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18, 71647-14-8; 19, 71647-15-9; methyltriphenoxyphosphonium iodide, 17579-99-6; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7; 6-(benzamidomercuri)purine, 71647-16-0; 2,2-dimethoxypropane, 77-76-9.

Hydrometalation. 3. Hydroalumination of Alkenes and Dienes Catalyzed by Transition Metal Halides

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Bis(dialkylamino)alanes, $\text{HAL}(\text{NR}_2)_2$, react with alkenes and dienes in the presence of a catalytic amount of Cp_2TiCl_2 to provide high yields of hydrometalation product. 1-Octene reacts with $\text{HAL}[\text{N}(i\text{-Pr})_2]_2$ in benzene at 40 °C in the presence of 5 mol % Cp_2TiCl_2 in 10 min to form $n\text{-C}_8\text{H}_{17}\text{Al}[\text{N}(i\text{-Pr})_2]_2$ in 93% yield. The formation of the hydrometalation product was determined by quenching the reaction mixtures with D_2O or iodine. The hydrometalation products react with benzaldehyde and benzophenone to form tertiary amines in high yield.

Considerable current interest in organic synthesis is centered around the use of transition metal hydrides for the hydrometalation of alkenes and dienes. For example, recent reports show that stoichiometric amounts of transition metal hydrides can reduce unsaturated organic compounds. Conjugated $\text{C}=\text{C}$ or $\text{C}=\text{N}$ bonds¹⁻⁶ have been reduced, and organic halides have been reductively dehalogenated by $[\text{HFe}(\text{CO})_4]^-$ and by several derivatives of "CuH".⁸⁻¹¹ In protic media,¹² the same transformations can be accomplished by $[\text{HFe}_3(\text{CO})_{11}]^-$. Wailes and Schwartz have reported independently that hydrozirconation of alkenes¹³⁻¹⁵ and alkynes^{16,17} also involves a hydrometalation intermediate.

The hydrozirconation of alkenes proceeds through the placement of the zirconium moiety at the sterically least hindered position of the alkene. The authors argue that the formation of the product involves either the regioselective addition of Zr-H to a terminal alkene or Zr-H addition to an internal alkene followed by rapid rearrangement via Zr-H elimination-readdition to place the metal in the least hindered position. Transition metal hydrides are also

catalysts for reactions of unsaturated hydrocarbons, e.g., hydroformylation, hydrogenation, hydrosilation, and isomerization.¹⁸

Recently, the reduction of alkenes and alkynes by the reagent LiAlH_4 -transition metal halide was reported.^{19,20} Although one might assume that this reaction proceeds through a hydrometalation intermediate, deuteration of the reaction mixture shows that only titanium catalysts are effective in the formation of such intermediates. We have found that other first row transition metal compounds (e.g., NiCl_2 and CoCl_2) are effective in catalyzing the formation of reduction products although no evidence for a stable transition metal intermediate has been found.

Our research has centered around an investigation of the hydrometalation of alkenes and dienes, using less expensive and more readily available hydrometalation systems than have been available so far. The importance of forming the hydrometalation intermediate rather than the reduction product (alkane or alkene) lies in the formation of an organometallic compound that can be easily functionalized. Although hydroboration proceeds readily between an olefin and diborane in THF in the absence of a catalyst, the C-B bond is relatively stable and not nearly as susceptible to functionalization as C-Mg or C-Al compounds. In addition, diborane is expensive, toxic, and explodes on contact with air. Although it has been reported that MgH_2 and AlH_3 do not hydrometalate alkenes or alkynes readily compared to B_2H_6 , we have found that the reaction does take place readily and in high yield when certain transition metal halide catalysts are present.

During our investigations, we discovered an excellent hydrometalation system which consists of a bis(dialkylamino)alane ($\text{HAL}(\text{NR}_2)_2$) as the hydrometalating agent, in the presence of a catalytic amount of transition metal halide (particularly bis(cyclopentadienyl)titanium dichloride, Cp_2TiCl_2). Since $\text{HAL}(\text{NR}_2)_2$ ²¹ compounds can be prepared by the reaction of aluminum metal, hydrogen, and dialkylamine in a one-step reaction in quantitative

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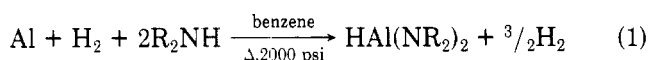
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yield (eq 1), and since the resulting compounds are soluble



in hydrocarbon solvents as well as ethers, these hydrometalating agents should be both versatile and economically attractive.

Our studies involving hydrometalation of alkynes by reaction of $\text{Al}(\text{NR}_2)_2$ compounds in the presence of Cp_2TiCl_2 is reported separately.

Experimental Section

Apparatus. Reactions were performed under nitrogen or argon, using Schlenk tube techniques, or in a glove box equipped with a recirculating system, using manganese oxide columns to remove oxygen and dry ice-acetone traps to remove solvent vapors.²²

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepfer pump.²³ Aluminum was determined by adding excess standard EDTA solution to hydrolyzed samples and then back titrating with standard zinc acetate solution at pH 4, using dithizone as an indicator. Amines in reaction mixtures were analyzed by GLC, using an internal standard. Carbon and hydrogen analyses were carried out by Atlantic Microlab, Inc., Atlanta, Ga.

Analysis of all products arising from the quenching of reactions of alkenes or dienes with hydride reagents with H_2O , D_2O , CO , CO_2 , I_2 , O_2 , or carbonyl compounds was by GLC and/or NMR. All products were isolated by GLC techniques and compared with authentic samples obtained commercially or synthesized by proven methods.

Materials. Solvents. Fisher reagent grade anhydrous diethyl ether was distilled under nitrogen from LiAlH_4 and/or sodium-benzophenone ketyl. Fisher reagent grade tetrahydrofuran (THF) was dried over NaAlH_4 and distilled under nitrogen, using diphenylmethane as a drying indicator. Fisher reagent grade benzene and hexane were stirred over concentrated H_2SO_4 , washed with Na_2CO_3 and distilled water, dried over anhydrous MgSO_4 , and distilled from NaAlH_4 under nitrogen or argon.

Alkenes and Dienes. 1-Octene, 1-methyl-1-cyclohexene, styrene, *cis*-2-hexene, *trans*-2-hexene, 1-hexene, methylenecyclohexene, 2-ethyl-1-hexene, cyclohexene, neohexene, 2,3-dimethyl-2-butene, 2-methyl-2-butene, 1,3-butadiene, 1,3-hexadiene, and 1,5-hexadiene were obtained from Chemical Samples Co. or Aldrich Chemical Corp. The liquids were stored over 4 Å molecular sieves, and the 1,3-butadiene was passed through a tube of 4 Å molecular sieve prior to use.

