Table VI

Separation of Constants

Metal	D.	k, min.$^{-1}$	K, M^{-1}	k, min.$^{-1}$	K, M^{-1}
			M^{+2}		M(Ph)$_2$$^{+2}$
		Letting $K' = 0$			
Mn	78	6.6×10^{-3}	61	0.15	11
Ni	78	0.124	95	0.50	20.3
Ni	61	0.21	1.9×10^3	0.38	6.6×10^2
		Letting $K'/K = 15$			
Mn	78	0.098	4.1	2.3	0.73
Ni	78	1.9	6.3	7.6	1.35
Ni	61	3.0	1.3×10^2	5.6	44

From the limiting values given in Table VI it is seen that lowering of the solvent dielectric constant greatly enhances K, the catalyst–substrate association, but has little effect on k, its rate of decarboxylation. Conversely, the effect of coordination by o-phenanthroline has a small effect on K (decreases it slightly as expected from statistics) but in the case of Mn^{+2}, it greatly increases the rate constant k. The fact that k for Ni^{+2} is not so strongly affected suggests that the specific enhancement of Mn^{+2} by enzyme is the result not of just a lowered dielectric constant which would cause a stronger binding of the substrate, but to a specific coordination of the metal by the enzyme such as to greatly speed the decarboxylation of the bound substrate.

Not all ligands enhance the catalytic activity of metal ions. It is seen from Table IV that EDTA, for example, destroys the catalytic activity of Ni^{+2}. This is taken to mean that this ligand, by using all the coordination positions of Ni^{+2}, prevents direct binding to the substrate which is apparently necessary for reaction. Similar results are found for high concentrations of other ligands, even o-phenanthroline. Less

obvious is the low reactivity of 8-hydroxyquinoline-5-sulfonic acid complexes. A possible explanation arises from the fact that this negatively charged ligand lowers the effective charge of the metal ion, and it has been found previously that $+1$ ions do not have catalytic activity.[3]

The fact that addition of dioxane to the solvent increases the extent of association between positive ions and the substrate anion is easily rationalized in terms of lowered dielectric constant of the medium. The fact that the rate of decarboxylation of the metal ion–substrate complex is increased by the presence of ligands such as o-phenanthroline is more unexpected. Apparently, the presence of the o-phenanthroline causes an increase in the shift of electron density from the carbonyl oxygen of the dimethyloxaloacetate ion to the metal ion. The fact that o-phenanthroline is generally a better base than water makes this behavior somewhat difficult to understand. It could arise, however, if in the o-phenanthroline samples there is some back π-bonding from the metal to the o-phenanthroline ring system. This could allow the metal ion to have a higher effective charge when coordinated to o-phenanthroline than when coordinated to water. The larger enhancement of Mn^{+2} than of Ni^{+2} could then be accounted for in terms of the smaller nuclear charge of Mn^{+2} which should allow greater back donation. It also might be that there is a finite amount of π-bonding from any coordinated oxygen base to metal. As o-phenanthroline is substituted for coordinated water of hydration, the π-bonding from the coordinated oxygens of the substrate increases, thus enhancing the rate of decarboxylation. Whatever the explanation, the results are most suggestive of a type of binding between metal ions and the enzyme, similar to that between metal ions and o-phenanthroline, perhaps through appropriately located imidazole rings.

Organogallium Compounds. IV. Exact Analysis of the Nuclear Magnetic Resonance Spectra of Trivinyl- and Tripropenylgallium–Trimethylamine Adducts[1,2]

By D. Moy, J. P. Oliver, and M. T. Emerson

Triiso-, tri-cis-, and tri-$trans$-propenylgallium–trimethylamine derivatives were prepared from the respective dipropenylmercury compounds and gallium metal followed by addition of trimethylamine. The n.m.r. spectra show that these reactions all proceed with complete retention of configuration. Exact analyses of the n.m.r. spectra of these adducts and the trivinylgallium–trimethylamine derivative were carried out giving a consistent set of coupling constants and chemical shifts.

