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Methyl Transfer from *trans*-Dimethylcobalt(III) Complexes to Metal Ion Electrophiles. 2. Reactions of Dimethyllead(IV), Trimethyllead(IV), and Lead(II) Ions

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Methyl transfer from $(CH_3)_2Co((1-)N_4)$ and $[(CH_3)_2Co(N_4)]ClO_4{\cdot}H_2O$ to Pb^{2+} and $(CH_3)_3Pb^+$ in acetonitrile is rapid. A monomethylcobalt(III) complex is always a product, but different lead ion electrophiles and reaction stoichiometries yield different lead products. $(CH_3)_3Pb^+$ and $(CH_3)_2Pb^{2+}$ form $(CH_3)_4Pb$. Reactions of excess Pb^{2+} and $(CH_3)_2Co(chel)$, (chel is $((1-)N_4)$ or (N_4)) form CH_3Pb^+, which has a half-life for methane formation of 7.2 or 5.4 h depending on chel. Methane is evolved via pseudo-first-order kinetics. Reactions of Pb^{2+} and $(CH_3)_2Co((1-)N_4)$ in a 1:2 Pb^{2+}:$(CH_3)_2Co((1-)N_4)$ stoichiometry yield lead metal and $(CH_3)_4Pb$.

Introduction

Recently Ahmad et al.[1] demonstrated that CH_3I methylates Pb^{2+} in water to form $(CH_3)_4Pb$. Interest in aquatic environment lead methylation is high because $(CH_3)_4Pb$ occurs in natural water, sediments, and fish.[2] For some years research groups have claimed that Pb^{2+} is microbiologically methylated to $(CH_3)_4Pb$ in the aquatic environment.[3,4] This conclusion is reasonable because microbiological transformations of metal ions are well-known.[5] More recently Craig[6] contended that it is unnecessary to assume a biological route for lead methylation. In biotic or chemical alkylation of Pb^{2+} to form $(CH_3)_4Pb$, $(CH_3)_2Pb$ is a reasonable intermediate because of its presumed disproportionation (eq 1). $(CH_3)_2Pb$

$$(CH_3)_2Pb \rightarrow 0.5Pb^0 + 0.5(CH_3)_4Pb \qquad (1)$$

has not been directly identified during Pb^{2+} methylation reactions, but is often assumed to be a reaction intermediate,[7-10] and a few dialkyllead(II) compounds are known.[11,12]

In addition to the above papers past work of this group lends evidence to the transient presence of $(CH_3)_2Pb$ in 2-propanol. The *trans*-diorganocobalt(III) complex of a macrocyclic ligand, $(CH_3)_2Co((1-)N_4)$,[13,14] transfers one methyl group to excess Pb^{2+}[15] in 2-propanol (eq 2a). The CH_3Pb^+ intermediate has

$$(CH_3)_2Co((1-)N_4) + Pb^{2+} \xrightarrow[\text{fast}]{\text{2-propanol}} CH_3Co((1-)N_4)^+ + CH_3Co((1-)N_4)^+ + CH_3Pb^+ \qquad (2a)$$

$$(CH_3)_2Co((1-)N_4) + CH_3Pb^+ \xrightarrow{\text{2-propanol}} CH_3Co((1-)N_4)^+ + (CH_3)_2Pb \qquad (2b)$$

a half-life of 60 h as measured by CH_4 evolution. Analogous reactions between Pb^{2+} and excess $(CH_3)_2Co((1-)N_4)$[16] formed $(CH_3)_2Pb$ in a biphasic reaction (eq 2). The reactive $(CH_3)_2Pb$ intermediate evolved 1 mol of CH_4 and a tan solid within 60 min, and no disproportionation to Pb^0 and $(CH_3)_4Pb$ occurs. The resulting precipitate, which contains 50% of the transferred methyl group, does not evolve CH_4 until H_3O^+ is added.

