catalyst.[7] Anal. Calcd for **13d**: Co, 4.78. Found: Co, 6.5 (CH_2Cl_2 reflux); Co, 5.5 (CH_2Cl_2 25 °C).

The reaction of 0.5 g of the soluble polymer-supported 7-methoxynorbornene (**9a**) with 0.3 g of sodium–potassium alloy in 20 mL of THF for 1 h at 28 °C also generated the cyclopentadienyl anion. Cross-linked, insoluble polymer (**9b**) did not react with the alloy. The cobalt and rhodium catalysts were prepared as described above.

Model Reactions of *syn*- and *anti*-7-Chloro-7-phenylnorborn-2-ene (4). A solution of phenylcyclopentadiene anion was prepared from **4** by a procedure similar to that described for polymers **9**. The anion was converted to phenylferrocene by using an iron–ferric chloride reagent[14] in a 56% crude yield. Separation of phenyl ferrocene was accomplished by column chromatography (SiO_2). Elution with pentane gave 0.5 g (31%) of product: mp 140 °C (lit.[9] mp 154 °C) (Table III).

Attempted Fischer–Tropsch Reaction. A mixture of 0.3 g of polymer-supported cobalt catalyst and 20–30 mL of *n*-octane was sealed in a 100-mL Monel Parr pressure reaction vessel under a nitrogen atmosphere. The system was flushed with carbon monoxide three times and finally pressurized with a mixture of hydrogen and carbon monoxide (3:1) to a pressure of 75 psi at 25 °C. The vessel was heated to 150 or 200 °C for 72–168 h. The vessel was then cooled to –78 °C and vented. The volatile components were then transferred to a trap and analyzed by GLC. Only *n*-octane was recovered.

Hydrogenation. A 100-mL Monel Parr pressure reaction vessel with a glass liner was charged with substrate and 0.2 g of polymer-bound rhodium catalyst (**12d**) under nitrogen. The reaction vessel was filled with hydrogen and evacuated four times and finally pressurized with

hydrogen at 25 °C (Table II). At the end of the indicated reaction time, the catalyst was removed by filtration and the products were determined by ^1H NMR, IR, and GLC (Table II).

Hydroformylation. Hydroformylation[5] was carried out by charging 0.1 g of polymer-attached catalyst (**12d**), 10 mL of benzene, and 2 mL (17.8 mmol) of 1-hexene into a 100-mL Monel Parr pressure reaction vessel. The system was flushed three times with hydrogen and twice with carbon monoxide. The vessel was pressurized to 200 psi with carbon monoxide and heated to 110 °C in an oil bath. After 40 min, during which time the system achieved equilibrium, a 1:1 carbon monoxide–hydrogen mixture was introduced to 1300 psi and the reaction vessel was heated at 110 °C for 1 h. The pressure dropped to ~1200 psi during this time. The vessel was cooled to 25 °C and the suspension was filtered to remove the catalyst. The solution was analyzed by GLC (SE-30, 10 ft) at 180 °C. The products were identified by comparison with authentic samples. The ^1H NMR spectrum of the solution showed no 1-hexene. The turnover rate was >148/h; linear/branched = 0.72.

The reaction was repeated with the use of the same catalyst. Complete conversion of aldehydes, linear/branched = 0.69, was achieved. The catalyst, by IR, showed absorptions at 2045 and 1980 cm^{-1}.

Alkylation of Tin by Alkylcobalamins. Kinetics and Mechanism

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Abstract: The reaction of methylcobalamin with stannous chloride in aqueous hydrochloric acid solution has been examined under aerobic conditions. The reaction occurs with a 1:1 stoichiometry, producing aquocobalamin and methyltin(IV) trichloride. The reaction follows a second-order rate expression: first order in methylcobalamin and first order in stannous chloride. Under anaerobic conditions, the reaction does not occur but does occur in the presence of stoichiometric amounts of aquocobalamin, producing a twofold excess of cob(II)alamin and methyltin(IV) trichloride. This reaction is first order in methylcobalamin, first order in stannous chloride, and zero order in aquocobalamin. Adding cob(II)alamin in large amounts does not affect the kinetics or stoichiometry of this reaction. The kinetics of dealkylation of ethylcobalamin and (chloromethyl)cobalamin by stannous chloride under aerobic conditions are also examined. Second-order rate constants for the dealkylation of methylcobalamin, ethylcobalamin, and (chloromethyl)cobalamin by stannous chloride at 23 °C, [HCl] = 1.0 M, were found to be 1.04 ± 0.10 M^{-1} s^{-1}, $(1.66 \pm 0.20) \times 10^{-2}$ M^{-1} s^{-1}, and 7×10^{-3} M^{-1} s^{-1}, respectively. The mechanism is described in terms of a direct bimolecular homolytic attack (S_H2) by stannous chloride at the saturated carbon center, producing cob(II)alamin and a strongly reducing methylstannyl(III) radical. This radical intermediate then reacts with oxygen or aquocobalamin to produce the stable methyltin(IV) trichloride.