The interest in vinylmetallic compounds has increased rapidly since the discovery of the vinyl Grignard[3] and the stereospecific reactions of vinyllithium[4] derivatives. This work has been extended to systems containing mercury and thallium by Nesmeyanov and others[5] who have demonstrated that a number of metal exchange reactions occur with retention of configuration of the vinyl group. In addition, a considerable amount of work has been undertaken to elucidate the mechanisms of cleavage reactions and the stabilities of carbon–metal bonds.[6] This work, however, has been carried

out primarily on compounds of group II and IV metals because of their stability, with little emphasis placed on compounds of group III except for boron.

Vinyl derivatives of the remaining group III metals have been reported but the work on these has been limited to studies without regard to stereochemistry except for thallium which does not have a stable metal–carbon–metal bridge bond. Thus, there have not been any reports on the stability of isomeric vinyl derivatives of aluminum or gallium. Furthermore, little information is available regarding the effect of the vinyl substituents on the electron density in the metal–carbon bond, although Ritter[7] has shown by a molecular orbital calculation that this effect should be primarily inductive rather than mesomeric for trivinylborane; and indirect thermodynamic data[8] has been

(1) This work was supported in part by the National Science Foundation, Grants NSF-G-15829 and NSF-G-19981.

(2) Based upon a dissertation submitted by David Moy in partial fulfillment of the requirements for the Doctor of Philosophy degree.

(3) H. Normant, Compt. rend., 239, 1510 (1954).

(4) E. A. Braude and J. A. Coles, J. Chem. Soc., 2012 (1950).

(5) For a recent review of this work see O. A. Reutov, Record Chem. Progr., 22, 1 (1961).

(6) R. E. Dessy and F. Paulik, J. Chem. Educ., 40, 185 (1963).

(7) C. D. Good and D. M. Ritter, J. Am. Chem. Soc., 84, 1162 (1962).

(8) L. G. Stevens, B. Park, and J. P. Oliver, J. Inorg. Nucl. Chem., in press.

reported which implies that this is a major factor in the bonding present in trivinylgallium.

The only other quantitative information on this series of compounds is the complete analysis of the n.m.r. spectrum of trivinylaluminum etherate[9] which is of interest because of the apparent anomolies in coupling constants when compared with other vinyl systems. This provides only a meager beginning in understanding the type of bonding present in these vinyl derivatives.

For these reasons it should be of particular interest to synthesize substituted vinyl derivatives of group III metals, determine if they can form stable isomeric products, and study properties which will give some direct measure of the influence of the substituent on the electron densities within the molecule. One approach to this problem is through the study of chemical shifts and coupling constants of the n.m.r. spectra of the molecules. The chemical shift is dependent on the electron distribution within the molecule which is related to the bonding present and which also has been correlated with the chemical reactivity at different molecular sites.[10] The chemical shift is also sensitive to the electronegativity of attached groups[11,12] and hence can be used either to confirm the presence of a particular metal or to determine the effect of changing the electronegativity of the attached metal on the bonding within the organic moiety.

Additional information can be gained from the proton-proton spin coupling constants which are dependent on the molecular geometry of the compound and the electronegativity of its substituents. In vinyl derivatives it has been shown experimentally[11,12] and via a valence bond calculation[13] that for the vinyl protons $J_{trans} > J_{cis} > J_{gem}$. The magnitude of these fall in the range $J_{trans} = 14-20$ c.p.s., $J_{cis} = 5-15$ c.p.s., and $J_{gem} = 0-5$ c.p.s. This information in conjunction with the other data furnished by n.m.r. has been shown to be particularly useful in the determination of the stereochemistry of isomeric propenylmetallic compounds.[14]

The purpose of this paper is to report the stereospecific synthesis and to present an exact analysis of the n.m.r. spectra of trivinyl-, tri-cis-, tri-trans-, and triisopropenylgallium–trimethylamine (TMA) adducts to obtain precise values of the chemical shifts and coupling constants. These are then compared to confirm the stereochemistry of the isomers and to check the consistency of the analysis.

