line product was made and the infrared spectrum taken. IX was made as reported[20] from $Al(C_2H_5)Cl_2$ and (3)-1,2-$B_9C_2H_{11}^{2-}$ in THF, yield 46.0%. A Nujol infrared spectrum of this product was found to be identical with that obtained from the THF adduct of IV.

Polymerization of Ethylene. Ziegler-type catalysts were prepared from compounds I and IV in a manner similar to that originally described for triethylaluminum.[21] Solutions were made under nitrogen of 0.50 g of I in 50 ml of dry heptane and 0.50 g of IV in 20 ml of dry benzene mixed with 30 ml of heptane. To these solutions was added 0.50 ml of $TiCl_4$, which immediately produced dark red-brown precipitates. These mixtures were then evacuated to the solvent vapor pressures and exposed to dry ethylene gas with stirring. Over several hours the mixtures became warm and viscous as ethylene was periodically added to maintain 1 atm of pressure. Finally they were cooled and hydrolyzed with 2-propanol; the polyethylene was filtered off and washed with methanol and water. After 6 hr of exposure to ethylene gas at 1 atm, 3.5 g of white, amorphous polyethylene had been produced. An infrared spectrum of a pressed disk confirmed its identity. In both cases it was possible to isolate (3)-1,2-$B_9C_2H_{12}^{-}N(CH_3)_3H^+$ from the hydrolyzed catalyst upon addition of trimethylammonium chloride.[2]

Acknowledgment. The authors wish to express their gratitude to Professor F. A. L. Anet and Dr. Craig Bradley of this department for the 250-Mcps proton and the 80-Mcps boron nmr spectra and to the Office of Naval Research for support of this research.

Effects of Solvent on the Rate and Mechanism of Exchange of Methyl Groups in the Systems Dimethylcadmium, Dimethylzinc–Trimethylindium, and Dimethylcadmium–Trimethylgallium Determined by Proton Magnetic Resonance Spectroscopy

Jamshid Soulati,[1a] Kenneth L. Henold,[1b] and John P. Oliver*[1c]

Contribution from the Departments of Chemistry, Pahlavi University,
Shiraz, Iran, the University of Detroit, Detroit, Michigan 48221,
and Wayne State University, Detroit, Michigan 48202.
Received February 8, 1971

Abstract: The self-exchange of $Cd(CH_3)_2$ in diethyl ether, the exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$ in cyclopentane and in toluene, and the exchange of $Zn(CH_3)_2$ with $In(CH_3)_3$ in diethyl ether and in triethylamine have been investigated. The activation energies and rate constants for each of these systems have been determined. These data show that the rate of reaction is dependent on the coordinating ability of the solvent and the nature of the metal atom. Strongly coordinating solvents have been shown to enhance the exchange rate between derivatives of group II metals, but decrease the exchange rate when one of the species is from group III. These effects are discussed in detail.

The exchange of ligands between alkyl derivatives of group II metals and between group II and group III metals has been under investigation for sometime. These studies have shown that "rapid" self-exchange occurs in dimethylcadmium[2,3] and in divinyl- and methylvinylcadmium.[4] They have also shown that rapid exchange of alkyl groups occurs between cadmium and zinc[3,5] and between zinc or cadmium and magnesium derivatives.[6] It has also been suggested that self-exchange occurs in zinc derivatives, as evidenced by lack of ^{13}C coupling across the C–Zn–C system[7] and by the appearance of an AX_4 spectrum in diallylzinc.[8] Exchange has been observed under a variety of conditions for magnesium derivatives.[9] Several research groups have demonstrated that groups such as alkoxide and halide,[2a] as well as the studies already cited on unsaturated organic derivatives,[4,8,10] tend to catalyze exchange in these systems and permit, in some cases, establishment of equilibria similar to the Schlenk equilibrium observed in Grignard reagents.[11]

Studies have been reported on the exchange between group II and group III derivatives, with the emphasis placed on the reactions of aluminum alkyls.[2a,3,12] These studies are limited, however, in the sense that the dominant feature is the stability of the bridge bond in aluminum trimethyl, which governs the rate of reaction. Limited studies have been reported on the exchange of other group III derivatives with group II compounds,

---

(1) (a) Pahlavi University; (b) University of Detroit; (c) Wayne State University.

(2) (a) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, 21, 1187 (1968); (b) W. Bremser, M. Winokur, and J. R. Roberts, *J. Amer. Chem. Soc.*, **92**, 1080 (1970).