Ketones and Aldehydes. Fisher Certified A.C.S. grade acetone was dried over MgSO_4 , filtered, distilled from P_2O_5 , and stored over 4 Å molecular sieves. Frinton 4-*tert*-butylcyclohexanone was sublimed under nitrogen. Eastman benzophenone and Aldrich benzaldehyde were distilled under vacuum and stored under argon in the dark.

Preparation of Inorganic Reagents. Alane, AlH_3 , was prepared by the reaction of 100% H_2SO_4 with LiAlH_4 in THF at -78°C and filtered in the drybox,^{24,25} using a fritted glass filter funnel and dry Celite as a filter aid.

H_2AlCl , HAlCl_2 , H_2AlBr , HAlBr_2 , and H_2AlI were prepared in THF by the redistribution reactions of AlH_3 with AlCl_3 , AlBr_3 , or AlI_3 .²⁶ These reagents were characterized by analyzing for aluminum and hydrogen.

$\text{H}_2\text{AlO-}t\text{-Bu}$, $\text{HAl(O-}t\text{-Bu)}_2$, H_2AlOMe , HAl(OMe)_2 , $\text{H}_2\text{AlN}(i\text{-Pr)}_2$, H_2AlNEt_2 , $\text{H}_2\text{AlN}(\text{SiMe}_3)_2$, $\text{HAlN}(i\text{-Pr)}_2$, $\text{HAl(NEt}_2)_2$, and $\text{HAlN}(\text{SiMe}_3)_2$ were prepared by simply adding the appropriate alcohol or amine to AlH_3 in THF in a 1:1 or 1:2 molar ratio.

Hydrogen was evolved during the addition, and the reaction was complete within 15 to 20 min except in the case of the reaction involving diisopropylamine and 1,1,1,3,3,3-hexamethyldisilazane when 3-h reaction times were required. The HAlX_2 compounds were identified by their Al-H stretching frequency assignments:²⁷ $\text{HAl(O-}t\text{-Bu)}_2$, 1850 cm^{-1} ; HAl(OMe)_2 , 1840 cm^{-1} ; $\text{HAlN}(i\text{-Pr)}_2$, 1810 cm^{-1} ; $\text{HAl(NEt}_2)_2$, 1820 cm^{-1} ; $\text{HAlN}(\text{SiMe}_3)_2$, 1800 cm^{-1} . These compounds were also analyzed for their aluminum content by titration with EDTA and back titration with zinc acetate and also by hydrogen analysis, using standard vacuum line techniques.²³

The alkoxy- and aminoalanes were also prepared in benzene by simply removing the THF from the appropriate reagent under vacuum followed by addition of freshly distilled benzene. This procedure was repeated three times until all of the THF had been removed. The solutions were then analyzed for aluminum and hydrogen content.

AlCl_3 , AlBr_3 , and AlI_3 (Alfa Inorganics) were sublimed just prior to use and crushed to a fine powder in the drybox.

The following transition metal halides were obtained from Fisher: TiCl_3 , TiCl_4 , CrCl_3 , MnCl_2 , and ZnBr_2 . Alfa Inorganics supplied the following transition metal halides: VCl_3 , FeCl_3 , FeCl_2 , CoCl_2 , NiCl_2 , Cp_2TiCl_2 , Cp_2ZrCl_2 , $\text{Cp}_2\text{Ni}(\text{PPh}_3)\text{Cl}$, $\text{Ni}(\text{acac})_2$, $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$, allyl $\text{Ni}(\text{dpe})\text{Br}$, Cp_2VCl_2 , and the polymer bound benzyltitanocene dichloride (Grubb's catalyst). All samples of transition metal halides were opened only in the drybox.

General Reactions of Alkenes and Dienes. To a tared $10 \times 18 \text{ mm}$ test tube with a Teflon coated magnetic stirring bar was added a transition metal halide (5 mol % in most cases). The test tube was sealed with a rubber serum cap, removed from the drybox, reweighed, and connected by means of a syringe needle to a nitrogen-filled manifold. In the case of Cp_2TiCl_2 , a saturated solution in benzene (0.02 M) or THF (0.125 M) was prepared (the solutions had to be made fresh each day). One or two milliliters of THF or benzene was introduced into the reaction vessel, the olefin or dienes were added, and after 2 to 3 min the reagent was added. The reaction mixture was then stirred at the appropriate temperature for up to 40 h in some cases. In general, the reactions involving terminal alkenes and dienes were complete in 20 min. The reactions were quenched by various means (see below, Quenching Reactions) and worked up by conventional methods (addition of water, followed by extraction with THF, diethyl ether, or hexane and drying over MgSO_4). Most products were separated by GLC, using a 6 ft 10% Apiezon L 60-80 column with a helium flow rate of 45 mL/min (1-octene (110°C), 1-methyl-1-cyclohexene (50°C), 2-ethyl-1-hexene (50°C), cyclohexene (50°C)) or a 20 ft 10% TCEP column with a helium flow rate of 45 mL/min (1-hexene, *cis*-2-hexene, *trans*-2-hexene, neohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene (45°C , flow rate 25 mL/min)).

General Quenching Techniques. Quenching with Water. After the desired reaction time, the reaction mixture was quenched with H_2O or D_2O or a saturated solution of ammonium chloride to produce the protonated species. The amount of recovered starting material (alkene or diene) and products was determined by the methods described above.

The regioselectivity of the hydrometalation reactions involving styrene was monitored by NMR. The product, ethylbenzene (98%), was deuterated with 90% of the deuterium located on C-1 (indicated by a quartet at 2.64 ppm (2 H), $J = 8 \text{ Hz}$, and a doublet (3 H) at 1.23 ppm, $J = 8 \text{ Hz}$).

Quenching with I_2 . Iodine in benzene was added to the catalytic hydroalumination reaction product after the desired reaction time. The mixture was stirred at room temperature for 1 h and water was added, followed by a saturated solution of sodium thiosulfate. The organic layer was separated and dried over sodium sulfate and analyzed by GLC or NMR. This procedure was followed for the following substrates: 1-octene, 1-hexene, *cis*-2-hexene, *trans*-2-hexene, and 3-hexene. The iodoalkanes prepared in this manner were confirmed by comparison with authentic samples.

