

**Reduction of  $(OC)_9Co_3CCO^+PF_6^-$  with Triethylsilane.** (a) **In the Absence of Aluminum Chloride.** The acylium hexafluorophosphate prepared from 2.0 mmol of  $(OC)_9Co_3CCO_2Et$  was slurried in 20 ml of dichloromethane under nitrogen, and 0.80 g (6.6 mmol) of triethylsilane (PCR Inc.) was added. The mixture was stirred at room temperature for 1 hr; a homogeneous solution resulted. The reaction mixture was evaporated under reduced pressure and the residue was extracted with hexane. The red extracts were filtered through a layer of silicic acid and evaporated. The red solid residue was sublimed *in vacuo* at 50° to give 0.65 g of red solid, melting in the range 95–115° with decomposition. Its ir spectrum suggested that a mixture of  $CH_3CCO_3(CO)_9$  and  $HCCO_3(CO)_9$  was present (bands at 2960 w, 2920 m, 2880 m, 2820 m, 1160 m, 1000 s, and 855 m  $cm^{-1}$ ). The entire sample was dissolved in deuteriochloroform and the nmr spectrum which was taken showed that these two products were present in 1 to 1.44 ratio (30 and 43% yields, based on the 0.65 g isolated), respectively, by integration of the resonances at  $\delta$  3.76 and 12.10 ppm.

(b) **In the Presence of Aluminum Chloride.** The acylium hexafluorophosphate was prepared from 2.0 mmol of  $(OC)_9Co_3CCO_2Et$  and slurried in 15 ml of dichloromethane under nitrogen. To this mixture was added 0.75 g (6.0 mmol) of aluminum chloride. A brief evolution of gas commenced but subsided quickly. Addition of 0.70 g (6.0 mmol) of triethylsilane followed. A brief evolution of gas again was observed and the solution turned from brown to red-brown. Tlc (benzene) showed the presence of a single brown material in the solution. After it had been stirred for 10 min at room temperature, the mixture was treated with 150 ml of 15% aqueous HCl and extracted with 100 ml of dichloromethane. The organic layer was dried and evaporated. The brown solid which remained was taken up in benzene. This solution was passed through a layer of silicic acid and evaporated. The residue was recrystallized from hexane to give 0.68 g (74%) of black needles which decomposed without melting around 115° and whose ir spectrum was identical with that of an authentic sample<sup>11</sup> of the aldehyde,  $(OC)_9Co_3CCHO$ .

An experiment in which only 2 mmol of aluminum chloride was added to the acylium hexafluorophosphate prepared from 2 mmol of the cluster-ester and in which this mixture was treated with 6 mmol of triethylsilane gave only  $CH_3CCO_3(CO)_9$  (25%) and  $HCCO_3(CO)_9$  (45%) and none of the aldehyde.

**Reaction of  $(OC)_9Co_3CCO_2CH_2C\equiv CCH_2O_2CCC_9(CO)_9$  with Dicobalt Octacarbonyl.** A 100-ml three-necked flask equipped with a magnetic stirring unit, a nitrogen inlet tube, and a no-air stopper was charged with a solution of the cluster-substituted

acetylene (0.42 g, 0.47 mmol) in 20 ml of anhydrous diethyl ether. Subsequently, a solution of 2.3 g (6.7 mmol) of dicobalt octacarbonyl in 50 ml of diethyl ether was added. The mixture was stirred under nitrogen at room temperature for 90 min, during which time a very slow gas evolution and the separation of a solid were observed. The solvent was evaporated and the red-brown solid remaining was recrystallized from diethyl ether to give 0.41 g (78%) of I, mp 120–121° dec.