Experimental

All reactions were carried out using standard high vacuum techniques or under a dry nitrogen atmosphere following the procedure of Oliver[15] with the exception that a solvent (carbon tetrachloride) was added to the reaction mixture to moderate the reaction and reduce polymerization of the products. In addition, the reaction vessel was covered with aluminum foil to exclude light and the products stored at low temperature to further decrease the side reactions.

The iso-, cis-, and trans-propenylmercuric bromide derivatives were prepared by reaction of the corresponding isomeric propenyllithium compounds with mercuric bromide and were then converted to the dipropenyl derivatives by reaction with Na_2SnO_2.[16] These products were purified by distillation. Both their isomeric and chemical purity were determined by n.m.r.[14] Gallium metal was obtained from Fairmount Chemical Co. and was 99.99% pure. Trimethylamine (TMA) was distilled directly into the

vacuum line and stored over sodium metal until used, then it was transferred directly to the reaction vessel. Trivinylgallium–TMA adduct was obtained from L. G. Stevens and was distilled into the sample tubes without further purification.

A typical reaction was carried out distilling 0.05 mmole of dipropenylmercury onto 0.04 mg.-atom of gallium metal (a slight excess) which had been covered with 10 ml. of carbon tetrachloride. The reaction was then allowed to proceed at room temperature with stirring for 10 hr. The carbon tetrachloride and any residual dipropenylmercury were distilled out of the vessel leaving the tripropenylgallium in a fairly pure state. This material was then treated with excess TMA to form the adduct. These adducts were purified by distillation or sublimation in the vacuum system.

Tri-cis-propenylgallium and triisopropenylgallium were viscous liquids at room temperature, whereas tri-trans-propenylgallium was a white solid, melting at approximately 40°. The adducts of tri-cis- and triisopropenylgallium were liquids distilling at 80 and 60° in vacuo. The adduct of the trans derivative was a white solid subliming at 35–40° in vacuo. The TMA adducts were thermally stable under vacuum, i.e., to decomposition or polymerization.

The chemical analyses were obtained in terms of the mmoles of propene and gallium. A weighed sample of the TMA adduct was hydrolyzed with dilute HCl and the amount of propene gas evolved was measured in the vacuum system. The propene was identified by its gaseous infrared spectrum.[17] The residue from the gas analysis was treated with 6 N H_2SO_4 to convert gallium chloride to gallium sulfate. The procedure of Renwanz[18] was followed for gallium analysis in which gallium sulfate is converted to the oxide by ignition and then weighed. The amount of TMA was obtained by integrating the n.m.r. spectra and comparing the areas from the TMA protons with that arising from the propenyl group. In all cases, the compounds were found to form a 1:1 adduct. The results of all of the analyses are contained in Table I.

TABLE I
CHEMICAL ANALYSIS OF TRIPROPENYLGALLIUM·TMA ADDUCTS

Compound	mmoles propene	mmoles gallium	TMA: propene	Propene: Ga:TMA
Triisopropenylgallium trimethylamine	2.13	0.692	1:3	3.08:1:1
Tri-cis-propenylgallium trimethylamine	3.85	0.916	1:3	3.10:1:1
Tri-trans-propenylgallium trimethylamine	4.72	1.61	1:3	2.93:1:1
Tri-trans-propenylgallium trimethylamine	3.23	1.06	1:3	3.05:1:1

The n.m.r. samples of all of the tripropenylgallium–TMA adducts and tri-trans-propenylgallium were made up in carbon tetrachloride with a concentration of 10–20%. Tetramethylsilane (TMS) was used as the internal standard. The trivinylgallium–TMA was dissolved in cyclohexane which was used both as solvent and internal standard. In all cases the solvent, internal standard, and compound were distilled directly from the high vacuum system into the n.m.r. sample tube and sealed under vacuum. The spectra were run on a Varian HR 60 spectrometer at 27°.

Experimental line positions were measured by a linear interpolation between bracketing side bands. The audio side-band frequencies were measured to one part in 10^5 using a H-P 523 CR counter operating in the period count mode. In all cases the reported positions are averages obtained from five to eight spectra. The observed average deviations are listed in the tables of experimental data.

