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Methylation of Zinc(II), Cadmium(II), and Lead(II) by a *trans*-Dimethylcobalt Complex

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The methylation reactions of Zn^{2+}, Cd^{2+}, and Pb^{2+} by the *trans*-dimethylcobalt complex $(CH_3)_2Co(BDM1,3pn)$ in 2-propanol are discussed (BDM1,3pn is a mononegative tetradendate dioxime–diimine ligand formed by the condensation of 2 mol of 2,3-butanedione monoxime and 1,3-propanediamine). The products of the 1:1 reactions are $CH_3Co^{III}(BDM1,3pn)^+$ and unstable CH_3Zn^+, CH_3Cd^+, and CH_3Pb^+. Kinetic studies were carried out on the decomposition of the CH_3M^+ intermediates resulting in the relative rates $CH_3Zn^+ >> CH_3Cd^+ \sim CH_3Pb^+$, with half-lives of 1.5, 52.6, and 60.1 h, respectively. A kinetic study of the demethylation of $(CH_3)_2Co(BDM1,3pn)$ by Zn^{2+} and Cd^{2+} revealed the presence of binuclear intermediates of the type $M^{2+}\cdot R_2Co(BDM1,3pn)$.

Introduction

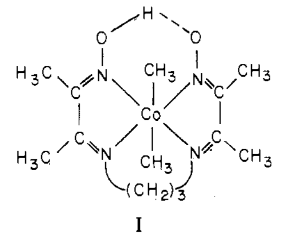
The dealkylation reactions of organocobalt chelates of the type RCo(chel)[30] (R = CH_3, C_2H_5, n-C_3H_7, etc.) by the Hg(II) electrophile has been a subject of considerable interest in recent years. The Co–Hg transalkylation reactions of cobaloximes have been extensively investigated, and a wealth of kinetic and stereochemical data has been accumulated for this system.[1-9] More recently, the reactions of $[RCo(BDM1,3pn)H_2O]^+$ [10,11] and of $CH_3Co(chel)$ (chel = tim, salen, and saloph)[12] with Hg(II) were studied in detail. These reactions invariably exhibit a 1:1 stoichiometry and result in the products shown in eq 1. The effect of the R group and of the chelating ligand on the rates of these reactions support a bimolecular electrophilic substitution (SE2) mechanism.

$$RCo(chel) + Hg^{2+} \rightarrow RHg^+ + Co^{III}(chel)^+ \qquad (1)$$

Of principal interest to our work are the reactions of alkylcobalt complexes with metal ions other than Hg^{2+}. Perhaps the most interesting reactions studied in this respect are the reactions of methylcobalamin with Cr^{2+} [13] and Tl^{3+} [9] to yield CH_3Cr^{2+} and CH_3Tl^{2+}, respectively. Analogous reactions of alkylcobaloximes with Cr^{2+} [14] and Tl^{3+} [5] to yield RCr^{2+} and RTl^{2+} were reported. Other metal ions including Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, and In^{3+} were shown to be unreactive toward monoalkylcobalt chelates.[9,15]

We are presently engaged in a comprehensive study of the cobalt–carbon bond reactivity in a series of *trans*-dialkylcobalt chelates toward metal ions and metalloids. Complexes of this type $R_2Co(chel)$ (chel = BDM1,3pn, tim, cr) remain relatively unstudied presumably because of their high reactivity. The Co–C bond of the $R_2Co(BDM1,3pn)$ complexes is readily cleaved by electrophiles such as ICl[16] or $Co^{III}(chel)$.[17] In addition, these complexes are extremely unstable to light as exemplified by the photolytic reactions of $(CH_3)_2Co(BDM1,3pn)$ (structure I) in methanol, ethanol, and 2-propanol.[18]

In this paper we will discuss the dealkylation reactions of I by Zn^{2+}, Cd^{2+}, and Pb^{2+} in i-C_3H_7OH. These metal ions were previously shown to be unreactive toward a variety of organocobalt species.[9,15] This study involves the elucidation of some very surprising reactions in which I is unusually effective among methylcobalt complexes as a carbanion donor. In addition, our data support the formation of relatively stable organometallic products of the type CH_3M^+ which is entirely unexpected in view of the protic solvent employed.



