(8) J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc. A*, 1847 (1970).
(9) M. Green, S. Heathcock, and D. C. Wood, *J. Chem. Soc., Dalton Trans.*, 1564 (1973).
(10) J. P. Williams and A. Wojcicki, *Inorg. Chim. Acta*, **15**, L21 (1975).
(11) S. R. Su and A. Wojcicki, *Inorg. Chim. Acta*, **8**, 55 (1974).
(12) J.-L. Roustan and C. Charrier, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 2113 (1969).
(13) (a) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, **10**, 2130 (1971); (b) W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader, *J. Chem. Soc. A*, 930 (1971).
(14) (a) D. W. Lichtenberg and A. Wojcicki, *Inorg. Chim. Acta*, **7**, 311 (1973); (b) J.-L. Roustan, J.-Y. Merour, J. Benaim, and C. Charrier, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **274**, 537 (1972).
(15) (a) Y. Yamamoto and A. Wojcicki, *Inorg. Chem.*, **12**, 1779 (1973); (b) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *J. Am. Chem. Soc.*, **94**, 8251 (1972).
(16) J. P. Williams, Ph.D. Thesis, The Ohio State University, 1975.
(17) D. W. Lichtenberg, Ph.D. Thesis, The Ohio State University, 1973.
(18) T. Yu. Orlova, P. V. Petrovskii, V. N. Setkina, and D. N. Kursanov, *J. Organomet. Chem.*, **67**, C23 (1974).
(19) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964).
(20) L. S. Chen, D. W. Lichtenberg, P. W. Robinson, Y. Yamamoto, and A. Wojcicki, *Inorg. Chim. Acta*, in press.
(21) M. R. Churchill and S. W.-Y. N. Chang, *J. Am. Chem. Soc.*, **95**, 5931 (1973).
(22) (a) K. L. Williamson and J. C. Fenstermaker, *J. Am. Chem. Soc.*, **90**, 342 (1968); (b) P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *ibid.*, **88**, 2459 (1966); (c) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).
(23) S. H. Burstein and H. J. Ringold, *Can. J. Chem.*, **39**, 1848 (1961).
(24) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).
(25) R. L. Downs, Ph.D. Thesis, The Ohio State University, 1968.
(26) J.-L. Roustan and P. Cadiot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 734 (1969).
(27) (a) P. W. Jolly and R. Pettit, *J. Organomet. Chem.*, **12**, 491 (1968); (b) M. D. Johnson and C. Mayle, *J. Chem. Soc. D.*, 192 (1969).

Contribution from the Department of Chemistry,
Parsons Hall, University of New Hampshire, Durham, New Hampshire 03824

Formation of Transient $(CH_3)_2Zn$, $(CH_3)_2Cd$, and $(CH_3)_2Pb$ Species via Methylation of Zn^{2+}, Cd^{2+}, and Pb^{2+} by a *trans*-Dimethylcobalt Complex

MARK W. WITMAN and JAMES H. WEBER*

Received March 11, 1977 AIC70192W

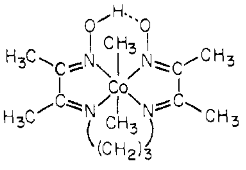
The methylation reactions in *i*-C_3H_7OH of Zn^{2+}, Cd^{2+}, and Pb^{2+} by an excess of the *trans*-dimethylcobalt complex, $(CH_3)_2Co(BDM1,3pn)$, are discussed. (BDM1,3pn is a mononegative, tetradentate dioxime diimine ligand formed by the condensation of 2 mol of 2,3-butanedione and 1 mol of 1,3-propanediamine.) With a 2:1 complex:metal ratio a very rapid reaction forms $CH_3Co(BDM1,3pn)^+$ and CH_3M^+ ($M^{2+} = Zn^{2+}, Cd^{2+}$, and Pb^{2+}). Then in a slower reaction CH_3M^+ reacts with a second mole of $(CH_3)_2Co(BDM1,3pn)$ to form unstable $(CH_3)_2M$ species. These compounds rapidly react yielding CH_4 and a variety of nonvolatile products such as $[CH_3Cd(i\text{-}C_3H_7O)]_4$. The progress of the reactions was followed by the absorbance decrease of $(CH_3)_2Co(BDM1,3pn)$ and a GC analysis of CH_4.