Analysis of Spectra

(1) **Trivinylgallium·TMA.**—The vinyl region of the experimental n.m.r. spectrum of trivinylgallium; TMA is shown in Fig. 1a. The three nonequivalent vinyl protons are strongly coupled giving a typical ABC type spectrum. The nine methyl protons of the trimethylamine moiety give a single peak at $\delta = 0.72$. Table II gives the experimental line positions determined by averaging the values obtained from eight recordings of the spectrum. Wherever possible, each individual line was bracketed by audio side bands for calibration. The average deviations for each line ranged from ± 0.4 to 0.17 c.p.s.

(9) D. W. Moore and J. A. Happe, J. Phys. Chem., **65**, 224 (1961).

(10) R. W. Taft, Jr., ibid., **64**, 1805 (1960).

(11) T. Schaeffer, Can. J. Chem., **40**, 1 (1962).

(12) C. N. Banwell and N. Sheppard, Mol. Phys., **3**, 351 (1960).

(13) M. Karplus, J. Chem. Phys., **30**, 11 (1959).

(14) D. Moy, M. T. Emerson, and J. P. Oliver, Inorg. Chem., **2**, 1261 (1963).

(15) J. P. Oliver and L. G. Stevens, J. Inorg. Nucl. Chem., **24**, 953 (1962).

(16) A. N. Nesmeyanov, A. B. Borisov, and N. V. Novikova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1216 (1959).

(17) R. H. Pierson, A. N. Fletcher, and E. Gantz, Anal. Chem., **28**, 1239 (1956).
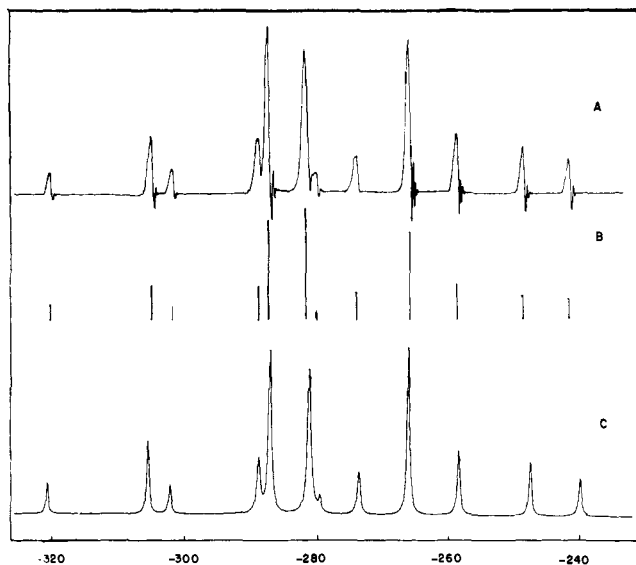
(18) J. Renwanz, Ber., **65**, 1308 (1932).

Fig. 1.—(A) The vinyl region of the experimental n.m.r. spectrum of trivinylgallium·TMA. (B) The calculated line spectrum of trivinylgallium·TMA. (C) The calculated spectrum of trivinylgallium·TMA plotted using the line shape function $G(\nu)$.

Of the fifteen possible transitions, twelve distinguishable lines were observed. Preliminary analysis of the spectrum proceeded by a method similar to that reported by Castellano and Waugh.[19] In this method,

TABLE II
EXPERIMENTAL AND CALCULATED LINE FREQUENCIES AND
RELATIVE INTENSITIES FOR THE VINYL PROTONS OF
TRIVINYLGALLIUM–TRIMETHYLAMINE