I

Results and Discussion

Stoichiometry and Products. In contrast to the reactions of the monoalkyl derivatives RCo(chel) with Hg^{2+} which demonstrate a simple 1:1 stoichiometry (eq 1), the reactions of I with Zn^{2+}, Cd^{2+}, and Pb^{2+} are unique. The demethylation of I by all three metal ions can be obtained with two different

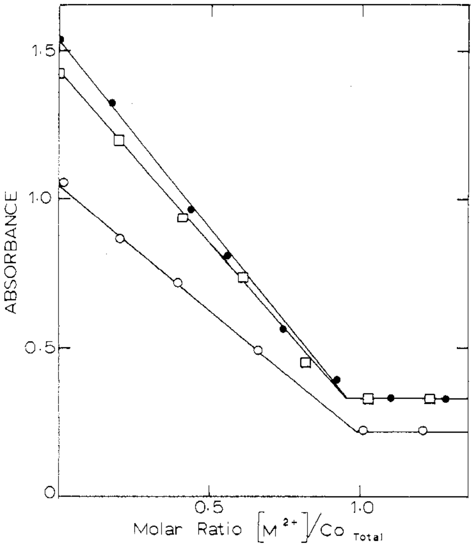


Figure 1. Representative spectral titrations of $(CH_3)_2$-Co(BDM1,3pn) with Cd^{2+} (●), Zn^{2+} (□), and Pb^{2+} (○) at 412 nm.

stoichiometries using a molar ratio complex/M^{2+} of 1.0 or 2.0. The 1:1 and 2:1 stoichiometries are shown in eq 2 and in eq 2 and 3, respectively. We will discuss only the former reactions

$$(CH_3)_2Co(BDM1,3pn) + M^{2+} \xrightarrow{\text{fast}} CH_3Co(BDM1,3pn)^+ + CH_3M^+ \quad (2)$$

$$(CH_3)_2Co(BDM1,3pn) + CH_3M^+ \xrightarrow{\text{slow}} CH_3Co(BDM1,3pn)^+ + (CH_3)_2M \quad (3)$$

in the present work. The latter reactions which result in the formation of unstable dimethylcadmium, dimethylzinc, and dimethyllead species will be presented in a subsequent paper.

Upon reaction of I with an equimolar or excess of Zn^{2+}, Cd^{2+}, or Pb^{2+} in i-C_3H_7OH the ultraviolet–visible spectrum changes instantaneously. These reactions can be monitored most conveniently by observing the disappearance of the visible maximum at 412 nm (ϵ_{max} 8380) which is characteristic of I. The complex product ion $CH_3Co(BDM1,3pn)^+$ was identified by comparison of the spectra of the final solutions with that of a solution made from an analyzed sample of $[CH_3Co(BDM1,3pn)H_2O]^+$. From a knowledge of the molar absorptivity of the product ion at 463 nm (ϵ_{max} 2120) it is evident that I is quantitatively converted to $CH_3Co(BDM1,3pn)^+$ in these reactions. Furthermore, this monoalkyl product is indefinitely stable in the presence of excess Zn^{2+}, Cd^{2+}, or Pb^{2+} in accord with the results of Magnuson[15] for the reactions of $CH_3Co(BDM1,3pn)^+$ with the same metal ions in aqueous solution.

The stoichiometries of these reactions were determined by spectral titration (Figure 1). This procedure was complicated by the slower but significant reaction of CH_3M^+ with a second mole of I (eq 3). As a consequence, a rapid titration technique was devised to minimize any error incurred due to the competing reaction (see Experimental Section). The titrations for Zn^{2+}, Cd^{2+}, and Pb^{2+} yield end points close to complex/M^{2+} = 1:1 in accord with eq 2. The fact that the molar ratios are slightly low reflects the contribution due to the competing reaction.

