bility in these states. Other specific factors may prevent a metal from exerting catalysis even though it fulfills these requirements. Thus, chromium, for example, forms such a stable oxo complex of the necessary acid strength that the reaction occurs through a different mechanism. Finally, it was shown that the effects of the recognized ammonium nitrate decomposition catalysts, copper chromite and Prussian Blue, were small compared to the catalysis observed with the best synergistic combinations described herein.

Alkyl Exchange Reactions Involving Organometallic Derivatives of Groups II and III[1]

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Abstract: Kinetic and activation energy studies were made on the methyl group exchange reactions between dimethylcadmium and trimethylgallium, trimethylindium, and dimethylzinc. The results indicate that all reactions are bimolecular in nature with the relative rates of reaction toward dimethylcadmium being $Ga(CH_3)_3 > In(CH_3)_3 \gg Zn(CH_3)_2$. The activation energies for these systems are 7.8 ± 0.8, 8.4 ± 0.2, and 17.0 ± 1.0 kcal/mole, respectively. All kinetic parameters have been obtained by complete line-shape analysis of the nmr spectra by use of modifications of the McConnell equations to simulate theoretical spectra. An attempt is made to correlate the rates of exchange to the Lewis acidity of the organometallic species.

Nuclear magnetic resonance techniques have made possible the study of exchange of alkyl groups in organometallic systems. In the past, however, little quantitative work has been done involving organometallic derivatives of groups II and III.

Much of the effort of group III alkyl exchange has been placed on the study of reactions involving aluminum compounds. It has been reported by Brown and Williams[3] that the rate of methyl group exchange between $Al_2(CH_3)_6$ and $Ga(CH_3)_3$ is determined by dissociation of the trimethylaluminum dimer, with an activation energy of 16.5 kcal/mole. The activated monomer of $Al(CH_3)_3$ then reacts with a molecule of $Ga(CH_3)_3$, thereby effecting exchange. Similar findings were reported for the $Al_2(CH_3)_6$–$In(CH_3)_3$ system.

This dissociation process is found only in the alkylaluminum series since these compounds are unique among the saturated derivatives of group III in that they exist as dimers in solution.[4] It appears, however, that other compounds of groups II and III can assume four-centered structures as intermediates for alkyl exchange and that the rate of formation of such an intermediate would determine the rate of alkyl exchange. It has been found that when two group III compounds are involved in the exchange studies, the rate of exchange is very fast. For example, self-exchange of methyl groups between molecules of $Tl(CH_3)_3$ proceeds in a bimolecular fashion with an activation energy of 6.3 kcal/mole.[5] The rate of exchange of methyl groups between $Ga(CH_3)_3$ and $In(CH_3)_3$ is so fast on the nmr time scale that only one resonance is observed at −70°.[3,6]

Exchange reactions of group II alkyls seem to be much slower. Self-exchange does not occur between $Cd(CH_3)_2$ molecules in the absence of catalytic impurities,[7,8] and neither $Cd(CH_3)_2$ nor $Zn(CH_3)_2$ exchanges with $Hg(CH_3)_2$ on the nmr time scale.[9] Exchange has been observed between $Zn(CH_3)_2$ and $Cd(CH_3)_2$.[10] The results, obtained using simplifying assumptions for the cadmium spectra, indicated a bimolecular reaction very much slower than the group III reactions.

These studies, along with the earlier investigations of McCoy and Allred,[10] show that alkyl exchange between compounds of group III and those of group II to be intermediate between the extremes mentioned above. In this work, we have studied the reactions of three organometallic compounds, $Ga(CH_3)_3$, $In(CH_3)_3$, and $Zn(CH_3)_2$, with one reference compound, $Cd(CH_3)_2$. This has been done in order to study the effect of the various compounds on the formation of the bridged activated species which is reflected in the rates of exchange.

Experimental Section

$Ga(CH_3)_3$,[11] $In(CH_3)_3$,[12] $Cd(CH_3)_2$,[13] and $Zn(CH_3)_2$[14] were all prepared by previously reported methods.

All nmr samples in this study were made by standard high vacuum techniques in 5-mm o.d. sample tubes with either dichloromethane

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(1) Presented in part by K. L. Henold, J. Soulati, and J. P. Oliver at the 156th National Meeting of the American Chemical Society, Atlantic City N. J., Sept 1968.