This paper extends our previous work discussed above in several ways. We studied the methyl transfer from neutral $(CH_3)_2Co((1-)N_4)$ and cationic $[(CH_3)_2Co(N_4)]^+$[14] to Pb^{2+}, $(CH_3)_3Pb^+$, and $(CH_3)_2Pb^{2+}$ in CH_3CN. Reactions in CH_3CN are different from those in protic 2-propanol discussed above. In addition the neutral and cationic methyl donors show surprisingly different behavior toward Pb^{2+}.

Results and Discussion

Characterization of $(CH_3)_3PbCl$ and $(CH_3)_2Pb(NO_3)_2$. The elemental analyses of $(CH_3)_3PbCl$ agreed with theoretical values, but those of $(CH_3)_2Pb(NO_3)_2$ consistently showed the compound to be low in nigrogen (i.e.: calcd, 7.76; found, 6.02). The use of various combustion catalysts (e.g., tungstic oxide) did not alter the results. The low nitrogen value was rather intriguing because observed carbon, hydrogen, and lead percentages were always in excellent agreement with the theoretical values for $(CH_3)_2Pb(NO_3)_2$. Determination of the nitrate content of the compound (for NO_3^-: calcd, 34.35; found, 34.65) also supports the contention that the compound is $(CH_3)_2Pb(NO_3)_2$. The reason for the apparent loss of nitrogen upon combustion in the furnace is not obvious, but the formation of a nonvolatile lead–nitrogen compound is likely.

^1H NMR chemical shifts and $J(^{207}Pb{-}H)$ for cationic methyllead(IV) compounds are highly solvent dependent. The ^1H chemical shift of the methyl protons moves to higher magnetic field, and $J(^{207}Pb{-}H)$ increases as the donor strength of the solvent molecule increases. For example, for $(CH_3)_2Pb(NO_3)_2$,[17] the shift is 2.33 ppm for CH_3 in $(CH_3)_2SO$, 2.42 ppm in CH_3OH, 2.55 ppm in H_2O, and 2.65 ppm in 20% aqueous $HClO_4$. The values of $J(^{207}Pb{-}H)$ vary from 149 to 133 Hz over the same range of solvents. In various solvents the shift for CH_3 was 1.5 ppm for Me_3PbCl with a $J(^{207}Pb{-}H)$ of ca. 80 Hz.[7,18] Our chemical shifts and coupling constants for $(CH_3)_2Pb(NO_3)_2$ and $(CH_3)_3PbCl$ in CH_3CN-d_3 agree with literature values. $(CH_3)_2Pb(NO_3)_2$ exhibits a doublet at 2.65 ppm ($J(^{207}Pb{-}H)$ = 140 Hz); $(CH_3)_3PbCl$ shows a doublet at 1.50 ppm ($J(^{207}Pb{-}H)$ = 79 Hz).

Reactions of $(CH_3)_3Pb^+$ and $(CH_3)_2Pb^{2+}$ with $(CH_3)_2Co((1-)N_4)$. Spectrophotometric titrations demonstrate that $(CH_3)_2Pb^{2+}$ reacts with $(CH_3)_2Co((1-)N_4)$ in a 1:2 reaction and $(CH_3)_3Pb^+$ reacts with a 1:1 stoichiometry (Figure 1). ^1H NMR titrations with $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ confirmed the 1:2 and 1:1 stoichiometries and that $(CH_3)_4Pb$ (0.75 ppm) was the final reaction product in both cases. Comparison to

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[14] Ligand abbreviations: $((1-)N_4)$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diolato-O^1(1−); (N_4) = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

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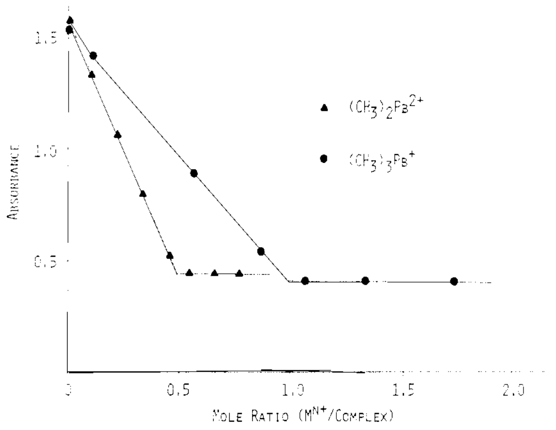

