

$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ and subsequently produces only the bridging iodonium system upon reaction with AgBF_4 in the presence of olefins.

Experimental Section

General Procedures. All reactions and subsequent manipulations were carried out by using standard Schlenk techniques under argon or purified nitrogen atmospheres. Solvents were routinely dried by standard procedures and stored under an inert atmosphere.¹¹ The NMR solvents were predried over 3-Å molecular sieves, subjected to three consecutive freeze-pump-thaw cycles, and then stored in a Schlenk flask under an inert atmosphere. In addition, NMR samples were routinely passed through a short column of Celite to remove finely divided decomposition particles.

Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian EM360, Bruker 250FT (at 250 MHz); ^{13}C NMR, Bruker 250FT (at 62.9 MHz); IR, Perkin-Elmer 281B or PE 398. NMR chemical shifts were reported in δ vs. Me_4Si with the CDCl_3 resonance in ^{13}C spectra assigned as 77.00 ppm. The reported ^{13}C NMR spectra were run with ^1H decoupling, and resonances may be assumed to be singlets unless multiplicity was specified (off-resonance spectra were run to confirm assignments). The compound $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ (**1**)³ and its dianion $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2^-$ (**2**)¹² were prepared by literature methods. The 3-chloropropene and 2-methyl-3-chloropropene were purchased from Aldrich and distilled prior to use. The $\text{HBF}_4\cdot\text{Me}_2\text{O}$ and NaBH_3CN were purchased from Aldrich and used without further purification.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)]_2$ (3**).** To 50 mL of THF containing 0.50 g (1.2 mmol) of **2** was added 1.0 mL (12 mmol) of $\text{ClCH}_2\text{CH}=\text{CH}_2$ at 0 °C with stirring. The reaction mixture was stirred for an additional 2 h at 0 °C, the solution filtered, and the solvent removed in vacuo at ambient temperature. The resulting oil was column chromatographed at low temperature (alumina III, -10 °C, pentane). The initial yellow band was collected and the solvent removed in vacuo to give a red-yellow oil identified by ^1H NMR and IR as **3**. ^1H NMR (CDCl_3): δ 6.32-5.5 (2, m, CH=), 5.00-4.28 (4, m, =CH₂), 4.72 (8, s, C₅H₄), 2.07 (4, d, J = 9 Hz, CH₃), 0.52 (6, s, SiCH₃). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 2002 and 1950.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}(\text{CH}_3)=\text{CH}_2)]_2$ (4**).** Compound **4** was synthesized by a method completely analogous to the preparation of **3** using 3-chloro-2-methylpropene as the allylic halide. Compound **4** was isolated after low-temperature chromatography as a red-yellow oil (0.23 g, 36%). ^1H NMR (CDCl_3): δ 4.73 (4, m, =CH₂), 4.51 (8, d, C₅H₄), 2.13 (4, s, CH₂), 1.78 (6, s, CH₃), 0.53 (6, s, SiCH₃). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 2002 and 1950.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_3)]_2[\text{BF}_4]_2$ (5**).** A pentane solution containing **3** (obtained directly from the alumina column described above) was added dropwise to a solution of $\text{HBF}_4\cdot\text{Me}_2\text{O}$ (0.30 g, 2.4 mmol) at -10 °C with stirring. The resulting bright yellow precipitate was collected by filtration, washed with cold THF (10 mL \times 2), and dried under vacuum to yield pure **5** (0.36 g, 45%). ^1H NMR (acetone- d_6): δ 6.04, 5.83 (8, s, s, C₅H₄), 5.30 (2, m, =CH), 4.01 (2, d, J = 8 Hz, CH₂=), 3.63 (2, d, J = 14 Hz, CH₂=), 1.86 (6, d, J = 6 Hz, CH₃), 0.94 (6, s, SiCH₃). IR spectrum (cm^{-1} in CH_3NO_2): $\nu(\text{CO})$ 2072, 2030. ^{13}C NMR (CD_3NO_2): δ 211.23, 209.69 (CO), 96.39, 94.91 (C₅H₄), 89.17 (=CH), 56.91 (CH₂=), 22.37 (CH₃), -2.36 (SiCH₃).

Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{B}_2\text{F}_8\text{Fe}_2\text{O}_4\text{Si}$: C, 39.57; H, 3.92. Found: C, 39.65; H, 4.01.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}_2)]_2[\text{BF}_4]_2$ (6**).** Similar treatment of **4** with $\text{HBF}_4\cdot\text{Me}_2\text{O}$ (0.30 g, 2.4 mmol) at -10 °C gave complex **6** as a yellow solid (0.45 g, 53%). ^1H NMR (acetone- d_6): δ 6.13 (8, s, C₅H₄), 4.03 (4, s, =CH₂), 1.98 (12, s, (CH₃)₂C=), 0.96 (6, s, SiCH₃). IR spectrum (cm^{-1} in CH_3NO_2): $\nu(\text{CO})$ 2067 and 2030. ^{13}C NMR (CD_3NO_2): δ 206.06, 203.31 (CO), 91.52, 90.26 (C₅H₄), 80.49 ((CH₃)₂C=), 48.86 (=CH₂), 23.92 (CH₃), -7.91 (SiCH₃).

Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{B}_2\text{F}_8\text{Fe}_2\text{O}_4\text{Si}$: C, 41.43; H, 4.34. Found: C, 41.58; H, 4.38.

Reduction of **5 with NaBH_3CN .** To a 15 mL THF slurry of **5** (0.25 g, 0.38 mmol) at 0 °C was added NaBH_3CN (0.048 g, 0.76 mmol) with stirring. The reaction mixture was stirred for an additional 1 h at 0 °C and then slowly allowed to warm to room temperature. This mixture was filtered and the solvent removed to yield a red-yellow oil. The oil was column chromatographed (alumina III, hexane) and the initial yellow band collected. The hexane was removed under vacuum to give an air-sensitive red-yellow oil identified as a mixture of η^1 -*n*-propyl and η^1 -isopropyl isomers (0.15 g, 79%). The mixture gave ^1H NMR (CDCl_3) signals at δ 4.68 (C₅H₄), 2.55 (m, J = 6 Hz, -CH(CH₃)₂), 1.23 (d, J = 6 Hz, CH(CH₃)₂), 1.23 (m, CH₂CH₂CH₃), 0.78 (m, CH₂CH₂CH₃), 0.38 (6, s, SiCH₃). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 1990 and 1940.

Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{Fe}_2\text{O}_4\text{Si}$: C, 53.53; H, 5.79. Found: C, 53.25; H, 5.69.

Reduction of **6 to $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}(\text{CH}_3)_2)]_2$ (**8**).** Complex **8** (0.38 mmol) was prepared by a method analogous to the preparation of complex **7**. The product was isolated as a red-yellow oil (0.17 g, 85%) and identified as **8**. ^1H NMR (CDCl_3): δ 4.70 (8, s, C₅H₄), 1.25 (6, m, CH₂CH(CH₃)₂), 0.80 (12, d, J = 5 Hz, CH₃), 0.3 (6, s, SiCH₃). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 1990 and 1942. ^{13}C NMR (CDCl_3): δ 217.88 (CO), 92.87, 89.33, 85.45 (C₅H₄), 34.81 (CH), 26.25 (CH₃), 13.68 (CH₂), -1.44 (SiCH₃).

Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{Fe}_2\text{O}_4\text{Si}$: C, 55.14; H, 6.39. Found: C, 54.98; H, 6.15.

Preparation of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2)_2][\text{BF}_4]$ (9**).** A solution of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{I}]_2$ (**8**) (0.50 g, 0.80 mmol) in 25 mL of CH_2Cl_2 was treated with AgBF_4 (0.35 g, 1.9 mmol) at 30 °C. After 5 min of reaction the color had changed from brown to deep red with contamination of the solution by AgI precipitation. The mixture was filtered, the solvent was removed under vacuum, and the residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give pure **9**. The results of this reaction were the same when a large excess of olefin was present when the AgBF_4 was added. ^1H NMR (acetone- d_6): δ 6.10, 5.47 (8 m, C₅H₄), 0.80 (6, s, SiCH₃). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 2037 and 1995. ^{13}C NMR (acetone- d_6): δ 211.94 (CO), 97.08, 91.33, 84.24 (C₅H₄), -2.20 (SiCH₃).

Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{BF}_4\text{Fe}_2\text{IO}_4\text{Si}$: C, 30.81; H, 2.26; I, 20.34. Found: C, 30.85; H, 2.27; I, 20.18.

Acknowledgment is made to the NSF (Grant CHE-8102918) for support of this work.