An interesting feature of this work is the fate of the liberated methyl group. The fast demethylation reactions described above are followed by relatively slow reactions in which methane is evolved. This is in contrast to the demethylation of I by H_3O^+ in which the methane is liberated instantaneously and quantitatively according to eq 4.

$$(CH_3)_2Co(BDM1,3pn) + H_3O^+ \xrightarrow{\text{fast}} CH_3Co(BDM1,3pn)^+ + CH_4 \quad (4)$$

For the Cd^{2+} and Pb^{2+} reactions the theoretical amount of methane was obtained only after ca. 200 h. The methane could be quantitatively recovered at any time during the course of the reaction, however, by the addition of H_3O^+.

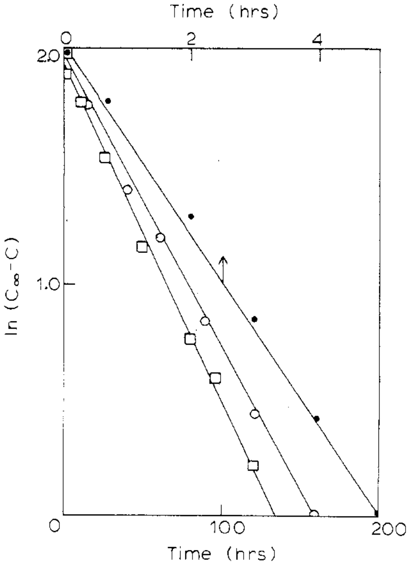


Figure 2. Rate of methane evolution for the reaction of $(CH_3)_2$-Co(BDM1,3pn) with Cd^{2+} (□), Zn^{2+} (●), and Pb^{2+} (○) at room temperature in i-C_3H_7OH.

Table I. Summary of Kinetic Data for Methane Evolution in i-C_3H_7OH

Electrophile	$10^6 k_{obsd}$, s^{-1}	$t_{1/2}$, h
Zn^{2+}	128	1.5
Cd^{2+}	3.6	52.6
Pb^{2+}	3.2	60.1
$H_3O^{+\,a}$		

[a] The theoretical amount of methane was obtained immediately after initiating the reaction.

On the basis of the slow evolution of methane, the sensitivity of the intermediate species to H_3O^+, and the indicated 1:1 stoichiometry, we postulate that intermediates of the type CH_3Zn^+, CH_3Cd^{2+}, and CH_3Pb^+ are formed in these reactions. Further support for these species comes from a study of the kinetics of their decomposition.

The rate of methane evolution was monitored by GC for the reactions of I with the three metal ions. Plots of ln (C_∞ – C) vs. time were linear over at least four half-lives as shown in Figure 2. The rates were independent of excess metal ion concentration, which precludes the possibility of redistribution equilibria of the type shown in eq 5. These results are

$$2CH_3M^+ \rightleftharpoons (CH_3)_2M + M^{2+} \quad (5)$$

consistent with a process in which the organometallic intermediate is decomposed by i-C_3H_7OH (eq 6). Because the

$$CH_3M^+ + i\text{-}C_3H_7OH \rightarrow CH_4 + M(i\text{-}OC_3H_7)^+ \quad (6)$$

solvent is in a large excess over the CH_3M^+ species the reaction is pseudo first order and the rate law (eq 7) is followed.

$$d(CH_4)/dt = k_{obsd}[CH_3M^+] \quad (7)$$

A summary of the kinetic data for the methane evolution reactions is presented in Table I. The relative stability $CH_3Cd^+ \gg CH_3Zn^+$ agrees with the known reactivity of saturated organometallic compounds of the group 2B metals, Zn > Cd > Hg.[19] The apparent stability of the CH_3M^+ intermediates is somewhat surprising in view of the protic nature of the solvent. Solvation of the CH_3M^+ species by

Table II. Summary of Second-Order Rate Constants as a Function of Metal Ion Concentration

Zinc(II)		Cadmium(II)	
$10^5[Zn^{2+}]$, M	$10^{-5}k_{obsd}/[Zn^{2+}]$, $M^{-1}\ s^{-1}$	$10^5[Cd^{2+}]$, M	$10^{-5}k_{obsd}/[Cd^{2+}]$, $M^{-1}\ s^{-1}$
7.25	11.7	3.75	28.7
10.7	10.7	5.62	25.3
12.9	10.1	7.50	22.6
16.5	9.2	15.0	15.4
22.5	8.0		

i-C_3H_7OH presumably contributes to the stabilization of these organometallic intermediates, since oxygen donors are known to stabilize alkyl zinc and alkyl cadmium bonds.[19] The isolations of stable alkyl zinc[20] and alkyl cadmium alkoxides[21] are good examples of this effect.