(3) C. R. McCoy and A. L. Allred, *ibid.*, **84**, 912 (1962).

(4) H. D. Visser, L. P. Stodulski, III, and J. P. Oliver, *J. Organometal. Chem.*, 24, 563 (1970).

(5) K. L. Henold, J. Soulati, and J. P. Oliver, *J. Amer. Chem. Soc.*, **91**, 3171 (1969).

(6) R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *ibid.*, **85**, 1191 (1963).

(7) F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968).

(8) K. H. Thiele and P. Zdunneck, *J. Organometal. Chem.*, **4**, 10 (1965).

(9) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, 32, 2481 (1967).

(10) J. Lorberth, *J. Organometal. Chem.*, **19**, 189 (1968).

(11) K. Cavanagh and D. F. Evans, *J. Chem. Soc. A*, 2890 (1969).

(12) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 5460 (1966).

but these are not sufficient to permit generalizations to be made.[5,12]

We now wish to report on several aspects of the problem of alkyl exchange involving exchange of group II derivatives and on the exchange of group II derivatives with those of group III which should allow much broader conclusions to be drawn. The main emphasis in this paper is on the effect of solvents which play a major role in these alkyl exchange reactions.

Experimental Section

Preparation of $Cd(CH_3)_2$,[13] $Zn(CH_3)_2$,[14] $Ga(CH_3)_3$,[15] and $In(CH_3)_3$[16] was carried out by procedures described in the literature. All were purified on a vacuum system by repeated distillations and stored under vacuum until used. Cyclopentane, toluene, diethyl ether, triethylamine, and diethylamine were refluxed over sodium–potassium alloy and distilled into the vacuum system for subsequent use. Dichloromethane was dried as reported earlier.[5]

Nmr samples were prepared as reported earlier[5] and were stored at low temperature. The samples containing dimethylcadmium were also protected from the light to prevent photoinduced decomposition.

A Varian A60-A nmr spectrometer equipped with variable-temperature accessories was used for all experiments. Temperatures were measured using the temperature dependence of the internal chemical shift of methanol or ethylene glycol as described by VanGeet.[17] Chemical shifts were determined by standard audiofrequency side-band techniques using an internal standard

Interpretation of Nmr Data. The manner in which lifetimes were obtained by fitting the experimental spectra to calculated curves by use of modifications of the McConnell equations has been discussed previously.[5]

Treatment of Data. The rate expression previously used to describe the reaction has been reexamined and found to contain some inconsistencies. The statistical factor introduced to account for the differing number of methyl groups on each species should not have been introduced prior to the formation of the activated complex. The proper treatment should be as follows.

$$Cd(CH_3)_2 + M(CH_3)_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AC] \xrightarrow{k_2} \text{exchange products} \quad (1)$$

$$\text{rate}_{\text{exc}} = k_2[AC] \quad (2)$$

$$d[AC]/dt = k_1[Cd(CH_3)_2][M(CH_3)_n] - k_{-1}[AC] - k_2[AC] \quad (3)$$

Applying the steady-state approximation, with $k_{-1} = k_2$, $d[AC]/dt = 0$ and then

$$2k_2[AC] = k_1[Cd(CH_3)_2][M(CH_3)_n] \quad (4)$$

$$[AC] = (k_1/2k_2)[Cd(CH_3)_2][M(CH_3)_n] \quad (5)$$

Then, from eq 2

$$\text{rate}_{\text{exc}} = (k_1/2)[Cd(CH_3)_2][M(CH_3)_n] = k_{\text{obsd}}[Cd(CH_3)_2][M(CH_3)_n] \quad (6)$$

This is the form the rate expression should take if one assumes that the formation of the activated complex is a simple bimolecular process and that once formed, the activated complex has a chance of yielding an exchange product. Thus, $k_{\text{obsd}} = k_1/2$, as seen in eq 6.

The lifetime of each individual carbon–metal bond can be related to the rate of exchange by taking into consideration the number of methyl groups on each of the organometallic moieties. Only $1/n$ of the times a molecule is involved in an exchange will a given carbon–metal bond be broken.

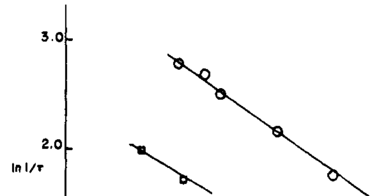


Figure 1. The Arrhenius activation energy plots (ln $1/\tau$ *vs.* $1/T$) for the self-exchange of $Cd(CH_3)_2$ in diethyl ether, □, $E_a{}^{\ddagger} = 5.6 \pm 0.2$ kcal,mol; and triethylamine, ○, $E_a{}^{\ddagger} = 6.9 \pm 0.2$ kcal/mol.