Registry No. **2**, 85319-98-8; **3**, 85319-99-9; **4**, 85320-00-9; **5**, 85320-02-1; **6**, 85320-04-3; **7**, 85320-09-8; **8**, 80399-47-9; **9**, 85320-07-6; $[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{CH}_3)]_2\text{SiMe}_2$, 85320-08-7; $[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}(\text{CH}_3)_2)]_2\text{SiMe}_2$, 85320-05-4; $\text{ClCH}_2\text{CH}=\text{CH}_2$, 107-05-1; 3-chloro-2-methylpropene, 563-47-3.

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Crystal Structure of a Molybdenum(VI) Compound with a Tetradentate N₂S₂ Ligand: Re-refinement in a Higher Symmetry Space Group

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Received October 13, 1982

The crystal structure of [bis(*p*-methoxyphenyl)diazenedo][*N,N'*-dimethyl-*N,N'*-bis(mercaptoethyl)ethylenediamine]molybdenum(VI) has been described in space group *Cc* (monoclinic; *a* = 22.557 (2), *b* = 8.483 (3), *c* = 18.030 (2) Å; β = 133.25 (1)°) and was refined to an *R* of 0.043 for 1505 reflections with $I(\text{obsd}) \geq 3.0\sigma(I(\text{obsd}))$.¹ Surprising

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Table I. Atomic Parameters ($\times 10^4$), Space Group $C2/c$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0	370 (1)	2500	381 (4)	320 (3)	339 (4)	0	276 (3)	0
S(1,2)	-512 (1)	-40 (2)	791 (1)	481 (9)	570 (11)	325 (8)	28 (7)	278 (8)	39 (6)
O(1,2)	-2135 (3)	5661 (6)	3574 (3)	642 (28)	718 (32)	620 (29)	160 (25)	458 (26)	-55 (25)
N(1,2)	791 (3)	-1735 (6)	2797 (4)	595 (35)	533 (33)	393 (30)	182 (27)	326 (29)	35 (25)
N(3,5)	-793 (3)	1817 (5)	2016 (4)	444 (30)	357 (27)	434 (28)	-34 (23)	349 (26)	-16 (22)
N(4,6)	-1387 (3)	2690 (5)	1564 (4)	467 (31)	400 (28)	397 (29)	64 (24)	302 (27)	81 (23)
C(1,6)	309 (5)	-1199 (9)	1130 (6)	1031 (62)	960 (58)	846 (59)	311 (49)	807 (57)	183 (45)
C(2,5) _a	608 (9)	-2335 (18)	1877 (11)	$B(\text{iso}) = 3.5$ (4) \AA^2 , $\text{Pop}^a = 0.43$ (2)					
C(2,5) _b	1003 (8)	-1462 (15)	2142 (9)	$B(\text{iso}) = 4.3$ (4) \AA^2 , $\text{Pop}^a = 0.57$					
C(3,4)	433 (5)	-3134 (8)	2820 (8)	836 (59)	392 (40)	1539 (94)	171 (40)	490 (68)	126 (51)
C(7,8)	1638 (5)	-1641 (9)	3779 (6)	632 (50)	842 (54)	834 (59)	303 (42)	465 (49)	117 (44)
C(9,16)	-1538 (3)	3409 (6)	2141 (4)	424 (33)	335 (30)	516 (37)	-16 (26)	372 (32)	13 (26)
C(10,21)	-998 (3)	3316 (6)	3188 (4)	397 (33)	426 (33)	488 (38)	110 (27)	303 (32)	70 (28)
C(11,20)	-1180 (4)	4070 (7)	3693 (4)	481 (36)	530 (37)	463 (35)	73 (29)	328 (32)	39 (29)
C(12,19)	-1901 (4)	4892 (7)	3148 (4)	528 (36)	465 (39)	596 (39)	15 (28)	453 (34)	-9 (28)
C(13,18)	-2439 (3)	4978 (6)	2094 (4)	383 (31)	453 (41)	570 (38)	47 (25)	334 (31)	39 (27)
C(14,17)	-2254 (3)	4259 (6)	1598 (4)	438 (33)	394 (35)	387 (32)	-4 (26)	274 (29)	36 (25)
C(15,22)	-1582 (5)	5788 (10)	4633 (6)	866 (54)	937 (62)	724 (51)	200 (47)	583 (48)	10 (45)

^a Site population factor.

results of this refinement included nonequivalence of the molybdenum–amine bonds, at 2.27 (1) and 2.37 (1) \AA , which was attributed to “inherent ligand strain”. Essentially the same R value and a considerably more satisfactory structure with equal Mo–amine distances can be attained if the space group is presumed to be $C2/c$.

