R value was 0.063 (weighted = 0.057). The final ΔF map contained no peaks higher than 0.5 e/Å^3. For the drawing (Figure 1), the SCHAKAL program[28] was employed.

MO Calculations. The following program systems were employed: ACIWERTE[29] and ACMORS;[30] CNDO/2 and QCPE No. 91; MINDO/3 and QCPE No. 279.

Parameters for overlap calculations: bond distances, $d(\mathrm{C{\equiv}C}) = 117$, $d(\mathrm{C{-}H}) = 90$, $d(\mathrm{C{-}P}) = 175$ pm; bond angles in $\mathrm{P(C{\equiv}CH)_3}$, idealized C_{3v} symmetry, 101° (adapted from ref 13); atomic orbital coefficients for valence orbitals, H(s), C(s), C(p), P(s), and P(p) Clementi's double-ζ's[31] and P(d) Richardson's 3d coefficients for V(0).[32] The overlap matrices for $\mathrm{C{\equiv}CH^-}$ and $\mathrm{P(C{\equiv}CH)_3}$ are given in Tables VII and VIII. To calculate the overlap integrals for $\mathrm{P(C{\equiv}CH)_3}$, collective $\mathrm{C{\equiv}CH^-}$ orbitals were used: $\sigma[\mathrm{H(s), C_a(s), C_b(s), C_a(p_z), (C_b(p_z)}]$; $\pi_v{}^*[\mathrm{C_a(p_y), C_b(p_y)}]$; $\pi_h{}^*[\mathrm{C_a(p_x), C_b(p_x)}]$ (the indices a and b refer to the carbon carrying the negative charge, $\mathrm{C_a}$, and the hydrogen, $\mathrm{C_b}$). Bonding $\pi(\mathrm{C{\equiv}CH^-})$ orbitals were excluded on the grounds of negligible interaction with P orbitals.

For the SCCC calculations on $\mathrm{C{\equiv}CH^-}$, valence orbital ionization potentials (VOIPs) of Basch, Viste, and Gray[14] for two limiting configurations ($2s^2p^2$ and $2sp^3$ in the case of C) and the electron distributions were fed into the program. The program first caculates Coulomb integrals and exchange integrals (on the basis of Cusachs' approach[33]) and then eigenvectors and eigenvalues, and finally a Mulliken population analysis is undertaken. This procedure is maintained until self-consistency is achieved. For the results, see Table VII. In the case of $\mathrm{P(C{\equiv}CH)_3}$, the following starting parameters were employed: P(3s) and P(3p), VOIPs by Basch, Viste, and Gray; P(3d), −0.7945 aJ (-40×10^3 cm^{-1}; this is the mean value of the VOIPs for the 3d orbitals of Ti(0) and V(0)); $\mathrm{C{\equiv}CH^-}$, −1.0927 (σ) and −0.5265 aJ (π) (cf. Table VII).

Spectra. Instruments: IR, Perkin-Elmer 325 and 225 spectrophotometers in cyclohexane (ν(CO) region) and CsI; FIR, Digilab FTS 14 spectrophotometer in polyethylene; Raman, Cary 82 (Varian) spectrophotometer, fitted with Kr or Ar laser (Spectra Physics), neat samples. For a complete set of all of the IR and Raman data of $\mathrm{P(C{\equiv}CPh)_3}$ and the complexes see ref 23. ^{31}P NMR of $\mathrm{W(CO)_5P(C{\equiv}CPh)_3}$: bruker WH 90 spectrometer in 7.5-mm vials at 306 K relative to 80% $\mathrm{H_3PO_4}$, ca. 0.02 M THF solution; $\delta(^{31}\mathrm{P})$ −41.2 (central line and ^{183}W satellite doublet, intensity ratio 7.1/1).

Registry No. 1, 83136-71-4; $\mathrm{W(CO)_5P(C{\equiv}CPh)_3}$, 83152-07-2.

Supplementary Material Available: Tables of thermal parameters, best planes, and structure factor amplitudes for $\mathrm{Cr(CO)_5P(C{\equiv}CPh)_3}$ (75 pages). Ordering information is given on any current masthead page.

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Oxidative Demethylation of Methylcobalamin by Hexachloroiridate(IV)

