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PREPARATION OF CATIONIC DIALKYLCOBALT COMPLEXES $[CoR_2(bpy)_2]$-$[AlR_4]$ (R = CH_3, C_2H_5) BY THE REACTIONS OF $Co(acac)_3$ WITH TRIALKYLALUMINUMS IN THE PRESENCE OF 2,2'-BIPYRIDINE

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Stable cationic dialkylcobalt complexes of composition $[CoR_2(bpy)_2]$-$[AlR_4]$ (R = CH_3, C_2H_5) were obtained in high yields from mixtures of $Co(acac)_3$, 2,2'-bipyridine (bpy), and trialkylaluminums (Al/Co > 7). Ion exchange reactions of the complexes with $Na[B(C_6H_5)_4]$ afforded $[CoR_2(bpy)_2]$-$[B(C_6H_5)_4]\cdot(H_2O)_n$ (R: CH_3, n=1; C_2H_5, n=0). Reactions of $[CoR_2(bpy)_2]$-$[AlR_4]$ with CH_2Cl_2 gave $[CoR_2(bpy)_2]Cl\cdot CH_2Cl_2$.

Formation of transition metal alkyls in various Ziegler type catalyst mixtures (transition metal compounds plus alkylaluminums) has been soundly established. However, most of the transition metal alkyls isolated from the Ziegler type catalyst mixtures are electrically neutral and examples of cationic transition metal alkyls are scarce.[1,2] We report here the isolation of cationic dialkylcobalt complexes of composition $[CoR_2(bpy)_2][AlR_4]$ (R = CH_3, C_2H_5) from the mixtures of $Co(acac)_3$ (acac = acetylacetonato), AlR_3, and 2,2'-bipyridine (bpy). Formation of alkylaluminate salts with transition metal alkyl cations has been sometimes suggested,[1,3] but isolation of this type of complex has no precedent.

When a mixture of $Co(acac)_3$ (2.4 g, 6.7 mmol), bpy (3.6 g, 23 mmol), and $Al(CH_3)_3$ (3.8 g, 53 mmol) in 60 ml of diethyl ether was warmed from -60°C to room temperature, a brown homogeneous solution was obtained. On stirring the solution for 1 hr a deep red solid began to precipitate, and the deep red solid separated from the solution after further reaction for 10 hr was washed with hexane thoroughly and dried in vacuum to obtain 2.7 g (5.5 mmol, y. = 82 %) of $[Co(CH_3)_2(bpy)_2][Al(CH_3)_4]$ (**1a**). $[Co(C_2H_5)_2$-$(bpy)_2][Al(C_2H_5)_4]$ (**1b**) was prepared in a similar manner (y. = 73 %). The complexes **1a** and **1b** are fairly stable in air.

$$\underset{1}{Co(acac)_3} + \underset{3.4}{bpy} + \underset{ca.8}{AlR_3} \longrightarrow [CoR_2(bpy)_2][AlR_4] \qquad (1)$$

1 : 3.4 : ca.8   R = CH_3 (**1a**), C_2H_5 (**1b**)

The Co-$\underline{CH}_3$ signal of **1a** in its ^1H-NMR spectrum (CD_2Cl_2, -50°C) appeared at a considerably lower field (0.60 ppm, s, 6H) compared with the electrically neutral transition metal methyl complexes.[4] The Al-$\underline{CH}_3$ signal appeared at -1.28 ppm (12H) as a complex multiplet due to the $^{27}Al-^1H$ coupling characteristic of $Al(CH_3)_4$ anion.[5] The NMR spectrum of **1b** (CD_2Cl_2, -50°C) showed Co-$\underline{CH}_2$- at 1.59 (q, 8Hz, 2H) and 1.74 (q, 8Hz, 2H) ppm, Co-CH_2-$\underline{CH}_3$ at -0.07 ppm (t, 8Hz, 6H), Al-$\underline{CH}_2$- at -0.61 ppm (m, 8H), and Al-CH_2-$\underline{CH}_3$ at 0.87 ppm (m, 12H), respectively. The appearance of the Co-$\underline{CH}_2$- signal as a couple of quartets indicates that the two ethyl groups are bonded to asymmetric cobalt[6] and therefore suggests a cis-configuration for the complex. The electronegativity of the cobalt atom in **1b** calculated from the difference between the positions of Co-$\underline{CH_2}$- and Co-CH_2-$\underline{CH_3}$ signals$^{7)}$ is 3.2. The value is much larger than Pauling's electronegativity of atomic cobalt (χ = 1.7) and it is consistent with the cationic structure of the cobalt complex. The IR spectra of **1a** and **1b** showed ν(Al-C) bands$^{8)}$ at 680 and 630 cm^{-1}, respectively. Table 1 shows the equivalent conductivities (Λ) of **1a** and **1b**. The data of non-ionic complexes are also given for the comparison.

Table 1. Equivalent Conductivities of Cationic Dialkyl Cobalt Complexes

Complex	**1a**	**1b**	**2b**	KI	$Co(acac)_3$	$Ni(C_2H_5)_2(bpy)$
$\Lambda^{a)}$	21.3	35.0	26.0	40.3	< 0.07	0.07

a) Equivalent conductivity ($\Omega^{-1}\cdot cm^2$) in dry acetone at -78°C.

It is seen in Table 1 that the complexes **1a** and **1b** have ionic structures.

The complexes **1a** and **1b** underwent facile ion exchange reaction with $Na[B(C_6H_5)_4]$ to afford red crystals of $[CoR_2(bpy)_2][B(C_6H_5)_4]\cdot(H_2O)_n$ ($R=CH_3$, n=1 **2a**; $R=C_2H_5$, n=0 **2b**). Furthermore the complexes **1a** and **1b** were converted to the complexes of composition $[CoR_2(bpy)_2]Cl\cdot CH_2Cl_2$ ($R = CH_3$ **3a**; $R = C_2H_5$ **3b**) by the reaction with CH_2Cl_2. Analytical data agreed with the compositions of the complexes **2a**, **2b**, **3a**, and **3b**. The iodide analogs of **3a** and **3b** have been prepared by reducing $CoCl_2\cdot 6H_2O$ with $NaBH_4$ in the presence of alkyl iodide and bpy.$^{9)}$

The methyl signals of **2a** and **3a** and the methyl and methylene signals of **2b** and **3b** in the NMR spectra appeared at almost the same positions as those of the methyl signal of **1a** and of methyl and methylene signals of **1b**, respectively, indicating that the dialkylcobalt cations $[CoR_2(bpy)_2]^+$ in the three different types of complexes (**1** - **3**) have essentially the same electronic structure. The ratios between the peak areas in the NMR spectra agreed with the structures of the complexes. All of the cationic complexes are thermally stable up to 100°C.

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