**Characterization of Compounds.** The new  $(OC)_9Co_3C$  derivatives prepared during the course of this study are listed in Table III. The ir and nmr spectra of all compounds were recorded. In general, all alkylidynetricobalt nonacarbonyl complexes show five bands in their ir spectrum (Table IV) in the region 2150–1950  $cm^{-1}$

**Table IV.** Ir Spectra of  $(OC)_9Co_3CR$  Complexes

R	C≡O bands, $cm^{-1}$ (in $CCl_4$ unless specified otherwise)
$CO_2H$	2120 m, 2075 vs, 2055 s, 2040 sh ( $CHCl_3$ )
$CO_2CMe_3$	2110 m, 2065 vs, 2044 s, 2018 w, 1980 vw
$C(O)SPh$	2110 m, 2065 vs, 2042 s, 2020 w, 1990 vw
$CONH_2$	2115 m, 2066 vs, 2044 s, 2015 w
$CONMe_2$	2114 m, 2065 vs, 2044 s, 2020 w, 1990 vw
$C(O)Et$	2110 m, 2065 vs, 2040 s, 2020 w, 1990 vw
$C(O)C_6H_4FeC_6H_5$	2108 m, 2065 vs, 2045 s, 2040 sh, 1983 vw
$C(O)C_6H_4NMe_2-p$	2108 m, 2065 vs, 2042 s, 2020 w, 1990 vw

(terminal carbonyl region) with the intensity pattern medium, very strong, strong, weak, and very weak. As such, they serve to identify an  $RCCO_3(CO)_9$  cluster complex, but shifts in these bands with change in apical substituent R among organic groups are so minimal as to have no diagnostic value. Accordingly, only a few such spectra in this region are described as typical examples.

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## Intramolecular Metal-Double Bond Interactions. VI. Metal- $\pi$ -Electron Interactions Observed in Trialkenylaluminum and -gallium Derivatives

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**Abstract:** <sup>1</sup>H nmr data and cryoscopic molecular weight data are presented for several terminal trialkenyl and trialkyl group III metal derivatives. The molecular weight data for the trialkenylaluminum derivatives correspond to a monomer in cyclohexane while under identical conditions the degree of association for the saturated trialkyl-aluminum derivatives is two. The nmr parameters for the trialkenyl group III metal derivatives are substantially perturbed. These data have been interpreted in terms of a direct intramolecular interaction between the metal center and the  $\pi$ -electron system of the olefinic site.

The interaction between a  $\pi$ -electron system and a metal atom has been shown to yield stable complexes with transition metals and it has been established that these complexes play an extremely important role in the stereochemically controlled reactions of these

systems. Similar metal-olefin complexes have been postulated for main group derivatives,<sup>1</sup> and a substantial body of evidence now exists supporting this type of

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interaction. Thus, it has been suggested that, in alkenyllithium, -magnesium, -zinc and -aluminum derivatives, intramolecular metal- $\pi$ -electron interactions occur.<sup>2-5</sup> This type of interaction has also been postulated as the initial step in the intramolecular cyclization processes observed for the 1-hex-5-enyl derivatives of group III metals,<sup>3</sup> for lithium,<sup>6</sup> and for the Grignard reagents.<sup>7-9</sup> These reactions are depicted as occurring *via* an internal addition across the double bond with the ease of reaction shown to be a function of chain length.<sup>10,11</sup> Furthermore, formation of metal- $\pi$ -electron complexes have been considered as the initial step in polymerization reactions catalyzed by aluminum alkyls. The latter has recently been discussed in detail by Egger and Cocks<sup>12</sup> who have proposed that a tight metal-olefin complex plays an important role in this reaction. They further stated that no complex of this type with sufficient stability to study had been reported.

In this paper we present the results of an investigation of group III metal- $\pi$ -electron intramolecular interactions and will demonstrate that the nmr parameters and molecular weight data indicate that these derivatives exist with a thermodynamically stable metal- $\pi$ -electron interaction. Our studies include the investigation of tri-*n*-butyl-, tri-1-but-3-enyl-, tri-*n*-pentyl-, tri-1-pent-4-enylaluminum, tri-1-pent-4-enylgallium, and their trimethylamine adducts.