Reactions with Carbonyl Compounds. A stoichiometric amount of carbonyl compounds (acetone or benzaldehyde) was added to the hydroalumination product followed by additional

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Table I. Reactions of 1-Octene with $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ in a 1:1 Ratio in the Presence of 5 mol % Catalyst^a

catalyst	% of octane ^b	% of deuterium incorp
TiCl_3	95	65
TiCl_4	97	80
VCl_3	10	0
CrCl_3	5	0
MnCl_2	3	0
FeCl_2	5	0
FeCl_3	7	0
CoCl_2	99	10
NiCl_2	99	10
Cp_2TiCl_2	99	93
Cp_2ZrCl_2	5	95
$\text{CpNi}(\text{dpe})\text{Cl}$	99	5
$\text{Ni}(\text{acac})_2$	5	0
$\text{Ni}(\text{PET}_3)_2\text{Br}$	90	7
$\pi\text{-allylNi}(\text{dpe})\text{Br}$	81	10
polymer bound benzyl-titanocene dichloride	99	0
Cp_2VCl_2	15	2
CuI	5	0
ZnBr_2	5	0

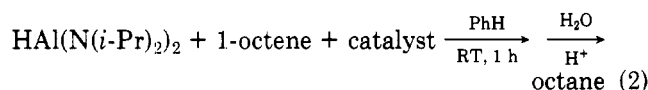
^a All reactions were carried out in benzene at room temperature for 30 min under an argon atmosphere. ^b The yield was determined by GLC, using hexane as the internal standard.

stirring for 10 h. The reaction mixtures were then worked up by addition of water. The organic layer was separated, dried over MgSO_4 , filtered, and analyzed by NMR techniques.

When $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ was allowed to react with 1-octene in the presence of 2 mol % of Cp_2TiCl_2 and then with benzaldehyde, the major product was diisopropylbenzylamine. The following data were obtained on the product: N^{D_5} 1.5300; NMR (CDCl_3 , Me_4Si) δ 1.01 (12 H doublet, $J = 5$ Hz), 2.66–3.34 (2 H multiplet), 3.63 (2 H singlet), 7.10–7.40 (5 H multiplet); mass spectrum, m/e (rel intensity) 191 ($M^+ 6$).

Results and Discussion

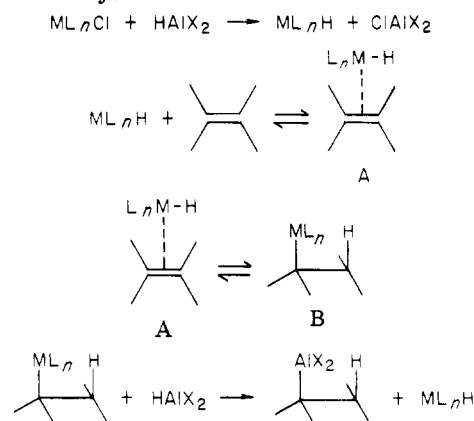
Reactions of Alkenes. 1-Octene was chosen for the initial evaluation of catalysts in the study of hydroalumination of olefins. Bis(diisopropylamino)alane, $[\text{HAL}(\text{N}(i\text{-Pr})_2)_2]$, a representative alane, was allowed to react with 1-octene in the presence of 5 mol % of various transition metal compounds (eq 2). Nearly quantitative yields



of octane were obtained when TiCl_4 , TiCl_3 , CoCl_2 , NiCl_2 , Cp_2TiCl_2 , polymer bound benzyltitanocene dichloride, $\text{CpNi}(\text{Ph}_3\text{P})\text{Cl}$, $\text{Ni}(\text{PET}_3)_2\text{Br}_2$, and $\pi\text{-allylNi}(\text{dpe})\text{Br}$ were used as catalysts (Table I). The intermediate formation of the octylaluminum compound was monitored by the deuterium incorporation when the reaction mixture was quenched with D_2O . Even though the yields of octane were high, for several catalysts, only the titanium catalysts provided high yields of product showing deuterium incorporation. The best catalyst for the hydrometalation reaction (eq 2) appears to be titanocene dichloride, Cp_2TiCl_2 .

Scheme I outlines the proposed mechanism involved in the catalytic hydrometalation process. The transition metal halide is proposed to react with the alane to form the transition metal hydride and ClAlX_2 . The active hydroalumination species is presumed to be the transition metal hydride, and the reducing ability of the active species is believed to be due to d-orbital overlap between the metal ion and the unsaturated carbon-carbon bond. Under this assumption, $\text{Cu}^{\text{I}}(\text{d}^{10})$ and $\text{Zn}^{\text{II}}(\text{d}^{10})$ have no empty d orbitals

Scheme I. Proposed Catalytic Hydrometalation Mechanism



to overlap with the olefin, and $\text{Mn}^{\text{II}}(\text{d}^5)$ with the d orbitals half filled would be predicted to have a lower activating ability. Under the conditions described above, Cu, Zn, and Mn catalysts are considerably slower reacting than the titanium cobalt or nickel catalysts.

Mixing the reactants produces a blue-violet color characteristic of the transition metal hydride.²⁸ Although Cp_2TiCl_2 is an effective catalyst,²⁹ in the case of Cp_2TiMe_2 , no color change was observed and the olefin was recovered unreacted. This result can be explained on the basis that the chloride in titanocene dichloride is a better leaving group than the methyl group in dimethyl titanocene.³⁰ Thus, the necessary Ti-H bond formation takes place much more readily in the reaction of Ti-Cl with H- AlX_2 than does Ti- CH_3 . The transition metal hydride then coordinates with the unsaturated substrate, forming the π complex A.

The next step involves addition of the transition metal hydride to the unsaturated substrate, forming compound B. Hoffman³¹ proposed that specific activation of the alkene or diene should be accomplished when a d^0 metal (e.g., $\text{Cp}_2\text{Ti}^{\text{IV}}\text{Cl}_2$) is involved. That is, the d^0 metalalkyl B should predominate over the unsaturated complex A at equilibrium. Once the alkyl transition metal compound is formed, a transmetalation step with the alane takes place. Hart and Schwartz³² have shown that alkyl groups can be transferred from zirconium to aluminum simply by treatment with AlCl_3 . It is suggested that a similar process occurs in the analogous titanium system. The transition metal hydride complex which is also formed in this step can react with more substrate to continue the hydrometalation process.

In order to determine the nature of the reaction intermediate when alkene is allowed to react with $\text{HAL}(\text{NR}_2)_2$ in the presence of transition metal halides, deuterium incorporation experiments were carried out by quenching the reaction mixture with deuterium oxide (Table I). These results imply that the hydrometalated transition metal halide intermediate is not stable under the conditions studied except for the titanium catalysts (Grubb's catalyst is an exception). In other words, the addition and transmetalation steps (Scheme I) involving first addition then alkyl transfer from the transition metal to aluminum

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Table II. Reactions of 1-Octene with $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ in a 1:1 Ratio in the Presence of 5 mol % Cp_2TiCl_2 Followed by D_2O Quench^a

temp, °C	time, min	solvent	atmosphere	% of deuterium incorp
RT	60	THF	N ₂	78
RT	60	THF	Ar	87
RT	60	benzene	N ₂	88
RT	60	benzene	Ar	93
40	10	THF	N ₂	75
40	10	THF	Ar	85
40	10	benzene	N ₂	88
40	10	benzene	Ar	93

^a All reactions were carried out in benzene solvent.