Figure 1. Representative spectral titrations for the reactions of $(CH_3)_2Co((1-)N_4)$ with $(CH_3)_3Pb^+$ (●) and $(CH_3)_2Pb^{2+}$ (▲).

the ^1H NMR spectrum of an authentic sample of $(CH_3)_4Pb$ confirmed the assignment. Attempts to observe directly the $(CH_3)_3Pb^+$ intermediate prior to $(CH_3)_4Pb$ formation in the $(CH_3)_2Pb^{2+}$ reaction failed at room temperature because of instantaneous $(CH_3)_4Pb$ formation. We also sought the $(CH_3)_3Pb^+$ intermediate during low-temperature NMR experiments, but, unfortunately, the −44 °C freezing point of CH_3CN and the solubility of $(CH_3)_2Co((1-)N_4)$ imposed a lower temperature limit of −35 °C and we observed only $(CH_3)_4Pb$.

Reactions of $(CH_3)_2Co((1-)N_4)$ with Pb^{2+}. As shown by earlier work of our group,[15,16] reactions of Pb^{2+} with $(CH_3)_2Co((1-)N_4)$ in 2-propanol occur by 1:1 (eq 2a) and 1:2 (eq 2) Pb^{2+}:cobalt complex stoichiometries. Reactions in CH_3CN show similar stoichiometries. Slow spectrophotometric titrations show an end point of mole ratio = 0.50 (Figure 2), which is indicative of a reaction in which 1 mol of Pb^{2+} reacts with 2 mol of dimethyl complex (eq 3). Attempts to titrate the fast first reaction of the overall biphasic reaction failed to yield the expected 1.0 end point predicted by eq 3a. The observed end point between mole ratios of 1.0 and 0.50 reflects the partial reaction of the organolead(II) ion CH_3Pb^+ formed in eq 3a with a second mole of the dimethyl complex (eq 3b).

$$(CH_3)_2Co((1-)N_4) + Pb^{2+} \xrightarrow{CH_3CN} CH_3Co((1-)N_4)(CH_3CN)^+ + CH_3Pb^+ \tag{3a}$$

$$(CH_3)_2Co((1-)N_4) + CH_3Pb^+ \xrightarrow{CH_3CN} CH_3Co((1-)N_4)(CH_3CN)^+ + (CH_3)_2Pb \tag{3b}$$

Solutions prepared from Pb^{2+} and excess $(CH_3)_2Co((1-)N_4)$ in CH_3CN yielded a black precipitate. Nephelometry demonstrated that the precipitate formed immediately upon the addition of Pb^{2+}. The Pb^0 solid, which was identified by its X-ray powder diffraction pattern, contained approximately 45% of the Pb^{2+} added. The only organolead ^1H NMR resonance in the solution was at +0.75 ppm, which is identical with the chemical shift of an authentic sample of $(CH_3)_4Pb$. GLC experiments demonstrated that approximately 49% of the Pb^{2+} added was converted to $(CH_3)_4Pb$ and indicated that about 3% of the transferred methyl group formed CH_4.

