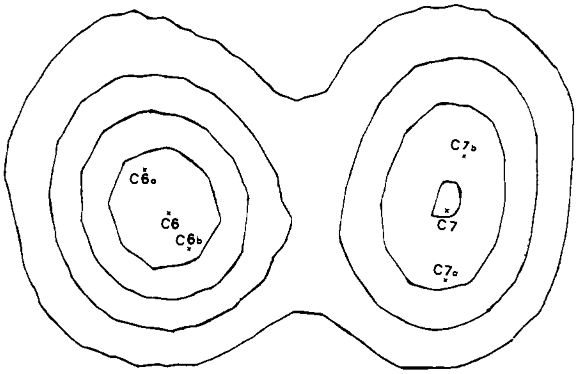

Figure 2. Difference electron density map of C6, C7 region of V=S(acen). This map is based upon a structure factor calculation from which C6 and C7 were omitted. Other atoms were given the final refined parameters of Tables II and III. Electron density contours start at 0.55 Å^{-3} and are in intervals of 0.55 Å^{-3}. The final coordinates for the ordered and disordered refinement models (see text) are indicated.

Cu(acen),[12] Cu(acen)·$^1/_2$H$_2$O,[13] and Cu(acen)·H$_2$O[14] are 1.55, 1.43, and 1.55 Å, respectively. These data suggest the likelihood of disorder both in V=O(acen) and in the copper hemihydrate.

Acknowledgment. Partial support from National Institutes of Environmental Health Sciences Grant ES-00966 (Arizona) and National Science Foundation Grant CHE 79-0643 (UCLA) is gratefully acknowledged. We thank the University of Arizona Computer Center for an allocation of computer time.

Registry No. V=S(acen), 74354-70-4.

Supplementary Material Available: Listings of final thermal parameters (Table III), atomic parameters for hydrogen atoms (Table V), observed and calculated structure factors for the data collected at the University of Arizona with Mo Kα radiation (Table VI), final atomic parameters, bond distances and angles, and observed and calculated structure factors (Tables VII–IX) for the data collected at UCLA with Cu Kα radiation (20 pages). Ordering information is given on any current masthead page.

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Effect of Halide Ions on the Rates of Reaction of Methylcobalamin with Heavy-Metal Species

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The reaction between methylcobalamin (I) and metal compounds plays a major role in biological transmethylation and may also be involved in the geochemical cycling of metals.[1,2] The kinetics and mechanism of this reaction have been reported in detail for Hg(II) salts,[3-5] tetrachloropalladate(II),[6] and chloroplatinum(IV) compounds.[7-11] More qualitative studies for various metal–I reactions have also appeared.[12-14] Methyl compounds of mercury, arsenic, selenium, and tin occur in nature.[15,16] As more and more details of such reactions have been reported, it has become increasingly apparent that the rate of methyl exchange between I and metal substrates depends very much on the nature of ligands on the metal. This paper will report some observed effects of halides.

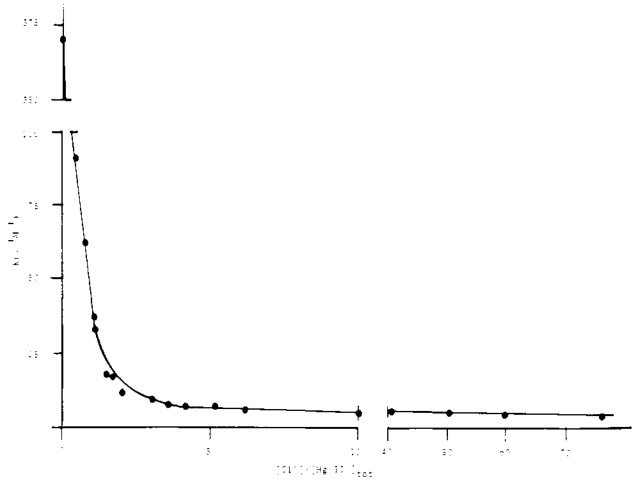

Figure 1. Effect of chloride ion on the Hg(OAc)$_2$–CH$_3$B$_{12}$ rate constant.

Experimental Section

Inorganic salts were purchased from various commercial sources and usually recrystallized before using. Methylcobalamin was purchased from Sigma Chemical Co. and stored in darkness at −10 °C. Solutions of reactants were prepared immediately before use. Reactions were carried out in spectroscopic cells or in sealed glass vessels protected from light. Reactions were studied until at least 75% of the methylcobalamin had reacted. The standard reaction medium was 0.10 M acetic acid–0.10 M sodium acetate buffer solution.