Introduction

Reactions in which alkyl groups are transferred from synthetic monoalkylcobalt complexes to metal electrophiles have been the subject of intensive investigations in recent years. Interest in these reactions has been heightened by the demonstrated microbiological methylation of mercury,[1] lead,[2,3] and selenium[4] in the aquatic environment. Studies on organocobalt complexes include alkyl transfer from $RCo^{III}(chel)$[5] and alkylcobalamins to Hg^{2+}, Cr^{2+}, and Tl^{3+}.[6-13] These reactions invariably exhibit a 1:1 stoichiometry and result in the products shown in eq 1.

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

Despite the ready cleavage of the Co–C bond by Hg^{2+}, Cr^{2+}, and Tl^{3+} a surprising number of other electrophilic reagents including H_3O^+, CH_3Hg^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Al^{3+} are unreactive toward monoalkylcobalt chelates.[14] Consequently, we became interested in studying the reactions of the *trans*-dimethyl complex $(CH_3)_2Co(BDM1,3pn)$ (structure I)



I

with light[15] and selected metal electrophiles. This interest was heightened by earlier studies with monomethylcobalt complexes which established the superior σ-donor and trans-labilizing character of CH_3 relative to other Lewis bases.[16,17] Our thinking in this regard was that one methyl group would be extremely susceptible to electrophilic attack and that methyl-transfer reactions with previously unreactive electrophiles might be made to occur.

In a recent paper we described the results of a detailed study on the 1:1 reactions of I with Zn^{2+}, Cd^{2+}, and Pb^{2+} in *i*-C_3H_7OH.[18] We reported that I reacts nearly instantaneously with a stoichiometric amount of all three metal ions to give quantitative yields of the corresponding monomethylcobalt derivative, $CH_3Co(BDM1,3pn)^+$, and surprisingly stable organometallic products of the type CH_3M^+ (eq 2). These

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

results are of particular interest since no reaction has been previously reported in which these metal ions bring about the cleavage of a Co–C bond in complexes of macrocyclic ligands. In the present work we will discuss the 2:1 (complex:metal) reactions of I with these same metal ions and present evidence for the formation of transient $(CH_3)_2Zn$, $(CH_3)_2Cd$, and $(CH_3)_2Pb$ species.

Results and Discussion

The anaerobic 2:1 (complex:metal) reactions of I with Zn^{2+}, Cd^{2+}, and Pb^{2+} in *i*-C_3H_7OH are markedly different from the 1:1 reaction of I with these same metal ions. Instead of a single instantaneous reaction (eq 2) a two-step reaction was observed in which an initial fast step was followed by a second slower reaction which was complete in a matter of minutes. The biphasic nature of this reaction was confirmed using the stopped-flow technique to follow the decrease in absorbance of I at 412 nm (ε 8380).

The presence of isosbestic points at 490 and 450 nm indicate that only one complex product was formed in solution. In

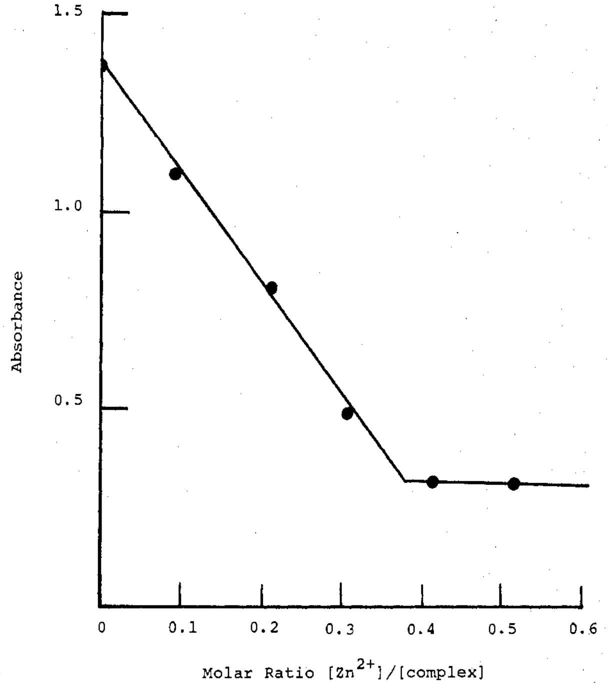


Figure 1. Representative spectral titration for the overall biphasic reaction between $(CH_3)_2Co(BDM1,3pn)$ and Zn^{2+}.