Reactions between alkylcorrinoids and tin are of environmental importance as well as mechanistic interest.[1] Reductive cleavage of alkylcorrinoids and of related B_{12} model compounds by Sn^{II} salts was initially proposed by Schrauzer et al.[2] More recently, it was suggested that tin could be methylated by methylcobalamin through reductive cobalt–carbon cleavage by a species which was generated by one-equivalent oxidation of Sn^{II}.[3] In this report, we present kinetic and mechanistic data on the alkylation of stannous chloride by methyl-, ethyl-, and (chloromethyl)cobalamin.

Alkyl transfer from cobalt to tin is discussed in terms of a mechanism of S_H2 displacement of cob(II)alamin by Sn^{II}.

Experimental Section

Materials. Stannous, Stannic, Methyltin(IV), and Dimethyltin(IV) chloride salts were obtained from Ventron, Inc., and were used as received. The stability of $SnCl_2$ solutions against air oxidation at room temperature was determined by standard $S_2O_3^{2-}$–Br_2 titration. Stock solutions of $SnCl_2$ were never stored under air for more than 2 h. [^{13}C]methyl iodide (90%) was obtained from Stohler Inc. Methylcobalamin (CH_3-B_{12}) was obtained from Sigma Co. $^{13}CH_3$-B_{12}, C_2-H_5-B_{12}, and CH_2Cl-B_{12} were synthesized in the dark from cyanocobalamin (Vitamin B_{12}) and $^{13}CH_3I$, C_2H_5I, and CH_2Cl_2, respectively.[4] Cob(II)alamin (B_{12r}) was generated by reducing H_2O-B_{12}^+ with equi-

(1) (a) Wood, J. M. *Science (Washington, D. C.)* 1974, *183*, 1049. (b) Johnson, M. D. *Acc. Chem. Res.* 1978, *11*, 57.

(2) Schrauzer, G. N.; Seck, J. A.; Beckhan, T. M. *Bioinorg. Chem.* 1973, *2*, 211.

(3) Dizikes, L. J.; Ridley, W. P.; Wood, J. M. *J. Am. Chem. Soc.* 1978, *100*, 1010.

(4) Dolphin, D. *Method Enzymol.* 1971, *18C*, 34.
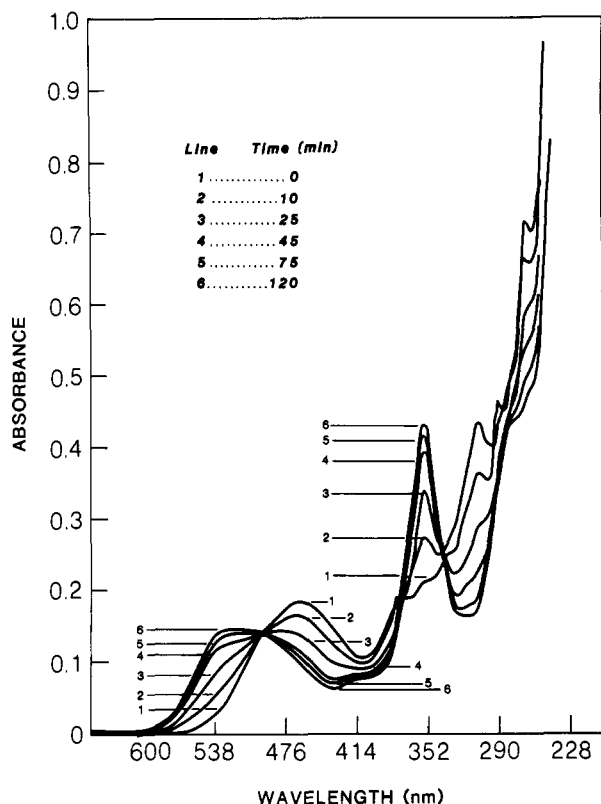
Figure 1. Repetitive spectral scans during the aerobic demethylation of CH_3-B_{12} (2.0×10^{-5} M) by $Sn^{II}Cl_x^{2-x}$ (5.2×10^{-4} M) in 1.0 M HCl solution (23 °C).

molar amounts of Eu^{2+} under an atmosphere of nitrogen or argon. Concentrations of CH_3-B_{12}, C_2H_5-B_{12}, CH_2Cl-B_{12}, H_2O-B_{12}^+, and B_{12r} were determined from absorption spectra by using the published molar absorptivities.[5] All other chemicals were reagent grade and were used as received.