## Experimental Section

**Reaction Conditions.** All reactions, sample preparations, and physical measurements were carried out either using high vacuum techniques or in an argon-filled inert atmosphere box scavenged with sodium-potassium alloy.

**Reagents.** All solvents were dried over sodium potassium alloy, degassed, and stored on the high vacuum line until needed. All alkenyl and alkyl chlorides were obtained from Chemical Samples Co. and dried over molecular sieves. The dialkenyl- and dialkylmercury compounds used as intermediates were prepared by disproportionation of their respective organomercuric chloride by method described by Nesmeyanov and coworkers.<sup>13</sup> Typically, the alkyl- and alkenylmercuric chlorides were prepared from their respective Grignard reagent and mercuric chloride.<sup>14</sup> All organomercury derivatives were purified by high vacuum distillations with subsequent handling performed in a sodium-potassium scavenged inert atmosphere box.

**Cryoscopic Molecular Weight Measurements.** The molecular weights were determined cryoscopically in cyclohexane ( $K_f = 20.0$ ) using a modified Beckmann<sup>15</sup> apparatus for air-sensitive

**Table I.** Nmr Parameters of Group III 1-But-3-enyl Derivatives<sup>a</sup>

$$R = \begin{array}{c} \text{H}_\alpha \quad \text{H}_D \quad \text{H}_C \quad \text{H}_B \\ | \quad | \quad | \quad / \\ -\text{C}-\text{C}-\text{C}=\text{C} \\ | \quad | \quad \backslash \\ \text{H}_\alpha \quad \text{H}_D \quad \text{H}_A \end{array} \quad R' = [-\text{CH}_2(\text{CH}_2)_2\text{CH}_3]$$

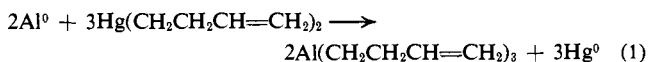
	R <sub>3</sub> Al	R <sub>3</sub> Al·N-(CH <sub>3</sub> ) <sub>3</sub>	R' <sub>3</sub> Al	R' <sub>3</sub> Al·N-(CH <sub>3</sub> ) <sub>3</sub>
$\delta_A$	4.960	4.841		
$\delta_B$	4.847	4.687		
$\delta_C$	5.985	5.888		
$\delta_\alpha$	0.380	-0.54	0.546	-0.107
$J_{AB}$	2.24	2.63		
$J_{AC}$	17.25	17.12		
$J_{AD}$	1.49	1.48		
$J_{BC}$	9.69	9.66		
$J_{BD}$	1.16	1.28		
$J_{CD}$	6.06	6.15		
$J_{\alpha D}$	8.25	8.53	7.75	8.10

<sup>a</sup> Chemical shifts and coupling constants were derived from first-order analysis and are presumed reliable to  $\pm 0.01$  ppm and  $\pm 0.3$  Hz, respectively. Line positions were calibrated by use of audio-frequency side band techniques on a Varian A60-A. All spectra were obtained on cyclopentane solutions with cyclopentane used as an internal standard. The chemical shifts were corrected to TMS by addition of 1.50 ppm to the observed value.  $J$  values are given in Hz.

compounds and a Beckmann thermometer. The reliability of the system was determined by repeated measurements of the molecular weight of Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> in cyclohexane which is dimeric in hydrocarbon solutions. The average deviation in this measurement was found to be 1.6% (experimental molecular weight = 141.7, calculated value = 144.0). The freezing points of the pure solvent and the solutions were determined graphically.<sup>16</sup>

**Nuclear Magnetic Resonance Techniques.** Nmr spectra were recorded on a Varian A60-A spectrometer. Chemical shifts and coupling constants were obtained from the first-order analysis and are reliable to approximately  $\pm 0.01$  ppm and  $\pm 0.3$  Hz, respectively. Line positions were calibrated by use of audiofrequency side band techniques of the solvent peak. Cyclopentane and benzene were used as internal standards. The chemical shifts of cyclopentane solutions were corrected to TMS = 0 by addition of 1.50 ppm to the observed value. The same procedure was employed for benzene solutions, only 7.24 ppm was added to the observed value. Coupling constant values are given in Hertz. All chemical shifts and coupling constant values were obtained from a minimum of two calibrations.