analogy to the 1:1 reactions, $CH_3Co(BDM1,3pn)^+$ was identified as the complex product ion by comparing the visible spectrum of the final reaction solution to that of a solution prepared from an analyzed sample of $[CH_3Co(BDM1,3pn)H_2O]ClO_4$. From a knowledge of the molar absorptivity of the product ion at 463 nm (ϵ 2120) it is evident that I is quantitatively converted to $CH_3Co(BDM1,3pn)^+$ in these reactions. The stoichiometries of the overall reactions were determined by spectral titration of I with standard solutions of the appropriate metal ion. The technique employed previously for the titration of the fast first reactions was utilized,[18] with the exception that the reactions were allowed to proceed to completion. The results of these titrations are presented graphically in Figure 1 for Zn^{2+} and Figure 2 for Cd^{2+} and Pb^{2+}.

It is readily apparent from these data that the end points for all three metal ions are close to the M^{2+}:complex molar ratio of 0.5; i.e. 1 mol of added metal ion reacts with 2 mol of I. This is consistent with a process in which the relatively stable CH_3M^+ intermediates formed in the initial fast reaction (eq 2) react with a second mole of I in a subsequent slower reaction as outlined in eq 3. The low molar ratio observed

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

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

for the Zn^{2+} titration (Figure 1) is in agreement with the fast protonolysis of CH_3Zn^+ by $i\text{-}C_3H_7OH$ (eq 4) which was

$$CH_3Zn^+ + i\text{-}C_3H_7OH \rightarrow CH_4 + Zn(i\text{-}C_3H_7O)^+ \quad (4)$$

discussed previously.[18] Thus, in the case of Zn^{2+}, eq 4 competes with eq 3b and the overall reaction is catalytic in the sense that Zn^{2+} is regenerated and is free to react further with I. This competing reaction does not occur with Cd^{2+} and Pb^{2+} however since the CH_3M^+ species formed from these ions are considerably more stable in $i\text{-}C_3H_7OH$.[18] Support for the scheme outlined here comes from experiments[19,20] on the alkyl-transfer reactions of I, $(CH_3)_2Co(tim)^+$, $(CH_3)_2Co(cr)^+$, and other dialkylcobalt complexes to CH_3Hg^+ and $C_6H_5Hg^+$ as exemplified in eq 5. These reactions occur with the indicated 1:1 stoichiometry and proceed to completion.

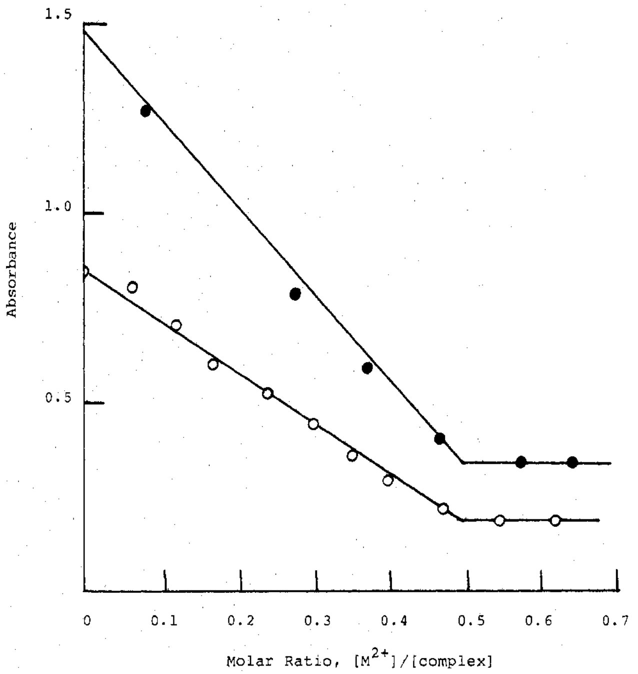


Figure 2. Representative spectral titrations for the overall biphasic reactions of $(CH_3)_2Co(BDM1,3pn)$ with Cd^{2+} (○) and Pb^{2+} (●).