Stoichiometries and Products. The comsumption ratio of $SnCl_2$:CH_3-B_{12} was determined by spectrophotometric titration with a GCA/ McPherson Instrument. The B_{12} products were identified spectrophotometrically. Organotin products were identified by using a Brüker 270-MHz proton NMR and a Varian XL 100 MHz ^{13}C NMR spectrometers. In a typical NMR experiment, 3 mM CH_3-B_{12} was mixed with a fivefold excess of $SnCl_2$ in 1.0 M DCl in D_2O in the dark. The same amounts of $SnCl_2$ were added to reaction solutions after 5 h, and air was bubbled through such solutions for approximately 3 min. After 1 week, the B_{12} products precipitated out and the reaction solution was filtered. The proton NMR spectrum of the filtrate was compared to the spectrum of an authentic sample of $(CH_3)SnCl_3$ recorded in 1.0 M DCl–D_2O. ^{13}C NMR spectra of reaction solutions were studied with $^{13}CH_3$-B_{12} (90% enriched) in the presence of stoichiometric amounts of H_2O-B_{12}^+. ^{13}C NMR spectra were recorded immediately after the reactions had reached completion.

Kinetic Measurements. Rates for the dealkylation of CH_3-B_{12}, C_2-H_5-B_{12}, and CH_2Cl-B_{12} by $SnCl_2$ under air were estimated by the absorbance increase at 351 nm (absorbance maximum for H_2O-B_{12}^+) at 23 °C in the dark. Rates for demethylation of CH_3-B_{12} by $SnCl_2$ in the presence of H_2O-B_{12}^+ (under N_2 or Ar) were estimated by the absorbance increase at 470 nm (absorbance maximum for B_{12r}) or by the absorbance decrease at 538 nm. Ionic strength was maintained at 1.0 M with NaCl and/or HCl throughout. The pH was controlled in the range 0–1 with HCl.

Results

It has been shown that in 1.0 M chloride pH 0–1 (NaCl, HCl) solution, Sn^{II} exists largely as a mixture of $SnCl_3^-$ and $SnCl_2$.[6] Therefore, stannous chloride solutions used in this study are referred to as $Sn^{II}Cl_x^{2-x}$. $Sn^{II}Cl_x^{2-x}$ is slowly oxidized by air to give $Sn^{IV}Cl_y^{4-y}$ in HCl solution. At room temperature (~23 °C), the
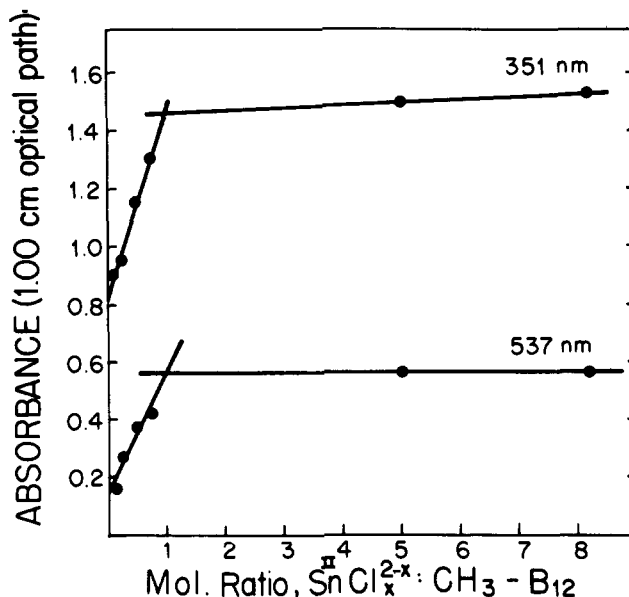
(5) Pratt, J. M. "Inorganic Chemistry of Vitamin B_{12}"; Academic Press: London, 1972; Chapter 5, p 44.
(6) Moodley, K. G.; Nicol, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 239.

