ORGANOMETALLICS

Volume 1, Number 4, April 1982

© Copyright 1982
American Chemical Society

Carbon-13 Nuclear Magnetic Resonance Studies of Tricyclopropylaluminum, -gallium, and -indium

Ruthanne D. Thomas and John P. Oliver*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received September 9, 1981

^{13}C NMR studies have been carried out on tricyclopropylaluminium, -gallium, and -indium. The concentration and temperature dependence of the NMR spectra of the aluminum derivative have been interpreted in terms of a singlely bridged intramolecular bridge–terminal exchange process with activation parameters of $E_a^{\ddagger}$ = 12.4 (2)kcal/mol, $\Delta H^{\ddagger}$ = 11.7 (2)kcal/mol, and $\Delta S^{\ddagger}$ −13.1 (1.2) eu. Investigation of the ^{13}C spin–lattice relaxation times at low temperature and calculation of the relative spinning rates, ρ, of the cyclopropyl groups shows that the bridging cyclopropyl groups and the terminal cyclopropyl groups lying on the same side of the Al–C–Al–C rings rotate at the same rate, while the terminal groups on the opposite side rotate at 5–8 times this rate. This confirms the proposal that the low-temperature averaging process observed is a result of the variations in the rotation rate of the bridging cyclopropyl group and not from freezing the terminal cyclopropyl groups in different configurations. The study of the gallium and indium derivatives shows that their ^{13}C chemical shifts are highly dependent on temperature, concentration, and solvent. The measurement of the temperature and concentration dependence of these chemical shifts leads to the conclusion that these species are involved in an equilibrium between monomer and dimer and that the shift in the relative concentration of these two species leads to the observed changes in chemical shift. On this basis, equilibrium constants and enthalpies of dissociation have been calculated. The enthalpies of dissociation obtained for toluene solutions are 5.6 and 4.0 kcal/mol for the gallium and indium compounds, respectively.

Introduction

The mechanisms of group transfer and other reorganization processes in simple organometallic systems have been under investigation for many years. Much of the earlier work has been reviewed,[1-4] and it now seems clear that simple alkylaluminum dimers undergo bridge–terminal exchange via a dissociation process. A second bridge–terminal exchange mechanism involving a monobridged intermediate in which rotation about the bridge bond effects exchange has been suggested as the path in aromatic[5] and in the unsymmetrically bridged system μ-cyclopropyl-μ-methyl-tetramethyldialuminum.[7]

Another type of exchange process which only involves the rotation of a bridging or terminal group without group transfer has been observed with the best studied of these systems, that of the cyclopropylaluminum dimers. Oliver et al.[6-8] have reported that the cyclopropyl bridging group undergoes rotation both in the di-μ-cyclopropyl- and the μ-cyclopropyl-μ-methyl-tetramethyldialuminum molecules as indicated by the nonequivalence of the terminal methyl groups. To account for a similar observation in tricyclopropylaluminum dimer, Olah et al.[9] have proposed a different mechanism with the nonequivalence of terminal groups arising from fixed conformations for them with the assumption that the bridging groups continue to rotate freely. These findings appear to be inconsistent with one another. In order to clarify this inconsistency, to explore the bridge–terminal exchange of the cyclopropyl groups (which had not been previously done because of the complexity of the ^{1}H NMR spectra), and to extend these studies to the gallium and indium derivatives, we have carried out an extensive ^{13}C NMR study of these systems.

(1) Oliver, J. P. *Adv. Organomet. Chem.* **1970**, *8*, 167.
(2) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235.
(3) Ham, N. S.; Mole, T. *Prog. Nucl. Magn. Reson. Spectrosc.* **1969**, *4*, 91.
(4) Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974.
(5) Stanford, T. B., Jr.; Henold, K. L. *Inorg. Chem.* **1975**, *14*, 2426.
(6) Sanders, D. A.; Scherr, P. A.; Oliver, J. P. *Inorg. Chem.* **1976**, *15*, 861.
(7) Rie, J. E.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *133*, 147.
(8) Moore, J. W.; Sanders, D. A.; Scherr, P. A.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 1035.
(9) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217.
(10) Oliver, J. P.; Sanders, D. A. *J. Am. Chem. Soc.* **1968**, *90*, 5910.

0276-7333/82/2301-0571$01.25/0 © 1982 American Chemical Society

Experimental Section

All laboratory manipulations involving the synthesis and sample preparation of air-sensitive compounds were performed in an argon-filled drybox or in a high vacuum system (10^{-5} torr or less). The drybox was a Vacuum Atmosphere Drilab equipped with an HE-493 Dritrain. All solvents were dried over $LiAlH_4$ or CaH_2 and degassed on the vacuum system.

Preparation Compounds. Dicyclopropylmercury. Dicyclopropylmercury was synthesized by the method of Reynolds[11] from the cyclopropyl Grignard reagent and mercuric chloride in tetrahydrofuran. Following the normal workup, the dicyclopropylmercury was vacuum distilled with the fraction collected from 96 to 98 °C at ~8 mm (lit. value 110–112 °C at 18 mm) was used. The ^{13}C NMR spectrum of a 20% soluion in benzene-d_6 (v/v) consists of two peaks, each with mercury satellites: 32.1 ppm (d, $^1J(^{13}C-^1H)$ = 153.9 Hz, $^1J(^{13}C-^{199}Hg)$ = 1097.6 Hz), 2.6 ppm (t, $^1J(^{13}C-^1H)$ = 161 Hz, $^2J(^{13}C-^{199}Hg)$ = 19.5 Hz).

Tricyclopropylaluminum Dimer. Tricyclopropylaluminum was synthesized by the direct reaction of aluminum dust (~5-fold excess) with neat dicyclopropylmercury (0.01 mol) by the procedure of Sanders.[6,10,12] The reactants were placed in a tube which was then attached to the vacuum system, evacuated, and sealed. The reaction tube was heated in an oil bath to 75 °C for 1 week. It was then taken to the drybox where it was opened, and the solid transferred to vacuum sublimator and sublimed at 50 °C and 10^{-6} torr; yield 95%. Tricyclopropylaluminum is a white crystalline solid (mp ~60 °C). The ambient-temperature ^{13}C NMR spectrum in toluene-d_8 consists of four peaks at δ_c 12.4, 1.6, −10.7, and −15.2 calculated relative to Me_4Si.

Tricyclopropylgallium. Tricyclopropylgallium was synthesized by metal exchange between gallium metal and dicyclopropylmercury.[12] The reaction was carried out by placing gallium metal (~3-fold excess) in a reaction vessel (simply a long tube with a standard taper joint and a constriction) and then adding the dicyclopropylmercury (0.01 mol) to this vessel. The apparatus was then evacuated, sealed at the constriction, and placed in a 65 °C oil bath for 2 weeks. The sealed vessel was removed and transferred to an argon drybox where it was opened, and the liquid above the gallium amalgam was transferred to an inverted Y-vessel used for distillation. The crude material was distilled at ~70 °C (10^{-6} torr). Tricyclopropyl gallium is a clear, colorless liquid (mp ~15 °C). Yields were essentially quantitative. The ^{13}C NMR spectrum consists of two peaks corresponding to the α- and β-carbon atoms with chemical shifts which show strong concentration, temperature, and solvent dependence as discussed below.