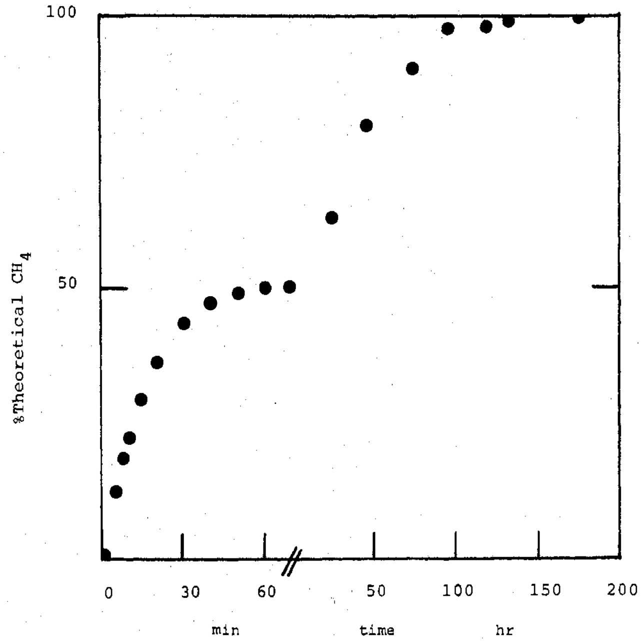


Figure 3. Rate of methane evolution for the reaction of $(CH_3)_2Co(BDM1,3pn)$ wth Cd^{2+} ($[Cd^{2+}]/[complex] = 0.5$).

$$(CH_3)_2Co(chel)^{n+} + CH_3Hg^+ \rightarrow CH_3Co(chel)^{(n+1)+} + (CH_3)_2Hg \quad (5)$$

In contrast to $(CH_3)_2Hg$, however, the proposed Me_2Zn, Me_2Cd, and Me_2Pb products of eq 3b are extremely reactive and readily decompose in solvents which contain an acidic hydrogen atom.[21,22] As a consequence, the rapid formation of methane was anticipated in these reactions. This was indeed the case for all three metal ions which further corroborates the proposed reaction scheme (eq 3).

This phenomenon can be exemplified by the 2:1 (complex:metal) reaction of I with Cd^{2+} which results in the

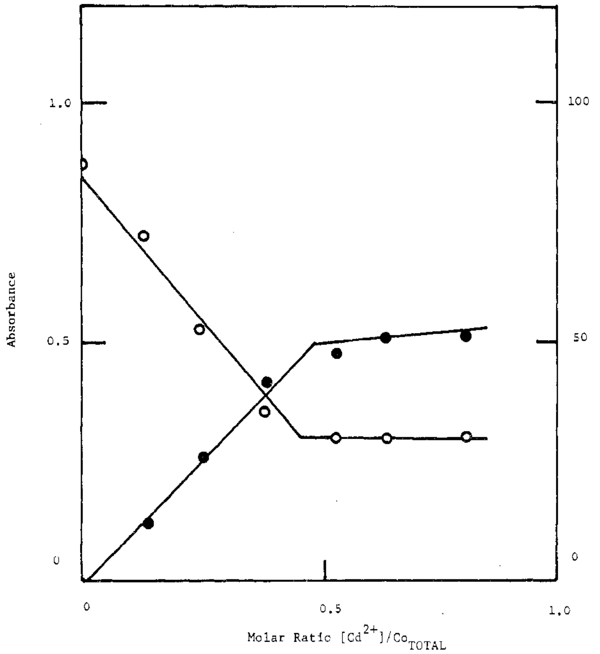


Figure 4. Simultaneous spectral titration (○) and % methane evolution (●) for the reaction of $(CH_3)_2Co(BDM1,3pn)$ with Cd^{2+} ($[Cd^{2+}]/[complex]$) = 0.5).