Therefore, equations for the lifetimes of all species can be written as

$$\frac{1}{\tau_{Cd-CH_3}} = \frac{(k_1/2)/[Cd(CH_3)_2][M(CH_3)_n]}{2[Cd(CH_3)_2]} = \frac{k_1[M(CH_3)_n]}{4} \quad (7)$$

and

$$\frac{1}{\tau_{M-CH_3}} = \frac{k_1[Cd(CH_3)_2]}{n} = \frac{k_1[Cd(CH_3)_2]}{2n} \quad (8)$$

where n is the number of alkyl groups in MR_n.

Results and Discussion

The self-exchange of $Cd(CH_3)_2$ has been known for some time and several papers have reported quantitative data on this system.[2,3] We have investigated it under somewhat different conditions. Data for the concentration dependence for the self-exchange of $Cd(CH_3)_2$ in ether are given in Table I and show unequivocally the second-order dependence of the exchange rate on $Cd(CH_3)_2$ concentration. This has been implied but not previously reported. The temperature dependence for this exchange in both diethyl ether and triethylamine is shown in Figure 1.

Table I. Concentration Dependence of the Self-Exchange of Dimethylcadmium in Diethyl Ether at +33.3°

$[Cd(CH_3)_2]$, M	$[Cd(CH_3)_2]_{\text{eff}}$,[a] M	$1/\tau_{Cd-CH_3}$, sec^{-1}	k_1,[b] l. mol^{-1} sec^{-1}
0.681	0.172	2.20	51.2
0.860	0.217	2.80	51.6
1.07	0.270	3.46	51.3
1.20	0.302	4.24	56.2
1.36	0.333	4.40	52.9
1.90	0.488	5.34	43.8
			$k_{1\text{av}} = 51 \pm 2$

[a] $[Cd(CH_3)_2]_{\text{eff}} = 0.252[Cd(CH_3)_2]$. This value is used in the determination of the rate constant because exchange with molecules of dimethylcadmium containing ^{112}Cd does not result in a change in the line shape of the nmr resonance line. [b] $k_1 = 2k_{\text{obsd}}$.

The data obtained in this and other studies dealing with the self-exchange of $Cd(CH_3)_2$ are summarized in Table II. The first point to be made is that the self-exchange of $Cd(CH_3)_2$ and the exchange of $Zn(CH_3)_2$ with $Cd(CH_3)_2$ proceed with a second-order concentra-

---

(13) H. Gillman and J. F. Nelson, *Recl. Trav. Chim. Pays-Bas*, **55**, 518 (1936).

(14) N. K. Hota and C. J. Willis, *J. Organometal. Chem.*, **9**, 171 (1967).

(15) L. M. Dennis and W. Pantode, *J. Amer. Chem. Soc.*, **54**, 182 (1932).

(16) L. M. Dennis, R. W. Work, and E. G. Rochow, *ibid.*, 56, 1047 (1934).

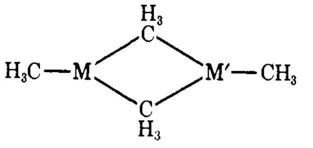
(17) A. L. VanGeet, *Anal. Chem.*, **40**, 2227 (1968).

Table II. Kinetic Parameters for the Self-Exchange of $Cd(CH_3)_2$ and for its Exchange with $Zn(CH_3)_2$ in Various Solvents

Reaction	Solvent	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	k_1, l. mol^{-1} sec^{-1} (25°)
Self-exchange	$N(C_2H_5)_3$	6.9 ± 0.2		
Self-exchange	$O(C_2H_5)_2$	5.6 ± 0.2	-38	38.5
Self-exchange	THF^a	6.8 ± 0.1	-28.3 ± 0.4	245
Self-exchange	py^b	13		
Self-exchange	Toluene^b	16		
Self-exchange	Neat^a	15.6 ± 0.1	-9.8	0.4
$Zn(CH_3)_2$–$Cd(CH_3)_2$	Methylcyclohexane^c	17.0 ± 1	-3	1.7

^{a} Reference 2b. ^{b} Reference 2a, with added methanol giving $Cd(OCH_3)CH_3$ which catalyzes the exchange. ^{c} Reference 5.