Product analysis and spectrophotometric titrations suggest the following overall stoichiometry for the biphasic reaction (eq 4). The presence of equal amounts of Pb^0 and $(CH_3)_4Pb$ in the product mixture implies that an organolead(II) species disproportionated. The literature[8-10,19] suggests that $(CH_3)_2Pb$ could disproportionate to yield a methyllead(IV) species and lead metal (eq 5). Alternatively, CH_3Pb^+, which has not been directly identified, could disproportionate (eq 6) and has been suggested as a possible intermediate in reactions of $(CH_3)_2Co((1-)N_4)$ in 2-propanol[15,16] and in the biotransformation of Pb^{2+} to $(CH_3)_4Pb$.[19] It is not possible to distinguish between the potential unstable intermediate CH_3Pb^+ and $(CH_3)_2Pb$ based on stoichiometry and product distribution. If $(CH_3)_2Pb$ is the intermediate, then the scheme outlined in eq 3a, 3b, and 5 could occur. The unstable intermediate CH_3Pb^+ results in the scheme outlined in eq 3a, 6, 7, and 8. Previously discussed spectrometric titrations with $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ establish that they react with $(CH_3)_2Co((1-)N_4)$ as predicted by eq 7 and 8. It is clear that both mechanisms would give the same reaction stoichiometry and product distribution. Unfortunately NMR titrations at −35 °C could not distinguish between the disproportionation of $(CH_3)_2Pb$ (eq 5) or CH_3Pb^+ (eq 6) because the reactions are too fast to observe any organolead compound except the $(CH_3)_4Pb$ product.

$$2(CH_3)_2Co((1-)N_4) + Pb^{2+} \xrightarrow[CH_3CN]{fast} 2CH_3Co((1-)N_4)(CH_3CN)^+ + 0.5(CH_3)_4Pb + 0.5Pb^0 \tag{4}$$

$$(CH_3)_2Pb \rightarrow 0.5(CH_3)_4Pb + 0.5Pb^0 \tag{5}$$

$$CH_3Pb^+ \rightarrow 0.5(CH_3)_2Pb^{2+} + 0.5Pb^0 \tag{6}$$

$$0.5(CH_3)_2Co((1-)N_4) + 0.5(CH_3)_2Pb^{2+} \rightarrow 0.5(CH_3)_3Pb^+ + 0.5CH_3Co((1-)N_4)(CH_3CN)^+ \tag{7}$$

$$0.5(CH_3)_2Co((1-)N_4) + 0.5(CH_3)_3Pb^+ \rightarrow 0.5(CH_3)_4Pb + 0.5CH_3Co((1-)N_4)(CH_3CN)^+ \tag{8}$$

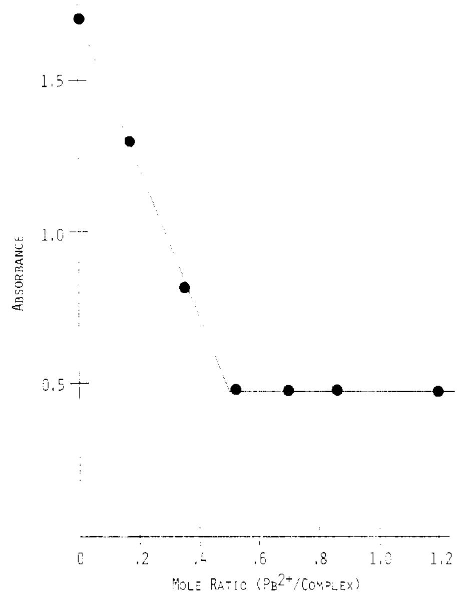

Figure 2. Representative slow spectral titrations for the reaction of $(CH_3)_2Co((1-)N_4)$ with Pb^{2+}.

We also studied reactions of $(CH_3)_2Co((1-)N_4)$ with equimolar or excess Pb^{2+}. Addition of an equimolar quantity of Pb^{2+} to $(CH_3)_2Co((1-)N_4)$ in CH_3CN results in a solution that contains a stoichiometric amount of $[CH_3Co((1-)N_4)(CH_3CN)]^+$, shows no precipitate or $(CH_3)_4Pb$, and evolves CH_4 slowly. This suggests that an organolead species generated in this reaction is relatively stable. The reaction stoichiometry and immediate recovery of the theoretical amount of CH_4 on addition of acid strongly suggest the presence of CH_3Pb^+. There is no evidence of the dispropor-