The reaction of $(CH_3)_2Co(BDM1,3pn)$ with Pb^{2+} is analogous to the reaction with Cd^{2+} in certain respects. Divalent organolead compounds are very unstable and frequently disproportionate into organolead(IV) species and lead metal.[22] This reaction was not observed here, however. The 1:1 stoichiometry of the reaction, the methane evolution data, and other evidence[23] suggest that a relatively stable CH_3Pb^+ species is formed. The reactivity of the organometallic compounds correlates with the ionic character of the carbon–metal bond, both decreasing in the order Li > Mg > Zn > Cd > Hg.[24] Consequently, the stability of CH_3Pb^+ observed here ($CH_3Pb^+ \sim CH_3Cd^+ \gg CH_3Zn^+$) agrees with the known covalent character of C–Pb bonds.[22]

Kinetics. The kinetic behavior of the 1:1 reaction (eq 2) of I with Zn^{2+} or Cd^{2+} was investigated by monitoring the decrease in absorbance due to the complex at 412 nm. The corresponding reaction with Pb^{2+} was not studied due to the extreme sensitivity of the reaction to oxygen. These reactions exhibited half-lives on the order of a few milliseconds and were studied using the stopped-flow technique.

Plot of ln $(A - A_\infty)$ vs. time were invariably linear over at least four half-lives for both metal ions. Since the metal ions were in excess over the complex, the observed kinetics were pseudo-first order. A least-squares analysis of the slopes of these lines yielded values for the observed rate constants (k_{obsd}) which ranged from 85 to 180 s^{-1} for Zn^{2+} and 108 to 231 s^{-1} for Cd^{2+}. The metal ion dependence of the reactions was determined by varying $[Zn^{2+}]$ and $[Cd^{2+}]$ from 7.25×10^{-5} to 2.25×10^{-4} M while maintaining the ionic strength constant at 1.8×10^{-3} M. The apparent second-order rate constants decreased markedly with increasing metal ion concentration throughout the range studied as can be seen in Table II.

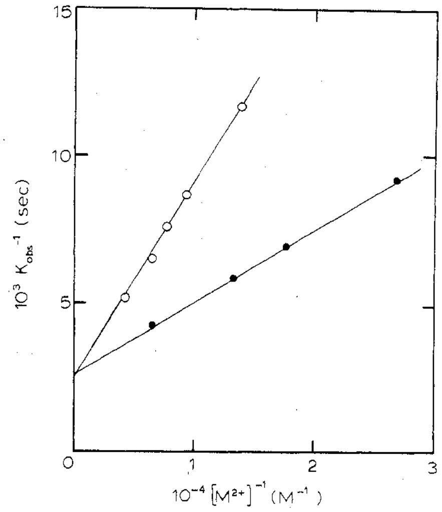


Figure 3. Variation of the reciprocal of k_{obsd} with $[M^{2+}]^{-1}$ for the reactions of $(CH_3)_2Co(BDM1,3pn)$ with Zn^{2+} (○) and Cd^{2+} (●) at 22.2 ± 0.1 °C and $\mu = 1.8 \times 10^{-3}$ M ($LiClO_4$) in i-C_3H_7OH.

Table III. Summary of Kinetic and Equilibrium Data[a] for the Reaction of $(CH_3)_2Co(BDM1,3pn)$ with Zn^{2+} and Cd^{2+}

Electrophile	$10^{-3}K$, M^{-1}	$10^{-2}k_1$, s^{-1}	$10^{-6}k_1K$, $M^{-1}\ s^{-1}$
Zn^{2+}	3.8	3.8	1.4
Cd^{2+}	10.6	4.0	4.2

[a] At 22.2 °C, $\mu = 1.8 \times 10^{-3}$ ($LiClO_4 \cdot 3H_2O$) in i-C_3H_7OH.