Figure 2. Spectrophotometric titration of 6.0×10^{-5} M CH_3-B_{12} with $Sn^{II}Cl_x^{2-x}$ at 351 and 537 nm ([HCl] = 1.0 M; temperature = 23 °C).

rate of air oxidation of $Sn^{II}Cl_x^{2-x}$ is first order in $Sn^{II}Cl_x^{2-x}$ with $k_{obsd} = 4.4 \times 10^{-6}$ s^{-1}.

$Sn^{IV}Cl_y^{4-y}$ does not react with CH_3-B_{12} under the experimental conditions reported here. $Sn^{II}Cl_x^{2-x}$ does not react with CH_3-B_{12} under strictly anaerobic conditions over 24 h. However, CH_3-B_{12} (2.0×10^{-5} M) was demethylated by $Sn^{II}Cl_x^{2-x}$ (5.0×10^{-4} M) in 1.0 M HCl solution under an atmosphere of air. The reaction proceeded with a half-life of approximately 20 min. H_2O-B_{12}^+ was identified as the B_{12} product with isosbestic points observed at 494, 373, and 339 nm (Figure 1).

H_2O-B_{12}^+ alone does not react with $Sn^{II}Cl_x^{2-x}$ at any detectable rate. However, in the presence of stoichiometric amounts of H_2O-B_{12}^+, CH_3-B_{12} (1.6×10^{-4} M) was demethylated by $Sn^{II}Cl_x^{2-x}$ (8.0×10^{-5} M) under an atmosphere of N_2 to produce twofold excess of B_{12r}. B_{12r} alone does not react with $(CH_3)SnCl_3$ or $(CH_3)_2SnCl_2$ at any appreciable rate.

The demethylation of CH_3-B_{12} by a large excess of $Sn^{II}Cl_x^{2-x}$ under air was followed by a slower reaction, producing a yellow corrinoid with a UV–visible spectrum similar to that of B_{12r} at low pH. This yellow corrinoid is stable in the air for several weeks and has similar properties to the yellow corrinoid produced by the reduction of vitamin B_{12} reported by Gruning et al.[7]

Products and Stoichiometry. The demethylation of CH_3-B_{12} by $Sn^{II}Cl_x^{2-x}$ under air occurs according to eq 1. Plots of ab-

$$CH_3\text{-}B_{12} + Sn^{II}Cl_x^{2-x} + H_2O \xrightarrow{O_2}$$
$$H_2O\text{-}B_{12}^+ + (CH_3)Sn^{IV}Cl_y^{3-y} \quad (1)$$
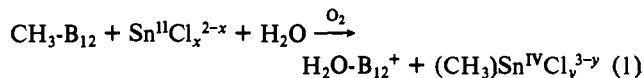
sorbance at 351 and 537 nm vs. the ratio of the added $Sn^{II}Cl_x^{2-x}$ and CH_3-B_{12} are shown in Figure 2. Titration endpoints are noted at a 1:1 ratio, supporting the stoichiometry of eq 1. This 1:1 stoichiometry can also be calculated by using the molar absorptivities of CH_3-B_{12} and H_2O-B_{12}^+.[8] $(CH_3)Sn^{IV}Cl_3$ was identified as the tin product for this reaction by proton NMR. The CH_3-Sn resonance appears at 1.18 ppm relative to TSP with a proton spin–spin coupling constant of 65 cps in 1.0 M DCl–D_2O solution, which agrees quite well with an authentic sample of $(CH_3)SnCl_3$ in 1.0 M DCl solution.[9]