tion dependence which is compatible with a four-centered transition state as shown in I. These reactions have also been shown to have very similar activation energies and rates when studied in nonpolar systems.[2b,5] In fact, it would appear that the reaction in which zinc is present proceeds more readily than the self-exchange of dimethylcadmium, since the self-exchange does not interfere with the observation of the $Zn(CH_3)_2$-$Cd(CH_3)_2$ exchange. The apparent contradiction between this statement and the studies reported by Bremser, Winokur, and Roberts[2b] appears to arise because of the difference in solvents and because these authors apparently overlooked the second-order concentration dependence of the reaction. Using the parameters which they reported, one can calculate the lifetime of $Cd(CH_3)_2$ to be approximately 2 sec at 70° for 0.5 *M* $Cd(CH_3)_2$. This relatively long lifetime makes exchange by line-shape analysis unobservable under these conditions.



I

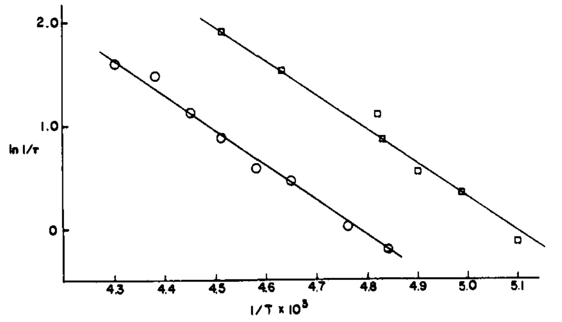


Figure 2. The Arrhenius activation energy plots (ln 1/τ *vs.* 1/*T*) for the exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$ in cyclopentane, □, $E_a{}^{\ddagger} = 6.7 \pm 0.4$ kcal/mol; and in toluene, ○, $E_a{}^{\ddagger} = 7.0 \pm 0.2$ kcal/mol.

In view of the proposed mechanism of the reaction, it is of fundamental interest to examine the effect of solvents on the reaction, since they may modify the transition state.

In going to strongly basic solvents, *i.e.*, THF, diethyl ether, and triethylamine, the activation energy drops dramatically to 5–7 kcal/mol, as seen in Table II. The differences are probably not significant owing to the possibility of side reactions producing products which might catalyze the reaction. With still more basic solvents, *i.e.*, pyridine, it appears that the activation energy for this process is increased, although additional data should be obtained to confirm this fact.

These changes in the activation energy may be interpreted if one examines the effect of the solvent on the transition state for the exchange process. The formation of the transition state will depend on several factors, three of which are the reorganization energy of the metal orbitals and the donor and acceptor character of the carbon and of the metal, respectively.

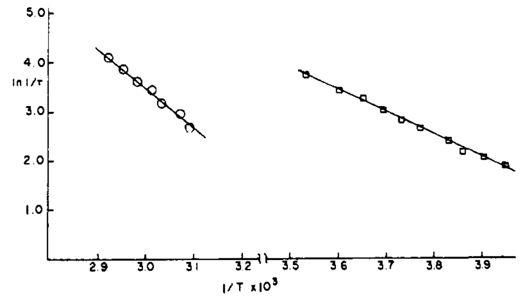
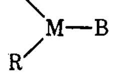


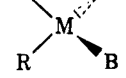
Figure 3. The Arrhenius activation energy plots (ln 1/τ *vs.* 1/*T*) for the exchange of $Zn(CH_3)_2$ with $In(CH_3)_3$ in ether, □, $E_a{}^{\ddagger} = 9.1 \pm 0.2$ kcal/mol; and in triethylamine, ○, $E_a{}^{\ddagger} = 16.3 \pm 0.7$ kcal/mol.

To assess the effects of these factors on the rate and mechanism of the exchange reactions we must look at the structure and interaction of the solvent with the alkyl derivatives. A group II metal alkyl is capable of forming either a mono- or dicoordinated derivative, as seen in II and III. In the monocoordinated system, the metal still has an unoccupied orbital, while the angles between the groups bonded to the metal are reduced from 180° in the free alkyl to near 120° in the complex. In addition, the electron density on the carbon bonded to the metal should be somewhat increased. These changes are either compatible with or in favor of a more easily formed transition state involving a four-centered species. This is particularly true since the C–M–C angle in stable complexes is between 100 and 120°.[18] Thus, only a small reorganization energy will be required to attain the transition state. This will be further aided by the enhanced electron density avail-



II

or



III

---

(18) A general discussion of this may be found in G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, 3rd ed, Methuen, London, 1967, Chapters 2 and 3.