methane evolution profile shown in Figure 3. Two distinct steps are observed. In the first step exactly 50% of the theoretical amount of methane (determined by GC after the acid hydrolysis of I, eq 6) is evolved in a matter of minutes.

$$(CH_3)_2Co(BDM1,3pn) + H_3O^+ \rightarrow CH_3Co(BDM1,3pn)H_2O^+ + CH_4 \qquad (6)$$

This is followed by a slow second step which liberates the remaining methane over a period of 150 h. The methane evolution pattern observed here is consistent with a process in which the $(CH_3)_2Cd$ product formed in eq 3b rapidly reacts with i-C_3H_7OH to form the well-known tetramer $[CH_3Cd(i\text{-}C_3H_7O)]_4$[23] and methane according to eq 7. The more

$$(CH_3)_2Cd + i\text{-}C_3H_7OH \xrightarrow{\text{fast}} {}^1/_4[CH_3Cd(i\text{-}C_3H_7O)]_4 + CH_4 \qquad (7)$$

stable tetramer is then slowly decomposed by i-C_3H_7OH to liberate the remaining methyl group as methane (eq 8). This

$$^1/_4[CH_3Cd(i\text{-}C_3H_7O)]_4 + i\text{-}C_3H_7OH \xrightarrow{\text{slow}} Cd(i\text{-}C_3H_7O)_2 + CH_4 \qquad (8)$$

interpretation is in agreement with recent kinetic and NMR investigations on the reactions of $(CH_3)_2Cd$ and $(C_2H_5)_2Cd$ with a variety of alcohols (ROH).[21] These studies demonstrate that the $[CH_3Cd(OR)]_4$ and $[C_2H_5Cd(OR)]_4$ products are formed much more rapidly than the $Cd(OR)_2$ products.

Further confirmation of the scheme outlined here is provided in Figure 4. In this experiment I was titrated with a standard Cd^{2+} solution in the usual manner while simultaneously monitoring the quantity of methane evolved. Figure 4 clearly shows the expected 2:1 (complex:Cd^{2+}) stoichiometry of the reactions. In addition it is evident that only 50% of the expected methane is liberated upon reaching the end point, as would be predicted from eq 7 and 8.

Perhaps the best evidence for the transient existence of $(CH_3)_2Cd$ comes from the isolation of $[CH_3Cd(i\text{-}C_3H_7O)]_4$ as a product of the reaction of I with Cd^{2+} in i-C_3H_7OH. The reaction was run on a preparative scale using a molar ratio $[Cd^{2+}]/[complex] = 0.5$. White crystals of $[CH_3Cd(i\text{-}C_3H_7O)]_4$ were recovered in low yield by freeze-drying the reaction mixture and subliming the residue. The tetramer was characterized by its instantaneous reaction with 1 M $HClO_4$ to yield methane (eq 9) and by comparing its mass spectrum

$$^1/_4[CH_3Cd(i\text{-}C_3H_7O)]_4 + H^+ \rightarrow Cd(i\text{-}C_3H_7O)^+ + CH_4 \qquad (9)$$

to that of an authentic sample which was prepared from the reaction of $(CH_3)_2Cd$ with i-C_3H_7OH.