(7) (a) Gruning, B.; Gossamer, A. "Vitamin B_{12}", Proceeding of the Third European Symposium on Vitamin B_{12} and Intrinsic Factor, Zagalak, B., Friedrich, W., Eds. Zurich, Switzerland, 1979, p 141. (b) Schlingmann, G.; Koppenhagen, V. B. *Ibid.*, p 149.
(8) in 1.0 M HCl solution, molar absorptivities of CH_3-B_{12} and H_2O-B_{12}^+ at 351 nm were determined to be 1.06×10^4 and 2.63×10^4 M^{-1} cm^{-1}, respectively. Absorbance of $Sn^{II}Cl_x^{2-x}$ at low concentration can be neglected.
(9) For NMR studies of methyltin chlorides, see: Sawyer, A. K., Ed.; *Organotin Compd.* **1971**, *1*, 106.
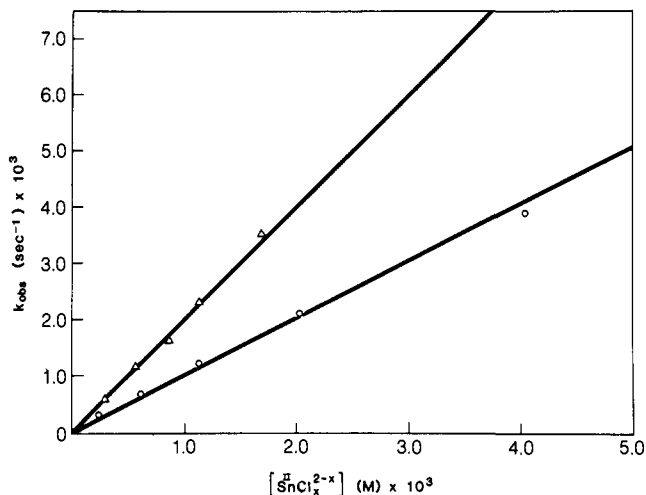
Figure 3. Kinetic measurements for the demethylation of CH_3-B_{12} by $Sn^{II}Cl_x^{2-x}$ in 1.0 M HCl solution 23 °C: (O) under aerobic conditions; (△) under anaerobic conditions (in the presence of stoichiometric amounts of H_2O-B_{12}^+).

The demethylation of CH_3-B_{12} by $Sn^{II}Cl_x^{2-x}$ in the presence of H_2O-B_{12}^+ (under N_2) is described in eq 2. $(CH_3)Sn^{IV}Cl_y^{3-y}$

$$CH_3\text{-}B_{12} + H_2O\text{-}B_{12}^+ + Sn^{II}Cl_x^{2-x} \rightarrow$$
$$2B_{12r} + (CH_3)Sn^{IV}Cl_y^{3-y} + H_2O \quad (2)$$
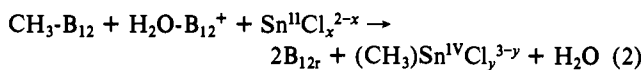
was identified as the tin product for this reaction by ^{13}C NMR. The ^{13}C NMR spectrum of the reaction solution (1.0 M DCl–D_2O) gave a $^{13}CH_3$ resonance which was downfield shifted from 1.43 ppm ($^{13}CH_3$-Co) relative to TSP to 22.6 ppm ($^{13}CH_3$-Sn^{IV}).

Kinetic Measurements. An excess of $Sn^{II}Cl_x^{2-x}$ over alkylcobalamin was used in all the rate measurements so that $[Sn^{II}Cl_x^{2-x}]$ remained essentially constant. The range of $[R\text{-}B_{12}]$ was (8–50) × 10^{-6} M. Plots of log ($A_\infty - A_t$) vs. time gave straight lines for more than 85% of the reaction. Kinetic data for the demethylation of CH_3-B_{12} by $Sn^{II}Cl_x^{2-x}$ under air and in the presence of H_2O-B_{12}^+ (under N_2) ae plotted in Figure 3. Data for the dealkylation of CH_3-B_{12}, C_2H_5-B_{12}, and CH_2Cl-B_{12} by $Sn^{II}Cl_x^{2-x}$ under air can be expressed in eq 3 with $k_{Me} = 1.04 \pm$

$$d[H_2O\text{-}B_{12}^+]/dt = k_R[Sn^{II}Cl_x^{2-x}][R\text{-}B_{12}]_T \quad (3)$$

0.10 M^{-1} s^{-1}, $k_{Et} = (1.66 \pm 0.20) \times 10^{-2}$ M^{-1} s^{-1}, and $k_{CH_2Cl} \simeq 7 \times 10^{-3}$ M^{-1} s^{-1} [10] at 0 (HCl) (23 °C).