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The stoichiometries and kinetics of the demethylation of $\mathrm{CH_3\text{-}B_{12}}$ by $\mathrm{IrCl_6{}^{2-}}$ in aqueous solution have been examined. In the presence of excess $\mathrm{IrCl_6{}^{2-}}$, this reaction occurs with a 2:1 ($\mathrm{IrCl_6{}^{2-}}$:$\mathrm{CH_3\text{-}B_{12}}$) stoichiometry, producing $\mathrm{H_2O\text{-}B_{12}{}^+}$, $\mathrm{CH_3Cl}$, and $\mathrm{IrCl_6{}^{3-}/IrCl_5(H_2O)^{2-}}$. With deficient $\mathrm{IrCl_6{}^{2-}}$, the reaction occurs with a ~1.3:1 ($\mathrm{IrCl_6{}^{2-}}$:$\mathrm{CH_3\text{-}B_{12}}$) stoichiometry, producing $\mathrm{H_2O\text{-}B_{12}{}^+}$, $\mathrm{IrCl_6{}^{3-}}$, and $\mathrm{C_2H_6}$ (the major demethylation product). The demethylation follows a second-order rate expression: first order in $\mathrm{CH_3\text{-}B_{12}}$ and first order in $\mathrm{IrCl_6{}^{2-}}$. This second-order rate constant is pH dependent in acidic solution, which is interpreted in terms of protonation of the 5,6-dimethylbenzimidazole moiety and its resulting base-on to base-off conversion. $\mathrm{IrCl_6{}^{3-}}$ inhibits the demethylation, while $\mathrm{Cl^-}$ pronouncedly enhances the rate. The mechanism is described as a one-electron transfer from $\mathrm{CH_3\text{-}B_{12}}$ to $\mathrm{IrCl_6{}^{2-}}$ (rate-determining step), yielding a transient $\mathrm{CH_3\text{-}B_{12}{}^+}$ intermediate. This intermediate rapidly releases a methyl radical which either abstracts a chlorine atom from a second $\mathrm{IrCl_6{}^{2-}}$ molecule to produce $\mathrm{CH_3Cl}$ or combines to yield $\mathrm{C_2H_6}$.

Introduction

The cleavage of the Co–C bonds in organocobalt compounds is a subject of considerable interest in $\mathrm{B_{12}}$-dependent biological reactions,[1] as well as in various homogeneous catalytic processes.[2] Several modes of reagent-induced cleavage of the Co–C bond of methylcobalamin ($\mathrm{CH_3\text{-}B_{12}}$) have already been described.[3] The reactions between $\mathrm{CH_3\text{-}B_{12}}$ and the electrophile are generally characterized as a direct displacement of the Co atom. However, some recent experiments on the methyl transfer from $\mathrm{CH_3\text{-}B_{12}}$ to platinum,[4] gold,[5] and tetracyanoethylene[6] in-

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dicate that an electron transfer may be involved in these reactions. It is important, therefore, to explore electron-transfer reactions of CH_3-B_{12}.

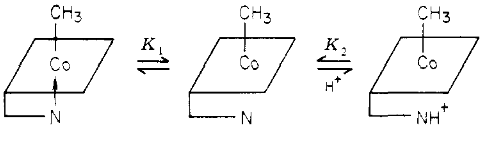
Hexachloroiridate(IV) is well-known as a one-electron oxidant capable of participating in both outer-sphere and inner-sphere processes.[7] More recently, Halpern et al. have shown that organobis(dioximato)cobalt(III) complexes can be oxidized to organocobalt(IV) by $IrCl_6^{2-}$, followed by a nucleophile-induced heterolytic cleavage of the Co–C bond to yield Co(II) ions.[8] Oxidative cleavage of metal–carbon bonds of organometals such as R′HgR, R_4Pb, and R_2PtL_2 by $IrCl_6^{2-}$ has also been described by Kochi et al.[9] A remarkable and noteworthy point lies in the fact that the oxidized organocobaloxime intermediate undergoes a nucleophilic displacement, while R_2Hg^+ or R_4Pb^+ releases an organic radical.

We report here the reaction of CH_3-B_{12} with $IrCl_6^{2-}$. It is described in terms of a one-electron oxidative demethylation. However, unlike alkylcobaloximes, the oxidized CH_3-B_{12} intermediate releases a methyl radical which undergoes further reactions.

Experimental Section

Materials. $Na_2IrCl_6{\cdot}6H_2O$ and $Na_3IrCl_6{\cdot}12H_2O$ were obtained from Goldsmith Inc. Their purity was checked with the published molar absorptivities. $^{13}CH_3I$ (90% enriched) was obtained from Stohler, Inc. CH_3-B_{12} and $^{13}CH_3$-B_{12} were synthesized in the dark from cyanocobalamin and CH_3I or $^{13}CH_3I$.[10] Cob(II)alamin (B_{12r}) was generated by reducing H_2O-B_{12}^+ with equimolar amounts of Eu^{2+} under an atmosphere of Ar. Concentrations of CH_3-B_{12}, H_2O-B_{12}^+, and B_{12r} were determined from their absorption spectra.[11] All other chemicals were reagent grade.

Base-On and Base-Off Equilibrium Constants of CH_3-B_{12}. Protonation of the 5,6-dimethylbenzimidazole moiety and the resulting base-on and base-off conversion can be expressed as in eq 1. pK_2 is taken as 4.7—the pK_a of free 5,6-dimethylbenzimidazole.[12] pK_1 at 1.0 M $NaClO_4$ and NaCl has been previously determined to be 0.90 and 1.74, respectively (23 °C).[5]



(1)

