonitrile at room temperature.

The time required to complete the polymerization of 20 mL (~0.3 mol) of acrylonitrile decreased as the amount of catalytic mixture of $[Co(dpa)_2(CH_3)_2]I$ and $NaBH_4$ (1:2.5 mol ratio) increased as shown in Table IV. When the amount of $NaBH_4$ was fixed in excess, the polymerization rate depended only on the amount of $[Co(dpa)_2(CH_3)_2]I$. This results also support that the actual catalytic species is the low-valent cobalt–alkyl compound. Table IV also indicates that the polymerization reaction gives high turnover numbers of substrate in the presence of an excess of reducing agent: 1 mol of a cocatalyst, $[Co(dpa)_2(CH_3)_2]I$, can cause the polymerization of several thousand moles of acrylonitrile.

Polymerization of acrylonitrile usually proceeds through an anionic mechanism or a radical mechanism.[40,41] These mechanisms, however, can be excluded for the present polymerization reaction on the following grounds. (1) The only anions present in the present system are I^- derived from $[Co(dpa)_2(CH_3)_2]I$, BH_4^- from $NaBH_4$, and OCH_3^- formed by the reaction of $NaBH_4$ with methanol. However, these anions are not the real catalytic species as discussed previously. (2) Polymerization proceeded even in the presence of a large amount of α-naphthol, a good scarvenger of free radicals. (3) The radical process is known to be inhibited by a trace amount of moisture and air.[40] However, the present polymerization reaction was not affected and proceeded in the air as well as under nitrogen.

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[37] Braundrop, J.; Immergut, F. H. *Polymer Handboodk*, 2nd ed.; Wiley: New York, 1975; pp 308–314.

[38] This phenomenon can be explained by that $[Co^{II}(dpa)_2Cl_2]{\cdot}CH_3OH$ is reduced to $[Co(dpa)_2Cl]$ by $NaBH_4$, and in the presence of $[Co(dpa)_2Cl_2]$ or $[Co^I(dpa)_2Cl]$ the methoxide ion may be used for the substitution of the ligand of the complex instead of oligomerization of acrylonitrile.

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[40] *The Chemistry of Acrylonitrile*, 2nd ed.; American Cyanamide Co.: New York, 1959; pp 29–32.

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A Ziegler–Natta type mechanism (Scheme III) is proposed for the present polymerization of acrylonitrile. In this scheme, five-coordinate cobalt(I)–methyl complexes are involved, which are formed by the reduction of cobalt(III) methyl with $NaBH_4$. Reduction of alkylcobalt(III) complex with $NaBH_4$ or Na(Hg) to give alkylcobalt(I) complex has been reported for other ligand systems.[18,42] The flexible bidentate ligand di-2-pyridylamine plays an important role of providing a vacant coordination site for acrylonitrile to form cobalt(I)–acrylonitrile π-complexes in the catalytic cycle.

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Registry No. 1, 81985-22-0; 3·I, 105763-88-0; 5·I, 105763-87-9; 5·ClO_4, 105763-90-4; 5·PF_6, 105763-91-5; acetonitrile, 107-13-1.

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[42] Pratt, J. M.; Craig, P. J. *Adv. Organomet. Chem.* 1973, 432.

Stereochemistries and Mechanisms of Reactions of Electrophiles with Organotin Compounds

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The effect of solvent and electrophile on halodemetalation reactions of carbon–tin bonds has been investigated. Both stereochemical results and ^{119}Sn NMR have been used as mechanistic probes. The effect of solvent is extreme; reactions performed in polar solvents such as acetonitrile and dimethylformamide yield cleavage products with predominantly inversion of configuration, whereas nonpolar solvents yield products with predominantly retention. Polar-aprotic solvents appear to be highly efficient in promoting inversion stereochemistry. Polar-protic solvents are not as efficient. This is explained in terms of some very specific solvation phenomena. Also, ^{119}Sn NMR studies of several trialkyltin halides in various solvents show that these specific solvation phenomena can be qualitatively assessed. The nature of the electrophile also plays an important role in eventual stereochemistry; Br_2, I_2, ICl, and IBr are compared and discussed.

Early work investigating electrophilic cleavages of organomercurials indicated that retention of configuration at carbon was the general stereochemical outcome for S_E2 reactions.[1] In an attempt to demonstrate the viability of an inversion mechanism, Jensen and Davis[2] sought to devise a system which would have properties favorable to an inversion pathway. An examination of the possible transition states for S_E2 reactions, Figure 1, reveals that the transition state leading to inversion of configuration at carbon, Figure 1c, would require (a) sufficient charge stabilization of both leaving groups Y and M and (b) steric hindrance to frontside attack by the electrophile Y–Z. Thus, Jensen and Davis synthesized trineopentyl-*sec*-butyltin, reacted it with bromine in methanol with added sodium bromide, and obtained inversion at carbon.[2] Since this finding, other groups have also demonstrated inversion stereochemistry for S_E2 processes at carbon–tin bonds. Rahm and Pereyre demonstrated that the severe steric congestion caused by neopentyl substitution on tin resulted in an abnormal stereochemical outcome and that retention was still the preferred pathway.[3] In a later study performed by McGahey and Jensen it was found that inversion pathways compete with retention pathways and there is *no* general preferred stereochemistry.[4] They studied the bromodemetalation of a series of tetraalkyltins of the form (*sec*-butyl)Sn(isopropyl)$_{3-N}$(neopentyl)$_N$, $N = 0–3$, in carbon tetrachloride, acetonitrile, and methanol. They observed that reactions in carbon tetrachloride gave predominantly retention of configuration, reactions in methanol yielded *sec*-butyl bromide with either net retention or inversion of configuration depending on alkyl substitution, and reactions performed in acetonitrile gave products with predominantly net inversion of carbon. This work demonstrated the separate influences exerted by alkyl substitution on tin and solvent on the eventual stereochemical pathway.

Gielen and Fosty also observed a dramatic medium effect for the bromodemetalation of tetraalkyltins in chlorobenzene: inversion of configuration at carbon in the presence of "naked" fluoride ion and retention in the absence of the fluoride salt.[5]

These media effects raised crucial questions about the role of media participation in determining the eventual stereochemistry of electrophilic cleavages at the carbon–tin bond. The primary questions are the following: what role does solvent play in determining the stereochemistry of reaction, and what solvent properties are especially important in this participation? Reported herein are the results of a systematic study of the effects of solvent on the halodemetalation of tetraalkyltin compounds. Both stereochemistry at carbon and ^{119}Sn NMR are utilized as mechanistic probes.

Also, it has been demonstrated that alkyl substitution on tin is vitally important in determining the stereochemistry of electrophilic cleavage,[2-4] and preliminary results indicate that solvent also plays a major role.[4,5] However, the effect of the electrophile has not yet been systematically investigated. The stereochemistry of S_E2 reactions at carbon–tin bonds by bromine has been studied fairly

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