The most reasonable explanation of this phenomenon is that there is a rapid preequilibrium between the reactants and a substitutionally labile 1:1 adduct that is being saturated as the concentration of the metal ion is increased (eq 8). This process

$$R_2Co(BDM1,3pn) + M^{2+} \underset{k_b}{\overset{k_f}{\rightleftarrows}} M^{2+}\cdot R_2Co(BDM1,3pn) \tag{8}$$

is followed by the rate-determining decomposition of the adduct to products (eq 9), where R = CH_3 in this scheme. If

$$M^{2+}\cdot R_2Co(BDM1,3pn) \xrightarrow[\text{solvent}]{k_1} RM^+ + RCo(BDM1,3pn)solv^+ \tag{9}$$

$K = k_f/k_b$ and $k_b \gg k_1$, the rate law (eq 10) is derived. Plots

$$\frac{-d[R_2Co(BDM1,3pn)]}{dt} = \frac{k_1K[M^{2+}][R_2Co(BDM1,3pn)]}{1 + K[M^{2+}]} \tag{10}$$

of the reciprocal of the observed pseudo-first-order rate constant vs. the reciprocal of the metal ion concentration are linear in agreement with this scheme. The data indicating this linear relationship are presented in Figure 3. The kinetic and equilibrium parameters were extracted from the slopes and intercepts of these lines and are summarized in Table III.

The proposed first-order decomposition of the adduct (eq 9) is not easily distinguished from a second-order reaction of metal ion with free $R_2Co(BDM1,3pn)$ (eq 11) since both

$$R_2Co(BDM1,3pn) + M^{2+} \rightarrow RM^+ + RCo(BDM1,3pn)^+ \tag{11}$$

processes lead to the same kinetics. However, we favor the former reaction (eq 9) in view of the nearly identical k_1 values observed for both the Zn^{2+} and Cd^{2+} reactions. If the leaving group RM^+ is loosely held in the adduct similar k_1 values are expected. The slight difference in $k_1[Cd^{2+}] > k_1[Zn^{2+}]$ may reflect the size difference and thus the lability of the leaving group in the order $RCd^+ > RZn^+$. Presumably adduct decomposition occurs by way of a five-coordinate intermediate since CH_3 is known to promote the dissociation of trans ligands in octahedral cobalt complexes.[25] Furthermore, five-coordinate alkyl cobalt intermediates are well known in the anation reactions of $RCo(BDM1,3pn)H_2O^+$ and alkyl cobaloximes.[26]

It is not surprising that adduct formation occurs in these reactions since 1:1 adducts were detected in the analogous reactions of the group 2B metal ion Hg^{2+} with the monoalkyl cobalt complexes $RCo(BDM1,3pn)H_2O^+$ and $RCo(salen)$[11] and with $ClCH_2Co(dmg)_2H_2O$.[3] The structure of $M^{2+}\cdot R_2Co(BDM1,3pn)$ presumably involves association of the metal ion with the methyl leaving group. This is reasonable because there is no isolated example of a compound in which a divalent metal ion has replaced the oxime hydrogen-bonded proton, in contrast to the RCo(salen) system. Adducts were not detected in the reactions of Hg^{2+} with other monoalkyl cobalt complexes. However, these reactions may be limiting cases in which $K[Hg^{2+}] < 1$ and thus simple second-order kinetics were observed.

Finally, it is of interest to compare the Co–C bond reactivity of the *trans*-dimethyl complex I observed here with that of the corresponding monomethyl complex $[CH_3Co(BDM1,3pn)H_2O]^+$. The superior trans labilizing influence of CH_3 relative to H_2O is reflected in the large k_1K values for the reactions of I with Cd^{2+} and Zn^{2+}. These same metal ions are unreactive toward $[CH_3Co(BDM1,3pn)H_2O]^+$.[15] In addition, the monomethyl complex is unreactive toward excess H_3O^+ while a second-order rate constant of 79.2 ± 6.2 $M^{-1}\ s^{-1}$ was observed for I in i-C_3H_7OH.[27] These results are presumably a manifestation of the superior σ-donor capability of CH_3[28] which activates the trans methyl group for electrophilic attack by Zn^{2+}, Cd^{2+}, and H_3O^+.