Tricyclopropylindium. Tricyclopropylindium was synthesized in an analogous manner from the reaction of indium metal (3-fold excess) and dicyclopropylmercury (0.01 mol). After 1 week of reaction at 70 °C, the viscous liquid above the indium amalgam was distilled at 80 °C (10^{-6} torr), yield 93%. Tricyclopropylindium forms large clear crystals, mp ~30 °C (lit.[12] value 33–34 °C). The ^{13}C NMR spectrum consists of two peaks with a strong concentration, temperature and solvent dependence as discussed below.

Preparation of NMR Samples. All NMR samples were prepared in the drybox by weight, with the material diluted to the desired concentration in a volumetric glassware with predried solvent. Each sample was transferred to an NMR tube fitted with a standard taper joint, capped with a stopcock, transferred to the vacuum system, and degassed by successive freeze–pump–thaw cycles. The sample was then sealed. All samples made in deuterated solvents were in 10-mm NMR tubes, while 8-mm NMR tubes were used for non-deuterated solvents so that they could be used coaxially in a 10-mm tube containing deuterated solvent.

Determination of NMR Spectra. ^{13}C NMR spectra were determined at 15 MHz on a JEOL FX-60 spectrometer or at 75 MHz on a Nicolet NT-300 spectrometer. Unless otherwise specified, all spectra were broad-band proton decoupled. Chemical shifts were assigned relative to internal solvent peaks as follows: toluene-d_8, 20.4 ppm; cyclopentane, 25.6 ppm.

T_1 measurements were made by using the standard inversion–recovery techniques.[13] For the infinity spectra, t was equal to at least 5 times the T_1 value. The standard deviations quoted are for the least-squares fit of a particular data set. All T_1 values were reproducible within 10%.

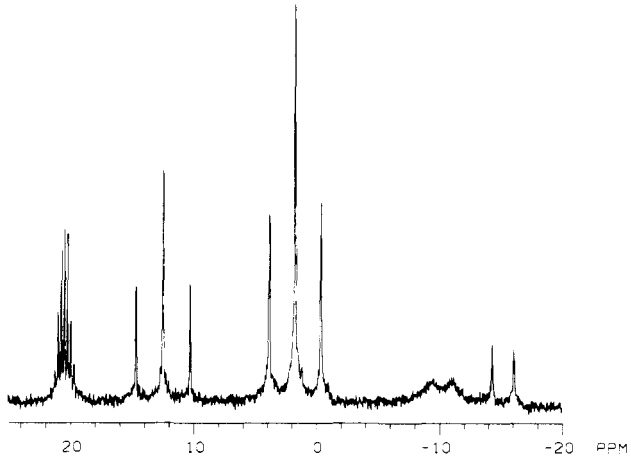


Figure 1. The 75-MHz ^{13}C NMR spectrum of a 0.2 M solution of tricyclopropylaluminum dimer in toluene-d_8 at 30 °C with proton coupling.

Temperature Calibration. FX-60. Temperature control of the sample with the FX-60 was achieved by using the standard JEOL temperature controller. The temperature at the sample was read by using a copper–constantan thermocouple inserted in an NMR tube which was maintained in the probe until a constant reading was achieved, and then the sample was transferred to the probe and allowed to equilibrate for a minimum of 30 min. After the spectrum was run, the temperature was read again. If this temperature was not within 1° of the initial reading, the spectrum was rerun.

NT 300. The Nicolet NT-300 uses the standard Nicolet temperature controller under NIC-1180 software control. Experience with this spectrometer has shown that the actual temperature at the sample is highly reproducible over a wide range of temperatures and nitrogen flow rates. This can be seen very clearly when the spectra of samples containing chemically exchanging systems which are strongly temperature dependent are compared. Spectra run on the sample at the same nominal temperature at exactly reproducible. To estimate the real sample temperature, a solution of Me_4Si/methyl iodide in the ratio of 1:3 was run over the range of +1 to −60 °C. Vidrine and Peterson's relationship[14] was then used to obtain a calibration curve for the sample temperature for the ^{13}C probe.

Determination of Exchange Lifetimes from NMR Spectra. The exchange lifetimes of particular species undergoing chemical exchange were determined by NMR line-shape analysis methods. Theoretical spectra generated from a line-shape equation were compared to the experimental spectra and the parameters alternatively changed until an acceptable fit was achieved.

The solution of the Bloch equation based on the McConnell modification[15] for the uncoupled AB system as derived by Carlson[16] was used. This had previously been adapted by Crotty[17] as a FORTRAN subroutine for use by the nonlinear least-squares fitting routine KINFIT.[18,19] Initial estimates were required for the difference between the two peaks, the rate constant, the equilibrium constant, the center of the peaks, and an experimental scale factor. The lifetimes of the two sites in the absence of exchange were used as parameters, although wide variations in these values had little or no effect on the final values for exchange lifetimes. The nonlinear least-squares program KINFIT was then used to alternately vary the parameters until a fit between the calculated and experimental spectra was achieved.

(11) Reynolds, G. F.; Dessy, R. E.; Jaffe, H. H. *J. Org. Chem.* **1958**, *23*, 1217.
(12) Sanders, D. A. Ph.D. Dissertation, Wayne State University, 1969.
(13) Farrar, T. C.; Becker, E. D. "Pulse and Fourier Transform NMR"; Academic Press: New York, 971.
(14) Vidrine, D. W.; Peterson, P. E. *Anal. Chem.* **1976**, *48*, 1301.
(15) McConnell, H. M. *J. Chem. Phys.* **1958**, *28*, 430.
(16) Carlson, E. H. Ph.D. Dissertation, Wayne State University, 1977.
(17) Crotty, D. Ph.D. Dissertation, Wayne State University, 1977.
(18) Dye, J. L.; Nicely, V. A. *J. Chem. Educ.* **1971**, *48*, 443.
(19) Scherr, P. A.; Oliver, J. P. *J. Mol. Spectrosc.* **1969**, *31*, 109.

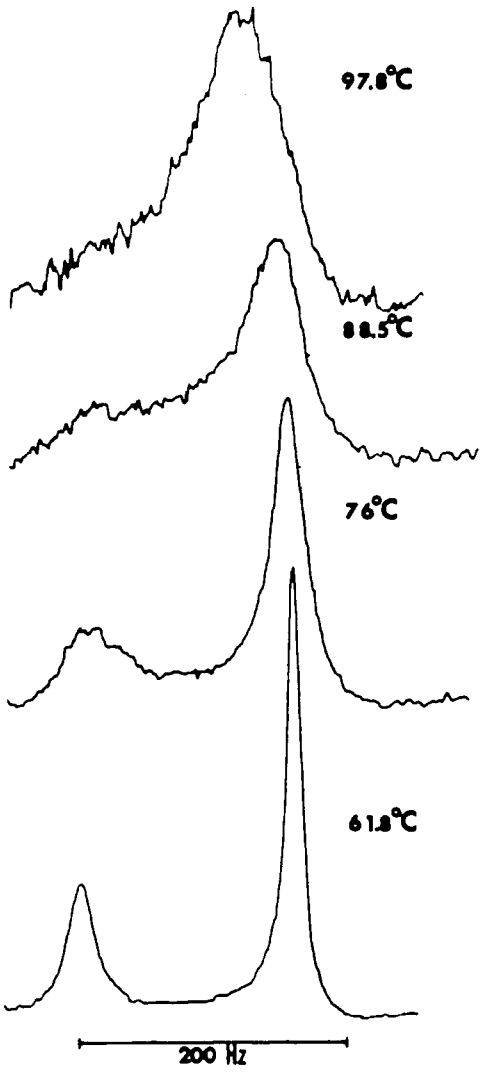


Figure 2. Temperature dependence of the 15-MHz $^{13}C\{^1H\}$ NMR spectrum of tricycloproylaluminum dimer in toluene-d_8. Only the lines associated with the bridging and terminal β-carbon atoms are shown.