Table III. Reactions of 1-Octene with $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ in a 1:1 Ratio in the Presence of 5 mol % Cp_2TiCl_2 : Effect of Temperature and Catalyst Concentration

mol % of Cp_2TiCl_2	temp, °C	time, h	% of octane ^b	% of deuterium incorp
5	58	2	100	88
10	58	1	100	83
20	58	0.25	100	86
5	25	12	100	86 ^c
5	25	1.5	10	

^a Reactions were carried out in benzene under a nitrogen atmosphere. ^b The yield was determined by GLC, using hexane as the internal standard. ^c The percentage of deuterium incorporation increased to 93% when the reaction was conducted under an argon atmosphere and was complete in 15 min.















proceed well only when titanium catalysts are used.

Several experiments were carried out in an attempt to stabilize the carbon-transition metal bond B by varying the ligands attached to the transition metal. It is expected that ligands are capable of stabilizing the transition metal compounds by dispersing the d orbitals of the transition metal through the attached ligands. The addition of triphenyl- or triethylphosphine to nickel chloride did not have much of an effect on the percent deuterium incorporation; however, the addition of cyclopentadienyl ligands to TiCl_4 had a pronounced effect on the formation of deuterium incorporation product (93%).

The amount of deuterium incorporation increased when the solvent was changed from THF (78%) to benzene (88%) and when the atmosphere was changed from nitrogen (88%) to argon (93%) (Table II). The changing of the atmosphere from nitrogen to argon increased the amount of deuterium incorporation observed, probably due to N₂ fixation by titanium. Changing the solvents from THF to benzene also increased the amount of deuterium incorporation presumably due to the inability of benzene to donate a hydrogen atom during homolytic cleavage of the intermediate R-Ti compound, as would be the case for THF.

The effect of catalyst concentration and temperature on the rate and extent of formation of hydroalumination product when $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ and 1-octene were allowed to react in the presence of Cp_2TiCl_2 in benzene was studied. The results (Table III) show that the reaction rate is substantially increased by both an increase in catalyst concentration (2 h to 15 min at 58 °C when the catalyst concentration is increased from 5 to 20 mol %) and by an increase in temperature (12 to 2 h at 5 mol % catalyst when the temperature is raised from 25 to 58 °C). The yield of octane is quantitative, and the deuterium incorporation is 93% when argon is used as an atmosphere. For

Table IV. Reactions of Alkenes with $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ in a 1:1 Ratio in the Presence of 5 mol % Cp_2TiCl_2 Followed by D_2O Quench^a

alkene	hydrolysis product (%)	% of deuterium incorp
1-octene ^c	octane (99)	93
<i>cis</i> -2-hexene	hexane (99)	83
<i>trans</i> -2-hexene	hexane (99)	81
	 (47)	20
	 (99)	72
	 (trace)	-
	<i>t</i> -BuCH ₂ CH ₃ (99)	10
	 (90)	75
	2-methylbutane (trace)	-
	 (0)	-
	 (100)	98 ^d

^a All reactions were carried out in benzene at 60 °C for 12 h. ^b The yield was determined by GLC, using hexane as the internal standard, except for *cis*- and *trans*-2-hexene, neohexene, and tetramethylethylene when octane was used. The only other compound observed was starting material, if any. ^c The reaction was over in 15 min at room temperature. ^d 90% of the deuterated ethylbenzene was determined to be PhCH(D)CH₃, with PhCH₂-CH₂D accounting for the other 10%.

most of these studies, 5 mol % catalyst, benzene solvent, and a reaction time of approximately 12 h were chosen as a reasonable compromise involving reaction rate, catalyst concentration, and reaction temperature.

Table IV contains the observed results from reaction of a series of alkenes with $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ in the presence of 5 mol % Cp_2TiCl_2 , demonstrating the scope of this reaction. Relative rates for the reactions were found to be styrene ~ 1-octene > 3,3-dimethyl-1-butene > methylenecyclohexane > 2-ethyl-1-hexene >> *cis*-2-hexene ~ *trans*-2-hexene >> cyclohexene >>> 2-methyl-3-butene ~ 2,3-dimethyl-2-butene ~ 1-methylcyclohexene. These rates parallel the rates found by Schwartz for hydrozirconation reactions.¹⁵

The percent deuterium incorporation, which monitored the production of the intermediate alkylaluminum compounds, is given in column 3. The yields were high in all cases except for 3,3-dimethyl-1-butene. A high yield of reaction product, 2,2-dimethylbutane, was obtained (99%), but only 10% deuterium was incorporated in the product. Cyclohexene and the trisubstituted or tetrasubstituted olefins provided only small or undetectable amounts of the corresponding alkanes. This implies that the greater the degree of substitution of the olefin, the slower the reaction.

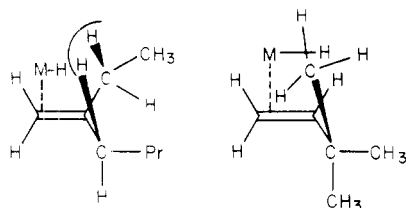
According to Scheme I, the critical step in the catalytic hydrometalation reaction is the production of A which leads to the formation of B in a regioselective manner where the transition metal proceeds to the terminal carbon for primarily steric reasons. The regioselectivity is sub-

Table V. Regioselectivity in the Reaction of $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ with Alkenes in a 1:1 Ratio in the Presence of 5 mol % Cp_2TiCl_2 , as Determined by Quenching with a Benzene Solution of Iodine^a

alkene	product (%) ^b
1-octene	1-iodooctane (80)
1-hexene	1-iodohexane (80)
<i>cis</i> -2-hexene	1-iodohexane (75)
<i>trans</i> -2-hexene	1-iodohexane (75)
3-hexene	1-iodohexane (72) + 3-iodohexane (5)

^a All reactions were carried out in benzene for 24 h at 58 °C, except for 1-octene which was complete in 15 min at room temperature. ^b The yield was determined by GLC, using dodecane as the internal standard.

stantiated by the fact that only 1-iodooctane is produced when the catalytic hydrometalation reaction product of 1-octene is quenched with iodine (Table V). When 2-ethyl-1-hexene is the substrate, the transition metal hydride complex can arrange itself in a manner where the compression effect is minimal. This allows the normal



reaction to proceed and hence a large percentage of deuterium incorporation. But for the neohexene reaction, the now present methyl group exerts a larger compression effect than the hydrogen in the 2-ethyl-1-hexene system. This, therefore, prevents the proper alignment of the groups and forces the reaction to follow a different pathway. Consequently, no deuterium incorporation is observed in the product.