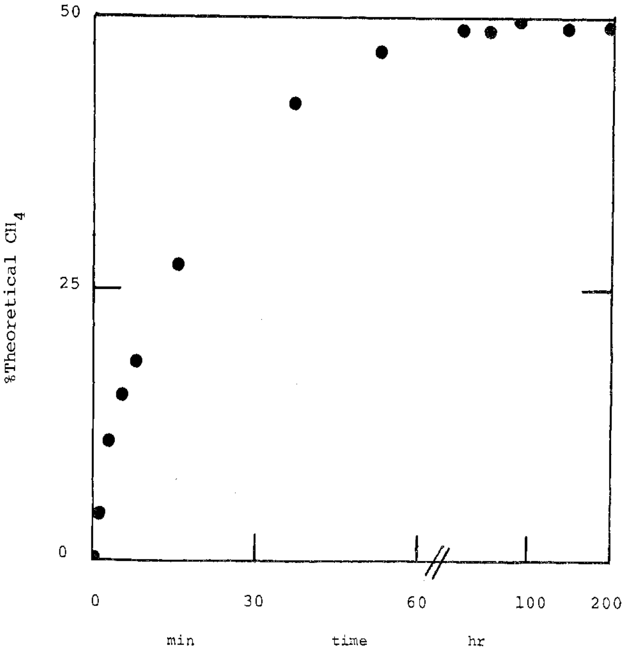


Figure 5. Rate of methane evolution for the reaction of $(CH_3)_2Co(BDM1,3pn)$ with Pb^{2+} ($[Pb^{2+}]/[complex] = 0.5$).

The 2:1 (complex:metal) reaction of I with Pb^{2+} in i-C_3H_7OH is analogous to the reaction of I with Cd^{2+} in certain respects. The titration data (Figure 2) are again consistent with a process in which CH_3Pb^+ formed in an initial fast reaction (eq 10) reacts with a second mole of I to form

$$(CH_3)_2Co(BDM1,3pn) + Pb^{2+} \xrightarrow{\text{fast}} CH_3Co(BDM1,3pn)^+ + CH_3Pb^+ \qquad (10)$$

$(CH_3)_2Pb$ (eq 11). Divalent organolead compounds of the

$$(CH_3)_2Co(BDM1,3pn) + CH_3Pb^+ \xrightarrow{\text{slow}} CH_3Co(BDM1,3pn)^+ + (CH_3)_2Pb \qquad (11)$$

type R_2Pb (R = alkyl) are known to disproportionate into organolead(IV) species and lead metal according to eq 12,[24]

$$2R_2Pb \rightarrow R_4Pb + Pb^0 \qquad (12)$$

but this reaction was not observed. Instead, the 2:1 (complex:metal) reaction of I with Pb^{2+} resulted in the methane evolution profile shown in Figure 5, and the simultaneous formation of an insoluble, tan material. Since only half of the expected methane is ultimately observed, we postulated that the precipitate is a relatively stable $CH_3Pb(i\text{-}C_3H_7O)$ compound formed from the protonolysis of $(CH_3)_2Pb$ by i-C_3H_7OH (eq 13). Presumably the $CH_3Pb(i\text{-}C_3H_7O)$ product

$$(CH_3)_2Pb + i\text{-}C_3H_7OH \rightarrow CH_3Pb(i\text{-}C_3H_7O) + CH_4 \qquad (13)$$

is polymeric in analogy to $[CH_3Cd(i\text{-}C_3H_7O)]_4$ since lead alkoxides reportedly exist as polymeric chains linked by oxygen atoms.[25] The addition of H_3O^+ to the solution decomposed the precipitate and liberated the remaining methane lending further support to this interpretation.

Elemental analysis of the isolated precipitate failed to confirm the presence of pure $CH_3Pb(i\text{-}C_3H_7O)$, however, since the material contained significant amounts of nitrogen. The presence of $CH_3Co(BDM1,3pn)^+$ was suspected and was confirmed spectrophotometrically by decomposing the solid in H_3O^+. Repeated washings with i-C_3H_7OH did not remove the $CH_3Co(BDM1,3pn)^+$ indicating that the complex is tightly held. Analogous precipitates were not observed in the reaction of $CH_3Co(BDM1,3pn)^+$ and Pb^{2+} or in the 1:1 anaerobic reaction of I and Pb^{2+}.[18] This precludes the presence of 1:1 lead–complex adducts that have been observed in the reactions of RCo(chel) with excess Hg^{2+}.[10] Nevertheless, the titration data (Figure 2), the methane evoution profile (Figure 5), and the formation of CH_4 upon the dissolution of the precipitate in H_3O^+ strongly suggest that $CH_3Pb(i\text{-}C_3H_7O)$ is at least a major product of the reaction.