Results and Discussion

The ^{13}C NMR spectra of tricyclopropylaluminum dimer with proton coupling is shown in Figure 1. The ambient-temperature spectrum consists of two triplets and two doublets with chemical shifts of δ_c 12.4, 1.6, −10.7, and −15.2, which corresponds to β-bridging, β-terminal, α-terminal, and α-bridging carbon atoms, respectively. The assignments of the α- and β-carbon atoms are unambiguous from the splitting observed. The bridge and terminal assignments are also quite certain from their relative intensities, from their relaxation behavior, and, also, are consistent with the assignments made by Olah et al.[9]

In earlier studies it was established that bridge–terminal exchange occurred, but no quantitative studies were carried out due to the complexity of the proton spectra.[10] The $^{13}C\{^1H\}$ NMR spectra cause no such difficulties and a typical series of spectra, as a function of temperature, for the β-carbon atoms is shown in Figure 2 with coalesence observed at ~88 °C (15 MHz) in toluene. Only the β-carbon atoms were used in this analysis because of their greater signal/noise ratio and to eliminate any possible interference from aluminum quadrupolar interaction which could alter the relaxation times of the α carbon atoms. Coalesence could not be observed below the boiling point of the solvent at 75 MHz as a result of the 5-fold increase in the frequency difference between the lines.

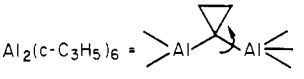
Table I. Tricyclopropylaluminum Dimer Bridge–Terminal Exchange Rates vs. Temperature and Concentration

M[a]	temp, °C	rate,[b] s^{-1}
0.49	61.8	75
	76	180
	80	230
	84.5	260
	87	267
	88.5	324
	93.5	377
	97.8	486
0.345	71	100
	81	203
	90	335
	92	350
0.2	73.5	125
	78	172
	81.5	207
	83	217
	87	272
	98.5	434
0.173	71	141
	81	226
	90	310
	92	385
0.12	76	165
	81	188
	86	209
0.034	71	121
	90	262

[a] Based on dimer in toluene-d_8. [b] $1/\tau_b$ is the lifetime of the cyclopropyl group in the bridging site.

Each spectrum, both as a function of temperature and concentration, was analyzed by the procedures described in the Experimental Section with the data collected in Table I. These data show no significant dependence of the lifetime on the concentration which implies a first-order reaction in dimer. This observation is consistent with either of the two mechanisms shown in eq 1 and 2 which

$$Al_2(c\text{-}C_3H_5)_6 = 2Al(c\text{-}C_3H_5)_3 \quad (1)$$



(2)

correspond to a dissociative process and to a simple bridge opening with rotation, respectively. Other mechanisms may be postulated but have been previously rejected as improbable for a variety of reasons.[1,2] The difference between the two proposed paths is apparent only in a detailed examination of the rate equations which leads to the expressions for the first-order rate constants of $k_1 = {}^3/_2\tau_b^{-1}$ and $k_1 = 3\tau_b^{-1}$ for the dissociative and bridged intermediate pathways, respectively, and does not permit an experimental test to be made between these two paths. Therefore, distinction between the two possible pathways must be made on the basis of other information and may not lead to a decisive choice.

The activation parameters for the process were obtained from the Arrhenius expression

$$\text{rate} = A \exp(-E_a^*/RT) \quad (3)$$

and from the Eyring equation

$$\ln (k/T) = \ln (k_B/h) + \Delta S^*/R - (\Delta H^*/RT) \quad (4)$$

The latter expression leads to slightly different values for the entropy of activation between the two mechanisms as a result of the differences in the rate expressions. The results of these calculations are given in Table II. The values of E_a^* and ΔH^* are quite low when compared to the

Table II. Activation Parameters for Tricyclopropylaluminum Bridge–Terminal Exchange

M[a]	$E_a^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]
0.49	12.4 ± 0.2	11.6 ± 0.2	−13.1 ± 1.4	−14.5 ± 1.4
0.345	13.9 ± 0.8	13.2 ± 0.8	−9.1 ± 6.6	−10.2 ± 6.6
0.2	11.5 ± 0.5	10.8 ± 0.5	−15.8 ± 4.0	−17.2 ± 4.0
0.173	11.2 ± 0.5	10.6 ± 0.5	−16.2 ± 3.9	−17.6 ± 3.9
0.12	5.8 ± 0.06	5.2	−32	−33
0.034	10.1	9.4	−20	−21
overall	12.4 ± 0.2	11.7 ± 0.2	−13.1 ± 1.2	−14.5 ± 1.2

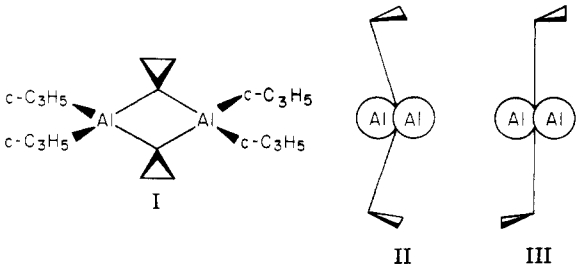
[a] Based on dimer in toluene-d_8. [b] Eu for open-intermediate mechanism. [c] Eu for dissociative mechanism.

simple alkylaluminum derivatives such as Al_2Me_6, while the entropy of activation is reasonably large and negative, in constrast to the generally positive values associated with the dissociative mechanisms.[1,2] These values are consistent with those obtained for the bridge–terminal exchange observed in μ-methyl-μ-(diphenylamino)-tetramethyldialuminum and also are consistent with the parameters obtained from the tolyl-bridged dimers which are thought to proceed through a single-bridged mechanism.[5] In addition, relatively low $E_a^{\ddagger}$ and $\Delta H^{\ddagger}$ values are inconsistent with a full dissociation assuming that the cyclopropyl groups form a more stable Al–C–Al bridge than do simple saturated alkyls.

On the basis of these considerations we, therefore, concluded that the most probable mechanism for the bridge–terminal exchange in tricyclopropylaluminum dimer is that indicated in eq 2, with only a single bridge opened during the course of the reaction. This exchange reaction then constitutes a second example, along with the tolyl-bridged system,[5] where there are identical bridging moieties in which bridge–terminal exchange occurs without complete dissociation.

Tricyclopropylaluminum Dimer Bridge Rotation. In addition to the high-temperature bridge–terminal exchange, there is a second, much faster, averaging process which leads to splitting of the lines associated with both the α- and β-carbon atoms of the terminal groups. This may be seen clearly in Figure 3. This had previously been observed for tricyclopropylaluminum,[6,9,10] for di-μ-cyclopropyl-tetramethyldialuminum[6,8] and for μ-cyclopropyl-μ-methyl-tetramethyldialuminum.