The kinetics for the demethylation of CH_3-B_{12} by $Sn^{II}Cl_x^{2-x}$ in the presence of H_2O-B_{12}^+ can be expressed in eq 4 with k_{Me}

$$d[B_{12r}]/dt = 2k_{Me}[Sn^{II}Cl_x^{2-x}][CH_3\text{-}B_{12}]_T \quad (4)$$

= 1.02 ± 0.10 M^{-1} s^{-1} at pH 0 (HCl) (23 °C). This reaction was found to be zero order in H_2O-B_{12}^+. The addition of B_{12r} did not affect the kinetics of this reaction. CH_3-B_{12} was quantitatively demethylated even the ratio of $[B_{12r}]/[H_2O\text{-}B_{12}^+]$ added to reaction solutions was 20. k_{Me} is $[H^+]$ dependent in the pH range 0–1 according to eq 5 with $k_1 = 0.32 \pm 0.03$ M^{-1} s^{-1} and $k_2 = 0.85 \pm 0.15$ M^{-2} s^{-1}.

$$k_{Me} = k_1 + k_2[H^+] \quad (5)$$

It should be noted that when $[CH_3\text{-}B_{12}] > 10^{-3}$ M, then the reaction of CH_3-B_{12} with $Sn^{II}Cl_x^{2-x}$ is much slower than the rate laws and rate constants of eq 3 and 4 predict. This observation can be explained by our recent NMR studies of CH_3-B_{12} in aqueous solution.[11] By using 270-MHz proton NMR, we have shown the existence of a dimer–monomer equilbrium for CH_3-B_{12}. An increase in $[CH_3\text{-}B_{12}]$ increases the concentraion of dimer,

which is much less reactive than the monomer.

Discussion

The methylation of tin compounds by methylcobalamin (C-H_3-B_{12}) was studied at low pH (0–1), so that sufficient tin salt was dissolved in reaction mixtures. CH_3-B_{12} in acid solution is subject to equilibria between species in which 5,6-dimethyl-benzimidazole is coordinated to the cobalt atom (base on), and in which it is protonated and therefore uncoordinated (base off).[5] In the pH range 0–1, the "base-on" form of CH_3-B_{12} is negligible. Examination of the tin products by NMR shows that the methyl group is transferred from CH_3-B_{12} to Sn^{II} quantitatively. This NMR study, together with the stoichiometries, rules out the possibility for the production of $(CH_3)_2Sn^{IV}Cl_2$ under present experimental conditions. Oxidants such as molecular oxygen or H_2O-B_{12}^+ play a crucial role in this methyl-transfer reaction. The oxidant chosen must be weak enough not to oxidatively cleave the Co–C bond. This precludes the use of oxidants such as Fe^{3+}, $IrCl_6^{2-}$, or Ce(IV).[12] Several lines of evidence suggest that the oxidant does not participate in the kinetics of the methyl-transfer reaction. First, the rate constant for demethylation of CH_3-B_{12} under air is identical within experimental uncertainty to that measured in the presence of H_2O-B_{12}^+ (under N_2). Second, the rate constant for demethylation of CH_3-B_{12} by $Sn^{II}Cl_x^{2-x}$ is much larger than the air oxidation of $Sn^{II}Cl_x^{2-x}$. Third, the demethylation of CH_3-B_{12} is zero order in H_2O-B_{12}^+. On the basis of these results, a mechanism can be proposed as following[13]

$$CH_3\text{-}B_{12} + Sn^{II} \rightleftharpoons B_{12r} + (CH_3)Sn^{III} \quad (6)$$

under aerobic conditions

$$(CH_3)Sn^{III} \overset{O_2}{\rightleftharpoons} (CH_3)Sn^{IV} \quad (7)$$

$$B_{12r} + H_2O \overset{O_2}{\rightleftharpoons} H_2O\text{-}B_{12}^+ \quad (8)$$

under anaerobic conditions

$$(CH_3)Sn^{III} + H_2O\text{-}B_{12}^+ \rightleftharpoons B_{12r} + (CH_3)Sn^{IV} + H_2O \quad (9)$$

The oxidation of B_{12r} by oxygen has been studied in detail by Abel et al.[14] One alternative mechanism for this methyl-transfer reaction is an S_N2 attack at the saturated carbon by Sn^{II}, which would result in the formation of $(CH_3)Sn^{IV}$ and cob(I)alamin (B_{12S}). This reaction could be followed by either air oxidation of B_{12S} or disproportionation reaction between H_2O-B_{12}^+ and B_{12S}. This mechanism is unlikely to occur, however, because B_{12S} is known to be an extremely reactive nucleophile.[15]