Stoichiometries and Products. The consumption ratios of $IrCl_6^{2-}$:CH_3-B_{12} were determined by spectrophotometric titration with a Cary 15 or GCA/McPherson spectrophotometer. When the reaction was performed with a large ratio of $IrCl_6^{2-}$ over CH_3-B_{12}, the titration was done at 487.5 nm (absorbance maximum for $IrCl_6^{2-}$) with an identical concentration of H_2O-B_{12}^+ in the reference cell to eliminate the B_{12} product absorption. When the reaction was performed with excess CH_3-B_{12}, the titration was done at 351 nm (γ band for H_2O-B_{12}^+) with an identical concentration of $IrCl_6^{3-}$ in the reference cell. The B_{12} products were identified spectrophotometrically. Organic products were examined by a gas chromatograph or a Brüker 250-MHz ^{13}C NMR at low temperature. The identity of the reduced Ir species was determined spectrophotometrically at pH 1. The reaction solution was oxidized with Cl_2. After removal of the excess chlorine, the spectrum was recorded and analyzed with respect to the $IrCl_6^{2-}/IrCl_5(H_2O)^-$ composition by using published spectral data.[13] An identical concentration of H_2O-B_{12}^+ (treated with Cl_2[14] was used in the reference cell to eliminate the B_{12} spectrum.

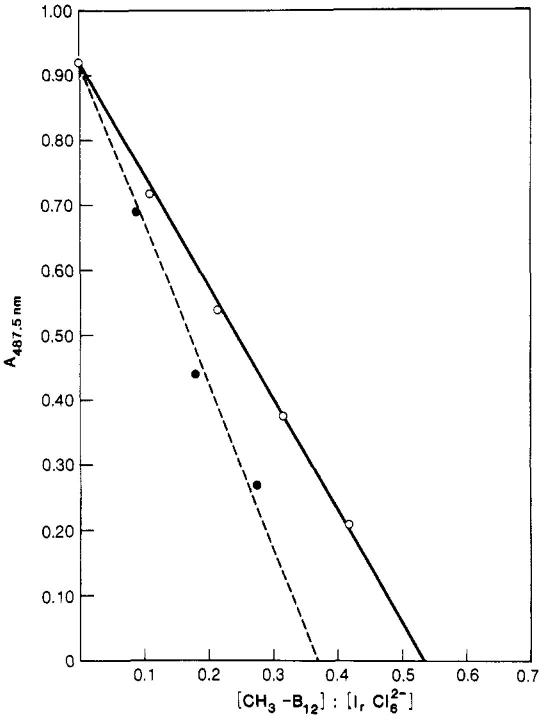


Figure 1. Spectrophotometric titration of 1.8 × 10^{-4} M $IrCl_6^{2-}$ with deficient amounts of CH_3-B_{12} at 487.5 nm (pH 2.91). An identical concentration of H_2O-B_{12}^+ was used in the reference cell to eliminate the absorbance of H_2O-B_{12}^+ produced during the reaction: (○), in 1.0 M NaCl; (●), in 1.0 M $NaClO_4$.

Kinetic Measurements. The rates for demethylation of CH_3-B_{12} by $IrCl_6^{2-}$ were estimated by the absorption increase at 351 nm at 23 °C under a dim light. Ionic strength was maintained at 1.0 M with $NaClO_4$ and/or NaCl throughout. The pH was controlled in the range of 0–3 with $HClO_4$.

Results

Preliminary Observations of the Oxidative Demethylation of CH_3-B_{12}. Similar to that of the B_{12} model compounds,[8] CH_3-B_{12} can be demethylated by a broad variety of oxidants. These include Fe^{3+}, $IrCl_6^{2-}$, Ce(IV), and Br_2. Several noteworthy aspects of the oxidative demethylation of CH_3-B_{12} were observed. (1) Fe^{3+} demethylates CH_3-B_{12} extremely slowly in perchloric acid solution. However, rapid demethylation occurs in the presence of Cl^-. This reaction is first order in both CH_3-B_{12} and Fe^{3+} at low $[Fe^{3+}]$ but approaches zero order in Fe^{3+} as its concentration is increased. (2) Similarly, appreciable demethylation of CH_3-B_{12} by Ce(IV) only occurs in the presence of Cl^-. However, mixing 1 equiv of Ce(IV) with CH_3-B_{12} at pH 7 (in the absence of Cl^-) results in a quantitative base-on to base-off conversion. (3) Br_2 rapidly demethylates CH_3-B_{12}. This reaction is complicated by

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(6) Fanchiang, Y.-T., unpublished results. A mixture of CH_3-B_{12} and tetracyanoethylene (TCNE) in CH_3OH/H_2O solution displays a sharp new absorption band at 420 nm, with ϵ 1.1 × 10^4 M^{-1} cm^{-1} and formation constant = 3.9 × 10^2 M^{-1} (23 °C). This band indicates the formation of a charge-transfer complex between corrin π orbitals and TCNE.

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(14) Treatment of H_2O-B_{12}^+ with Cl_2 results in an immediate color change from red to orange and in some cases the decomposition of cobalamin.