This intramolecular averaging process has been interpreted in two ways. The first interpretation, proposed for the methyl-substituted derivatives, was based on the analysis of temperature-dependent NMR studies and was on the assumption that the bridging cyclopropyl groups were free to rotate at elevated temperatures, but that this rotation slowed at lower temperatures, with these groups ultimately remaining in the syn configuration at very low temperatures as observed in the solid state.[8,20] The structure and views of the two conformations are shown in I–III. The exchange process is consistent with the



(20) Ilsley, W. H.; Glick, M. D.; Oliver, J. P.; Moore, J. W. *Inorg. Chem.* **1980**, *19*, 3572.

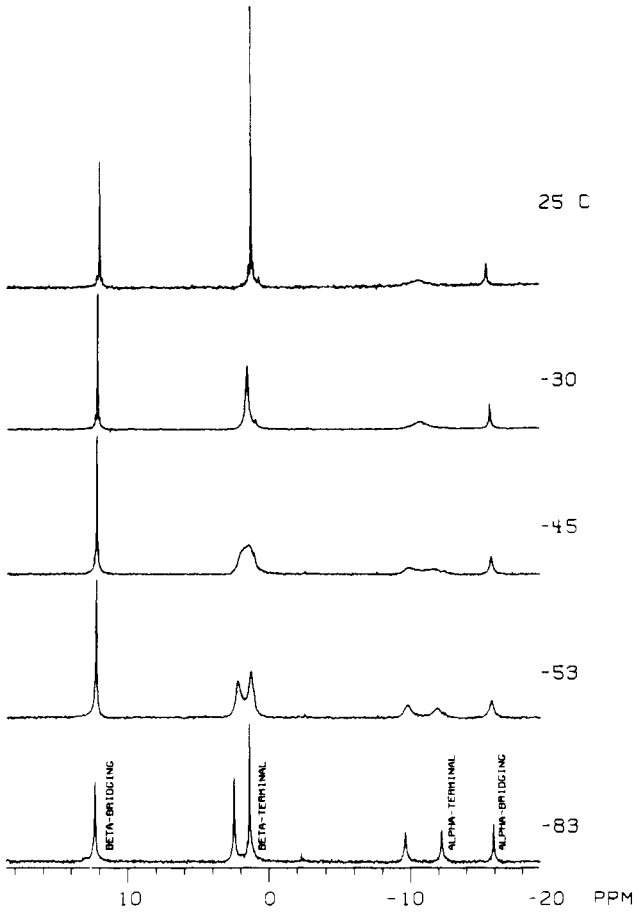


Figure 3. The temperature dependence of the 75-MHz $^{13}C\{^1H\}$ NMR spectrum of a cyclopentane solution of tricyclopropylaluminum dimer. Assignments are given from left to right in the −83 °C spectrum with two lines assigned to the β terminal and α terinal groups.

observed experimental data and is supported by calculations of the barrier to rotation for the bridging group between the syn and anti conformations.[6,8] The second mechanism proposed for this averaging process is based on the assumption that the bridging cyclopropyl groups are free to rotate even at low temperatures while the terminal groups become fixed in a specific conformation under these conditions.[9] This path is consistent with the observations reported for tricyclopropylaluminum dimer, providing that the set of assumptions made is correct but in no case can it account for the nonequivalence of the terminal methyl groups in di-μ-cyclopropyl- or μ-cyclopropyl-μ-methyl-tetramethyldialuminum.

In an effort to clarify this situation and to determine if there are two different averaging processes occurring, a study of the ^{13}C spin–lattice relaxation times has been carried out, since these relaxation times may be related to the molecular tumbling and internal rotational motion of molecules.[21,22] The relaxation of ^{13}C nuclei may result from a number of mechanisms, but for nuclei directly bonded to protons, ^{13}C–^1H dipole–dipole relaxation is usually predominant. For isotropic tumbling of the molecule, the relaxation time will be a function of a rotational correlation time. If, however, rotational reorientation is anisotropic or if internal motion must be considered, an additional correlation time for the internal

(21) Lyerla, J. R., Jr.; Levy, G. C. "Topics in Carbon-13 NMR Spectroscopy"; Wiley-Interscience: New York, Vol. 1, p 79.
(22) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

Table III. ^{13}C Spin-Lattice Relaxation Times for Tricyclopropylaluminum Dimer as a Function of Temperature[a]

temp, °C	T_1 relaxatn times, s (% T_1^{DD})					
	β_b	β_t		α_t		α_b
30	1.78	1.84		b		b
−42	0.26 (100)	0.39 (96)		0.76 (61)		0.50 (126)
−50	0.16	0.19[c]	0.29[d]	0.34[c]	0.80[d]	0.35
−55	0.16 (89)	0.18[c] (92)	0.32[d] (101)	0.36[c] (89)	0.62[d] (83)	0.30 (83)
−67	0.14	0.16[c]	0.32[d]	0.28[c]	0.66[d]	0.32
−70	0.10	0.12[c]	0.22[d]	0.19[c]	0.50[d]	0.19

[a] At 15 MHz. [b] Not measured at this field strength due to low signal/noise for these broad peaks. [c] Downfield peak. [d] Upfield peak.

motion of the group also must be included. This fact permits assignments of relative rotation rates to be made for internal motions in a molecule. The efficiency of a given internal rotation in shortening the overall effective correlation time (and lengthening T_1) for a given carbon is governed by the angle, θ, between the C–H bond vector and the preferred rotational axis.

Allerhand[23] has derived an expression to evaluate T_1^{DD} as a function of three parameters: (1) the overall reorientation correlation time, (2) the internal motion correlation time, and (3) the angle, θ, between the C–H bond vector and the internal rotational axis. Thus, for a given system, if the following two conditions hold, (1) the ^{13}C T_1 relaxation is via the dipole–dipole mechanism and (2) θ can be defined, then the T_1 relaxation times will provide information about molecular tumbling and internal rotation.

For the terminal cyclopropyl rings in tricyclopropylaluminum dimer, the angle between each of the carbon–proton vectors and the α-carbon–aluminum bond (about which rotation would take place) is constant. Each of the carbon–proton vectors will undergo reorientation from two sources: (1) the overall isotropic tumbling of the molecule and (2) the internal rotation of the cyclopropyl group about the carbon–aluminum bond. However, the overall tumbling of the molecule will be constant for all of the nuclei. Therefore, the T_1^{DD} will provide a means of directly comparing the rotations of the various cyclopropyl groups. The ^{13}C T_1 relaxation data are summarized in Table III.

To confirm the assumption that the relaxation is predominantly dipole–dipole, the nuclear Overhauser effect (NOE) was also determined at several temperatures. The percentage of the dipole–dipole mechanisms, where measured, is in parentheses. As is typical of this experiment, there is a large degree of error in these numbers. However, at least for the β-carbon atoms, the dipole–dipole mechanism appears to be nearly the sole relaxation mechanism. For the α-carbon atoms at low temperature the NOE is constant, indicating at least an equivalent contribution from the dipole–dipole mechanism for all of the α-carbon atoms.

Despite possibly large errors in the T_1 values, several observations may be made. First of all the T_1 values obtained for the α- and β-carbon atoms in a given ring from the low temperature data show that the relaxation behavior of the individual groups are in the approximate ratio of 2:1 as predicted from the relative numbers of directly bonded protons at each site with the assumption that there are no differences in the reorientation, either isotropic tumbling or internal rotation, between the α- and β-carbon atoms on a particular cyclopropyl ring. This further supports that the ^{13}C–^1H dipole–dipole mechanism as the predominant mechanism for relaxation of both the α- and β-carbon atoms.