No.	$\nu_{exptl}{}^{a}$ (c.p.s.)	$\nu_{1/2}$ (c.p.s.)	ν_{calcd} (c.p.s.)	I_{calcd}
1	...	...	−328.39	0.0069
2	−320.94 ± 0.04	0.389	−320.91	.3098
3	−305.79 ± .15	.436	−303.76	.8358
4	−302.38 ± .17	.466	−302.43	.3480
5	−289.01 ± .09	.608	−289.10	.8424
6	−287.35 ± .10	.550	−287.39	2.3290
7	−281.42 ± .07	.660	−281.46	2.4923
8	−280.15 ± .09	.508	−279.83	0.1886
9	−273.90 ± .06	.571	−273.95	.6471
10	−266.61 ± .08	.459	−266.50	1.8480
11	...	...	−266.41	0.1806
12	−258.85 ± .05	.487	−258.86	.8178
13	−248.12 ± .09	.464	−248.03	.6440
14	−240.39 ± .08	.502	−240.49	.4899
15	...	...	−227.05	.0188

^{a} All line positions are given relative to cyclohexane which was used as an internal reference. Negative values indicate a downfield shift.

the observed lines are classified by making use of repeated spacings and sum rules obtained by considering the traces of the various submatrices which make up the spin Hamiltonian. Initially a table of the differences of line positions was made up. Those lines which were related by repeated differences were grouped together. From these sets the lines were arranged in an assignment table according to the sum rules.

Analysis of the spectrum was simplified by measuring all chemical shifts relative to a point in the spectrum such that $\delta^{*}{}_{A} + \delta^{*}{}_{B} + \delta^{*}{}_{C} = 0$. In terms of the lines in Table II

$$\nu(A_1) + \nu(B_1) + \nu(C_1) + \nu(A_4) + \nu(B_4) + \nu(C_4) = 0 \quad (1)$$

This corresponds to finding a new reference for the vinyl lines in terms of the vinyl spectrum. The line

(19) S. Castellano and J. S. Waugh, J. Chem. Phys., 34, 295 (1961).

positions with respect to the new reference then are given by $\delta^{*}{}_{i} = \delta_{i} + \delta_{0}$ where δ_{0} is the shift of the new reference from that of cyclohexane. $\delta_{0} = -278.45$ c.p.s. for this spectrum. Table III gives the line assignments for the vinyl region. Castellano and Waugh[19] have pointed out that such an assignment is not unique and one can obtain several possible solutions from one set of data. Therefore, it is necessary to either consider all possible arrangements or find a criterion for choosing a particular assignment. It is known that the values of J_{ij} in vinyl groups are strongly dependent on the electronegativity of the atom or group attached to the vinyl group. Schaeffer[11] has found a linear relationship between electronegativity and the sum of the vinyl coupling constants. Using a value of 1.6 for the electronegativity of gallium,[20] $J_{AB} + J_{AC} + J_{BC}$ is predicted to be ~ 41 c.p.s. It can also be seen from the trace of the Hamiltonian that

$$\nu(A_1) + \nu(B_1) + \nu(C_1) = -\nu(A_4) - \nu(B_4) - \nu(C_4) = J_{AB} + J_{AC} + J_{BC} \quad (2)$$

The assignment shown in Table III was chosen so that the absolute value sums of the above line positions (eq. 2) were ~ 41 c.p.s.

TABLE III
VINYL LINE ASSIGNMENTS FOR TRIVINYLGALLIUM·TMA

	A lines	B lines	C lines
1	$E_1-E_3 = -42.49$	$E_1-E_3 = -10.56$	$E_1-E_2 = 11.84$
2	$E_2-E_6 = -27.34$	$E_2-E_7 = -2.97$	$E_3-E_7 = 19.60$
3	$E_3-E_5 = -23.93$	$E_4-E_5 = 4.55$	$E_4-E_6 = 30.33$
4	$E_7-E_8 = -8.90$	$E_6-E_8 = 11.84$	$E_5-E_8 = 38.06$
X^{a}	$E_4-E_7 = (51.36)$	$E_3-E_6 = -1.70$	$E_2-E_5 = (-49.91)$