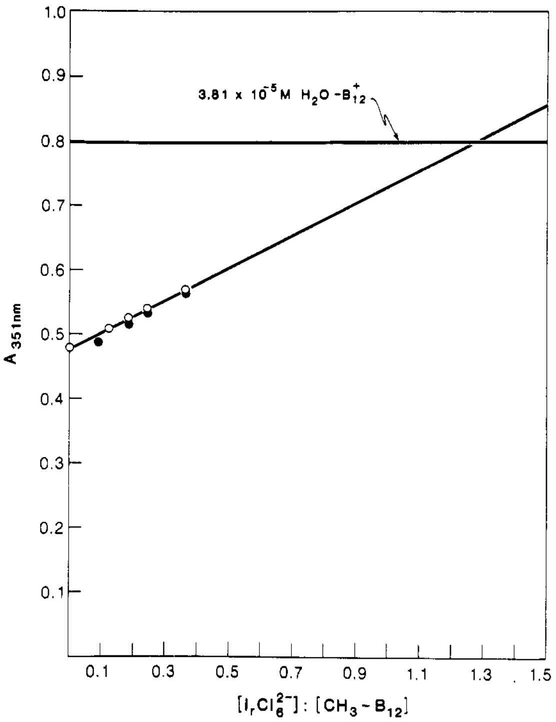

Figure 2. Spectrophotometric titration of 3.81×10^{-5} M CH_3-B_{12} with deficient amounts of $IrCl_6{}^{2-}$ at 351 nm (pH 2.91). An identical concentration of $IrCl_6{}^{3-}$ was used in the reference cell to eliminate the absorbance of $IrCl_6{}^{3-}$ produced during the reaction: (○), in 1.0 M NaCl; (●), in 1.0 M $NaClO_4$.

the Br_2 oxidation of the corrin ring.[15] Detailed stoichiometric and kinetic data of the oxidative demethylation of CH_3-B_{12} by $IrCl_6{}^{2-}$ are presented below.

Stoichiometries and Reaction Products. CH_3-B_{12} (3.5×10^{-5} M) was quantitatively demethylated to H_2O-$B_{12}{}^+$ by a sixfold excess of $IrCl_6{}^{2-}$ in 1.0 M $NaClO_4$ solution. This reaction proceeded with a half-life of ~13 min (pH 3; 23 °C) with isosbestic points at 515, 364, and 335 nm. Reactions performed under Ar yielded the same B_{12} product with no significant change in the demethylation rate. H_2O-$B_{12}{}^+$ was produced under all experimental conditions (i.e., with $IrCl_6{}^{2-}$ in excess over CH_3-B_{12} or vice versa, aerobic or anaerobic). No B_{12r} was detected. $IrCl_6{}^{2-}$ rapidly oxidized B_{12r} to H_2O-$B_{12}{}^+$. H_2O-$B_{12}{}^+$ does not react with $IrCl_6{}^{2-}$.

In 1.0 M NaCl solution, consumption ratio of $[IrCl_6{}^{2-}]$:$[CH_3$-$B_{12}]$ was determined to be 1.95:1 when $IrCl_6{}^{2-}$ used was in large excess over CH_3-B_{12} (Figure 1).[16] Spectrophotometric titration in perchlorate solution with excess $IrCl_6{}^{2-}$ is also shown in Figure 1. The results in perchlorate solution are less satisfactory, with $[IrCl_6{}^{2-}]$:$[CH_3$-$B_{12}] \approx 2.7$:1. We failed to identify the cause. The results of spectrophotometric titration with CH_3-B_{12} in excess over $IrCl_6{}^{2-}$ are shown in Figure 2. The consumption ratios of $[IrCl_6{}^{2-}]$:$[CH_3$-$B_{12}]$ measured under this condition are considerably smaller than 2. As shown in Figure 2, $[IrCl_6{}^{2-}]$:$[CH_3$-$B_{12}]$ was found to be ~1.3:1 in both the Cl^- and $ClO_4{}^-$ media.

The ^{13}C resonance of methyl-transfer product appeared at 26.0 ppm (relative to external Me_4Si) when the reaction of $^{13}CH_3$-B_{12} with a large ratio of $IrCl_6{}^{2-}$ was complete. This indicates that with a large excess of $IrCl_6{}^{2-}$, CH_3Cl is the main organic product generated under all experimental conditions (i.e., in the presence and absence of Cl^- or pyridine, aerobic or anaerobic). No other organic products are detected either by gas chromatograph or by ^{13}C NMR analyses. However, CH_3OH is not definitely ruled out. When reactions were carried out with deficient $IrCl_6{}^{2-}$ in perchlorate solution, C_2H_6 is the major organic product (^{13}C resonance appeared at 6.027 ppm relative to external Me_4Si). A minor amount of CH_3Cl was also generated. The generation of C_2H_6 under this condition is confirmed by GC analysis of the vapor above the reaction solution (the reaction flask (2 cm³) was sealed with a serum cap and warmed to ~40 °C).[17]