(23) Allerhand, A.; Doddrell, D.; Komoroski, R. *J. Chem. Phys.* **1971**, *55*, 189.

Table IV. Cyclopropyl Ring Rotation Ratios for Tricyclopropylaluminum at Low Temperatures

temp, °C	α_t[b] T_1, s	T_1(t)/T_1(b)	ρ[a]	α_t[c] T_1, s	T_1(t)/T_1(b)	ρ[a]
−50	0.34	0.97	1	0.80	2.3	6
−55	0.36	1.2	2	0.62	2.1	5
−67	0.28	0.9	1	0.66	2.1	5
−70	0.19	1.0	1	0.50	2.6	8

[a] Ratio of rates of rotation of terminal group to bridging group as calculated from T_1 ratios.[24] [b] Downfield peak. [c] Upfield peak.

Of far more importance, is the fact that the relaxation times for the α- and β-carbon atoms in the bridging and the downfield terminal cyclopropyl groups are approximately the same, whereas these for the upfield cyclopropyl groups are about double these values. This implies that there are significant differences in the rotational rates of the two types of terminal groups and that one class of terminal groups has relaxation behavior similar to that of the bridging units.

In an effort to quantify these relationships, Levy,[24] making use of Allerhand's relationship[23] for evaluation of T_1^{DD}, has calculated the spinning ratio, ρ, as a function of the T_1 ratio for a variety of angles between the C–H vector and the axis of rotation. In the present system, the T_1 ratio between the bridging α-carbon atoms and the downfield terminal α-carbon atom is approximately 1, while the ratio between the bridging and terminal T_1 values for the upfield peak ranges between 2.1 to 2.6 and the angle between the C–H vector and the carbon–aluminum bond for the terminal α-carbons of tricyclopropylaluminum dimer is approximately 60° (60° assuming idealized sp^2 geometry or 56.9° based on the H–C–H angle in cyclopropane[25]). With use of Levy's calculations for 60°, ρ can be estimated as 1 between the bridging and downfield (α-carbon atom) terminal group and in the range of 5–8 for the upfield group (Table IV).

Thus, there is a significant difference in the rates of rotation of the two sets of terminal groups of tricycloaluminum dimer at low temperature with the bridging group rotating at a rate approximately equal to that of the slower group. These observations lead to several conclusions. (1) Olah et al.[9] misinterpreted these data in terms of the process leading to the magnetic nonequivalence of the terminal groups. (2) The predominant form in solution at low temperatures is the syn conformation, similar to that in the solid state. (3) The terminal group which give rise to lines at 2.51 and −9.65 ppm is the group on the same side as the bridging cyclopropyl group and undergoes hindered rotation as a result of this. The group giving rise to lines at 1.39 and −12.47 ppm is on the opposite side of

(24) Levy, G. C.; Cargioli, J. D., Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527.
(25) Bastiansen, O.; Hassel, O. *Tidsskr. Kjemi, Bergves. Metall.* **1946**, *6*, 71. *Chem. Abstr.* **1946**, *60*, 6059.
(26) Yamamoto, O.; Hayamizu, K. *J. Phys. Chem.* **1968**, *72*, 822.

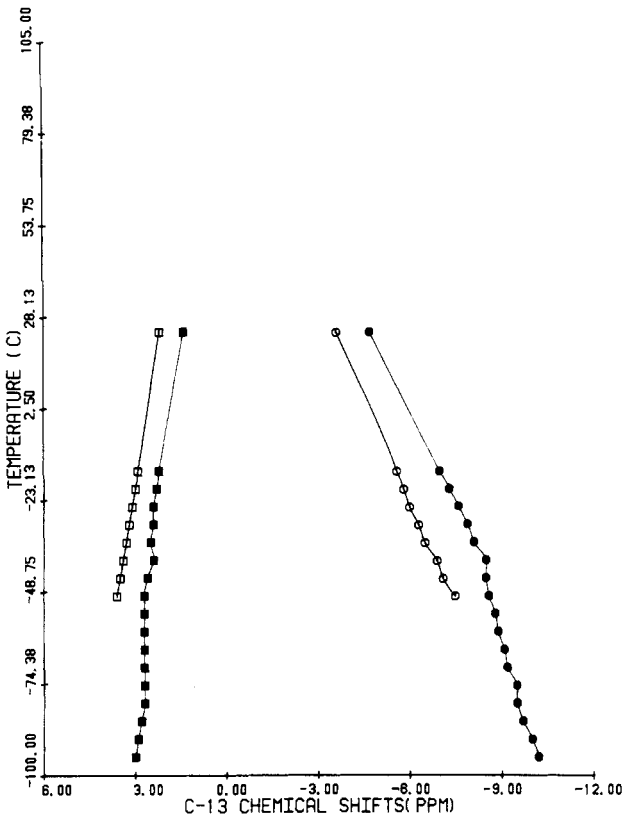


Figure 4. The temperature dependence of the chemical shifts of both the α- and β-carbon atoms of tricyclopropylgallium in cyclopentane and toluene solutions: 1.4 M in cyclopentane, β-carbon atom (■) and α-carbon atom (●); 1.4 M in toluene-d_8, β-carbon atom (□) and α-carbon atom (○).

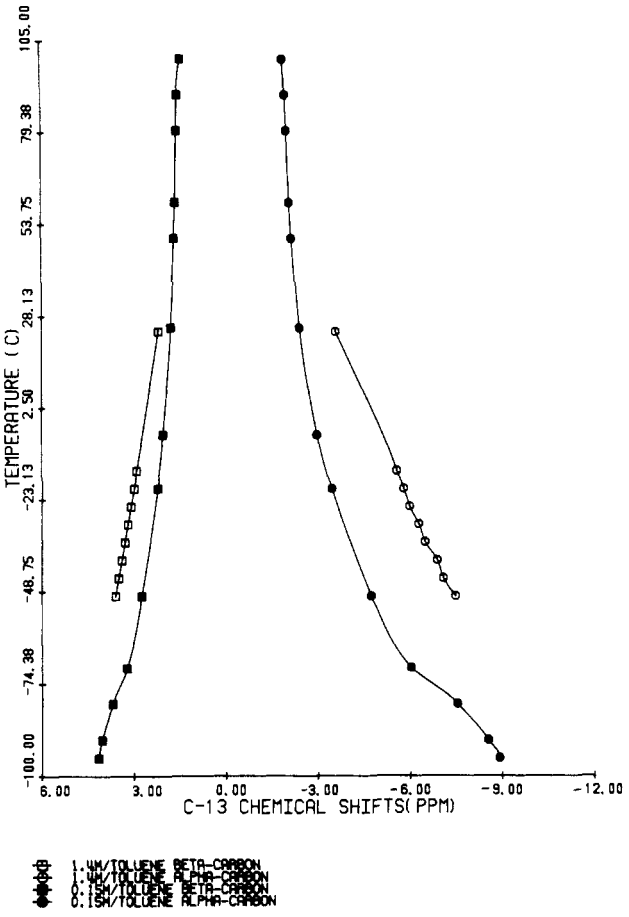


Figure 5. Effect of concentration and temperature on the chemical shifts of the α- and β-carbon atoms of tricyclopropylgallium in toluene-d_8.

the molecule in a less hindered site with the groups rapidly rotating even at low temperature. (5) Despite the steric interactions which lead to differentiation between the rotational rates of the various groups, the cyclopropyl group forms a very stable bridged dimer.