Spectroscopic investigations were performed, by methods described elsewhere,[14] on a Cary 14 recording visible–ultraviolet spectrophotometer. Certain gas-phase infrared spectra were obtained with the use of a 10-cm NaCl gas cell and a Perkin-Elmer Model 337 recording infrared spectrophotometer. Vapor-phase chromatographs were determined on a Hewlett-Packard Dual Column Model 5730 Chromatograph, using a 2-m glass column with DEGS packing. Helium served as the carrier gas, and the column temperature was 30–40 °C. Identities of methyl halides were confirmed by comparison of retention times with known samples. No other gaseous products were observed.

Results

Representative Metal Compounds. When the Tl(OAc)$_4^-$–I

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Table I. Rate Constants for Metal-Methylcobalamin Reactions

10^5[M]	10^5[CH_3B_{12}]	10^3k_{obsd}, s^{-1}	K, M^{-1} s^{-1}
		$Tl(OAc)_4^-$	
867	5.53	67.4	77.7
33.6	2.14	23.2	69.0
28.0	2.14	20.2	72.1
12.2	1.07	9.91	81.2
11.7	1.07	8.26	70.6
10.1	0.214	6.37	63.1
6.46	0.214	4.45	68.9
5.88	0.214	4.42	75.2
4.19	0.214	3.26	77.8
3.15	0.214	2.13	67.6
			$K^a = 72.3 \pm 5.6$
		$C_6H_5Pb(OAc)_3$	
248	2.68	0.133	0.0536
155	2.68	0.0762	0.0492
71.0	5.72	0.0356	0.0520
35.5	2.68	0.0178	0.0501
11.6	0.0536	0.00602	0.0519
			$K^a = 0.0510 \pm 0.018$
		$AuCl_4^-$	
392	9.07	99.2	25.3
310	6.28	77.2	24.9
131	11.2	29.6	22.6
38.5	3.14	9.09	23.6
8.27	0.243	1.98	23.9
			$K^a = 24.1 \pm 1.1$
		$HgCl_4^{2-}$ ^{b}	
514	2.55	18.49	3.60
343	2.55	11.22	3.27
229	2.55	9.52	4.16
180	2.55	7.70	4.28
171	2.55	6.36	3.72
144	2.55	4.95	3.44
120	2.55	3.77	3.14
100	2.55	3.16	3.16
			$K^a = 3.59 \pm 0.44$
		$HgBr_4^{2-}$ ^{b}	
628	2.55	3.00	0.477
458	2.55	2.16	0.471
229	2.55	1.12	0.488
93.0	2.55	0.357	0.384
41.1	2.55	0.169	0.421
35.2	2.55	0.143	0.406
			$K^a = 0.441 \pm 0.043$
		$TlCl_4^-$ ^{c}	
17.6	0.571	3.34	19.0
9.50	0.571	2.11	22.2
8.36	0.571	1.57	18.8
7.60	0.571	1.42	18.7
6.84	0.571	1.26	18.4
			$K^a = 19.4 \pm 1.6$
		$TlBr_4^-$ ^{c}	
17.6	0.571	1.29	7.32
15.4	0.571	1.07	6.97
14.8	0.571	1.06	7.16
13.1	0.571	0.977	7.46
12.3	0.571	0.955	7.76
9.71	0.571	0.754	7.77
			$K^a = 7.41 \pm 0.31$

[a] Average rate constant. Uncertainties are the standard deviations. [b] Halide to mercury ratio = 75:1. [c] Halide to thallium ratio = 300:1.

Table II. Effect of Chloride Ion on Rate Constants for CH_3HgOAc-Methylcobalamin Reaction[a]

Cl/Hg	10^4k_{obsd}, s^{-1}	$k_{obsd}/k_{obsd}^{\circ}$
0.000	1.20	1.000
0.346	1.18	0.983
0.692	1.12	0.933
2.07	1.04	0.867
2.36	1.02	0.850
26.55	0.927	0.773