(2) Recipient of a NASA Traineeship, 1966–1969.

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(4) Unsaturated derivatives of other group III metals have been proven dimeric in solution: J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, **24**, 953 (1962); E. A. Jeffery and T. Mole, *J. Organometal. Chem.*, **11**, 393 (1968).

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or methylcyclohexane solvent and cyclopentane internal standard. Dichloromethane was dried by refluxing over barium oxide, and methylcyclohexane was dried by refluxing over sodium–potassium alloy. Nmr samples were run on a Varian A-60A or Joelco JNM-4H-100 spectrometer with standard variable-temperature accessories. Chemical shifts were determined by linear interpolation between audiofrequency side bands.

The concentrations of $Ga(CH_3)_3$ and $Zn(CH_3)_2$ were determined by pressure–volume measurements on the vapor, and that of $In(CH_3)_3$ by weight. Since $Cd(CH_3)_2$ reacts with mercury metal, vacuum distillation results in the formation of some $Hg(CH_3)_2$, thereby making it difficult to know the accurate amount of $Cd(CH_3)_2$ present in solution by the direct measurement of the $Cd(CH_3)_2$ added. The method by which this concentration was obtained for use in this work is discussed later. An nmr investigation showed that the $Hg(CH_3)_2$ present in solution does not interfere with the exchange studies since it undergoes no exchange with any of the individual components on the nmr time scale.

Interpretation of Nmr Data

When treating systems containing dimethylcadmium, three naturally occuring isotopes of cadmium must be considered. These are Cd^{111} (12.9%, $I = 1/2$), Cd^{112} (74.8%, $I = 0$), and Cd^{113} (12.3%, $I = 1/2$). Since both of the nuclei of spin $1/2$ can exist in each of two spin states, there are five sites with which the other reacting moiety could exchange methyl groups. Therefore, considering all species in solution this may be treated as a six-site exchange problem at rates slow enough to keep the methyl groups on the cadmium atoms from approaching equivalence (*i.e.*, only those spectra were used which exhibited cadmium satellites with proper coupling constants).

Within this region the McConnell modification to the Block equations[15] as expanded to include six sites. To simplify the calculations three assumptions were made: (1) there is no exchange of methyl groups between dimethylcadmium molecules on the nmr time scale; (2) the lifetimes of methyl groups on all cadmium species are equal; and (3) the probabilities of the gallium, indium, or zinc moieties reacting with any given cadmium isotope is a function of the relative abundance of that isotope.

For the modified Block equations of McConnell, the rate of change of the complex magnetic moment, G_j, for the *j*th site is given by

$$\frac{dG_j}{dt} + \alpha_j G_j = -i\gamma H_1 p_j M_0 + \sum_k (\tau_{kj}^{-1} G_k - \tau_{jk}^{-1} G_j)$$

where $\alpha_j = T_{2j}^{-1} - i(\omega_j - \omega)$, where ω is the chemical shift in radians and τ_{jk}^{-1} is the probability per unit time of the group jumping from the *j*th to the *k*th site. Since the measurements are made under steady-state conditions, $dG_j/dt = 0$. The resulting six linear equations are solved for the complex magnetic moment, $G = \sum_j G_j$. The absorption spectra are represented by the imaginary part of the complex moment.

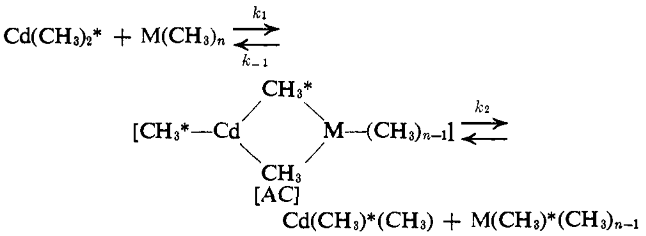
A program was written for an IBM 360-50 computer to simulate the nmr spectra. Input parameters included chemical shift differences between the reacting species, coupling constants, and natural line widths. An estimated value of the mole fraction of the protons on both species relative to the total number of protons of the interacting species (obtained from integration of the spectra under nonexchange conditions), an estimation of the lifetime for a methyl group in a given environment, and a series of intensities obtained at regular intervals along the experimental spectra are also included.