In order for the structure to be described in $C2/c$, the x coordinates (Table II, ref 1) must be reduced by 0.25, so that the Mo atom lies on a twofold axis; coordinates of the remaining atoms must be adjusted by amounts ranging up to 0.4 \AA to achieve pairing about this axis. (The atoms paired with C(9) and C(12)—presumably C(16) and C(19)—are missing from the published table.) Our least-squares refinements in $C2/c$ were based on 1503 values of F_o obtained as indicated in the supplementary material for ref 1 (two of the entries were illegible). The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$; since weights w (or σ 's) were not available, we took them equal to $1/F_o^2$ for $F_o \geq 4F_{\text{min}}$ and to $1/4(F_o)(F_{\text{min}})$ otherwise, with $F_{\text{min}} = 13.2$; this is the function originally suggested by Hughes² for refinement on F for visual data, and we have found it appropriate for F^2 refinement using diffractometer data.³ The full matrix included anisotropic U_{ij} 's for Mo, S, N, C, and O; the hydrogen atoms were held fixed in idealized positions, as in ref 1.

Convergence was initially reached at $R = 0.048$. However, the U 's for atom C(2,5) of the $\text{SCH}_2\text{CH}_2\text{N}$ group were very large and anisotropic, corresponding to an rms displacement of about 0.7 \AA , and an electron density map clearly showed that this atom should be distributed between two sites, perhaps with slightly different occupancy factors. (The other C atom of this group, C(1,6), and atom C(3,4) of the en group also showed enlarged, but somewhat smaller, U 's; electron density maps indicated that they could be satisfactorily represented as single atoms.) This disordered model, with the two partially occupied sites of C(2,5) assigned isotropic B 's and an adjustable occupancy parameter, converged (maximum shift, 0.2σ) at a final R of 0.044 for 150 parameters, compared to the R of 0.043 for 296 parameters (misprinted as 286) in the Cc model.¹ Our final $C2/c$ parameters are given in Table I. The site populations for C(2,5), 0.43 (2) and 0.57, are marginally unequal.

Aside from the disorder in the mercaptoethylamine group (a not unusual occurrence for this type of ligand), there are no surprises in the $C2/c$ structure. The two Mo–amine distances are equal by symmetry, at 2.313 (6) \AA , as are other

Table II. Selected Bond Lengths (\AA) for the $C2/c$ (This Study) and Cc (Ref 1) Models

bond	$C2/c$	Cc
Mo–S(1,2)	2.464 (2)	2.456 (7); 2.472 (8)
–N(1,2)	2.313 (6)	2.27 (1); 2.37 (1)
–N(3,5)	1.825 (6)	1.81 (1); 1.81 (2)
S(1,2)–C(1,6)	1.794 (10)	1.80 (3); 1.85 (2)
N(1,2)–C(2,5)	1.50 (2); 1.57 (2)	1.53 (3); 1.57 (2)
–C(3,4)	1.453 (13)	1.47 (3); 1.53 (4)
–C(7,8)	1.468 (12)	1.44 (3); 1.58 (3)
N(3,5)–N(4,6)	1.228 (8)	1.20 (3); 1.28 (2)
N(4,6)–C(9,16)	1.435 (9)	1.38 (2); 1.51 (2)
O(1,2)–C(12,19)	1.360 (9)	1.31 (2); 1.41 (2)
–C(15,22)	1.396 (11)	1.30 (3); 1.53 (3)

pairs of chemically equivalent bond lengths which were surprisingly discordant in the Cc description (Table II). The esd's are generally smaller by a factor of 2 or 3. The surprising bond lengths and relatively large esd's reported for the Cc refinement can almost surely be blamed on the near singularities associated with the refinement of an approximately centrosymmetric structure in a noncentrosymmetric space group.⁴

Although the $C2/c$ model is more reasonable than the Cc model, we cannot assert that it is correct; small departures from a centrosymmetric structure would have negligible effect on the strong reflections that comprised the data set. Indeed, the departures need not be “small” in the sense usually associated with crystallographic results; as noted earlier, the Cc structure derived in ref 1 requires that atoms be displaced by as much as 0.4 \AA (20–30 esd's) from their symmetrized positions, with no significant change in R . There are undoubtedly many other models in Cc , differing in the pattern of displacements of the various atoms from their symmetric, $C2/c$ positions, which would give equivalent agreement indices.