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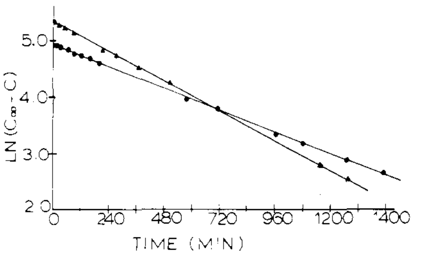

Figure 3. Rate of methane evolution for the reactions of a fourfold molar excess of $(CH_3)_2Co((1-)N_4)$ (●) or $[(CH_3)_2Co(N_4)]^+$ (▲) with Pb^{2+}.

tionation product lead metal (eq 6). Thus the Pb^0 and $(CH_3)_4Pb$ products in the 1:2 reactions discussed above undoubtedly occur via disproportionation of $(CH_3)_2Pb$ not CH_3Pb^+.

Determination of the stability of CH_3Pb^+ in CH_3CN by monitoring the rate of CH_4 evolution by GLC yielded a plot of ln $(C_\infty - C)$ vs. time that was linear over several half-lives (Figure 3). This data yields a half-live of CH_4 formation of 7.2 h ($k_{obsd} = 1.6 \times 10^{-3}$ min^{-1}) compared to a 60 h half-life in 2-propanol.[15] The pseudo-first-order kinetics are consistent with a process in which CH_3Pb^+ is slowly decomposed by excess water present from the hydrated Pb^{2+} (eq 9).

$$CH_3Pb^+ + H_2O \xrightarrow{CH_3CN} CH_4 + Pb(OH)^+ \qquad (9)$$

Because ^1H NMR studies confirmed the presence of organozinc and organocadmium intermediates in our previous Zn^{2+} and Cd^{2+} studies,[20] we performed NMR studies to confirm the presence of CH_3Pb^+. The ^1H NMR spectrum of a solution prepared from $(CH_3)_2Co((1-)N_4)$ and excess Pb^{2+} (mole ratio > 1.0) consisted only of the spectrum of $[CH_3Co((1-)N_4)(CH_3CN)]^+$ between −4.0 and +5.0 ppm. Because CH_3Pb^+ is uncharacterized we do not know its ^1H NMR chemical shift. A survey of ^1H NMR chemical shifts[21,22] suggests a +2.0 to −1.0 ppm range for organolead(II) compounds by comparison to $(CH_3)_2Tl^+$ (1.8 ppm), CH_3Hg^+ (1.0 ppm), $(CH_3)_4Pb$ (0.75 ppm), $(CH_3)_3Tl$ (0.5 ppm), $(CH_3)_2Hg$ (0.2 ppm), $(CH_3)_2Cd$ (−0.6 ppm), and $(CH_3)_2Zn$ (−0.8 ppm). Careful examination of the +2.0 to −1.0 ppm region of the ^1H NMR spectra revealed no peak attributable to organolead species. If, however, the chemical shift of the methyllead(II) species was greater than +1.95 ppm, it would be obscured by the resonances due to proton impurities in CH_3CN-d_3 and protons of the macrocycle. Alternatively line broadening due to exchange reactions[21] might make the resonance difficult to observe.

Despite the failure to find direct evidence for the existence of an organolead(II) compound, all available data, including the kinetics of methane evolution, the sensitivity of the species formed to acid, the indicated 1:1 reaction stoichiometry, and the similarity to the Zn^{2+} and Cd^{2+} chemistry in CH_3CN,[20] support the postulate that CH_3Pb^+ is indeed formed in these reactions.

Reactions of $[(CH_3)_2Co(N_4)]ClO_4$ with Excess Pb^{2+}. Addition of an equimolar or excess amount of Pb^{2+} to $[(CH_3)_2Co(N_4)]^+$ in CH_3CN results in the quantitative conversion of the dimethyl complex to $[CH_3Co(N_4)(CH_3CN)]^{2+}$ and a small amount of a yellow solid. Its X-ray powder diffraction pattern is not consistent with any of the lead oxides listed in the powder diffraction file.[23] Elemental analysis showed the compound to be approximately 40% lead by weight and to contain small amounts of carbon (2.9%), hydrogen (1.5%), and nitrogen (0.35%). The IR spectrum of the solid suggested that trace amounts of water and perchlorate ion might be present. Because the total amount of lead present in this compound approximates only 5% of the Pb^{2+} used in the 1:1 reaction, the unknown compound must be the product of a minor side reaction, and we did not pursue its identity further.