The program calculated an intensity for each of the frequencies for which an experimental intensity was submitted. Both the experimental and calculated intensities were normalized, and the sum of the squares of the differences between the experimental and calculated curves were determined. The lifetime of the methyl groups and the mole fractions were varied until the sum of the squares of the differences was minimized.

As mentioned previously, the concentration of $Cd(CH_3)_2$ cannot be determined directly with the techniques used. However, since the mole fraction of protons on the interacting species can be first estimated by integration and further refined by the iterative procedures just outlined, and the concentration of the gallium, indium, or zinc species is known, the $Cd(CH_3)_2$ concentration can be determined. It must be emphasized, though, that the accuracy of the concentration of the cadmium species is limited by the accuracy of the concentration of the other reacting moiety, and is not independently determined. Despite this fact, it is meaningful to compare the cadmium concentration so determined with the lifetime of the methyl group on the various sites to further substantiate the postulated mechanisms. A comparison of a typical calculated and experimental spectra is shown in Figure 1.

Results and Discussion

The results of variable-temperature nmr studies on the alkyl exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$, $In(CH_3)_3$, and $Zn(CH_3)_2$, respectively, are shown in Table I. The studies on the gallium system were done at −54°, the indium at −41°, and the zinc at +70°. The results indicate that in each system the rate of exchange is proportional to the concentration of each species, suggesting the bimolecular reaction path shown by the following equation.



M = Ga, In, or Zn

n = 3 for Ga and In; 2 for Zn

Using the steady-state approximation for the concentration of the activated complex, we obtain

$$\frac{d[Ac]}{dt} = 2nk_1[Cd(CH_3)_2][M(CH_3)_n] - k_{-1}[AC] - k_2[AC] = 0$$

$$[AC] = \frac{2nk_1[Cd(CH_3)_2][M(CH_3)_n]}{k_{-1} + k_2}$$

but

$$k_{-1} = k_2$$

$$\text{rate} = k_2[AC]$$

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[15] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10, and references therein.

Table I. Kinetic Data for Alkyl Exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$, $In(CH_3)_3$, and $Zn(CH_3)_2$

$[M(CH_3)_n]$, *M*	$[Cd(CH_3)_2]$, *M*	$1/\tau_{M-CH_3}$, sec^{-1}	$1/\tau_{Cd-CH_3}$, sec^{-1}	$(2/\tau_{Cd-CH_3})/n[M(CH_3)_n]$, l. $mole^{-1}$ sec^{-1}	$(1/\tau_{M-CH_3})/[Cd(CH_3)_2]$, l. $mole^{-1}$ sec^{-1}
		M = Ga,[a] *n* = 3, −54°, Dichloromethane Solvent			
0.197	0.335	6.9	6.1	20.6	20.6
0.327	0.306	5.4	8.7	17.7	17.7
0.414	0.317	6.5	12.8	20.6	20.5
0.421	0.343	5.3	9.8	15.5	15.5
0.545	0.512	6.2	9.9	12.1	12.1
0.573	0.533	6.2	10.0	11.6	11.6
0.413	0.642	10.7	10.3	16.6	16.7
0.450	0.386	5.5	9.6	14.2	14.2
0.248	0.661	15.5	8.7	23.4	23.4
0.260	0.923	15.6	6.6	16.9	16.9
0.752	1.05	11.5	12.3	10.9	10.9
0.940	0.917	11.5	17.6	12.5	12.5
				k_1 = average = 16.1 ± 4.0 l. $mole^{-1}$ sec^{-1}	
		M = In, *n* = 3, −41°, Dichloromethane Solvent			
0.170	0.260	4.7	4.6	18.0	18.1
0.148	0.180	3.3	4.1	18.4	18.4
0.138	0.358	9.3	5.4	25.9	25.9
0.259	0.097	2.0	7.9	20.3	20.3
0.282	0.227	6.1	11.4	26.8	26.9
0.221	0.531	11.4	7.1	21.4	21.4
				k_1 = 21.8 ± 3.8 l. $mole^{-1}$ sec^{-1}	
		M = Zn, *n* = 2, +70°, Methylcyclohexane Solvent			
0.167	0.210	3.6	2.8	16.8	17.1
0.140	0.192	2.8	2.0	14.3	14.6
0.337	0.785	14.5	6.2	18.4	18.5
0.497	0.883	19.5	11.0	22.1	22.1
				k_1 = 18.9 ± 3.0 l. $mole^{-1}$ sec^{-1}	