Experimental Section

All of the reactions were studied in i-C_3H_7OH at room temperature and carried out anaerobically in the dark. The choice of solvent was dictated in part by the reactivity of I in acidic solvents including H_2O and CH_3OH. I decomposes only very slowly in dry i-C_3H_7OH. Tetrahydrofuran was employed with success although the formation of peroxides made its use inconvenient. The metal perchlorates $Zn(ClO_4)_2{\cdot}6H_2O$, $Cd(ClO_4)_2{\cdot}6H_2O$, $Pb(ClO_4)_2{\cdot}3H_2O$, and $LiClO_4{\cdot}3H_2O$ were purchased from Smith Chemical Co., Columbus, Ohio. The $LiClO_4{\cdot}3H_2O$ which was found to be contaminated with H_3O^+ was neutralized with LiOH and recrystallized from H_2O.

Preparation of $(CH_3)_2Co(BDM1,3pn)$. The complex was prepared by a modification of the method used by Costa et al.[29] $[Co(BDM1,3pn)(H_2O)_2](ClO_4)_2$ was used as the starting material instead of $[Co(BDM1,3pn)I_2]$. In this way, contamination of the product by $[CH_3Co(BDM1,3pn)I]$ was avoided and yields in excess of 85% were obtained with regularity. Anal. Calcd: C, 47.56; H, 7.66; N, 17.06. Found: C, 47.64; H, 7.78; N, 17.14.

Spectral Titrations. The titrations were carried out anaerobically in a 1-cm quartz cell using a Cary Model 14 recording spectrophotometer. Typically 10^{-4} M solutions of I were titrated with standard solutions of the metal salts by following the absorbance decrease due to I at 412 nm. The fast first reaction of the overall biphasic reaction was titrated by injecting small volumes of the M^{2+} titrant from a 1-μl syringe directly into the cell containing the appropriate volume of complex. Mixing times were on the order of 5 s using this procedure. By repeating this process as rapidly as possible, the titration could be completed in a few minutes, thereby minimizing any error due to the second slower reaction (eq 3).

Kinetics of Methane Evolution. Typically $(CH_3)_2Co(BDM1,3pn)$ (0.03 g, 0.1 mmol) was dissolved in 100 ml of i-C_3H_7OH in a specially designed apparatus in which the reaction vessel and serum cap were separated by a stopcock. The reactions were initiated using 0.2 M metal ion solutions. The liberated methane was sampled in 20-μl aliquots using a 50-μl Hamilton Co. Gas-Tight syringe and detected by GC using a Varian Aerograph Series 1860-1 Chromatograph equipped with a flame ionization detector and a 6 ft × $^1/_8$ in. Porapak Q (80–100) mesh column maintained at 110 °C.

Kinetics of Dealkylation by Electrophiles. The rates of the reactions were followed spectrophotometrically at 412 nm using either a Cary Model 14 spectrophotometer for the slower reactions with H_3O^+ or a Durrum-Gibson stopped-flow spectrophotometer for the fast reactions with Zn^{2+} and Cd^{2+}. The kinetics were studied at 22.2 ± 0.1 °C in freshly distilled i-C_3H_7OH using ca 7.5 × 10^{-6} M solutions of $(CH_3)_2Co(BDM1,3pn)$ and an excess of metal ion. The $k_{obsd}/[M^{2+}]$ values summarized in Table II represent the mean values of at least five independent determinations for each concentration of metal ion. Standard deviations were on the order of 5–10% for both the Zn^{2+} and Cd^{2+} reactions. The solutions were thoroughly deoxygenated with nitrogen prior to running the reactions; however, the solutions used in the stopped-flow experiments could not be kept entirely air free.

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Registry No. $(CH_3)_2Co(BDM1,3pn)$, 33569-60-7; Zn^{2+}, 23713-49-7; Cd^{2+}, 22537-48-0; Pb^{2+}, 14280-50-3; $[Co(BDM1,3pn)(H_2O)_2](ClO_4)_2$, 32090-02-1.

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