It is interesting that 98% of the ethylbenzene produced from styrene incorporated deuterium after quenching with D_2O (Table IV). Of that 98%, 90% of the deuterium was located in the 1 position of $\text{PhCH}(\text{D})\text{CH}_3$. This result is very unusual in that hydrometalation of styrene with diborane gives about 75% attack of the metal at the terminal carbon, although sterically hindered reagents, such as 9-BBN and disiamylborane, give similar results to those observed for the reaction using $\text{HAL}(\text{NR}_2)_2$ compounds.³³

When 1-hexene, 1-octene, *cis*-2-hexene, and *trans*-2-hexene were allowed to react under the conditions listed above but were quenched with iodine, only the corresponding 1-iodo compounds were produced (Table V). This observation is consistent with previous findings of Schwartz observed for the hydrozirconation process.¹⁵ Zirconium(IV) and titanium(IV) salts can catalyze the isomerization of secondary to primary aluminum reagents.³⁴

Survey of Catalysts for Hydrometalation of Internal Alkenes. According to the literature, all attempted catalytic hydrometalation reactions of internal olefins result in isomerization to the terminal alkane products on hydrolysis. We would like to hydrometalate internal alkenes without isomerization. Therefore, a series of transition metal halides were reacted (as catalysts) with $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ and *cis*-2-hexene in benzene at 60 °C for 24 h (Table VI). The reactions were quenched with iodine and

Table VI. Reaction of *cis*-2-Hexene and $\text{HAL}(\text{N}(i\text{-Pr})_2)_2$ in a 1:1 Ratio with Various Catalysts^a and Quenched with a Benzene Solution of Iodine^{b,c}

catalyst	% of <i>cis</i> -2-hexene	% of <i>trans</i> -2-hexene	% of hexane	% of 1-iodohexane ^e
TiCl_3	20	15	10	55
TiCl_4	19	13	12	56
VCl_3	93	2	0	0
CrCl_3	93	2	5	0
MnCl_2	95	3	2	0
FeCl_2	70	20	10	0
FeCl_3	75	13	12	0
CoCl_2	0	1	99	0
NiCl_2	0	1	99	0
Cp_2ZrCl_2	90	2	5	3
Cp_2TiCl_2	8	12	5	75
$\text{Cp}_2\text{TiCl}_2^d$	85	15	trace	0
$\text{CpNi}(\text{Ph}_3\text{P})\text{Cl}$	3	0	97	trace
$\text{Ni}(\text{acac})_2$	90	0	10	0
$\text{Ni}(\text{PET}_3)_2\text{Br}_2$	10	0	90	0
π -allyl $\text{Ni}(\text{dpe})\text{Br}$	15	0	85	2
Cp_2VCl_2	90	3	7	0

^a 5 mol % in benzene. ^b All reactions were carried out in benzene at 60 °C for 24 h. ^c Yields were determined by GLC with octane as the internal standard and normalized by $\%(\textit{cis}\text{-2-hexene}) + \%(\textit{trans}\text{-2-hexene}) + \%(\text{hexane}) + \%(1\text{-iodohexane})$ 100%. ^d Reaction was carried out in benzene or THF at room temperature for 24 h and monitored every 3 h by GLC. ^e 2-Iodo-hexane was not detected in any of the cases studied.

Table VII. Reactions of 1-Octene with Substituted Alanes in a 1:1 Ratio in the Presence of 5 mol % Cp_2TiCl_2 in Benzene at Room Temperature for 12 h

alane	workup	product (%) ^a
$\text{HAL}(\text{N}(i\text{-Pr})_2)_2$	I_2	1-iodooctane (80)
	D_2O	octane- <i>d</i> ₁ (93)
$\text{HAL}(\text{NEt}_2)_2$	I_2	1-iodooctane (86)
	D_2O	octane- <i>d</i> ₁ (90)
$\text{HAL}[\text{N}(\text{SiMe}_3)_2]_2$	I_2	1-iodooctane (53)
	D_2O	2-iodooctane (47)
	D_2O	octane- <i>d</i> ₁ (93)
H_2AlCl	I_2	1-iodooctane (70)
	D_2O	octane- <i>d</i> ₁ (85)
HALCl_2	I_2	1-iodooctane (68)
	D_2O	octane- <i>d</i> ₁ (83)
$\text{H}_2\text{AlOMe}^{b,c}$	I_2	1-iodooctane (10)
	D_2O	octane- <i>d</i> ₁ (10)
$\text{HAL}(\text{OMe})_2^{b,c}$	I_2	1-iodooctane (0)
	D_2O	octane- <i>d</i> ₁ (0)
$\text{HAL}(\text{O}-i\text{-Pr})_2^{c,d}$	D_2O	octane- <i>d</i> ₁ (15)
$\text{HAL}(\text{O}-t\text{-Bu})_2^{c,d}$	D_2O	octane- <i>d</i> ₁ (15)

^a Yields were determined by GLC based upon 1-octene. ^b Insoluble. ^c The reagents were prepared in THF; however, the solvent was removed under vacuum and replaced by freshly distilled benzene. This procedure was repeated three times. According to GLC, only 5–10% of THF remained. ^d Slightly soluble.





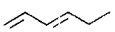
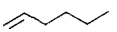
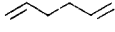
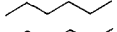

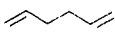

the products analyzed by GLC. No 2-iodohexane was observed, although the cobalt and nickel catalysts produced nearly quantitative yields of hexane (99%). The titanium catalysts (TiCl_3 , TiCl_4 , and Cp_2TiCl_2) provided 1-iodohexane in 55, 56, and 75% yields, respectively, accompanied by 5–15% *trans*-2-hexene. The reaction with Cp_2TiCl_2 is a good one since 20% of the product is recovered starting material, 5% hexane, and 75% 1-iodohexane, indicating approximately 95% yield of $\text{C}_6\text{H}_{13}\text{Al}(\text{NR}_2)_2$. One can conclude from these data that catalytic hydrometalation of internal alkenes proceeds with isomerization of the resulting $\text{RAL}(\text{NR}_2)_2$ product.

Survey of Other Alanes as Hydrometalating Agents. Although bis(diisopropylamino)alane in the

(33) H. C. Brown, Evard F. Knights, and Charles G. Scouter, *J. Am. Chem. Soc.*, **96**, 7765 (1974).