**Tri-1-but-3-enylaluminum.** Tri-1-but-3-enylaluminum, Al(CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>3</sub>, was prepared using a modified method of Buckton<sup>17</sup> by the reaction of an excess of aluminum dust with di-1-but-3-enylmercury in a sealed Pyrex tube with a magnetic stirring bar enclosed for agitation. A mixture of 0.02 mol of di-1-but-3-



enylmercury and 0.03 mol of aluminum dust was added to a Pyrex tube and sealed off, once evacuated to  $10^{-6}$  Torr. The mixture was stirred vigorously for 2 weeks at room temperature. The tube was broken open in a drybox and the liquid decanted into a high vacuum distillation apparatus for further purification. The product, tri-1-but-3-enylaluminum, distilled at 70-75° at  $10^{-5}$  Torr as a colorless liquid. The purity was determined from its nmr spectrum which indicated the presence of a 1-but-3-enyl species bonded to an electropositive metal. Cryoscopic molecular weight measurements showed it to be monomeric having a molecular weight of 187.7 (calculated value for R<sub>3</sub>Al = 192.0;  $n = 0.98$ ). Tri-1-but-3-enylaluminum formed a 1:1 trimethylamine adduct when mixed at room temperature with excess trimethylamine. On removal of the excess amine by vacuum distillation, the compound was a

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**Table II.** Nmr Parameters for Group III 1-Pent-4-enyl Derivatives<sup>a</sup>

$$R = \begin{bmatrix} H_\alpha & H_\beta & H_D & H_C & & H_B \\ | & | & | & | & & / \\ -C & -C & -C & -C & = & C \\ | & | & | & & & \backslash \\ H_\alpha & H_\beta & H_D & & & H_A \end{bmatrix} \quad R' = [-CH_2(CH_2)_3CH_3]$$

	1-Pentene <sup>b</sup>	R <sub>3</sub> Al	R <sub>3</sub> Al · N(CH <sub>3</sub> ) <sub>3</sub>	R <sub>3</sub> Ga	R <sub>3</sub> Ga · N(CH <sub>3</sub> ) <sub>3</sub>	R'Al	R'Al · N(CH <sub>3</sub> ) <sub>3</sub>
δ <sub>A</sub>	4.945	5.058	4.883	4.973	4.883		
δ <sub>B</sub>	4.888	5.050	4.822	4.965	4.822		
δ <sub>C</sub>	5.733	5.97	5.81	5.848	5.805		
δ <sub>α</sub>		0.012	-0.0133	0.47	0.245	0.362	-0.170
J <sub>AB</sub>	2.0	2.7	2.6	2.7	2.7		
J <sub>AC</sub>	17.0	17.9	17.0	17.7	17.0		
J <sub>AD</sub>	-1.7	-1.2	-1.4	-1.2	-1.3		
J <sub>BC</sub>	10.1	8.9	9.7	8.9	9.7		
J <sub>BD</sub>	-1.3	-0.8	-1.0	-1.0	-1.0		
J <sub>CD</sub>	6.2	6.5	6.3	6.5	6.3		
J <sub>αβ</sub>		7.8	7.5	7.0	7.0	7.7	7.8

<sup>a</sup> Chemical shift and coupling constants were derived from first-order analyses and are presumed reliable to ±0.01 ppm and ±0.3 Hz, respectively. Line positions were calibrated by used of audiofrequency side band techniques on a Varian A60-A. All spectra were obtained on cyclopentane solutions with cyclopentane used as the internal standard. The chemical shifts were corrected to TMS by addition of 1.50 ppm to the observed value. *J* values are given in Hz. <sup>b</sup> Reference 2.

viscous colorless liquid. The nmr parameters of tri-1-but-3-enylaluminum and tri-1-but-3-enylaluminum trimethylamine adduct are listed in Table I.