If a definitive choice between the two space groups is to be made, it must be based on the weaker reflections,⁵ and these are missing from the data set. (The 1505 retained reflections comprise only about 63% of the total number expected in the sphere of data.) It is also probable that omission of these weaker reflections was at least partly responsible for the misleading intensity statistics⁵ that led to the choice of Cc in the first place; these statistics may also have been distorted because of the presence of only a small number (4) of heavy atoms in the unit cell.⁶

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Registry No. [Bis(*p*-methoxyphenyl)diazenido][*N,N'*-dimethyl-*N,N'*-bis(mercaptoethyl)ethylenediamine]molybdenum(VI), 80228-56-4.

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Kinetic Studies of Dealkylation of Ethylcobalamin by Tetrachloroaurate

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Received August 23, 1982

In a recent paper,¹ we have described the reaction between methylcobalamin ($\text{CH}_3\text{-B}_{12}$) and AuX_4^- ($\text{X} = \text{Cl}$ or Br). This reaction proceeds with a 2:1 stoichiometry ($\text{AuX}_4^-:\text{CH}_3\text{-B}_{12}$) under an atmosphere of Ar, yielding CH_3X , metallic gold, and $\text{H}_2\text{O-B}_{12}^+$ with an oxidized corrin ring. The stoichiometry and products are inconsistent with a mechanism involving a direct displacement of Co atom by attack at the α -carbon. Consequently, they are interpreted in terms of a one-electron transfer that generates a $\text{CH}_3\text{-B}_{12}^+$ and Au(II) radical pair, which then collapses to the final products. Since the reactions of $\text{CH}_3\text{-B}_{12}$ with an electrophile such as Hg^{2+} or PdCl_4^{2-} are widely discussed in terms of direct electrophilic attack, we seek further evidence to support the electron-transfer mechanism. A criterion that has been frequently used for the electrophilic attack mechanism is the very great difference in the dealkylation rates of $\text{CH}_3\text{-B}_{12}$ and $\text{C}_2\text{H}_5\text{-B}_{12}$.^{2a} Therefore, we extended the kinetic study to the dealkylation of ethylcobalamin by AuCl_4^- . Comparison of the dealkylation rate of $\text{C}_2\text{H}_5\text{-B}_{12}$ with that of $\text{CH}_3\text{-B}_{12}$ indeed provides additional evidence for the electron-transfer mechanism.

Experimental Section

Materials. $\text{C}_2\text{H}_5\text{-B}_{12}$ was a generous gift from Dr. Hogenkamp.⁴ $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ was purchased from Goldsmith Metal & Chemicals Inc. and was used as received. All other chemicals were reagent grade.

Stoichiometry and Kinetics. The stoichiometry was determined spectrophotometrically at 350 nm (γ band of $\text{H}_2\text{O-B}_{12}^+$) or at 315 nm (absorbance maximum of AuCl_4^-) under an atmosphere of N_2 . B_{12} products were examined spectrophotometrically with a Cary 15 instrument. Dealkylation products were examined with a Becker gas chromatograph, Model 417.

Kinetic measurements were carried out with a McPherson/GCA spectrophotometer at 525 or 350 nm, as they provided the most convenient spectral changes during the course of reaction. The temperature was kept at $23 \pm 0.3^\circ\text{C}$ with a circulating-water jacket. A large excess of AuCl_4^- was used in all the rate measurements to provide the pseudo-first-order conditions in $\text{C}_2\text{H}_5\text{-B}_{12}$. The plots of $\log(A_\infty - A_t)$ vs. time gave straight lines for at least 80% of the reactions. pH was controlled in a range of 0-3 with HCl. At higher pH, both the quality and reproducibility of the kinetic measurements became poor, apparently because of the interference by buffer solution. Ionic strength was maintained at 1.0 M with NaCl and HCl.

Results and Discussion

In the demethylation of $\text{CH}_3\text{-B}_{12}$ by AuCl_4^- ,¹ we have demonstrated that the reaction occurs with a 2:1 stoichiometry