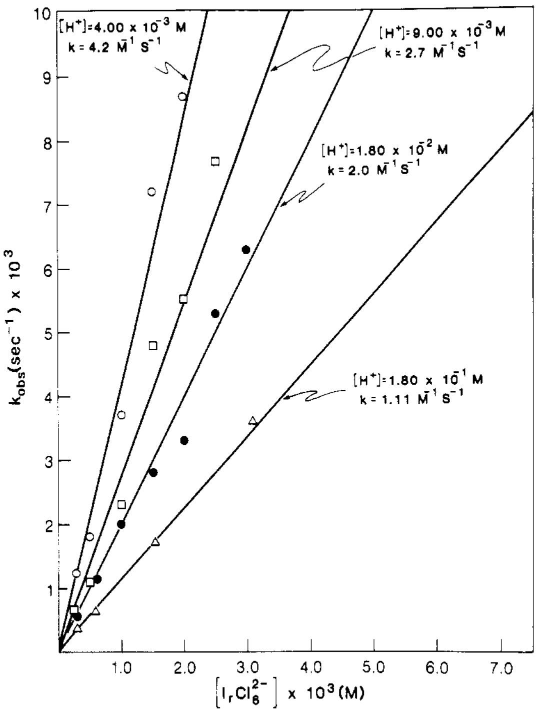

Figure 3. Kinetic data for the demethylation of CH_3-B_{12} by $IrCl_6{}^{2-}$ ($[CH_3$-$B_{12}] = (1\sim3) \times 10^{-5}$ M; $\mu = 1.0$ M ($HClO_4$ + $NaClO_4$); temperature, 23 °C): (○), $[H^+] = 4.00 \times 10^{-3}$ M; (□), $[H^+] = 9.00 \times 10^{-3}$ M; (●), $[H^+] = 1.80 \times 10^{-2}$ M; (△), $[H^+] = 1.80 \times 10^{-1}$ M.

With $IrCl_6{}^{2-}$ in excess over CH_3-B_{12}, 1 equiv of $IrCl_6{}^{3-}$ and $IrCl_5(H_2O)^{2-}$ is generated for each equivalent of CH_3-B_{12} consumed. With deficient $IrCl_6{}^{2-}$, $IrCl_6{}^{3-}$ is the main Ir product. No significant amount of $IrCl_5(H_2O)^{2-}$ was found under this condition.

In summary, the demethylation of CH_3-B_{12} by an excess of $IrCl_6{}^{2-}$ can be expressed in eq 2. With deficient $IrCl_6{}^{2-}$, the main reaction is eq 3.

$$CH_3\text{-}B_{12} + 2IrCl_6{}^{2-} + 2H_2O \rightarrow H_2O\text{-}B_{12}{}^+ + CH_3Cl + IrCl_6{}^{3-} + IrCl_5(H_2O)^{2-} \quad (2)$$

$$CH_3\text{-}B_{12} + IrCl_6{}^{2-} + H_2O \rightarrow H_2O\text{-}B_{12}{}^+ + {}^1/_2C_2H_6 + IrCl_6{}^{3-} \quad (3)$$

Kinetic Measurements. An excess of $IrCl_6{}^{2-}$ over CH_3-B_{12} was used in all the rate measurements so that $[IrCl_6{}^{2-}]$ remained essentially constant. The range of $[CH_3$-$B_{12}]$ was $(1$-$3) \times 10^{-5}$ M. Plots of log $(A_\infty - A_t)$ vs. time gave straight lines for more than 90% of the reactions. Reproducibility was found to be better than 7%. Kinetics data at various pH values are plotted in Figure 3. The

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[15] Bonnett, R.; Cannon, J. R.; Clark, U. M.; Johnson, A. W.; Parker, L. F. J.; Smith, E. L.; Todd, A. *J. Chem. Soc.* **1957**, 1158.

[16] The 2:1 stoichiometry was confirmed by calculation with ϵ 5.1×10^3 M^{-1} cm^{-1} for $IrCl_6{}^{2-}$ at 487.5 nm.

[17] Reaction of CH_3-B_{12} with a deficient amount of $IrCl_6{}^{2-}$ in CH_3OH/H_2O media presaturated with $CHCl_3$ yields a small amount of CH_4 at the expense of C_2H_6. However, CH_3OH production is not ruled out. Furthermore, we failed to obtain a quantitative measurement because of experimental difficulties.

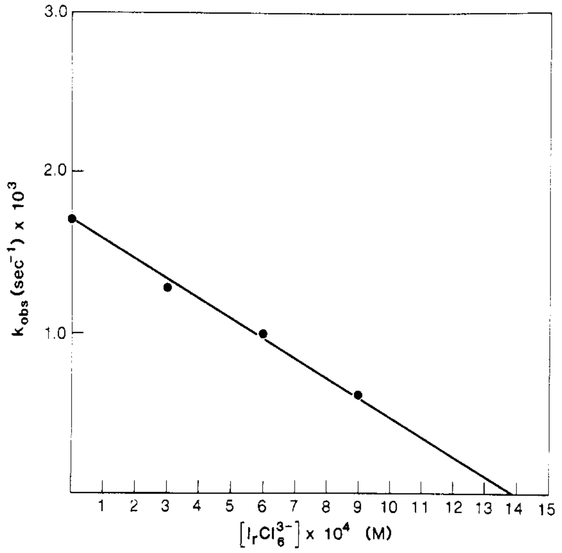

Figure 4. Effect of addition of $IrCl_6^{3-}$ on the kinetic measurements of the demethylation of CH_3-B_{12} by $IrCl_6^{2-}$ ($[IrCl_6^{2-}] = 1.55 \times 10^{-3}$ M; $[H^+] = 0.18$ M; $\mu = 1.0$ M ($HClO_4$ + $NaClO_4$); temperature, 23 °C).