^{a} The parentheses indicate lines which were not observed because of vanishingly weak intensities.
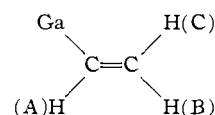
The following coupling constants and chemical shifts were obtained, via perturbation theory, from these assignments

$$J_{AC} = J_{trans} \approx 18 \text{ c.p.s.} \quad \delta^{*}{}_{A} = -25.65 \text{ p.p.m.}$$
$$J_{AB} = J_{cis} \approx 15 \text{ c.p.s.} \quad \delta^{*}{}_{B} = 0.65 \text{ p.p.m.}$$
$$J_{BC} = J_{gem} \approx 7.5 \text{ c.p.s.} \quad \delta^{*}{}_{C} = 25.00 \text{ p.p.m.}$$

From the coupling constant values the protons were identified as follows

$$\begin{array}{ccc} \text{Ga} & & \text{H(C)} \\ & \diagdown \quad \diagup & \\ & \text{C}=\text{C} & \\ & \diagup \quad \diagdown & \\ \text{(A)H} & & \text{H(B)} \end{array}$$

These approximate values of the constants were used to calculate a set of theoretical energy levels by diagonalization of the spin Hamiltonian. The calculated transitions produced a spectrum which had the same characteristics as the observed spectrum, but the line positions and intensities did not agree well with the observed values.

Rather than carry out an exact solution via the Castellano and Waugh method,[19] which would require an arbitrary adjustment of the experimental data to give exact agreement with the sum and repeated difference rules, an iterative procedure, similar to those proposed by Hoffman,[21] was used. This procedure is outlined as follows: Let us define H^0 to be an approximate Hamiltonian obtained by using approximate values of δ_{i} and J_{ij}. The true Hamiltonian H can be written as

$$H = H^0 + \Delta H \quad (3)$$

where ΔH is a correction to H^0 made up of $\Delta \delta_{i}$ corrections to the chemical shifts and ΔJ_{ij} corrections to the coupling constants. We can solve H^0 for its associated

(20) A. Allred and E. Rochow, J. Inorg. Nucl. Chem., 5, 264 (1958).
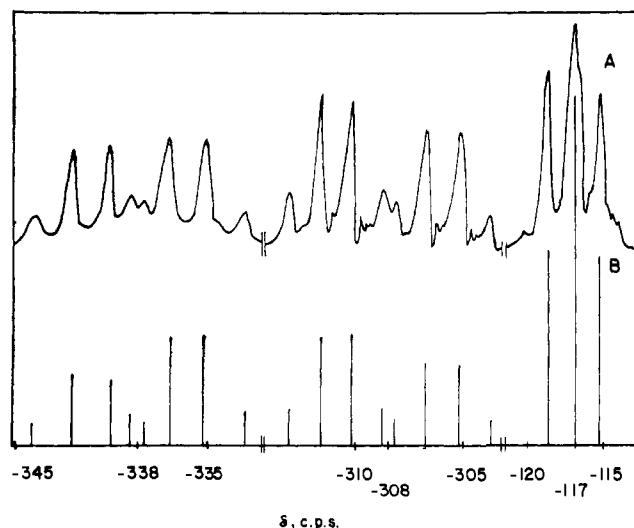(21) R. A. Hoffman, J. Chem. Phys., 33, 1256 (1960).

Fig. 2.—(A) The experimental n.m.r. spectrum of triisopropenylgallium·TMA. (B) The calculated line spectrum of triisopropenylgallium·TMA.

eigenvalues and the unitary transformation $\mathbf{U}^0$ which diagonalizes $\mathbf{H}^0$, i.e.

$$\tilde{\mathbf{U}}^0\mathbf{H}^0\mathbf{U}^0 = \Lambda^0 \qquad (4)$$

A similar transformation when carried out on the correct Hamiltonian $\mathbf{H}$ by $\mathbf{U}$ gives the energy levels Λ which reproduce the observed spectrum. It has been shown that if a transformation $\mathbf{U}$, correct to only the first order, is used, the resulting set of eigenvalues will differ from the correct eigenvalues by a second-order error.[22] Thus

$$\tilde{\mathbf{U}}^0\mathbf{H}\mathbf{U}^0 = \tilde{\mathbf{U}}^0\mathbf{H}^0\mathbf{U}^0 + \tilde{\mathbf{U}}^0\Delta\mathbf{H}\mathbf{U}^0 \qquad (5)$$

therefore

$$\tilde{\mathbf{U}}^0 = \Delta\mathbf{H}\mathbf{U}^0 = \Delta\Lambda \qquad (6)$$

where $\Delta\Lambda$ is the difference between the observed energy levels and those obtained from the approximate parameters.