The absence of change of the UV-vis spectrum of the monomethyl complex indicates that it is stable in the presence of Pb^{2+} and any organolead products formed. These results suggest the 1:1 reaction shown in eq 10. GLC analysis of the

$$(CH_3)_2Co(N_4)^+ + Pb^{2+} \xrightarrow{CH_3CN} CH_3Co(N_4)(CH_3CN)^{2+} + CH_3Pb^+ \qquad (10)$$

atmosphere prepared from $[(CH_3)_2Co(N_4)]^+$ and a fourfold excess of Pb^{2+} in CH_3CN showed that CH_4 evolved slowly. A linear plot of ln $(C_\infty - C)$ vs. time (Figure 3), which yielded a CH_4 evolution half-life of 5.4 h ($k_{obsd} = 2.1 \times 10^{-3}$ min^{-1}), is consistent with the decomposition of the intermediate CH_3Pb^+ by the excess water added as hydrated Pb^{2+} (eq 9). The longer half-life of CH_3Pb^+ in the presence of the oxime-containing $((1-)N_4)^-$ ligand compared to the (N_4) ligand agrees with our CH_3Zn^+ and CH_3Cd^+ studies.[20] As in the analogous $(CH_3)_2Co((1-)N_4)$ reactions discussed above, we could not observe CH_3Pb^+ by ^1H NMR.

Although 1:1 reactions of $[(CH_3)_2Co(N_4)]^+$ and $(CH_3)_2Co((1-)N_4$ with Pb^{2+} are similar, reactions of excess $[(CH_3)_2Co(N_4)]^+$ and excess $(CH_3)_2Co((1-)N_4)$ with Pb^{2+} are very different. In fact, reactions of excess $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ with Pb^{2+} in CH_3CN have a complex mechanism that is not at all similar to mechanisms discussed previously in this paper or our other papers.[15,16,20] First, spectral titrations give no definite endpoints. Second, the Pb^0:$(CH_3)_4Pb$ product ratio is not indicative of disproportionation of an organolead(II) species. And third, less than one-half of transferred methyl occurs as CH_4 or an organolead compound. We are presently studying the mechanism of the reaction of excess $[(CH_3)_2Co(N_4)]^+$ with Pb^{2+} in CH_3CN and other solvents.

Experimental Section

General Information. Reactions of the dimethylcobalt complexes with Pb^{2+}, $(CH_3)_2Pb^{2+}$, and $(CH_3)_3Pb^+$ were carried out in CH_3CN in the dark under an atmosphere of purified nitrogen. $Pb(ClO_4)_2 \cdot 3H_2O$, which was obtained from G. F. Smith, was recrystallized from deionized water. Tetramethyllead (80% in toluene) was a gift of the Ethyl Corp. and was used as received.

Physical Measurements. Elemental analyses (C, H, N) were performed on a Perkin-Elmer Model 204B elemental analyzer or an F and M model 185 CHN analyzer. ^1H NMR spectra were recorded on a Varian EM360 or JEOL FX-90Q FT spectrometer. Electronic spectra in the 200–700-nm range were recorded on a Cary 14 or Cary 219 recording spectrophotometer. A Varian series 1860-1 Chromatograph equipped with a flame ionization detector and a 6 ft × $^1/_8$ in. OV-17 column (3% on Chromsorb-W, 80–100 mesh) maintained at 60 °C or a 6 ft × $^1/_8$ in. Porapak-Q (80–100 mesh) column maintained at 115 °C was used to determine volatile reaction products. With a 25 mL/min flow rate, the following retention times were observed: CH_4, 66s (OV-17), 30 s (Porapak-Q); $(CH_3)_4Pb$, 128 s (OV-17); C_2H_6, 54 s (Porapak-Q); CH_3CN, 90 s (OV-17), 21.5 min (Porapak-Q). X-ray powder diffraction patterns were determined with a North American Phillips X-ray generator using Ni-filtered Cu Kα radiation. Solution scattering experiments were done at 500 nm with a Perkin-Elmer Model 204 spectrofluorometer.