[a] [CH_3HgOAc] = 1.7×10^{-3} M; [CH_3B_{12}] = 8.75×10^{-5} M. These figures give a rate constant of $6.9_8 \times 10^{-2}$ M^{-1} s^{-1}, in excellent agreement with reported values.[14]

reaction was run under pseudo-first-order conditions and the logarithm of the observed rate constants was plotted against the logarithm of the Tl concentration, a straight line of slope 1.02 resulted. This indicates first-order dependence on Tl(III) and second order overall, in agreement with previously reported kinetic studies on related systems.[3,5,6,12,14] Similar straight-line plots resulted from Hg^{II}–I or Tl^{III}–I studies done in the presence of chloride or bromide. Rate data are listed in Table I. The decreased rate of reaction of Hg(II) toward I in the presence of chloride (Figure 1) agrees with reports by other workers.[4,15,17] Our value of 3.56 s^{-1} M^{-1} found for $HgCl_4^{2-}$ is in reasonable agreement with the value of 4.0 s^{-1} M^{-1} reported by Robinson et al.[4] We could find no evidence for the formation of any "base-off" complex formed in the $HgCl_2$–I system.[4,5]

Addition of nitrate ion, even in 15-fold excess, had no noticeable effect on the rate of reaction between I and either Hg(II) or Tl(III), nor did the presence of Tl^+ show any effect in the latter reaction. When an equimolar solution of Tl(III) and I were allowed to react to completion and treated with a solution of iodide ion, there was a precipitate of yellow TlI. Extraction with carbon tetrachloride gave no violet color attributable to iodine. The same Tl(III) solution in the absence of I gave iodine upon extraction. The TlX_4^-–I reaction slowly generated halomethanes as products, which could be determined by vapor-phase chromatography. Halomethanes were not generated by Hg(II) salts under the same conditions.

Phenyllead triacetate reacts with I; this reaction is first order in respect to each reactant. The experimentally determined rate constant of 5.10×10^{-2} s^{-1} M^{-1} is comparable in magnitude to that for CH_3HgOAc (6.88×10^{-2} s^{-1} M^{-1}).[14] The rate of reaction was not affected by the presence of Pb(II). In the presence of halides, phenyllead triacetate decomposes rapidly, forming halobenzenes and Pb(II) halides. The presence of halides does affect the CH_3HgOAc–I reaction, however. The rate decreases, just as with inorganic Hg(II); however, the effect is much less drastic, as the data in Table II show.

Transition-Metal Compounds. Yamamoto et al. reported that $CuCl_2$ reacts with I only at very high Cl^- concentrations and that methyl chloride forms as product.[21] We find similar results for the $CuBr_2$ system; the rate of reaction depends very much on the Br^- concentration, as shown by Figure 2. Methyl bromide forms as product. Bromide causes a greater rate enhancement than chloride under comparable conditions. Addition of solid CuCl caused no noticeable rate enhancement in the chloride system.

Scovell reported that the reaction rate of I with $PdCl_4^{2-}$ increased with increasing chloride concentration[5] and that CH_3Cl and Pd metal were the products (eq 1). We found

$$PdCl_4^{2-} + CH_3B_{12} \rightarrow [CH_3PdCl_3^{2-}] \rightarrow CH_3Cl + Pd + 2Cl \quad (1)$$

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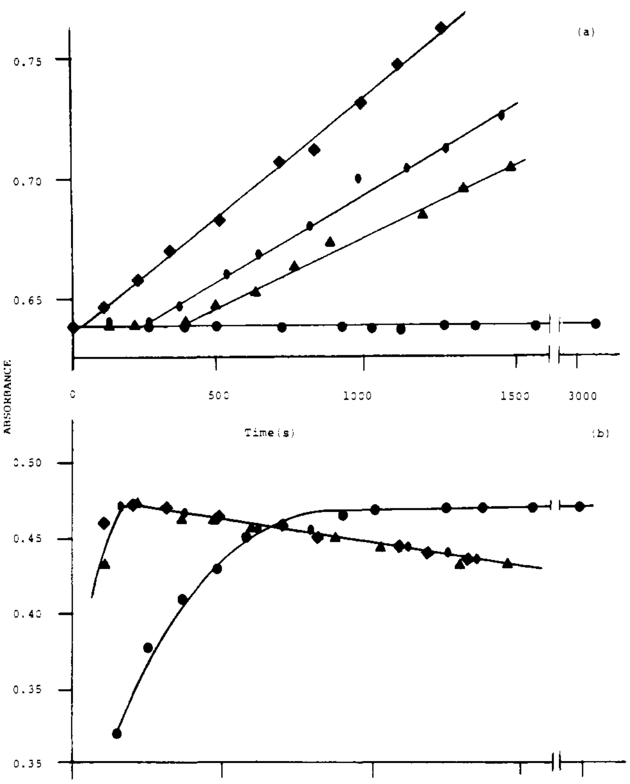

Figure 2. Change in peak absorbances in the K_2PdCl_4-methylcobalamin reaction ($[PdCl_4^{2-}] = 3.66 \times 10^{-4}$ M; $[CH_3B_{12}] = 9.41 \times 10^{-5}$ M): (a) 350 nm, (b) 440 nm. Circle, triangle, oval, and box: $[Br^-]$ = 0.0000, 0.0088, 0.0175, and 0.0218 M, respectively.