**Tri-*n*-butylaluminum.** Tri-*n*-butylaluminum, Al<sub>2</sub>[(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>3</sub>, was prepared in a similar manner from di-*n*-butylmercury and aluminum dust. The mixture was heated to 65° for 1 week at which time quantitative conversion to tri-*n*-butylaluminum had occurred. The product was purified by distillation at 82–84° at 10<sup>-5</sup> Torr. Tri-*n*-butylaluminum formed a 1:1 adduct when mixed with trimethylamine. Cryoscopic molecular weight measurements indicated it to be associated with a molecular weight of 387.9 (calculated value for R<sub>3</sub>Al = 198.0; *n* = 1.96; *m* = 0.081).

**Tri-1-pent-4-enylaluminum.** Tri-1-pent-4-enylaluminum, Al[(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub>)<sub>3</sub>], was prepared similarly by mixing 0.02 mol of di-1-pent-4-enylmercury and 0.03 mol of aluminum dust in a sealed Pyrex tube at 10<sup>-6</sup> Torr. The reaction was quantitative after the mixture was vigorously stirred at room temperature for 2 weeks. The product was purified by distillation at 80–82° at 10<sup>-5</sup> Torr. The product formed a 1:1 trimethylamine adduct when mixed with trimethylamine. Typically, the mass spectral analysis gave evidence for the Al[(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ion as the most abundant metal species.<sup>18</sup> The nmr parameters of tri-1-pent-4-enylaluminum and its trimethylamine adduct are listed in Table II. Cryoscopic molecular weight measurements indicated it was monomeric with a molecular weight of 232.8 (calculated value for R<sub>3</sub>Al = 234.3; *n* = 0.99; *m* = 0.057).

**Tri-1-pent-4-enylgallium.** Tri-1-pent-4-enylgallium, Ga[(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub>)<sub>3</sub>], was prepared and characterized in a similar manner. The mixture of gallium metal and di-1-pent-4-enylmercury was heated at 110° for 3 weeks. The mass spectra showed the most abundant metal-containing species to be Ga[(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ion. The product was purified by distillation and the purity determined by nmr spectroscopy. The nmr parameters of tri-1-pent-4-enylgallium and tri-1-pent-4-enylgallium trimethylamine adduct are listed in Table II.

**Tri-*n*-pentylaluminum.** Tri-*n*-pentylaluminum, Al<sub>2</sub>[(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>]<sub>3</sub>, was prepared by vigorously stirring 0.05 mol of aluminum dust and 0.03 mol of di-*n*-pentylmercury in a sealed tube at 65° for 1 week. The product was distilled at 90–95° at 10<sup>-5</sup> Torr. The purity and completeness of the reaction were determined from its nmr spectrum. Cryoscopic molecular weight measurements indicated it to be associated with a molecular weight of 437.3 (calculated value for R<sub>3</sub>Al = 240.0; *n* = 1.80; *m* = 0.057).