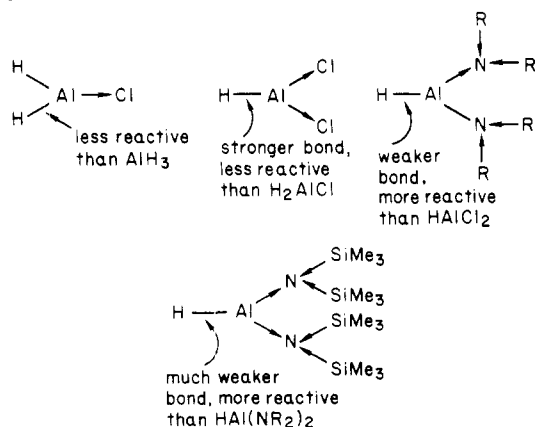
(34) (a) Reinacker, *Angew. Chem., Int. Ed. Engl.*, **68**, 721 (1967); (b) K. Ziegler, *Angew. Chem.*, **68**, 721 (1956).

Table VIII. Reactions of Dienes with $\text{HAL}(\text{N}(\text{i-Pr})_2)_2$ in a 1:2 Ratio in THF or Benzene at Room Temperature for 12 h

diene	solvent	% of recovered diene ^a	products (%) ^a	% of deuterium incorp
	THF	40	 (60) ^b	41
	benzene	42	 (58) ^b	45
	benzene or THF	45	 (55) ^b	45
	THF	10	 (80)  (10)	75
	benzene	10	 (90)	90

^a Yields were determined by GLC with octane as the internal standard. ^b Total yield of olefinic products.

presence of 5 mol % Cp_2TiCl_2 has been shown to be an excellent reagent for accomplishing catalytic hydrometalation, we decided to investigate the effects of other substituted alanes in the catalytic hydroalumination reaction. Table VII lists the results of this investigation, using 1-octene as a representative olefin. As discussed earlier, the bis(diisopropyl)- and bis(diethylamino)alanes produced high yields of 1-iodooctane (80 and 86%, respectively) and octane-*d*₁ (93 and 90%, respectively) when quenched with the appropriate reagent. The mono- and dichloralanes under catalytic hydroalumination conditions produced 97% octane with 85 and 83% deuterium incorporation, respectively. Sato et al.¹⁹ reported a 90% yield of hexane when AlH_2Cl or AlHCl_2 reacted with 1-hexene in the presence of 2% TiCl_4 at 15 °C for 6 or 16 h, respectively. Unfortunately, these reactions were not quenched with D_2O or halogen, which would indicate the extent to which the hydroalumination species was formed. The decrease in rate for HALCl_2 compared to H_2AlCl observed by Sato et al.^{19c} was also observed in the present work. We found that 2–5% of Cp_2TiCl_2 increased the rate of reaction compared to that observed by Sato,^{19b,c} but a relative rate decrease was also observed going from H_2AlCl to HALCl_2 (2 to 6 h for complete reaction). The relative decrease in reaction rate may be due to the electron-withdrawing ability of the chlorine atom which results in the strengthening of the Al–H bond, thus making it less reactive than



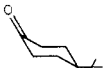

AlH_3 toward Cp_2TiCl_2 as well as the transmetalation step described in Scheme 1. When two chlorine atoms are present, the effect is greater, resulting in an even slower rate. This effect is predictable when comparing $\text{HAL}(\text{NR}_2)_2$

compounds with HALCl_2 on the basis of electronegativities. The electronegativities of nitrogen and chlorine are the same (3.0); however, because alkyl groups are attached to the nitrogen atom, the effect of nitrogen is diminished somewhat by the electron-donating effect of the R groups attached to nitrogen, and therefore, the H–Al bond is weaker and accordingly more reactive. As a result, reactions with $\text{HAL}(\text{NR}_2)_2$ compounds are complete in approximately 15 min, whereas the corresponding reaction with HALCl_2 took 6 h. In the case of $\text{HAL}[\text{N}(\text{SiMe}_3)_2]_2$, a similar effect is also observed, but to a greater degree. When this reaction was quenched with iodine, both 1- and 2-iodooctane were produced in a relative ratio of 53:47 in 90% yield. This was surprising since all of the other reactions quenched with iodine produced only 1-iodooctane. On the electronegativity scale, aluminum, silicon, and nitrogen have values of 1.5, 1.8, and 3.0; therefore, the electron density on aluminum is not decreased as much in $\text{HAL}[\text{N}(\text{SiMe}_3)_2]_2$ as it is in HALNR_2 . The overall result is a more reactive H–Al bond for $\text{HAL}[\text{N}(\text{SiMe}_3)_2]_2$. In Scheme II, we propose an equilibrium between the two complexes A_1 and A_2 . If the formation of $\text{Cp}_2\text{TiH}(\text{Cl})$ or the transmetalation step depends on the reactivity of the alane, then the more reactive the alane, the greater the possibility of forming compound B_2 , which would eventually lead to 2-iodooctane. This evidently is the case with $\text{HAL}[\text{N}(\text{SiMe}_3)_2]_2$, since the reaction with olefin was over in about 10 min at room temperature. Once compounds B_1 and B_2 are formed, both are likely to undergo a transmetalation reaction with $\text{HAL}(\text{NR}_2)_2$ to form C_1 and C_2 . These products in turn can produce the 1- and 2-deuterio- or iodoalkanes when quenched with D_2O or iodine. Presumably, B_2 isomerizes more slowly to B_1 and C_2 to C_1 when the $\text{AL}(\text{NR}_2)_2$ group is $\text{AL}[\text{N}(\text{SiMe}_3)_2]_2$ due to steric reasons.

When a more electronegative atom is incorporated into the reagent, such as oxygen (electronegativity value of 3.5), the reaction is slowed down even more because of a stronger and less reactive H–Al bond, which was demonstrated for H_2AlOMe , $\text{HAL}(\text{OMe})_2$, $\text{HAL}(\text{O-}i\text{-Pr})_2$ and $\text{HAL}(\text{O-}t\text{-Bu})_2$. For the methoxy derivatives which were insoluble in THF or benzene, only the monomethoxy reagent produced 10% octane after 24 h of reaction at room temperature. The diisopropoxy and di-*tert*-butoxy derivatives which were soluble in THF produced only 15% octane.