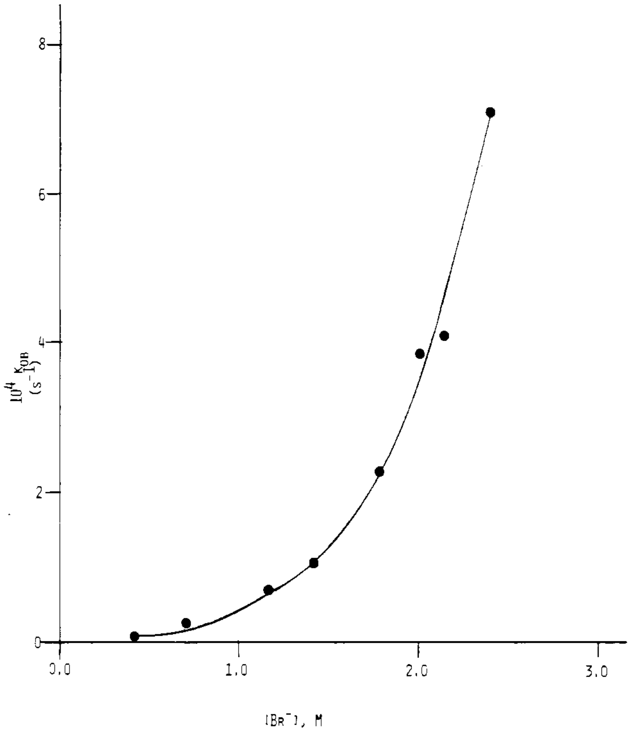

Figure 3. Effect of $[Br^-]$ on the pseudo-first-order rate constants for the $Cu(NO_3)_2$-methylcobalamin reaction: $[Cu^{2+}] = 2.70 \times 10^{-3}$ M; $[CH_3B_{12}] = 1.12 \times 10^{-4}$ M.

that addition of bromide ion to this system noticeably increased the rate of formation of "base-off" complex and that in the subsequent demethylation reaction. This is shown in Figure 3, which portrays the change in spectrophotometric absorbances at 440 nm ("base-off" complex) and 350 nm (aquocobalamin) as a function of time and Br^- concentration.

Table III. Effect of Halides on Platinum and Gold Reaction Rates with Methylcobalamin[a]

metal species	$10^5 \times$ [M], M	$10^5 \times$ $[CH_3B_{12}]$, M	$10^5 \times$ $[X^-]$, M	K, $M^{-1} s^{-1}$
$PtCl_6^{2-}$	6.56	6.04		10.2
	13.1	8.13		12.2
	6.56	6.04	Cl, 443	19.6
	13.1	8.13	Cl, 136	22.4
	13.1	8.13	Br, 156	>300
$PtBr_6^{2-}$	1.29	8.13		61.5
	1.94	6.04		64.2
	2.58	4.07		59.2
	2.58	8.13		59.7
	1.29	8.13	Cl, 102	86.9
	1.94	6.04	Cl, 443	86.3
	2.58	4.07	Cl, 67.9	90.1
	1.29	8.13	Br, 117	>300
	1.94	6.04	Br, 434	>300
	2.58	4.07	Br, 77.8	>300
$AuCl_4^-$	17.4	6.04		22.6
	17.4	8.13		22.3
	17.4	6.04	Cl, 98.5	14.4
	17.4	8.13	Cl, 98.5	11.5
	17.4	6.04	Br, 96.5	53.4
	17.4	8.13	Br, 96.5	54.3

[a] Reactions run in 0.10 M buffered acetic acid. Rate constants calculated by method of initial rates.