## Results and Discussion

The molecular weights of tri-*n*-butyl-, tri-*n*-pentyl-, tri-1-but-3-enyl- and tri-1-pent-4-enylaluminum have been determined cryoscopically and are given in Table III. These data represent the weighted average molecular weight for the equilibrium mixture represented

**Table III.** Average Degree of Association for Several Alkyl- and Alkenylaluminum Derivatives

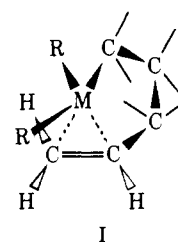
<i>n</i> <sup>a</sup>	Compound	<i>n</i> <sup>a</sup>	Compound
1.97	Al(CH <sub>3</sub> ) <sub>3</sub>	1.80	Al[(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> ] <sub>3</sub>
1.96	Al[(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>3</sub>	0.99	Al[(CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub> ] <sub>3</sub>
0.98	Al[(CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub> ] <sub>3</sub>		

<sup>a</sup> *n* = (K<sub>F</sub>[wt solute (g)]/Δ*T*)[wt solvent (kg)] (mol wt monomer), where K<sub>F</sub> = molal freezing point depression constant and Δ*T* = difference in freezing point between the pure solvent and solution.

in eq 2 and provide a measure of this equilibrium



constant.<sup>19</sup> Examination of the data in Table III clearly shows the dramatic shift in the equilibrium from dimer to monomer upon substitution of an olefinic moiety on the aluminum and leads directly to the structure proposed in I. Furthermore, this observed



shift in the equilibrium places a lower limit on the energy of the metal-olefin interaction since the shift in the equilibrium represents a one for one exchange of metal-carbon-metal bridge bond for a metal-olefin interaction. Since it has been established that the energy for a metal-carbon bridge bond is in the range of 2–7 kcal/mol.<sup>20,21</sup> These values represent the lower range for the metal-olefin interaction shown in I.

To provide additional information on these systems several nmr studies have been carried out. In order to make these studies significant one must devise a system which permits comparison of interacting and

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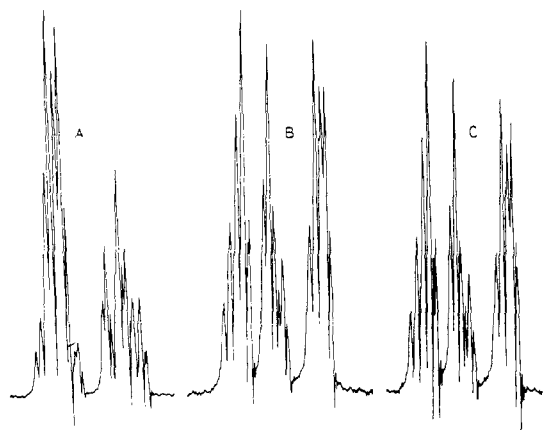


Figure 1. The nmr spectra of  $H_A$  and  $H_B$  regions of (A) tri-1-pent-4-enylaluminum, (B) tri-1-pent-4-enylaluminum trimethylamine adduct, and (C) 1-pentene.

noninteracting species. This can be achieved by comparing the nmr parameters of the trialkenylaluminum and trialkenylaluminum trimethylamine adducts. To establish this comparison the nmr spectra of tri-1-but-3-enyl- and tri-1-pent-4-enylaluminum and their trimethylamine adducts were analyzed. The nmr parameters were obtained on cyclopentane solutions and are listed in Tables I and II.

The data of most interest are the chemical shifts of the vinyl protons and the  $H_\alpha$  protons adjacent to the metal center. Normally the chemical shift of the  $H_\alpha$  protons adjacent to the metal center are determined by the electronegativity of the metal and fall into a narrow range for a given metal. Ramey<sup>22</sup> and coworkers have studied the nmr spectra of several alkylaluminum derivatives and have found that the  $H_\alpha$  proton of triethyl-, tri-*n*-propyl- and tri-*n*-butylaluminum compounds in toluene to have chemical shifts of 0.39, 0.37, and 0.42 ppm, respectively. The  $H_\alpha$  protons for the tri-*n*-pentylaluminum are reported (Table II) at 0.36 ppm which is well within the chemical shift range reported by Ramey. However, on investigation of the  $H_\alpha$  protons in the unsaturated tri-pent-4-enylaluminum derivative, the chemical shift has shifted upfield to 0.01 ppm. This is surprising and suggests that the  $H_\alpha$  protons in the unsaturated 1-pent-4-enyl derivative are experiencing a greater screening than the analogous *n*-pentyl derivative.