Table III. Concentration Dependence for $Cd(CH_3)_2 + Ga(CH_3)_3$ in Cyclopentane at −61.8°

				k_1	
$[Cd(CH_3)_2]$, M	$[Ga(CH_3)_3]$, M	$\frac{1}{\tau_{\mathrm{Cd-CH_3}}}$, sec^{-1}	$\frac{1}{\tau_{\mathrm{Ga-CH_3}}}$, sec^{-1}	$\frac{4}{\tau_{\mathrm{Cd-CH_3}}[Ga(CH_3)_3]}$, l. mol^{-1} sec^{-1}	$\frac{6}{\tau_{\mathrm{In-CH_3}}[Cd(CH_3)_2]}$, l. mol^{-1} sec^{-1}
0.194	0.137	15.1	14.3	441	442
0.154	0.043	4.75	11.4	442	444
0.201	0.095	10.9	15.4	459	460
0.403	0.118	12.4	28.2	420	420
0.280	0.127	14.5	21.3	457	456
					$k_{1_{\mathrm{av}}} = 440 \pm 10$

Table IV. Concentration Dependence for $In(CH_3)_3 + Zn(CH_3)_2$

				k_1	
$[In(CH_3)]$, M	$[Zn(CH_3)_2]$, M	$\frac{1}{\tau_{\mathrm{In-CH_3}}}$, sec^{-1}	$\frac{1}{\tau_{\mathrm{Zn-CH_3}}}$, sec^{-1}	$\frac{6}{\tau_{\mathrm{In-CH_3}}[Zn(CH_3)_2]}$, l. mol^{-1} sec^{-1}	$\frac{4}{\tau_{\mathrm{Zn-CH_3}}[In(CH_3)_3]}$, l. mol^{-1} sec^{-1}
		(a) Diethyl Ether Solvent, −8.8°			
0.258	0.238	10.9	17.2	275	267
0.320	0.131	8.3	30.5	380	381
0.248	0.170	11.4	24.9	402	402
0.199	0.174	10.7	18.4	369	370
0.099	0.280	13.0	6.9	279	279
0.164	0.198	12.4	15.4	376	376
0.132	0.066	4.1	12.3	373	373
					$k_{1_{\mathrm{av}}} = 350 \pm 40$
		(b) Triethylamine Solvent, 70.5°			
0.063	0.110	13.8	11.9	753	756
0.078	0.122	14.7	14.6	723	718
0.320	0.285	30.3	51.2	638	640
0 397	0.465	51.7	66.0	667	665
					$k_{1_{\mathrm{av}}} = 690 \pm 40$

Table V. Summary of Data for Methyl Group Exchange between Group II and Group III Derivatives

Reaction	Solvent	$E_a^{\ddagger}$, kcal/mol	k_1 (25°), l. mol^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$ (25°), eu
$Cd(CH_3)_2 + Ga(CH_3)_3$	Cyclopentane	6.7 ± 0.4	45,000	8.1	−17
	Dichloromethane[a,b]	7.3	4,250	6.7	−19
	Toluene	7.0 ± 0.2	1,500	6.4	−23
$Cd(CH_3)_2 + In(CH_3)_3$	Dichloromethane[a]	8.4 ± 0.2	7,800	7.8	−14
$Zn(CH_3)_2 + In(CH_3)_3$	Dichloromethane[c]	<5			
	Diethyl ether	9.1 ± 0.2	2,900	8.5	−14
	Triethylamine[d]	16.3 ± 0.7	17.4	15.7	+2
$Zn(CH_3)_2 + Cd(CH_3)_2$	Methylcyclohexane[a]	17.0 ± 1.0	1.7	16.4	−3

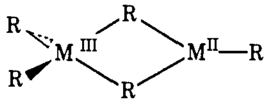
[a] Reported in ref 5. The rate constants are recalculated using the modified data treatment. [b] The activation energy has been redetermined from that in ref 5 and is lowered by 0.5 kcal mol^{-1}. [c] The lines could not be separated at −90°. [d] The reaction appears to proceed at a lower temperature in diethylamine; however, decomposition occurs which prevents determination of kinetic parameters.

able on the organic moiety entering into the bridge bond. Opposed to these will be steric crowding and reduced Lewis acidity of the central metal atom entering into the bridge.