reaction was found to be first order in CH_3-B_{12} and first order in $IrCl_6^{2-}$ according to eq 4 at all pH values. The

$$\frac{d[H_2O\text{-}B_{12}^+]}{dt} = k[IrCl_6^{2-}][CH_3\text{-}B_{12}] \qquad (4)$$

values of k are pH dependent. Considering eq 1, rate law 5 is obtained. Here k' represents the reaction path of

$$k = \frac{k'K_2 + k''K_1[H^+]}{K_2 + K_1K_2 + K_1[H^+]} \qquad (5)$$

base-on CH_3-B_{12}, while k'' represents the path of the protonated base-off form. We have neglected the unprotonated base-off form, since its concentration is extremely small. Under the present experimental conditions, rate law 5 can be simplified into rate law 6. Plots of k vs. $[H^+]^{-1}$ yielded $k' = 83$ M^{-1} s^{-1} and $k'' = 1.1$ M^{-1} s^{-1} (μ = 1.0 M ($HClO_4$ + $NaClO_4$); 23 °C).

$$\frac{d[H_2O\text{-}B_{12}^+]}{dt} = \frac{k'K_2 + k''K_1[H^+]}{K_1[H^+]}[IrCl_6^{2-}][CH_3\text{-}B_{12}] \qquad (6)$$

Addition of large amounts of $IrCl_6^{3-}$ inhibits the demethylation at low pH. This is plotted in Figure 4. Addition of $IrCl_6^{3-}$ ((1.56~7.84) × 10^{-3} M) at $[H^+] = 0.0040$ M does not affect the kinetic measurements. The Cl^- effect on the reaction rates at a constant ionic strength is shown in Figure 5. This experiment was carried out at pH 0.74 so that rate law 6 can be simplified into eq 7. This is nec-

$$\frac{d[H_2O\text{-}B_{12}^+]}{dt} = k''[IrCl_6^{2-}][CH_3\text{-}B_{12}] \qquad (7)$$

essary because Cl^- anion has a pronounced effect on the value of K_1. The Cl^- effect can be expressed in eq 8. Plots of k'' vs. $[Cl^-]$ yield $k''_1 = 0.97$ M^{-1} s^{-1} (i.e., perchlorate path) and $k''_2 = 24$ M^{-1} s^{-1} (i.e., chloride path).

$$k'' = k''_1 + k''_2[Cl^-] \qquad (8)$$

Discussion

The reactions of $IrCl_6^{2-}$ with $RCo(DH)_2H_2O$[8] and with R_2Hg or R_4Pb[9] have been described in terms of a one-electron transfer mechanism. A similar mechanism is adopted here for the reaction between CH_3-B_{12} and $IrCl_6^{2-}$, which is depicted in Scheme I.

Scheme I

$$CH_3\text{-}B_{12} + IrCl_6^{2-} \overset{k}{\rightleftharpoons} CH_3\text{-}B_{12}^+ + IrCl_6^{3-} \qquad (9)$$

with excess $IrCl_6^{2-}$

$$CH_3\text{-}B_{12}^+ + IrCl_6^{2-} + 2H_2O \xrightarrow{\text{fast}} H_2O\text{-}B_{12}^+ + CH_3Cl + IrCl_5(H_2O)^{2-} \qquad (10)$$

with deficient $IrCl_6^{2-}$

$$CH_3\text{-}B_{12}^+ + H_2O \xrightarrow{\text{fast}} H_2O\text{-}B_{12}^+ + {}^1/{}_2C_2H_6 \qquad (11)$$

An alternative path for the demethylation is a direct electrophilic attack at the carbon atom. However, this mechanism is not likely to occur. Electrophilic attack is essentially a one-step reaction. The stoichiometry and $IrCl_6^{3-}$ inhibition on the demethylation of CH_3-B_{12} virtually eliminate this mechanism.

The $IrCl_6^{3-}$ inhibition on the $IrCl_6^{2-}$ oxidation of $RCo(DH)_2(H_2O)$ and the redox potential measurements have allowed Halpern et al. to estimate rates of the electron transfer and of the cleavage of Co–C bonds for these reactions.[8] Although a similar $IrCl_6^{3-}$ effect was observed on the reaction of $IrCl_6^{2-}$ with CH_3-B_{12} at low pH, this effect cannot be interpreted in terms of the reverse reaction of electron transfer from CH_3-B_{12} to $IrCl_6^{2-}$. This is because the 2:1 stoichiometry at the experimental conditions of kinetic measurements and the high flux of C_2H_6 when the reactions were performed with deficient $IrCl_6^{2-}$ demand that the rate of cleavage of Co–C of CH_3-B_{12}^+ to be much larger than the electron-transfer rate under all experimental conditions. The retardation by $IrCl_6^{3-}$ is also unlikely due to an inverse salt effect, because all the rate measurements were performed in 1.0 M ClO_4^- media ($HClO_4$ + $NaClO_4$). Therefore, we propose that the $IrCl_6^{3-}$ retardation can be interpreted in the framework of Scheme II, which involves a preequilibrium between CH_3-B_{12} and $IrCl_6^{2-}$. In the presence of stoichiometric amounts of $IrCl_6^{3-}$, complex **b**, which is inert to the electron-transfer reaction, would compete with complex **a** and retardation by $IrCl_6^{3-}$ would result.