Fanchiang et al. reported that the rate of reaction of I with $PtCl_6^{2-}$ varied with ionic strength and proceeded faster in the presence of chloride ion than in the presence of perchlorate at the same concentration.[11] We found that there was a minor enhancement of reaction rate in the presence of additional chloride ion but that addition of bromide ion markedly increased the reaction rate (cf. Table III). Kinetic studies on the K_2PtBr_6–I system have proven difficult because of the strong absorbance of $PtBr_6^{2-}$ at 350 nm.[22] Under comparative conditions, the bromoplatinate(IV) ion seems to behave in identical fashion with the chloro analogue toward I. Chromatographic studies indicate that methyl halides form in both systems, but only slowly over the first few hours and at a rate considerably less rapid than the rate of I demethylation. This is in sharp contrast to the Cu system where methyl halide formation occurs almost immediately. This observation is consistent with the mechanisms proposed by other groups[8,9,11] that involve methylplatinum intermediates; apparently such intermediates can be quite long-lived. Studies on mixed systems ($PtCl_6^{2-}$–Br^- or $PtBr_6^{2-}$–Cl^-) showed that methyl bromide always formed as the dominant product (>98%), with only small quantities of methyl chloride.

The reaction of I with $AuCl_4^-$ is similar in its behavior to the $PtCl_6^{2-}$ system; however, reproducible kinetic results have proven more difficult to obtain. The data shown in Tables I and III were obtained with the use of initial rates and freshly prepared Au solutions. As in the preceding systems, addition of bromide noticeably accelerates the rate of reaction. Gas chromatographic studies showed that methyl chloride formed, and, in the presence of Br^-, methyl bromide was the dominant halomethane present.

Discussion

DeSimone et al., in their report on the $Hg(OAc)_2$–I reaction, proposed that the methyl group was transferred as an anion and that the metal served as an electrophile.[3] This S_E2 mechanism has also been proposed for the reaction of Hg(II) salts with methylgold[23] and methylchromium[24] compounds and

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Table IV. Dissociation Constants for Hg(II) and Tl(III) Complexes

metal	anion	$p\beta_1$	$p\beta_2$	$p\beta_3$	$p\beta_4$	ref
Hg(II)	OAc^-	5.56	9.30	13.28	17.08	*b*
	Cl^-	7.07	13.98	14.73	16.11	*c, d*
	Br^-	9.40	17.98	20.30	22.23	*d*
Tl(III)	OAc^-	6.17	11.28	15.10	18.30	*e*
	Cl^-	7.54	13.38	16.79	19.58	*f*
	Br^-	9.62	17.08	22.59	26.73	*f*

[a] $\beta_n = ([M^{m+}][X^-]^n)/[MX_n^{m-n}]$. $p\beta_n = -\log \beta_n$. [b] Banerjea, D.; Singh, I. P. *Z. Anorg. Allg. Chem.* **1964**, *331*, 225. [c] Sillen, L. G. *Acta Chem. Scand.* **1949**, *3*, 539. [d] Arnek, R. *Ark. Kemi* **1965**, *24*, 531. [e] Kul'ba, F. Y.; Yakovlev, Y. B.; Mironov, V. E. *Russ. J. Inorg. Chem.* **1965**, *10*, 886. [f] Ahrland, S.; Grenthe, I.; Johansson, L.; Noren, B. *Acta Chem. Scand.* **1963**, *17*, 1567.

may well apply to reactions between I and other representative metals.[2,5,6,13,14,25-27] If such a mechanism be correct, then anything altering the electrophilic nature of the metal species will correspondingly affect the reaction rate of that species with methylcobalamin. Alkyl and aryl groups bonded to metals serve as electron donors; monoorganometals should, therefore, be less reactive toward I than the purely inorganic analogues. This is indeed observed.[1,3,13,14,26,27] As may be seen from Table IV, the strength of the metal–ligand bond varies: $Br^- > Cl^- > OAc^-$, which is the converse of the order of the reaction rates toward I. Our experiments also show that the effect is greatest for the first halide and decreasingly important for subsequent ones—a trend observed elsewhere.[2,5,26] It should also be noted that transmethylation *does not cease*, even at ratios of X^- to metal of 50:1 and higher. The addition of one methyl group has a much greater repressive effect on transmethylation rates than any inorganic ligand; consequently, halides have a much smaller to repressive effect on CH_3HgOAc than on $Hg(OAc)_2$. On the basis of their work, Chu and Gruenwedel concluded,[5] "The effect of anions is not merely a question of ionic dissociation." Our evidence supports this statement. The proposed S_E2 mechanism, involving electrophilic attack by a metal on an anionic methyl group, is fully consistent with all reported results. The electrophilic nature of the metal, however, will depend very much on what ligands are present, and this is a factor that must be considered when discussing transmethylation of representative metals, especially under environmental conditions.