Espenson et al. have reported the reaction between CH_3-B_{12} and Cr^{2+}.[16] This reaction produces B_{12r} and $(CH_3)Cr(H_2O)_5^{2+}$. Two mechanisms were proposed for this reaction, one of which is a direct bimolecular homolytic attack (S_H2) at the saturated carbon center. Mechanism proposed here for methyl transfer from CH_3-B_{12} to $Sn^{II}Cl_x^{2-x}$ can also be described as a reductive homolytic cleavage of the Co–C bond, in which a strongly reducing $(CH_3)Sn^{III}$ intermediate is produced. It then quickly reduces the oxidant to give a stable $(CH_3)Sn^{IV}$ product. In the absence of oxidant, eq 6 lies far to the left and no reaction is observed. Organostannyl radicals are well-known in the reactions of organotin compounds in photochemical and free radical processes.[17] In fact, organostannyl radicals have been directly detected upon
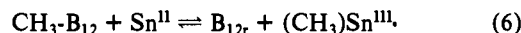
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(10) Because of the slow reaction for CH_2Cl-B_{12}, initial rates were used in this kinetic study, with $\epsilon = 2.63 \times 10^4$ and 1.33×10^4 M^{-1} cm^{-1} for H_2O-B_{12}^+ and CH_2Cl-B_{12} at 351 nm, (1.0 M HCl), respectively.

(11) Pignatello, J.; Fanchiang, Y.-T., manuscript in preparation.

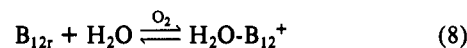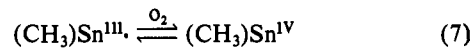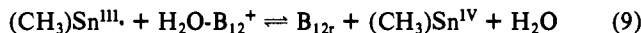(12) Fanchiang, Y.-T., unpublished results.

(13) The mechanism which was proposed in ref 3 should be disregarded because the assumption which was required to derive the rate law was incompatible with the stoichiometry that was observed.

(14) Abel, E. W.; Pratt, J. M. Whelan, R.; Wilkinson, P. M., S. Afr. *J. Chem.* **1977**, *30*, 1.

(15) Schrauzer, G. N. *Adv. Chem. Ser.* **1971**, *No, 100*, 1.

(16) Espenson, J. H.; Sellers, T. D., Jr., *J. Am. Chem. Soc.* **1974**, *96*, 94.

(17) (a) Sakurai, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973, Vol. 2, Chapter 25. (b) Howard J. A.; Tait, J. C.; Tong, S. B. *Can. J. Chem.* **1979**, *57*, 2761; (c) Howard, J. A.; Tait, J. C.; Tong, S. G. *J. Am. Chem. Soc.* **1977**, *99*, 8349.

using laser flash photolysis.[18] It is worth noting that the reaction ratio of k_{Me}/k_{Et} (=65) for the reactions of alkylcobalamins with $Sn^{II}Cl_x^{2-x}$ is quite similar to the reported rate ratio of k_{Me}/k_{Et} (=80) for the reactions of alkylcobalamins with Cr^{2+}.[16] The smaller rate constant for C_2H_5-B_{12} than for CH_3-B_{12} is probably due to the steric hindrance of methyl group of C_2H_5-B_{12}.

Endicott et al. have recently unified the mechanisms of halide- and methyl-bridged electron-transfer reactions of cobalt complexes with macrocyclic ligands.[19] The relatively slow rates for methyl-bridged reactions are interpreted in terms of a three-center–three-electron (Co–CH_3–Co) bonding description of the transition state. This three-center–three-electron bonding description can also be applied to the methyl transfer from CH_3-B_{12} to $Sn^{II}Cl_x^{2-x}$. It should be noted that the one-electron reduction potential of base-off CH_3-B_{12} has been estimated to be −1.46 V (vs. aqueous SCE) at 19 °C.[20] Consequently, compared with the reduction potential of H_2O-B_{12}^+ which has been measured to be 0.15 V under the same experimental conditions,[21] CH_3-B_{12} is an extremely weak oxidant. Indeed, we have shown that there is no reaction between

CH_3-B_{12} and $Ru(NH_3)_6^{2+}$, an apparent outer-sphere one-electron reductant, for several days under argon. Apparently, the rate constant of 1.04 M^{-1} s^{-1} (at 23 °C, 1.0 M HCl) for the methyl transfer from CH_3-B_{12} to Sn^{II} is due to the "bridging" of the methyl group.