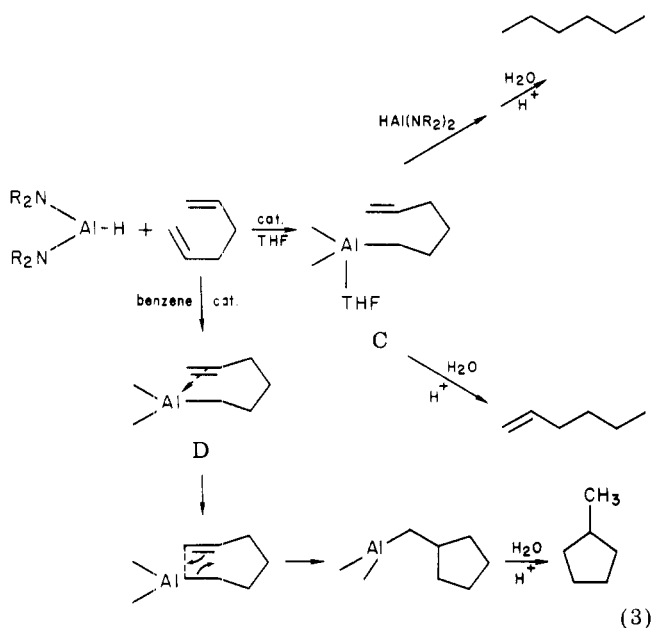
Reactions of Dienes. When dienes (Table VIII) were reacted under the standard conditions, the conjugate dienes (1,3-butadiene and 1,3-hexadiene) yielded only a

Table IX. Reactions of the Hydrometalated Species with Carbonyl Compounds, Oxygen, or Carbon Dioxide in a 1:1 Ratio in Benzene at Room Temperature for 24 h^a

reagent	added carbonyl	% of recovered carbonyl	reduced carbonyl (%)	% of carbonyl addition product	other products (%)
HAl(N(<i>i</i> -Pr) ₂) ₂	acetone	35	(40) 2-propanol		
	benzaldehyde	0	(100) benzyl alcohol		
	benzophenone	0	(100) benzhydrol		
HAl(N(<i>i</i> -Pr) ₂) ₂	 (THF)	30	(45) axial alcohol (18), equatorial alcohol (82)		
	 (benzene)	30	(45) axial alcohol (30), equatorial alcohol (70)		
HAl(N(<i>i</i> -Pr) ₂) ₂ + 1-octene	acetone	70	(5)	2	
	benzaldehyde	0	(10)	trace	PhCH ₂ N(<i>i</i> -Pr) ₂ (90)
	benzophenone	0	(35)	trace	Ph ₂ CHN(<i>i</i> -Pr) ₂ (65)
HAl(NEt ₂) ₂ + 1-octene	acetone	65	(5)	2	
	benzaldehyde	0	(10)	trace	PhCH ₂ NEt ₂ (90)
	benzophenone	0	(38)	trace	Ph ₂ CHNEt ₂ (62)
HAl(N(<i>i</i> -Pr) ₂) ₂ + 1-octene	O ₂	<i>b</i>			
	CO ₂	<i>b</i>			

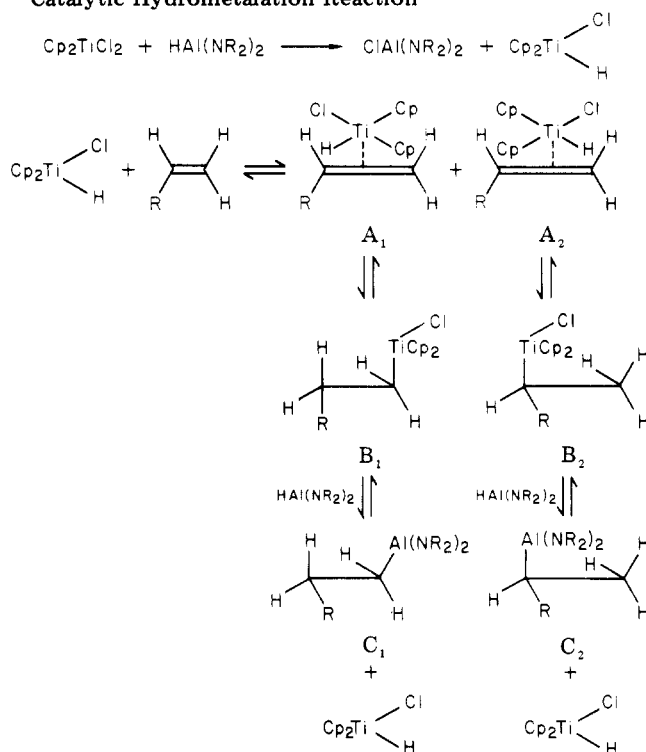
^a Yields for the acetone reactions were determined by GLC based on added carbonyl. Yields for the benzaldehyde and benzophenone reactions were determined by NMR, using acetone as the internal standard. ^b No reaction.

mixture of butenes and hexenes without any alkanes. Also, when quenched with D₂O, only 41–45% of the product showed deuterium incorporation. On the other hand, the nonconjugated diene, 1,5-hexadiene, in THF yielded a mixture of 1-hexene and hexane in 90% yield with 75% deuterium incorporation. However, in benzene, methylcyclopentane was formed in 90% yield with 90% deuterium incorporation. It is interesting that in benzene cyclization takes place,³⁵ whereas in THF it does not (eq 3).



It is suggested that intermediate D, involving complex formation between the vacant orbital of aluminum and the π electrons of the olefinic bond, results in cyclization. Since intermediate C has no vacant p orbital on aluminum to complex with the olefinic bond, the product is either 1-hexene or hexane, depending on whether or not the intermediate reacts with more HAl(NR₂). The hydro-

Scheme II. Proposed Mechanism for the Production of the Kinetic and Thermodynamic Products from the Catalytic Hydrometalation Reaction



alumination and subsequent cyclization of nonconjugated dienes in high yield represents an important synthetic tool and is being explored further in this laboratory.

Reaction of Hydrometalated Product with Carbonyl Compounds. In order to evaluate the extent to which further reactions (other than reactions with D₂O or iodine) can be applied to the newly formed hydroaluminated species, stoichiometric amounts of acetone, benzaldehyde, and benzophenone were added to the reaction mixtures at room temperature. The results of these reactions are listed in Table IX. HAl(N(*i*-Pr)₂)₂, without catalyst, reduced the nonenolizable carbonyl compounds, benz-

aldehyde and benzophenone, quantitatively to the corresponding alcohols. However, acetone was reduced in only 40% yield to 2-propanol with 35% of the starting ketone being recovered presumably because of enolization. This alane also reduced 4-*tert*-butylcyclohexanone to provide 18% axial alcohol and 92% equatorial alcohol in 45% yield with 30% recovered ketone. The relative ratio of alcohols is approximately the same as that observed using AlH_3 ³⁶ in THF (19% axial alcohol). However, in benzene, $\text{Al}(\text{N}(i\text{-Pr})_2)_2$ in a 2:1 ratio of reagent to ketone provided 30% of the axial alcohol and 70% of the equatorial alcohol in 45% yield with 30% the ketone recovered. These experiments served as controls for the reactions which followed in which the hydrometalation product containing catalyst was reacted with a series of ketones.