Scheme II

$$CH_3\text{-}B_{12} + IrCl_6^{2-} \overset{K}{\rightleftharpoons} \underset{\textbf{a}}{CH_3\text{-}B_{12}, IrCl_6^{2-}} \qquad (12)$$

$$CH_3\text{-}B_{12} + IrCl_6^{3-} \overset{K'}{\rightleftharpoons} \underset{\textbf{b}}{CH_3\text{-}B_{12}, IrCl_6^{3-}} \qquad (13)$$

$$\underset{\textbf{a}}{CH_3\text{-}B_{12}, IrCl_6^{2-}} \overset{k_{et}}{\rightleftharpoons} CH_3\text{-}B_{12}^+ + IrCl_6^{3-} \qquad (14)$$

In a recent paper,[5] we have demonstrated that the reaction between CH_3-B_{12} and AuX_4^- is zero order in AuX_4^- at high gold concentration. This kinetic behavior is interpreted as "complexation" between CH_3-B_{12} and AuX_4^- prior to the electron-transfer reaction. "Complexation" has also been demonstrated in the methyl transfer from CH_3-B_{12} to Pt^{IV}/Pt^{II} systems (in which an electron transfer is involved) by kinetic and spectroscopic methods.[4] On the basis of these experiences, the suggestion of "complexation" between CH_3-B_{12} and $IrCl_6^{2-}$ in Scheme II seems to be reasonable. It is noteworthy that the reaction rates of $IrCl_6^{2-}$ with organometals such as R_4Sn were found to be faster than that estimated from an outer-sphere model.[18]

It has been shown that the base-on CH_3-B_{12} has a much larger formation constant than the base-off form when

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(18) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

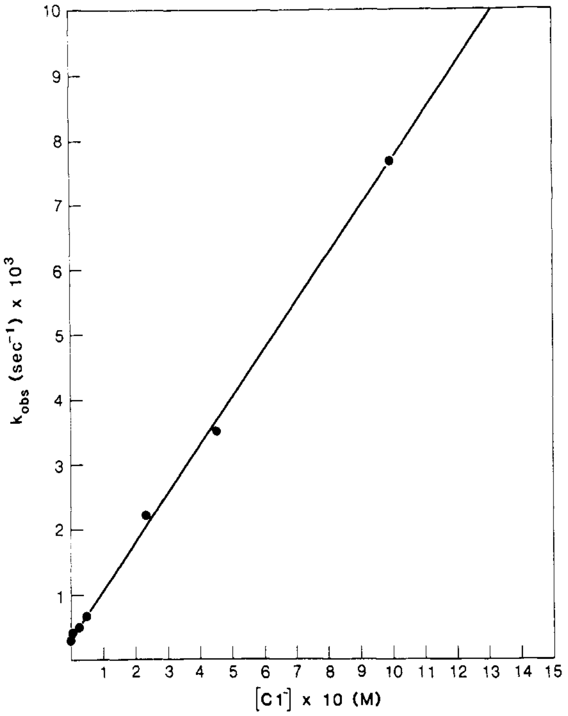

Figure 5. Cl^- effect on the kinetic measurements of demethylation of CH_3-B_{12} by $IrCl_6^{2-}$ ($[CH_3\text{-}B_{12}] = (1 \sim 3) \times 10^{-5}$ M; $[IrCl_6^{2-}] = 3.2 \times 10^{-4}$ M; $[H^+] = 0.18$ M; $\mu = 1.0$ M (maintained with $NaClO_4$); 23 °C).

complexing with platinum or gold complexes.[4,5] Similarly, $k' (= k_{et}K)$ is found to be $\sim$80-fold larger than k''. This suggests that K for the base-on CH_3-B_{12} is larger than that for the base-off form. However, since k_{et} is not separated from K in the present study, this suggestion should remain tentative for the $IrCl_6^{2-}$ oxidation of CH_3-B_{12}.

Figure 5 shows that Cl^- has a pronounced effect on the $IrCl_6^{2-}$ oxidation rate, with $k''_{Cl^-}/k''_{ClO_4^-} = 24$. Indeed. the Cl^--assisted demethylation of CH_3-B_{12} by electrophile has been frequently observed. This includes Fe^{3+}, Ce(IV), Pt(IV)/Pt(II),[4] and Au(III).[5] In cases of platinum and gold complexes in which k_{et} and K can be separated,[19] it is found that $[Cl^-]$ does not affect k_{et}, while K is significantly larger at high Cl^- concentration.