[a] The data obtained for the gallium–cadmium systems show a very small additional broadening of the $Cd-CH_3$ resonances which cannot be accounted for on the basis of the exchange mechanism present here. It should not effect the results appreciably as indicated by the measured lifetime of the gallium-methyl species which can be directly determined.

$$\text{rate} = \frac{2nk_1k_2[Cd(CH_3)_2][M(CH_3)_n]}{2k_2}$$

$$\text{rate} = nk_1[Cd(CH_3)_2][M(CH_3)_n]$$

$$\frac{1}{\tau_{Cd-CH_3}} = \frac{nk_1[Cd(CH_3)_2][M(CH_3)_n]}{2[Cd(CH_3)_2]} = \frac{n}{2}k_1[M(CH_3)_n]$$

$$\frac{1}{\tau_{M-CH_3}} = \frac{nk_1[Cd(CH_3)_2][M(CH_3)_n]}{n[M(CH_3)_n]} = k_1[Cd(CH_3)_2]$$

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

Since the methyl groups are nondistinguishable, the effective concentrations of the group II and group III species are taken as two and three times the molar concentrations, respectively.

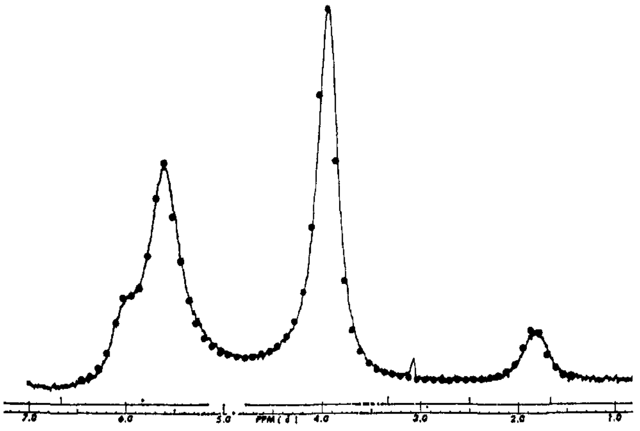

Figure 1. Comparison of an experimental and calculated (●) spectra for the $In(CH_3)_3$–$Cd(CH_3)_2$ system. The spectrum is on a 100-cps sweep width.

In the last two columns of Table I are listed rate constants calculated from the methyl group lifetimes and molar concentration of the reacting species. It is clear that the data obtained are consistent with the mechanism for which the rate equations were derived.

The Arrhenius plot of ln $1/\tau_A$ *vs.* $1/T$ for each of these systems is shown in Figure 2. The values for the activation energies are summarized in Table II with other kinetic and activation parameters. The negative entropies of activation, shown in the last column, are consistent with the bridged activated species. From the values of the

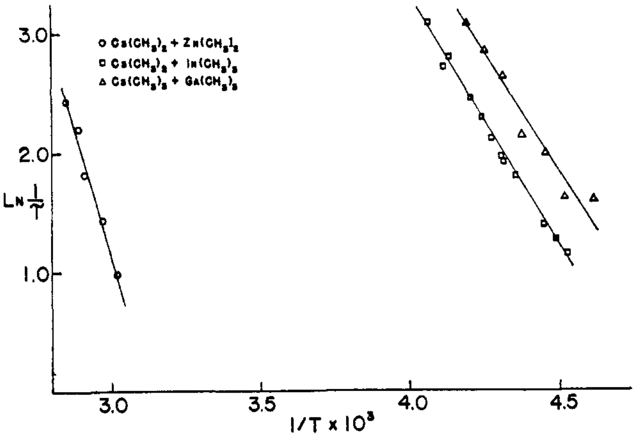

Figure 2. Arrhenius activation energy plots of log $1/\tau$ *vs.* $1/T$(°K).