Tricyclopropylgallium and -indium. In general, the heavier group 3 metals have less tendency to form higher aggregation states via electron-deficient bonding than aluminum with the only confirmed dimeric species, trivinylgallium[27,28] and the phenylethynyl derivatives of both gallium[29] and indium.[30] Even the phenyl derivatives of gallium and indium are monomeric in the solid state.[31] Thus, the earlier indication, based on limited cryoscopic data, that the tricyclopropylgallium and -indium derivatives were slightly associated[12] is of particular interest since it would serve as an indication of the stability of the metal–cyclopropyl–metal bridge as compared to other bridging units.

The $^{13}C\{^1H\}$ spectra of both tricyclopropylgallium and -indium consist of only two peaks, corresponding to the α- and β-carbon atoms even at low temperatures. This indicates that either of these derivatives consist only of monomer or of some monomer–dimer mixture with rapid interchange of groups under all conditions studied. Examination of the chemical shifts of both the α- and β-carbon atoms in the gallium and indium derivatives as a function of concentration, temperature, and solvent as seen in Figures 4, 5, and 6 shows each of these factors causes major changes on the chemical shift values.

In both systems the separation between the lines associated with α- and β-carbon atoms increases with a decrease in temperature, an increase in concentration, and a decreae in solvent coordinating ability. This shows that these changes in conditions affect the chemical shifts of the α- and β-carbon atoms to significantly different degrees. These observations can most easily be interpreted in terms of a monomer–dimer equilibrium in which the cyclopropyl groups are undergoing rapid exchange between different metals and different sites.

With the assumption of a monomer–dimer equilibrium, with rapid exchange on the NMR time scale, then the chemical shift of the carbon atoms at any given time will be a weighted average of three sites: monomer (δ_m), dimer bridging (δ_{db}), and dimer terminal (δ_{dt}). If the monomer is similar to the dimer-terminal groups and the terminal and bridging groups behave in the same manner as they do in tricycopropylaluminum dimer, then the observed changes in chemical shift would correspond to increases in dimer concentration with increasing concentration, decreasing temperature, and decreasing interaction.

An alternative explanation for the observed changes in chemical shift might involve some type of specific complex formation between the solvent molecule and the monomer such as that reported for trimethylgallium in benzene, with an enthalpy of formation of the complex of 2.8 (0.15) kcal/mol.[32] This does not, however, appear to explain the results of the present study since similar results were obtained in both cyclopentane and toluene, and the concentration dependence cannot be accounted for through this approach.

(27) Oliver, J. P.; Stevens, L. G. *J. Inorg. Nucl. Chem.* **1962**, *21*, 137.
(28) Visser, H. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1968**, *90*, 3579.
(29) Tecle, B.; Ilsley, Wm. H.; Oliver, J. P *Inorg. Chem.* **1981**, *20*, 2335.
(30) Fries, W.; Schwarz, W.; Hansen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1978**, *159*, 373.
(31) McDonald, W. S.; Malone, J. F. *J. Chem. Soc. A* **1970**, 3362.
(32) Gusakov, G. M.; Kozyrkin, B. I.; Gribov, B. G.; Zorina, E. N. *Dokl. Akad. Nauk SSSR* **1974**, *215*, 168.

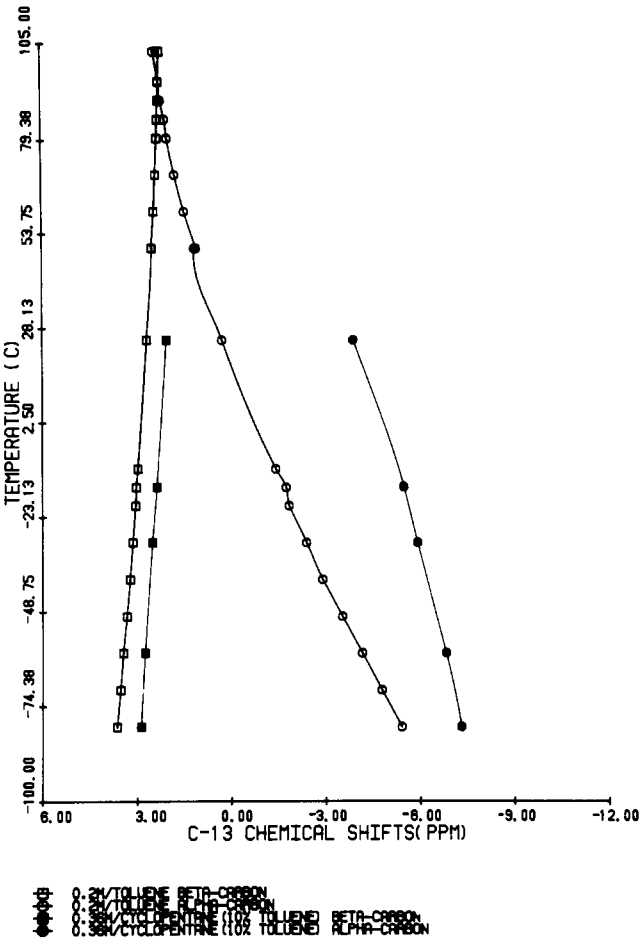


Figure 6. The temperature and solvent dependence of the chemical shifts of the α- and β-carbon atoms of tricyclopropylindium.

Since the tricyclopropylgallium and -indium derivatives represents the first cases in which formally saturated groups appear to provide sufficiently strong bridging units to lead to dimer formation with these metals, we have attempted to provide a more quantitative description of these systems. This has been done by analyzing the change in the chemical shifts as a function of temperature and of concentration.

The change in chemical shift of the cyclopropyl groups with temperature is assumed to result from a change in the relative populations of the groups among different magnetically nonequivalent sites in the monomer–dimer equilibrium. Higher aggregation states such as trimers or tetramers cannot be rigorously excluded, but there is no evidence for these in the group 3 metal–carbon-bridged systems.

The concentration of the dimer [D] and the monomer [M] may be expressed as $[D] = (C - x)$ and $[M] = 2x$ where C is the initial concentration, assuming all dimer, and x is the amount of dimer dissociated. The general expression for the observed chemical shift of a rapidly exchanging system is then given by the mole fractions of the specific sites times their nonexchange chemical shifts.

$$\delta_{obsd} = (1/6C)[6x(\delta_m) + 4(C - x)(\delta_{dt}) + 2(C - x)(\delta_{db})] \quad (5)$$

There are two limiting cases for this expression. As the dissociation, x, goes to zero, i.e., all dimer, then

$$\delta_{obsd} = \tfrac{2}{3}(\delta_{dt}) + \tfrac{1}{3}(\delta_{db}) \quad (6)$$

or as x approaches C, i.e., all monomer, then

$$\delta_{obsd} = \delta_m \quad (7)$$

Table V. Association Constants vs. Temperature for 0.15 M Tricyclopropylgallium in Toluene

temp, °C	chem shift,[a] ppm	K_{eq}[b]
105	−1.9	4.12×10^{-3}
95	−2.0	4.65×10^{-2}
85	−2.0	4.65×10^{-2}
65	−2.1	9.10×10^{-2}
55	−2.2	1.38×10^{-1}
30	−2.4	2.38×10^{-1}
0	−3.0	6.12×10^{-1}
−15	−3.5	1.03
−45	−4.8	2.91
−65	−6.0	6.94
−75	−7.5	2.43×10
−85	−8.5	7.94×10
−90	−8.9	1.57×10^{2}

[a] α-Carbon. [b] Defined as $K_{eq} = [\text{dimer}]/[\text{monomer}]^2$; calculated using upper chemical shift limit = −1.89 ppm and lower chemical shift limit = −10.0 ppm.