The principal new contributions of the present study relate to the reactions of I with CH_3Zn^+, CH_3Cd^+, and CH_3Pb^+ since reactions of organocobalt complexes with these electrophiles have not been observed previously. It is not surprising that methyl transfer occurs, however, in view of the superior σ-donor capability of CH_3 which activates the trans Co–C bond for electrophilic attack.[16,17] In this regard it is interesting to compare the relative rates of methyl transfer from I to M^{2+} and CH_3M^+. The order $M^{2+} \gg CH_3M^+$ is entirely consistent with the lower positive charge and therefore reduced electrophilic character of CH_3M^+. Finally, the transient $(CH_3)_2Zn$ and $(CH_3)_2Cd$ species formed in these reactions are analogous to the RCH_3Hg (R = alkyl or aryl) products formed in the reactions of I and RHg^+.[19,20] This similarity in reactivity is expected in view of the position of Zn, Cd, and Hg in the periodic table. The formation of $(CH_3)_2Pb$ was somewhat surprising, however, since it is not well-characterized.[22]

Experimental Section

All of the reactions were studied in i-C_3H_7OH at room temperature and carried out anarobically in the dark. The metal perchlorates $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, and $Pb(ClO_4)_2 \cdot 3H_2O$ were purchased from Smith Chemical Co., Columbus, Ohio. The Hypo-Vials, Tuf-Bond serum caps, and Mininert valves were purchased from Pierce Chemical Co. A Varian Aerograph Series 1860-1 chromatograph equipped with an FID and a 6 ft × 1/8 in. i.d. Porapak Q (80–100 mesh) column was used to identify the methane hydrocarbon product. A sample of analyzed hydrocarbons (C_1–C_4) for use in the GC experiments was obtained from Scott Research Laboratories.

Preparation of Organocobalt Complexes. The dimethyl complex was prepared as described previously.[18,26] $[CH_3Co(BDM1,3pn)H_2O]ClO_4$ was prepared by reacting I with 1 M $HClO_4$ followed by the addition of $NaClO_4$ which precipitates the monomethyl complex.

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 the loss of I at 412 nm. The overall biphasic reaction was titrated by injecting small volumes of the M^{2+} titrant from a 1-μL syringe directly into the cell which contained the appropriate volume of complex solution. Following the addition of each aliquot of M^{2+} and prior to adding the next volume of titrant the reactions were allowed to proceed until no change in absorbance was observed for a period of 5 min.

Methane Evolution. Typically I (0.3 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 a serum cap were separated by a stopcock. The reactions were initiated using the appropriate volumes of standardized 0.2 M metal ion solutions. The liberated methane was sampled in 20-μL aliquots using a 50-μL Hamilton Co. gastight syringe and detected by GC. The theoretical value was determined by the acid hydrolysis of an equivalent amount of I employing the same conditions of temperature and ionic strength.

Simultaneous Spectral Titration and Methane Evolution. I (0.3 g, 0.1 mmol) was dissolved in 100 mL of i-C_3H_7OH in a 125 mL Hypo-Vial. The vial was sealed either with a Tuf-Bond serum cap or a Mininert valve, and the solution thoroughly deoxygenated with N_2. The complex was titrated with a 0.25 M Cd^{2+} solution in 50-μL increments. Following the addition of titrant the reaction was allowed to proceed for ca. 30 min to ensure the completion of both steps of the biphasic reaction. The amount of methane produced after each addition of Cd^{2+} was monitored in the usual manner. Subsequently, a 0.3-mL aliquot of the reaction solution was diluted 10:1 in i-C_3H_7OH and the absorbance recorded at 412 nm. The procedure was repeated until constant absorbance and methane values were obtained.

Isolation of $[CH_3Cd(i\text{-}C_3H_7O)]_4$. A sample of I (0.33 g, 1 mmol) was ground in an agate mortar and pestle and dissolved in 200 mL of i-C_3H_7OH in a two-neck, round-bottom flask. The flask was fitted with a stopcock and Schlenk tube which contained a wad of glass wool for the purpose of filtering any insoluble materials. The solution was purged with nitrogen and the reaction initiated with 0.25 M Cd^{2+} (2.0 mL, 0.5 mmol; in i-C_3H_7OH). An instantaneous color change from orange to red-orange was observed. The reaction was allowed to continue for 1 h at which point the solution was frozen in liquid nitrogen and the solvent removed by freeze-drying. The residue which remained was extracted with hexane and filtered into the Schlenk tube. After removal of the hexane from the filtrate in vacuo, the residue was sublimed at 10^{-3} atm and 115 °C. A small amount of an air-sensitive white crystalline material was recovered; it was soluble in hexane, decomposed in H_3O^+ to yield methane, and gave a mass spectrum that agreed with that of an authentic sample.