Synthesis of Organocobalt and Organolead Compounds. The preparation of the organocobalt complexes was previously described.[20] Both $(CH_3)_3PbCl$[24] and $(CH_3)_2Pb(NO_3)_2$[17,25,26] were prepared from

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$(CH_3)_4Pb$ by literature procedures. Anal. Calcd for $C_2H_6PbN_2O_6$: C, 6.65; H, 1.66; N, 7.76; Pb, 57.34; NO_3^-, 34.35. Found: C, 6.66; H, 1.66; N, 6.02; Pb, 57.48; NO_3^-, 34.65. Anal. Calcd for C_3H_9PbCl: C, 12.52; H, 3.13; Pb, 72.01. Found: C, 12.64; H, 3.15; Pb, 72.85.

Determination of Pb^{2+} and NO_3^-. Pb^{2+} was determined by EDTA titration[27] or atomic absorption spectrometry (Techtron AA5 Spectrometer, Varian Corp.) and NO_3^- by gravimetry.[28]

Spectrophotometric Titrations. Titrations were performed anaerobically in 1-cm quartz cells. Typically 10^{-4} M solutions of $(CH_3)_2Co(chel)$ were titrated with standard solutions of Pb^{2+}, $(CH_3)_3PbCl$, or $(CH_3)_2Pb(NO_3)_2$ by following the absorbance decrease at 442 nm for $[(CH_3)_2Co(N_4)]ClO_4{\cdot}H_2O$ or at 405 nm for $(CH_3)_2Co((1-)N_4)$. The overall reactions were titrated by injecting small volumes of the electrophile from a 1-μL syring directly into the cuvette containing a known amount of the organocobalt complex solution. Within several minutes, absorbances decreased to a constant value, and more titrant was added. Attempts to observe the first step of the biphasic reactions of Pb^{2+} and $(CH_3)_2Pb(NO_3)_2$ failed although titrant additions were separated by only 10s.

^{1}H NMR Titrations. All titrations were performed anaerobically in 5-mm NMR tubes. In a typical experiment a 0.50 mL aliquot of a 0.030 M solution of $(CH_3)_2Co(chel)$ in CH_3CN-d_3 was titrated with standard electrophile solutions from a 100-μL syringe. ^{1}H NMR studies were done after cooling the titrant to −40 °C by means of a dry ice-*o*-xylene-*m*-xylene slush.

GLC Studies. Anaerobic solutions of $(CH_3)_2Co(chel)$ (4×10^{-3} M) were placed in 50-mL Hypo vials that were sealed with serum caps. An appropriate amount of a standardized electrophile solution was added, and the evolved CH_4 and $(CH_3)_4Pb$ were sampled with a gastight syringe and determined by GLC.

Determination of Pb. $[(CH_3)_2Co(N_4)]ClO_4{\cdot}H_2O$ (13.67 mg, 0.301 mmol) was dissolved in 5.00 mL of CH_3CN in a Hypo vial. The vial was sealed with a serum cap and purged with nitrogen before 34 μL of a 0.220 M Pb^{2+} solution was added. After completion of the reaction, the solution was filtered through a 0.40 μm polycarbonate membrane. The resulting black solid was washed with CH_3CN and air-dried. The solid was placed in a glass capillary, and its X-ray diffraction pattern was obtained. A similar experiment with $(CH_3)_2Co((1-)N_4)$ also gave a black solid. Both solids were identified as Pb^0 on the bases of their X-ray diffraction patterns.