The observed effects of halides on transition-metal species may also be explained in terms of ligand effects on the metal atom. The mechanism proposed for the $PdCl_4^{2-}$–I reaction is exactly the same as that proposed for Hg(II) species[6]. Spectroscopic evidence (Figure 3) indicates that $PdCl_{4-n}Br_n^{2-}$ species behave in the same way toward I as $PdCl_4^{2-}$ and presumably follow the same mechanism. In their proposed mechanism for methyl exchange between $PtCl_6^{2-}$ and I, Fanchiang et al. present evidence for the formation of an intermediate complex that labilizes the Co–C σ bond to electrophilic attack—i.e., the methyl group transfers as an anion.[11] The bromo complexes of both Pd and Pt are more stable than the chloro analogues;[22a,b,28] in mixed systems, it is these bromo complexes that react preferentially. Transmethylation of Cu(II) occurs only at quite high halide concentration. $Cu(NO_3)_2$ does not react with I in 2 M $NaNO_3$,[21] nor did we find any reaction for Cu(II) in buffered acetic acid. Figure 2 indicates that transmethylation involving $CuBr_2$ accelerates markedly at higher bromide ion concentrations and similar effects occur in the chloro system.[21] There was no evidence to indicate the formation of any cobalamin(II) derivative during the exchange,[21] and it seems probable that the methyl group transfers as an anion in this system also.

The AuX_4^- system is more difficult to evaluate. Experimental results tend to vary more than with other systems, and reproducibility becomes more of a problem. The presence of Au(I) species in solution certainly catalyzes methyl exchange.[12] Fanchiang et al. proposed formation of a Au(II) species as the active intermediate.[29] Exchange reactions involving Au(III) complexes follow the rate law

$$-d[Au]/dt = (k_1 + k_2[Y])[Au] \qquad (2)$$

where [Au] is the concentration of the initial gold complex and [Y] is the concentration of reagent.[30] Uncatalyzed exchange of Cl^- with $AuCl_4^-$ proceeded by the S_N2 mechanism, but the addition of Fe(II) catalyzed this exchange via a proposed Au(II) intermediate.[30b] As with other transition metals studied, addition of Br^- causes the $AuCl_4^-$–I reaction to accelerate. Considerably more work will be required for complete understanding of this particular system.

For all four transition metals, the bromo complexes are more stable than the chloro complexes. For three of these (and possibly all four), the methyl group transfers as an anion—i.e., by the S_E2 mechanism. In these two respects, the transition metals are exactly like Hg(II) and Tl(III). Yet, exactly the opposite effect happens to the rate of transmethylation when bromide ion is added to the chloro complexes and (for Cu) chloride is added to the aquo complex. One possible explanation may be the "symbiotic effect" proposed by Jørgensen.[31] Bromide ion is a "softer" base than chloride ion. Replacement of chloro ligands on a transition metal by bromo ligands would make the metal more receptive to the extremely "soft" base CH_3^-, hereby enhancing the rate of reaction. Therefore, although both representative and transition metals may show electrophilic attack on the methyl group of methylcobalamin, ligands on the two types of metals will affect their electrophilic nature quite differently.

There is no reason to suppose that methyl exchange between metals in aqueous media is any different in its intrinsic nature than other exchange reactions under the same conditions. As these systems become more completely understood, the relationship of aqueous transmethylation itself to both ligand-exchange reactions generally and to organometallic chemistry will become apparent, opening up new areas for further investigations.

Acknowledgment. Certain chemicals and spectroscopic cells used in this research were purchased under a University Research Council grant from the University of Cincinnati. The author wishes to thank his University of Cincinnati colleagues Dr. Carl Seliskar (for the use of a NaCl gas cell), Dr. Estel Sprague, and Dr. Darl McDaniel (for helpful discussions on kinetics and mechanisms). He gratefully acknowledges the kindness of Dr. Frederick Brinckman (National Bureau of Standards) for making available the use of his chromatographic equipment and for continuing encouragement and support.

Registry No. Methylcobalamin, 13422-55-4; Cl^-, 16887-00-6; Br^-, 24959-67-9; Tl, 7440-28-0; Pb, 7439-92-1; Au, 7440-67-5; Hg, 7439-97-6; Pt, 7440-06-4; Pd, 7440-05-3; Cu, 7440-50-8.

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