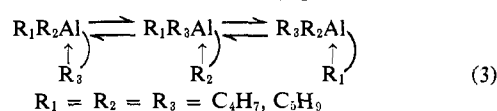
On formation of the trimethylamine adduct of tri-*n*-pentyl- and tri-1-pent-4-enylaluminum, one finds that the chemical shifts of the  $H_\alpha$  protons are now very similar,  $-0.13$  vs.  $-0.17$  ppm, respectively. This illustrates that on complexation the electron environments of the  $H_\alpha$  protons are similar and demonstrates that once the  $sp^3$  orbital is occupied by a strong coordinating Lewis base that the olefinic site no longer has an effect on the electron environment at the aluminum center.

The vinyl protons also experience similar perturbations. The vinyl protons in tri-1-pent-4-enylaluminum are shifted downfield relative to those of 1-pentene. This is opposite to the shift expected on substitution of an electropositive group for a hydrogen atom. The vinyl protons are shifted back upfield on formation of

the tri-1-pent-4-enylaluminum trimethylamine adduct. Figure 1 illustrates the changes in chemical shifts of the vinyl protons of 1-pentene, tri-1-pent-4-enylaluminum, and tri-1-pent-4-enylaluminum trimethylamine adduct. The nmr spectra of a series of samples of tri-1-pent-4-enylaluminum varying in concentration were analyzed and indicated no change in chemical shift vs. concentration. These data also establish evidence for an intramolecular rather than a possible intermolecular olefin-metal interaction.

It is also of interest that in the trimethylamine complexes of  $Al[CH_2(CH_2)_2CH=CH_2]_3$  and  $Ga[CH_2(CH_2)_2CH=CH_2]_3$  the chemical shifts of the vinyl protons are all similar. This demonstrates that the perturbations experienced in the uncomplexed derivatives are not caused by simply changing the electronegativity of the metal center. It has also been reported that the formation of addition compounds with trimethylamine effectively increases the electronegativity of the metal center which is reflected in the upfield shifts of the  $H_\alpha$  protons but has little or no effect on protons removed from the metal center by four or five bonds.<sup>23</sup>

On comparison of the vinyl protons  $H_A$ ,  $H_B$ , and  $H_C$  of the tri-1-but-3-enylaluminum and tri-1-pent-4-enylgallium derivatives, there exist similar changes in chemical shifts; however, these differences are small and indicate that these derivatives are not interacting with the aluminum atom as strongly as was observed for the tri-1-pent-4-enylaluminum. Finally, a low-temperature nmr experiment was conducted on the tri-1-but-3-enyl- and tri-1-pent-4-enylaluminum derivatives. The uncomplexed tri-1-but-3-enylaluminum compound shows some splitting of the  $H_\alpha$  protons in a temperature range from  $50$  to  $-10^\circ$  and at temperatures below  $-10^\circ$  only broaden the multiplet further. The low-temperature nmr spectra of  $H_\alpha$  protons of tri-1-pent-4-enylaluminum showed no significant change from  $20$  to  $-60^\circ$ . However, the region of the spectrum associated with the vinyl protons became broad and could not be analyzed. These data, along with the fact that at room temperature only one type of terminal olefinic site is observed in the nmr spectrum, suggest that a rapid exchange exists among all three olefinic sites for interaction on the aluminum atom (eq 3).



All of these findings support the model proposed in I for the metal-olefin interaction and establish the energy of this interaction to be a minimum of 2-5 kcal/mol, thus stabilizing the monomeric form of the aluminum derivative.

It is suggested here that these systems provide a convenient model for the study of metal-olefin interactions and supports the position that the Lewis acidity of the metal and the electron-donating ability of the multiple bond are directly related to the ability of these systems to undergo addition or polymerization.

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