Nephelometric Titration. Solutions of $(CH_3)_2Co(chel)$ (10^{-4} M) were titrated with small aliquots of 0.220 M Pb^{2+}. Changes in solution scattering were monitored during titration by Pb^{2+} by irradiating the solutions at 500 nm and measuring scattered light at the same wavelength.

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Registry No. $(CH_3)_2Co((1-)N_4)$, 33569-60-7; $[(CH_3)_2Co(N_4)]ClO_4$, 77310-45-3; Pb^{2+}, 14280-50-3; $(CH_3)_2Pb(NO_3)_2$, 39152-70-0; $(CH_3)_3PbCl$, 1520-78-1; $(CH_3)_4Pb$, 75-74-1.

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Electronic Effects and Trans Substitution in Octahedral Complexes of Chromium(III)

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Kinetics and equilibrium data were determined for the formation of 1:1 adducts of NCS^- with four complexes of the general formula $(H_2O)_5CrR^{2+}$ (R = CH_2OH, CH_2OCH_3, CH_2CN, and $CH(CH_3)_2$). The kinetic data for the approach to equilibrium follow the rate law $k_{obsd} = (A[SCN^-] + B)/(1 + C[SCN^-])$ and are consistent with both a limiting S_N1 (or D) and a dissociative ion-pairing (I_D) mechanism. The rate constants of the trans-water exchange in these and two previously studied complexes of the same general type (R = $CHCl_2$ and CH_2Cl) were approximated as a ratio A/C. The correlation of these rate constants and ones for the trans-water exchange in complexes $Cr(H_2O)_5X^{2+}$ (X = I^-, Cl^-, and SCN^-) with the electron-donating ability of the labilizing groups R and X as measured by a Hammett substituent constant was examined. The same correlation was obtained for a limited number of available rate constants for the Cr–NCS bond breaking in the adducts *trans*-$Cr(H_2O)_4R(NCS)^+$, indicating that the trans-labilizing ability of group R does not depend on the nature of the leaving group. The complex $(H_2O)_5CrCH(CH_3)_2^{2+}$ reacts with SCN^- more slowly than predicted by this correlation.

Introduction

The position trans to the alkyl group in some (halomethyl)pentaaquochromium(III) complexes is by several orders of magnitude kinetically more labile than the same position in the corresponding inorganic complexes of chromium(III).[1] Substitution of one water molecule in $(H_2O)_5CrCHCl_2^{2+}$ and $(H_2O)_5CrCH_2Cl^{2+}$ by thiocyanate ions (eq 1 and 2) occurs on the same time scale of several minutes

$$(H_2O)_5CrCHCl_2^{2+} + SCN^- = \textit{trans}\text{-}(H_2O)_4Cr(NCS)(CHCl_2)^+ + H_2O \tag{1}$$

$$(H_2O)_5CrCH_2Cl^{2+} + SCN^- = \textit{trans}\text{-}(H_2O)_4Cr(NCS)(CH_2Cl)^+ + H_2O \tag{2}$$

rather than hours or days normally seen for the complexes of the general formula $(H_2O)_5CrX^{2+}$. Another report[2] gives much higher rate constant for reaction 2. We return to this discrepancy later in the paper.

Malik et al.[3] reported a rapid substitution of the fluoride ion into the coordination sphere of $(H_2O)_5CrCF_3^{2+}$. The product of this reaction, $(H_2O)_4CrF(CF_3)^+$, undergoes a Cr–C bond cleavage more rapidly than the parent pentaaquo complex. The complexes *trans*-$Cr(H_2O)_4(NCS)(CHCl_2)^+$ and *trans*-$(H_2O)_4Cr(NCS)(CH_2Cl)^+$, the products of reactions 1 and 2, also decompose by Cr–C bond-cleavage reactions more rapidly than do the parent complexes. The acceleration by anions of the Cr–C bond cleavage in the benzylpentaaquochromium(III) cation is most likely also brought about by a rapid substitution of the anions into its coordination sphere.[4]

The studies of the kinetics and mechanisms of the oxidation of α-hydroxyalkyl complexes of chromium(III)[5-7] suggested

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