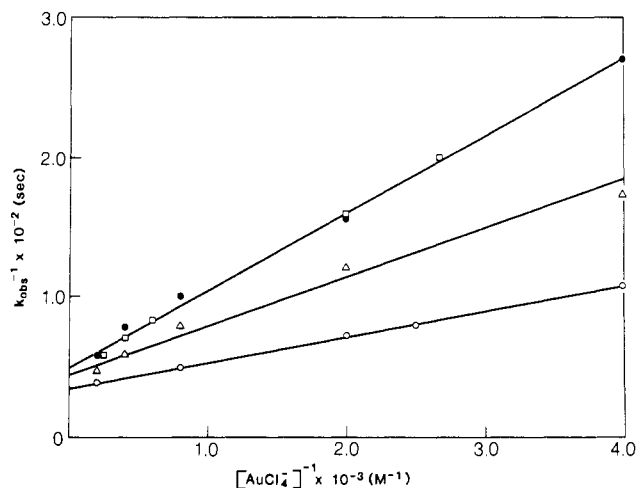


Figure 1. Kinetic measurements for the dealkylation of ethylcobalamin by AuCl_4^- ($[\text{C}_2\text{H}_5\text{-B}_{12}] = 6.0 \times 10^{-5} \text{ M}$, $\mu = 1.0 \text{ M}$ ($\text{HCl} + \text{NaCl}$); temperature $23 \pm 0.3^\circ\text{C}$): (O) pH 3.00; (Δ) pH 2.00; (\square) pH 1.30; (\bullet) pH 0.558.

Table I. Kinetic Parameters for the Dealkylation of Alkylcobalamins by AuCl_4^- ^a

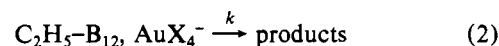
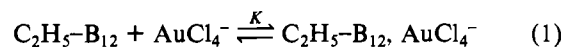
pH	$\text{C}_2\text{H}_5\text{-B}_{12}$		$\text{CH}_3\text{-B}_{12}$	
	$10^3 k, \text{ s}^{-1}$	$10^{-3} K, \text{ M}^{-1}$	$10^3 k, \text{ s}^{-1}$	$10^{-3} K, \text{ M}^{-1}$
0.558	20	0.91	8.6	2.3
1.30	20	0.91	9.3	4.4
2.00	23	1.21	10.3	6.6
3.00	29	1.46	13.0	9.2

^a $\mu = 1.0 \text{ M}$ ($\text{HCl} + \text{NaCl}$); $23 \pm 0.3^\circ\text{C}$.

under an atmosphere of Ar ($\text{AuCl}_4^-:\text{CH}_3\text{-B}_{12}$), yielding CH_3Cl , metallic gold, and $\text{H}_2\text{O-B}_{12}^+$ with an oxidized corrin ring. It should be stressed that the exclusion of oxygen from the reaction solution is crucial for the stoichiometric study. This is because Au(II) is an intermediate. Thus, in the absence of O_2 , Au(II) would be reduced to Au(0) by the corrin ring, while in the presence of O_2 , it would be reoxidized to AuCl_4^- for further demethylation.

$\text{C}_2\text{H}_5\text{-B}_{12}$ ($3.5 \times 10^{-5} \text{ M}$) is quantitatively dealkylated to $\text{H}_2\text{O-B}_{12}^+$ by AuCl_4^- ($5.0 \times 10^{-4} \text{ M}$) with isosbestic points at 480 and 370 nm (pH 2, 1.0 M NaCl). Although similar stoichiometry and products for the dealkylation of $\text{C}_2\text{H}_5\text{-B}_{12}$ by a high level of excessive AuCl_4^- (under N_2) were observed, a complication should be noted: when $\text{C}_2\text{H}_5\text{-B}_{12}$ is dealkylated by a deficient amount of AuCl_4^- under N_2 , a stoichiometry of $\sim 1:1$ is observed. This implies that the $\text{C}_2\text{H}_5\text{-B}_{12}^+$ intermediate (vide infra) undergoes a different reaction when deficient amounts of AuCl_4^- are used. The change of stoichiometry from 2:1 to 1:1 has also been observed for the reaction of IrCl_6^{2-} with $\text{CH}_3\text{-B}_{12}$ as the IrCl_6^{2-} concentration is decreased.⁵

The dealkylation of $\text{C}_2\text{H}_5\text{-B}_{12}$ by AuCl_4^- is first order in $\text{C}_2\text{H}_5\text{-B}_{12}$, as demonstrated by the straight-line plots of $\log(A_\infty - A_t)$ vs. time. Similar to that for $\text{CH}_3\text{-B}_{12}$,¹ the reaction is first order in AuCl_4^- at low $[\text{AuCl}_4^-]$ but approaches zero order in gold as its concentration is increased. The hyperbolic dependence of k_{obsd} on $[\text{AuCl}_4^-]$ is interpreted in terms of eq 1 and 2. Plots of k_{obsd}^{-1} vs. $[\text{AuCl}_4^-]^{-1}$ are various pHs are



straight lines, as shown in Figure 1. These data can be de-

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