Table II. Activation Parameters for the $Cd(CH_3)_2$ Exchange with $Ga(CH_3)_3$, $In(CH_3)_3$, and $Zn(CH_3)_2$

	$\Delta E^{\ddagger}$, kcal/mole	Temp, °C	k, l., mole^{-1} sec^{-1}	$\Delta S^{\ddagger}$,[a] eu
$Cd(CH_3)_2 + Ga(CH_3)_3$	7.8 ± 0.8	25	1860	-19
$Cd(CH_3)_2 + In(CH_3)_3$	8.4 ± 0.2	25	1300	-18
$Cd(CH_3)_2 + Zn(CH_3)_2$	17.0 ± 1	25	0.42	-5.3

[a] $\Delta S^{\ddagger}/2.303R = (-\Delta H^{\ddagger}/2.303RT) + \log K/h + \log T - \log k_1$: K = Boltzmann's constant, k_1 = rate constant, and $\Delta H^{\ddagger} = \Delta E^{\ddagger} - RT$.

rate constants given earlier, and the activation energies, rate constants were calculated for each of the systems at a common temperature using the Arrhenius equation. These values are given in Table II and allow a basis for comparison.

In the light of these results we can make some reasonable conclusion as to the factors which influence the rate of alkyl exchange in organometallic systems. Assuming a bimolecular reaction path with a bridged species as the transition state, those factors which increase the bridge stability would increase the rate of exchange. This would have as its limit, of course, those systems for which the bridged species becomes a stable moiety. Such a case is trimethylaluminum, where the determining factor in the rate of bridge-terminal exchange is the activation of the dimer.[3]

A common compound, $Cd(CH_3)_2$, was used in all of these systems in an attempt to establish a reference by which the bridging ability of the other three species could be compared. The solvents used, dichloromethane for $Ga(CH_3)_3$ and $In(CH_3)_3$ and methylcyclohexane for the $Zn(CH_3)_2$, were necessary because of solubility and temperature requirements of the individual systems. The difference in observed rates in these two solvents is thought to be small for the systems under investigation. Using dichloromethane for the $Zn(CH_3)_2$-$Cd(CH_3)_2$ system should, however, tend to reduce the large difference among the rates of the systems since it appears that a coordinating solvent tends to decrease the rate of exchange for group III exchange reactions, but increases similar reaction for group II systems.[7,8] Further work on solvent effects are now underway.

The second-order rate constants shown in Table II are 1860, 1300, and 0.42 l. mole^{-1} sec^{-1} for the $Ga(CH_3)_3$, $In(CH_3)_3$, and $Zn(CH_3)_2$ systems, respectively, at 25°. Based on the previous discussion this would indicate an order of bridging stability with dimethylcadmium as follows: $Ga(CH_3)_3 > In(CH_3)_3 \gg Zn(CH_3)_2$. If the methyl group of $Cd(CH_3)_2$ which acts as a bridging group is considered a Lewis base, the formation of the bridged species can be compared to an acid-base reaction that results in formation of an adduct. The stability of the bridge and, therefore, the rate of exchange could be compared to the heat of formation of each of the three species with an unidentate base, such as trimethylamine. Such a comparison is feasible because of the factors involved in the formation of the acid-base adduct including those factors involved in the formation of the bridged transition state, namely, the distortion of the molecule from its normal configuration to that in the complex, and the ability of the metal to accept electrons once in the proper geometric configuration.

In the case of the trimethylamine adducts, the heats of formation are 21.0 kcal/mole for trimethylgallium,[16] and 19.9 kcal/mole for trimethylindium.[17] There is no value available for the dimethylzinc adduct, but since it is extensively dissociated at room temperature,[18] the value for the heat of formation must be substantially lower than the gallium and indium counterparts.

Our results on this limited series of compounds show that the rate of exchange of alkyl groups between organometallic species and a reference compound are roughly proportional to the Lewis acidity of the organometallic species. Further tests are needed to show if this sample criterion for estimating the exchange rate in these systems is generally valid.

Acknowledgment. The authors thank the National Science Foundation for partial support of this work under Grant GP-6762 and GP-8323, and Mr. Paul Scherr for his help in writing the computer programs used herein.

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