Table VI. Association Constants for Tricyclopropylgallium and Tricyclopropylindium

concn	solvent	source of data	K_{eq}[a]
	Tricyclopropylgallium		
0.15 M	toluene	β-carbon	0.58
		α-carbon	0.24
1.4 M	cyclopentane	β-carbon	2.1×10^{-3}
		α-carbon	0.12
1.4 M	toluene	β-carbon	0.12
		α-carbon	0.11
	Tricyclopropylindium		
0.2 M	toluene	β-carbon	2.1
		α-carbon	0.88
0.36 M	cyclopentane/ 10% toluene	β-carbon	0.17
		α-carbon	0.27

[a] At 30 °C.

Table VII. Enthalpies of Dissociation for Tricyclopropylgallium and Tricyclopropylindium

concn	solvent	enthalpies of dissociatn, kcal/mol: α-carbon	β-carbon
	Tricyclopropylgallium		
0.15 M[a]	toluene-d_8	5.9 ± 0.4	5.2 ± 0.5
1.4 M	toluene-d_8	5.6 ± 0.2	5.6 ± 0.08
1.4 M	cyclopentane	5.7 ± 0.3	6.3 ± 0.9
	Tricyclopropylindium		
0.2 M	toluene-d_8	4.0 ± 0.1	3.9 ± 0.09
0.36 M	cyclopentane/ 10% toluene	3.9 ± 0.5	6.0 ± 0.6

[a] Based on monomer.

Values for these cases can be estimated from the experimental spectra if two assumptions are made. (1) At low temperature the dissociation approaches zero, making the observed chemical shift equal to that in eq 6. (2) At high temperature the dimer is completely dissociated and the observed shift is that of the monomer. Letting the average chemical shift for the dimer equal δ_d, then eq 5 becomes

$$\delta_{obsd} = [(\chi/c)(\delta_m - \delta_d)] + \delta_d \quad (8)$$

Thus, from an estimate of the low- and high-temperature chemical shift limits and from the observed chemical shift at any given temperature, the degree of dissociation and equilibrium constant may be calculated.

If the further assumptions are made that the solution behaves ideally and that the change in enthalpy for the

Table VIII. ^{13}C Chemical Shifts of Triorganoaluminum Compounds with a Comparison to the Parent Hydrocarbon

	^{13}C chem shifts[a]					
	bridging			terminal		
R group	α	β	γ	α	β	γ
methyl[b]	−5.6			−8.2		
	(−3.4)[c]			(−6.0)		
ethyl[d]	0.5	8.2		0.0	9.4	
	(−5.0)	(1.7)		(−5.5)	(3.9)	
n-propyl[d]	13.5	18.4	20.3	12.5	19.5	21.2
	(−2.0)	(2.9)		(−3.0)	(4.0)	
tert-butyl[e]	···	···		26.3	30.5	
				(1.4)	(6.5)	
cyclopropyl[f]	−15.2	12.4		−10.7	1.6	
	(−11.8)	(15.8)		(−7.1)	(5.1)	

[a] Ppm relative to Me_4Si. [b] Reference 9. [c] Values in parentheses are defined as chemical shift of the compound minus the chemical shift of the parent alkane (chemical shifts of the alkanes from ref 22). [d] In toluene: Yamamoto, O.; Hayamiyu, K.; Yanagisawa, M. *J. Organomet. Chem.* **1974**, *73*, 17. [e] In benzene: Muller, H.; Rosch, L.; Erb, W. *Ibid.* **1977**, *140*, C17. [f] In toluene-d_8 (this work).

dissociation is not a function of temperature, then

$$\ln K_{eq} = -(\Delta H/RT) + \text{constant} \quad (9)$$

and an analysis of the chemical shift as a function of temperature yields an estimate of the enthalpy of dissociation.

A typical set of equilibrium constants as a function of temperature is shown in Table V for 0.15 M tricyclopropylgallium in toluene. Tables VI and VII give a summary of equilibrium constants for both the gallium and indium compounds and of their enthalpies of dissociation. The agreement obtained between different samples and from the calculations using both the α and β atom chemical shifts is quite good considering the number of assumptions made. This is especially true for the calculations using the β-carbon chemical shift because of the relatively small change in this value which make it particularly sensitive to the estimates used for the chemical shifts of monomer and dimer. Additional support for the values obtained comes from the previous obervation by Sanders[12] that 0.085 M solution of tricyclopropylgallium in cyclohexane at 6 °C was 8 (5%) associated. The present study gives an equilibrium constant of 0.33 at 6 °C or 5% association, clearly within the error limits of the experiment.

An examination of these data permit several conclusions to be drawn. First, the observed dissociation energies of 5.7 kcal/mol for tricyclopropylgallium and of 4.0 kcal/mol for tricyclopropylindium fall into the trend which one would expect with the increasing sizes of the metal atoms. Further, the value for the gallium derivative fits between the estimates made by Matteson,[4] who set an upper limit for the dissociation energy of trimethylgallium dimer of 5 kcal/mol (a compound which is monomer under the condition used in this set of studies) and that estimated by Oliver[33] for trivinylgallium of less than 10 kcal/mol (trivinylgallium is dimeric under these same conditions). Additional support for this range for the dissociation energies comes from examination of the alkylaluminum derivatives with dissociation enthalpies in solution of 16.3 kcal/mol for Al_2Me_6,[34] 12.5 kcal/mol for Al_2Et_6,[34] and 8.1 kcal/mol for $Al_2(i\text{-}Bu)_6$.[35] The first two of the derivatives are predominately dimeric at elevated temperatures, while the latter undergoes significant dissociation at room temperature, much as do tricyclopropylgallium and -indium.

(33) Moy, D.; Emerson, M. T.; Oliver, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 371.

(34) Hay, J. N.; Hooper, P. G.; Robb, J. C. *J. Organomet. Chem.* **1971**, *28*, 193.

Table IX. One Bond Carbon-Proton Coupling Constants (Hz) for Group 3 Tricyclopropyl Compounds

	$^1J(^{13}C-^1H)$	
	β-carbon	α-carbon
Tricyclopropylindium[a]		
30 °C	160	148
103 °C	160	150
Tricyclopropylgallium		
30 °C		
1.4 M[b]	162	147
0.15 M[c]	162	148
Tricyclopropylaluminum[d]		
30 °C		
bridging	166	133
terminal	160	126
−78 °C		
bridging	166	133
terminal downfield	159	136
terminal upfield	159	131

[a] 0.2 M in toluene-d_8. [b] For both 1.4 M in toluene-d_8 and 1.4 M in cyclopentane. [c] In toluene-d_8. [d] 0.5 M in toluene-d_8.