Registry No. I, 33569-60-7; Zn^{2+}, 23713-49-7; Cd^{2+}, 22537-48-0; Pb^{2+}, 14280-50-3; $[CH_3Cd(i\text{-}C_3H_7O)]_4$, 12189-91-2; $(CH_3)_2Zn$, 544-97-8; $(CH_3)_2Cd$, 506-82-1; $(CH_3)_2Pb$, 63588-56-7.

References and Notes

(1) J. M. Wood, *Science*, **183**, 1049 (1974).
(2) U. Schmidt and F. Huber, *Nature (London)*, **259**, 157 (1976).
(3) P. T. S. Wong, Y. K. Chau, and P. L. Luxon, *Nature (London)*, **253**, 263 (1975).
(4) Y. K. Chau, P. T. S. Wong, B. A. Silverberg, P. L. Luxon, and G. A. Bengert, *Science*, **192**, 1130 (1976).
(5) chel: $(dmg)_2$, bis(dimethylglyoximato); salen, bis(salicylaldehyde)-1,2-ethane; BDM1,3pn, 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olato; saloph, *N,N'-o*-phenylenebis(salicylideniminato); tim, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; cr, 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.11]heptadeca-1(17),2,11,13,15-pentaene.
(6) G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971).
(7) H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *J. Am. Chem. Soc.*, **96**, 2378 (1974).
(8) P. Abley, E. R. Dockal, and J. Halpern, *J. Am. Chem. Soc.*, **95**, 3166 (1973).
(9) V. E. Magnuson and J. H. Weber, *J. Organomet. Chem.*, **74**, 135 (1974).
(10) G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Organomet. Chem.*, **81**, 107 (1974).
(11) J. H. Espenson, W. R. Bushey, and M. E. Chielewski, *Inorg. Chem.*, **14**, 1302 (1975).
(12) G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Williams, *J. Chem. Soc. D*, 850 (1971).
(13) J. H. Espenson and T. D. Sellers, Jr., *J. Am. Chem. Soc.*, **96**, 94 (1974).
(14) V. E. Magnuson, Ph.D. Dissertation, University of New Hampshire, 1974, p 48.
(15) M. W. Witman and J. H. Weber, *Inorg. Nucl. Chem. Lett.*, **11**, 591 (1975).
(16) H. A. O. Hill, K. G. Morallee, F. Cernivez, and G. Pellizer, *J. Am. Chem. Soc.*, **94**, 277 (1972).
(17) G. Pellizer, G. R. Tauszik, G. Tauzher, and G. Costa, *Inorg. Chim. Acta*, **7**, 60 (1973).
(18) M. W. Witman and J. H. Weber, *Inorg. Chem.*, **15**, 2375 (1976).
(19) J. H. Espenson, H. L. Fritz, R. A. Heckman, and C. Nicolini, *Inorg. Chem.*, **15**, 906 (1976).
(20) G. Mestroni, G. Zassinovich, A. Camus, and G. Costa, *Transition Met. Chem.*, **1**, 32 (1975/76).
(21) G. Emptoz and F. Huet, *J. Organomet. Chem.*, **82**, 139 (1974).
(22) D. P. Arnold and P. R. Wells, *J. Organomet, Chem.*, **111**, 269 (1976).
(23) G. E. Coates and A. Lauder, *J. Chem. Soc. A*, 264 (1966).
(24) H. Shapiro and F. W. Frey, "The Organic Compounds of Lead", Interscience, New York, N.Y., 1968.
(25) E. Amberger and R. Hönigschmid-Grossich, *Chem. Ber.*, **98**, 3795 (1965).
(26) M. W. Witman and J. H. Weber, *Synth. React. Inorg. Met.-Org. Chem.*, **1**, 143 (1977).