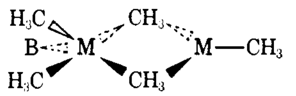
From the data so far available it appears that these features favor increased reactivity, and that the nature of the base involved determines the extent of this increase. Examples supporting this are the dimethylcadmium studies carried out in diethyl ether, THF, and triethylamine. When substantially stronger bases are used, stable diadducts are possible. If these are formed, then an important feature of the reaction will be the dissociation of the adduct to give a vacant site on the metal which may be used for formation of the bridged transition state. It would appear that the studies on pyridine solutions of dimethylcadmium are in this group, but an alternate explanation might be that this base forms a stable monoadduct in which the steric crowding and reduced acidity of the metal dominate, thus reducing the rate of reaction. Additional work needs to be carried out to determine if either of these postulates is correct.

Further information may be gained concerning the role of the solvent on the reaction mechanism by examination of the solvent dependence of the reactions of group II derivatives with group III compounds. The data for the exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$ and of $Zn(CH_3)_2$ with $In(CH_3)_3$ are summarized in Tables III, IV, and V. Data for the activation energies are provided in Figures 2 and 3.

From the data in Table V and those given earlier,[6] one can establish the following order of reaction rates for the methyl derivatives, Ga + Zn > In + Zn > Ga + Cd $\sim$ In + Cd > Zn + Cd $\gtrsim$ Cd + Cd, when the solvent is not capable of forming a stable complex with any of the species present. If the solvent interacts weakly with the metal, as it does with zinc and cadmium, then the rate of exchange between derivatives of these metals or the cadmium self-exchange is increased, while the exchange of substituents between a group II and a group III derivative is slowed depending on the nature and strength of the solvent interaction with the vacant site on the group III compound. This occurs because the most likely transition state for a group II–group III exchange is as shown in IV, which makes full use of the vacant orbital on the group III derivatives. With a sufficiently strong donor solvent, the rate-determining step is modified, giving rise to one of the following situations. A transition state can be formed, involving a five-coordinate intermediate such as V. An intermediate of this type has been proposed by Mole to account for the exchange of alkyl groups between aluminum alkyls in pyridine.



IV



V

This mechanism should show a second-order concentration dependence, first order in each of the components, and should also have a large negative entropy of activation. An alternate path is through the prior dissociation of the adduct

$$R_3M \cdot B \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_3M + B \qquad (9)$$

followed by the exchange reaction

$$R_3M + R_2M' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AC] \xrightarrow{k_2} \text{exchange products} \qquad (10)$$

In this case the observed concentration dependence will depend on the relative magnitudes of reactions 9 and 10. If the dissociation in eq 9 is rate determining, *i.e.*, if $k_1 \gg k_3$, then the reaction will be first order in the concentration of $R_3M \cdot B$ and independent of the concentration of R_2M. On the other hand, if $k_3 \gg k_1$ and a steady-state concentration of free R_3M is established, then the exchange reaction will be first order in R_3M and R_2M or overall second order. For intermediate values of k_1 and k_3 the reaction order may become complex. The entropy of activation for the processes involving dissociation are difficult to estimate, since they will depend to a great extent on the details of both the transition state and the extent of reordering of the solvent system, but may be near zero or positive if the major contribution is from the dissociation step.

From the data presented, it can be seen that all of the reactions are second order, thus no case has been observed in which the dissociation step is rate controlling. The data collected in Table V, however, may be interpreted as evidence for changes in the mechanism of the reaction in going from a noncoordinating solvent (dichloromethane, low activation energy) to a "weakly" coordinating solvent (diethyl ether, $E_a^{\ddagger} = 9.1$ kcal/mol^{-1}, $\Delta S^{\ddagger} = \mp -14$ eu) to a strongly coordinating solvent (triethylamine, $E_a^{\ddagger} = 16.3$ kcal/mol^{-1}, $\Delta S^{\ddagger} = +2$ eu) for the reaction of $Zn(CH_3)_2$ with $In(CH_3)_3$. The reaction in triethylamine appears to proceed through a dissociation path, which would account for the high activation energy and the near-zero entropy of activation. The reaction in ether may also proceed by this route, but could also proceed by the path involving the five-coordinate transition state V. The difference in entropy of activation is indicative of this change in mechanism but is not a sufficiently compelling argument to permit one to rule out the other possibility.

It is anticipated that additional studies may provide data to distinguish among these cases and, clearly, further examination of solvent effects is necessary to determine if five-coordinate paths are generally available for the exchange of alkyl groups on organometallic compounds.

Acknowledgment. The authors wish to thank the National Science Foundation for support of this work through NSF Grants No. GP-6762 and GP-8323. K. L. H. also thanks NASA for a Traineeship from 1966 to 1969.