The pH-dependent kinetics for the reaction between methylcobalamin and $Sn^{II}Cl_x^{2-x}$ are somewhat puzzling, because it has been shown that there is no pH dependence for the reactions between platinum(IV) and $Sn^{II}Cl_x^{2-x}$ (at pH 0–1),[6] and between CH_3-B_{12} and Cr^{2+}.[16] One explanation for the increasing rate with increasing [H^+] in the present study is that the base-off CH_3-B_{12} includes forms in which water occupies the sixth coordination position and in which it does not. An increase in [H^+] may increase the five-coordinated CH_3-B_{12} which is more reactive to $Sn^{II}Cl_x^{2-x}$ than the six-coordinated form.

In conclusion, our observation that CH_3-B_{12} possesses the capability of methylating inorganic tin is noteworthy because the organometallic forms of heavy metals are invariably more toxic than their inorganic precursors. This study may be pertinent to the toxicity of tin in the environment.

(18) Scaiano, J. C. *J. Am. Chem.* **1980**, *102*, 5399.
(19) (a) Durham, B.; Endicott, J. F.; Wong, C. L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847. (b) Endicott, J. F.; Wong, C. L.; Ciskowski, J. M.; Balakrishman, K. P. *Ibid.* **1980**, *102*, 2100. (c) Endicott, J. F.; Balakrishman, K. P.; Wong, C. L. *Ibid.* **1980**, *102*, 5519.
(20) Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3220. The reduction potential for base-off CH_3-B_{12} is taken from the reduction potential of methylcobinamide.
(21) Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 2786.

Novel Boron-to-Sulfur Alkyl Group Transfer in Reactions of Lithium Triethylborohydride-Derived Bis(μ-thiolato)-bis(tricarbonyliron) Dianion with Mercuric Chloride and Alkylmercuric Chlorides
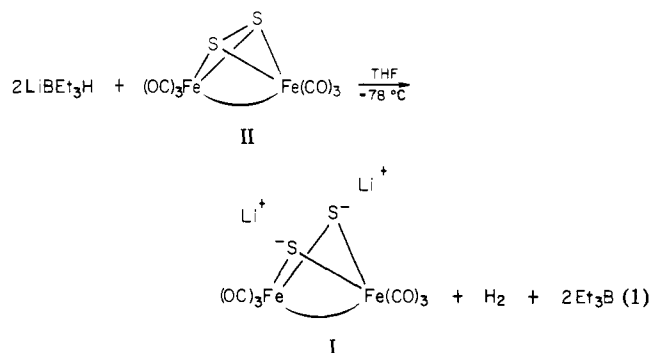
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Abstract: In addition to the expected products, $(\mu$-$RHgS)_2Fe_2(CO)_6$, the reaction of LiBEt$_3$H-derived $(\mu$-$LiS)_2Fe_2(CO)_6$ with methyl- and ethylmercuric chloride gave products of the type $(\mu$-$C_2H_5S)(\mu$-$RHgS)Fe_2(CO)_6$, i.e., into which ethyl groups from the complex hydride had been incorporated. An experiment in which KB(s-C_4H_9)$_3$H was used to generate the dianion from $(\mu$-$S_2)Fe_2(CO)_6$ gave evidence of the generality of this process. Possible intermediates in this novel chemistry are considered.

We have reported previously concerning the generation of the bis(μ-thiolato)-bis(tricarbonyliron) dianion (I) by reaction of (μ-dithio)-bis(tricarbonyliron) (II) with lithium triethylborohydride (eq 1).[1] The reactions of dianion I with various organic, inorganic,

and organometallic halides were quite straightforward, giving the products expected from nucleophilic displacement of halogen from the carbon or the metal(loid) atom, e.g., eq 2 and 3.[1,2]

(1) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.
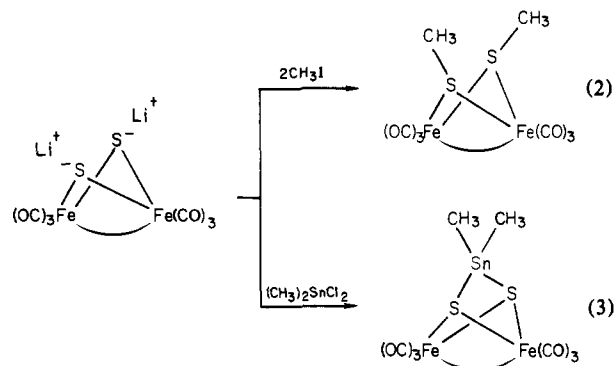
(2) Seyferth, D.; Henderson, R. S.; Gallagher, M. J. *J. Organomet. Chem.* **1980**, *193*, C75.