When 1-octene was added to $\text{Al}(\text{N}(i\text{-Pr})_2)_2$ and catalyst and allowed to react under hydrometalation conditions, and then the reaction mixture was added to acetone or vice versa, it produced only 5% 2-propanol, 2% of the addition product (2-methyl-2-decanol), and 70% recovered acetone. When benzaldehyde was allowed to react with the hydrometalated species formed from the reaction of 1-octene with $\text{Al}(\text{N}(i\text{-Pr})_2)_2$ and Cp_2TiCl_2 , the major product was benzyldiisopropylamine (90%). When $\text{Al}(\text{NET}_2)_2$ was used as the hydrometalating agent, 90% benzyldiethylamine was produced. When benzophenone was allowed to react with $\text{Al}(\text{NET}_2)_2$ or $\text{Al}(\text{N}(i\text{-Pr})_2)_2$, 62–65% of the corresponding amine (Ph_2CHNR_2) was formed in addition to 38% benzhydrol. Only a trace of the expected addition product was observed. Since the normal addition products were observed only in low yields in these reactions, they will not be discussed further, except that this reaction type is being pursued as a route to tertiary amines.

Reaction of the Hydrometalation Product with Oxygen or Carbon Dioxide. R_3Al compounds undergo rapid oxidation in the presence of O_2 to produce, on hydrolysis, alcohols¹⁹ or with CO_2 to produce tertiary alcohols or carboxylic acids, depending on the reaction conditions.³⁷

(36) K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, *Justus Liebig's Ann. Chem.*, **629**, 251 (1960).

When oxygen or carbon dioxide was passed through the hydrometalation reaction mixture of 1-octene and $\text{Al}(\text{N}(i\text{-Pr})_2)_2$ in the presence of Cp_2TiCl_2 , only octane was observed by GLC after workup with saturated ammonium chloride or 10% HCl. The reason for the lack of oxidation can be argued on the basis of inductive effect where nitrogen withdraws electron density from the adjacent carbon atom thereby strengthening the aluminum-carbon compared to R_3Al compounds. The electron-donating ability of the NR_2 group by resonance is diminished because the orbital size different between aluminum and nitrogen prohibits good overlap; thus the overall effect of the NR_2 group on Al-NR_2 compounds is one of electron withdrawal.

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Registry No. 1-Octene, 111-66-0; octane, 111-65-9; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; hexane, 110-54-3; cyclohexene, 110-83-8; cyclohexane, 110-82-7; methylenecyclohexane, 1192-37-6; methylcyclohexane, 108-87-2; 1-methylcyclohexene, 591-49-1; neohexene, 558-37-2; 2,2-dimethylbutane, 75-83-2; 2-ethyl-1-hexene, 1632-16-2; 2-ethylhexane, 589-81-1; 2-methyl-2-butene, 513-35-9; 2-methylbutane, 78-78-4; 2,3-dimethyl-2-butene, 563-79-1; 2,3-dimethylbutane, 79-29-8; styrene, 100-42-5; phenylethane, 100-41-4; 1-hexene, 592-41-6; 3-hexene, 592-47-2; 1-iodooctane, 629-27-6; 1-iodohexane, 638-45-9; 3-iodohexane, 31294-91-4; 1,3-butadiene, 106-99-0; 1,3-hexadiene, 592-48-3; 1,5-hexadiene, 592-42-7; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; 2-iodohexane, 18589-27-0; 1(2)-octane-*d*₁, 71501-04-7; 2-iodooctane, 557-36-8; methylcyclopentane, 96-37-7; acetone, 67-64-1; 2-propanol, 67-63-0; benzaldehyde, 100-52-7; benzyl alcohol, 100-51-6; benzophenone, 119-61-9; benzhydrol, 91-01-0; 4-*tert*-butylcyclohexanone, 98-53-3; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *N,N*-diisopropylbenzylamine, 34636-09-4; *N,N*-diisopropyl- α -phenylbenzylamine, 68714-11-4; *N,N*-diethylbenzylamine, 772-54-3; *N,N*-diethyl- α -phenylbenzylamine, 519-72-2; AlH_3 , 7784-21-6; H_2AlCl , 14644-71-4; HAlCl_2 , 13497-97-7; H_2AlBr , 54844-46-1; HAlBr_2 , 15576-93-9; H_2AlI , 58602-50-9; $\text{H}_2\text{AlO-}t\text{-Bu}$, 15649-64-6; $\text{Al}(\text{O-}t\text{-Bu})_2$, 15649-65-7; H_2AlOMe , 36803-31-3; $\text{Al}(\text{OMe})_2$, 15649-68-0; $\text{H}_2\text{AlN}(i\text{-Pr})_2$, 2826-21-3; H_2AlNET_2 , 24848-99-5; $\text{H}_2\text{AlN}(\text{SiMe}_3)_2$, 71501-02-5; $\text{Al}(\text{N-}i\text{-Pr})_2$, 2826-40-6; $\text{Al}(\text{NET}_2)_2$, 17039-99-5; $\text{Al}[\text{N}(\text{SiMe}_3)_2]_2$, 71501-03-6.

Concerning the Effects of Added Salts on the Stereoselectivity and Rate of Organometallic Compound Addition to Ketones

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The addition of CH_3Li to 4-*tert*-butylcyclohexanone in the presence of LiClO_4 increased the formation of the axial alcohol from 65 to 92% compared to the reaction in the absence of LiClO_4 . This result was attributed to complexation of the ketone by LiClO_4 followed by the addition of CH_3Li to the carbonyl group rather than by addition of a $\text{CH}_3\text{Li-LiClO}_4$ complex directly to the uncomplexed ketone. To complete a more detailed investigation of this unusual result, other organometallic compounds, ketones, and salts were studied in a similar manner. In addition to CH_3Li , *t*-BuLi, PhLi, $(\text{CH}_3)_2\text{Mg}$, and $(\text{CH}_3)_3\text{Al}$ were also allowed to react with 4-*tert*-butylcyclohexanone, 2-methylcyclohexanone, 3,3,5-trimethylcyclohexanone, and norcamphor in the presence of equalmolar ratios of ten different salts in order to study their effect on the stereochemistry of the alcohol products. In addition to stereochemical effects, a major result of the reactions with RLi and R_2Mg in the presence of LiClO_4 was a dramatic increase in the rate of reaction.

Recently, it was reported that a mixture of CH_3Li and $\text{LiCu}(\text{CH}_3)_2$ provides unusually high rate enhancement and

stereoselectivity (92% equatorial attack in diethyl ether) in the methylation of 4-*tert*-butylcyclohexanone compared