A final point which is of some interest is the fact that no difference was noted between the equilibrium constants or dissociation energies obtained in cyclopentane and toluene solution. This implies that the often invoked solvent interaction in aromatic compounds has a small effect on these parameters which lies within the experimental error with the upper limit set from the studies on the $GaMe_3$–benzene system of ~2 kcal/mol.[32]

^{13}C Chemical Shift Values. The ^{13}C chemical shifts of a number of aluminum derivatives are collected in Table VIII along with the relative chemical shifts of these groups from the parent alkane. These data show that the cyclopropyl group is particularly sensitive to the influence of the aluminum atom, with the α-carbon atoms more deshielded than for any of the other examples. Further, the chemical shift difference between the α- and β-carbon atoms of the bridging group of 27.6 ppm is far greater than that (12.2 ppm) observed between the α- and β-carbons in the terminal group. Whereas for the saturated derivatives the Δδ values between α- and β-carbon atoms on the bridging and terminal groups is far less. For example, in triethylaluminum dimer, the differences are 6.7 and 9.4 ppm and in tri-*n*-propylaluminum dimer these values are 4.9 and 7.0 ppm, respectively. This is what would be anticipated from the interaction of the cyclopropyl ring with the nonbonding orbitals on aluminum leading to the sttabilization of the bridged unit.[6]

This same type of interaction may be implied for the gallium and indium derivatives from the marked chemical shift changes associated with dimer formation. However, quantitative information on this is unavailable since the independent chemical shifts for the bridging and terminal groups could not be obtained because of the rapid exchange processes.

Examination of Table IX which lists the $^{13}C-^1H$ coupling constants for the tricyclopropylmetal derivatives provides some additional information. These data show that C–H coupling constants for the β-carbon–hydrogen pair are essentially uneffected by the metal or by the position of the ring in the dimeric molecules. The α-carbon–proton

(35) Smith, M. B. *J. Organomet. Chem.* **1970**, *22*, 273.

coupling is significantly altered by the metal, decreasing in absolute value with decreasing electronegativity of the element with the $^1J(^{13}C-^1H)$ values in the order In > Ga > Al.

There is essentially no difference observed between the coupling constants for the bridging and terminal cyclopropyl groups in dimeric tricyclopropylaluminum. Thus, further supporting the proposed mode of stabilization of the bridge bond in these tricyclopropylmetal derivatives through the interaction of the nonbonding metal orbitals with the p orbitals of the α-carbon atom. These interactions would leave the s orbitals essentially unperturbed should not effect the $^{13}C-^1H$ coupling to any great extent.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. R.D.T. was a recipient of a Wayne State University Graduate Fellowship during the years 1977–1979 and the Knoller Fellowship 1979–1980.

Registry No. tricyclopropylaluminum dimer, 21892-05-7; tricyclopropylgallium, 23719-82-6; tricyclopropylindium, 23719-81-5.

Metal Carbonyl Anion Generation Using Potassium Fluoride or Tetrabutylammonium Fluoride

Howard Alper*[1] and Leslie C. Damude

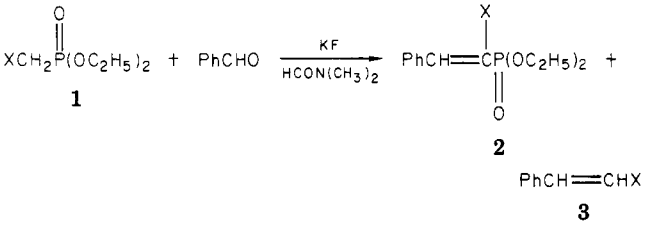
Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Received September 14, 1981

Triiron dodecacarbonyl reacts with dry potassium fluoride and commercial 18-crown-6, in tetrahydrofuran, to give the hydridoundecacarbonyltriferrate anion. The latter is also efficiently produced from $Fe_3(CO)_{12}$ and a 1 M solution of tetrabutylammonium fluoride. The quarternary ammonium fluoride can catalyze the reduction of nitrobenzenes to anilines by either $Fe_3(CO)_{12}$ or $Mn_2(CO)_{10}$. While $Co_2(CO)_8$ and $Co(CO)_3NO$ react with tetrabutylammonium fluoride, the resulting species are incapable of reducing nitrobenzene but can carbonylate 2-(bromomethyl)naphthalene.

Numerous publications have appeared in recent years on the utilization of fluoride ion as a base[2] and as a nucleophile[3] in organic synthesis. The fluoride used in these reactions is usually in the form of potassium fluoride or tetraalkylammonium fluorides.

There are many examples illustrating the ability of 18-crown-6 to solubilize potassium fluoride in relatively nonpolar solvents, thereby generating so-called "naked" fluoride ion. However, the exceedingly hygroscopic nature of potassium fluoride, tetraalkylammonium fluorides, and crown ethers cannot be overemphasized. The presence of water can have a major influence on the course of a variety of reactions involving fluoride ion. An example is the reaction of a phosphonate (1, X = CN, $COOC_2H_5$) with



benzaldehyde in *N,N*-dimethylformamide. In the presence of a small amount of "dry" potassium fluoride, the Knovenagel product (2) is the major product with little of the Wittig–Horner adduct (3) being obtained. Crown ether can accelerate this reaction. The proportion of 3 increases when some (but not too much) water is present, with the highest yield of 3 being attained with $KF{\cdot}2H_2O$.[4]

Liquid–liquid and solid–liquid phase-transfer catalysis is a useful technique in organometallic as well as in organic chemistry.[5] Crown ethers have been employed as catalysts for certain organometallic phase transfer processes, including the synthesis of ferrocenes[6] and bridging hydroxo complexes of platinum,[7] as well as the iron carbonyl induced reduction of nitroarenes to anilines.[8]

This paper describes the reactions of potassium fluoride and tetrabutylammonium fluoride with triiron dodecacarbonyl, dimanganese decacarbonyl, and several other metal carbonyls. Water plays a significant role in all of these reactions, with the facile generation of metal carbonyl hydrides being important in certain cases.

Results and Discussion

When triiron dodecacarbonyl was treated with an approximately equimolar amount of potassium fluoride and 0.25 equiv of "dry" 18-crown-6 in tetrahydrofuran, the solution remained intense green $[Fe_3(CO)_{12}]$ after being stirred at room temperature for 1 day. If, however, "wet" (i.e., commercial) 18-crown-6 was used instead, the reaction mixture turned deep red in less than 30 min. Under the latter conditions, the hydridoundecacarbonyltriferrate anion was generated and could be isolated as the bis(triphenylphosphin)iminium salt on addition of bis(triphenylphosphin)iminium chloride. The hydride was characterized on the basis of elemental analysis and the occurrence of an absorption maximum (methanol) at

(1) E.W.R. Steacie Fellow, 1980–1982.
(2) Clark, J. H. *Chem. Rev.* **1980**, *80*, 429 and references cited therein.
(3) Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag, Berlin, 1977; pp 117–124.
(4) Texier-Boullet, F.; Foucaud, A. *Tetrahedron Lett.* **1980**, *21*, 2161.
(5) Alper, H. *Adv. Oganomet. Chem.* **1981**, *19*, 183.
(6) Salisova, M.; Alper, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 792.
(7) Fakley, M. E.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1444.
(8) Alper, H.; DesRoches, D.; des Abbayes, H. *Angew. Chem. Int. Ed.* **1977**, *16*, 41.

0276-7333/82/2301-0579$01.25/0 © 1982 American Chemical Society