Anion-assisted outer-sphere electron-transfer reactions between $Co(en)_3^{3+}$, $Co(NH_3)_6^{3+}$, $Co(phen)_3^{3+}$, and Cr^{2+} or V^{2+} and between Fe^{3+} and $Co(phen)_3^{2+}$ have been thoroughly investigated.[20] This assistance is interpreted in terms of the orbital symmetries of the electron donor, electron acceptor, and the anion. More recently, Burdett has developed a molecular orbital model to rationalize the counterion effect.[21] This effect is suggested to be threefold: (i) acting as an electrostatic glue, (ii) reducing the barrier to reaction, and (iii) ensuring adiabatic behavior. This argument can be applied to the bridging inner-sphere reactions as well. The accelerating effect of Cl^- on the electron transfer between CH_3-B_{12} and $IrCl_6^{2-}$ can be readily interpreted by this molecular orbital model. However, it should be noted that CH_3-B_{12} is basically a neutral molecule. Thus, we suggest that the Cl^- anion interacts with the π orbitals of corrin ring to increase the formation constant (K) of the "complex" between CH_3-B_{12} and $IrCl_6^{2-}$. It should also be noted that the chloride acceleration is unlikely due to the reversibility in eq 14 in competition to nucleophilic attack of Cl^- on CH_3-B_{12}^+,[8] because CH_3-B_{12}^+ undergoes a homolytic scission of the Co–C bond to generate a $CH_3\cdot$ radical, even the reaction was performed in 1.0 M Cl^- media (vide infra).

A key question that should be asked about the oxidation of organometals is how does the metal–carbon bond of the oxidized intermediate cleave? Two modes are readily available for CH_3-B_{12}^+. One is a nucleophilic displacement resulting in the production of B_{12r}, $IrCl_6^{3-}$ and CH_3OH (with H_2O as the nucleophile) or CH_3Cl (with Cl^- as the nucleophile), or N-methylated pyridine (with pyridine as the nucleophile). Two lines of evidence are against this mechanism. First, when a large excess of $IrCl_6^{2-}$ is used, CH_3Cl is the only detectable organic product generated under all experimental conditions. Second, $IrCl_5(H_2O)^{2-}$ is produced with excess $IrCl_6^{2-}$. We have shown that the reaction between B_{12r} and $IrCl_6^{2-}$ yields H_2O-B_{12}^+ and $IrCl_6^{3-}$, thus the production of $IrCl_5(H_2O)^{2-}$ can be considered as a compelling evidence for the generation of $CH_3\cdot$ radical as described below.

The other mode of cleavage is for CH_3-B_{12}^+ to release a transient $CH_3\cdot$ radical, which then quickly abstracts a chlorine atom from a second $IrCl_6^{2-}$ molecule to form CH_3Cl and $IrCl_5(H_2O)^{2-}$. The rate of the $CH_3\cdot$ extraction of a chlorine atom from $IrCl_6^{2-}$ in aqueous solution has been determined to be 1.15×10^9 M^{-1} s^{-1} (22 ± 2 °C, pH 4–6).[22] In the absence of excess $IrCl_6^{2-}$, $CH_3\cdot$ combines to generate C_2H_6. This mode is remarkably similar to the homolytic scission of CH_3–Co bonds in cations derived from the macrocyclic complexes $(CH_3)_2Co(DpnH)$.[23] In this respect, $(CH_3)_2Co(DpnH)$ is more closely related to CH_3-B_{12} than that of methylcobaloximes. It should be noted that photolysis of CH_3-B_{12} in the presence of O_2 yields H_2O-B_{12}^+ and HCHO as the major products; traces of CH_3OH, CH_4 and C_2H_6 are also formed.[24] This photolysis is generally believed to involve homolysis of Co–C bond to yield $CH_3\cdot$ and B_{12r} as the initial products. The remarkable point that should be stressed in the $IrCl_6^{2-}$ oxidation of CH_3-B_{12} is that it generates a high flux of C_2H_6 with deficient $IrCl_6^{2-}$.

The high flux of C_2H_6 can be interpreted in terms of the relative ease of electron transfer from CH_3-B_{12} to $IrCl_6^{2-}$ and the very fast cleavage of Co–C bond of CH_3-B_{12}^+. In particular, our recent discovery that CH_3-B_{12} forms a head-to-head dimer in aqueous solution at a $[CH_3\text{-}B_{12}] > 10^{-3}$ M[25] greatly enhances the chance of generating C_2H_6 from $CH_3\cdot$ by confining them close together. The high flux of C_2H_6 has also been observed in the cations derived from $(CH_3)_2Co(DpnH)$.[23]

In summary, $IrCl_6^{2-}$ oxidation of CH_3-B_{12} involves a one-electron transfer from CH_3-B_{12} to $IrCl_6^{2-}$ as the rate-determining step. The transient CH_3-B_{12}^+ intermediate then releases a $CH_3\cdot$ radical which either abstracts a chlorine atom from a second $IrCl_6^{2-}$ molecule or combines with another $CH_3\cdot$ radical to generate C_2H_6. $IrCl_6^{3-}$ inhibits the $IrCl_6^{2-}$ oxidation, while Cl^- significantly enhances the rate of reaction.

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Registry No. Na_2IrCl_6, 16941-25-6; Na_3IrCl_6, 15702-05-3; CH_3-B_{12}, 13422-55-4; $^{13}CH_3$–B_{12}, 43184-67-4.

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