One can make the very crude approximation that $\mathbf{U} = \mathbf{E}$, the identity matrix, and obtain a set of linear equations

$$\Delta H_{ii} \approx \lambda_i - \lambda_i^0 \qquad (7)$$

which can be solved simultaneously for the corrections to the coupling constants and chemical shifts. A better approximation can be obtained by solving eq. 4 for $\mathbf{H}$ giving

$$\mathbf{H} \approx \mathbf{U}^0\Lambda_{exptl}\tilde{\mathbf{U}}^0 \qquad (8)$$

which is useful after one has gone through a complete diagonalization of a trial Hamiltonian and is close to the correct solution.

Six iteration cycles were required before satisfactory agreement between experimental and calculated spectra were obtained. The parameters which reproduce the observed spectrum are shown in Table IV.

Using the values found in Table IV, the calculated line spectrum is shown in Fig. 1b. One usually compares the height of an observed line with the calculated relative intensity. However, if lines overlap or there is a variation in the widths of the observed lines, these factors must be taken into account since they contribute to the peak shapes and heights. The line widths were observed to be different for different lines in the vinyl spectrum as shown in Table II. The line shapes were taken into account by using the Lorentzian line shape function

(22) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1956, Chapter 9.

$$G(\nu) = \sum_i \frac{2T_{2(i)}}{1 + 4\pi^2 T_{2(i)}^2[\nu_i^0 - \nu]^2} I_i \qquad (9)$$

where $T_{2(i)}$ is the spin–spin relaxation time, (ν_i^0) is the center of the i-th absorption peak, i.e., the calculated line position, and I_i is the relative calculated intensity of the i-th line. A plot of $G(\nu)$ is shown in Fig. 1c for comparison with the experimental spectrum and the calculated line intensities.

TABLE IV

δ_i AND J_{ij} FOR TRIVINYL- AND TRIPROPENYLGALLIUM
DERIVATIVES

	Trivinyl-gallium[a] TMA	Triisopropenylgallium[b] TMA	Tri-cis-propenylgallium[b] TMA	Tri-trans-propenylgallium[b] TMA	Tri-trans-propenylgallium[b]
δ_A	−6.586		−5.823	−5.787	−5.752
δ_B	−6.265	−5.634	−6.439		
δ_C	−5.873	−5.144		−6.073	−6.272
δ_X		−1.947	−1.755	−1.798	−1.837
J_{AB}	14.92		13.51		
J_{BC}	5.03	4.36			
J_{AC}	21.16			18.22	
J_{AX}			−1.24	−1.59	−1.59
J_{BX}		−1.67	6.18		
J_{CX}		−1.33		5.61	5.0

[a] The chemical shifts for trivinylgallium–TMA which were obtained using cyclohexane as an internal standard were corrected to tetramethylsilane by addition of 1.60 p.p.m. to each value. [b] All chemical shifts are relative to tetramethylsilane, which was used as the internal standard.

The very close agreement of the theoretical with the experimental spectrum verifies the accuracy of the computed parameters. These constants are also consistent with previously observed spectra of vinyl compounds with regard to the magnitudes of the coupling constants. The absolute sign of the coupling constants cannot be determined.[23] However, it was established that all have the same sign. No other combinations of signs gave good agreement between experimental and calculated intensities.

If one uses the Castellano–Waugh exact method[19] to obtain coupling constants and chemical shifts and the assignment of lines given in Table III, a second set of constants are found which also reproduce the line positions very well. This second set, however, does not reproduce the observed intensities and, therefore, was discarded. The set of constants obtained above also agrees well with those found for the various propenyl derivatives presented below.

(2) Tripropenylgallium–Trimethylamine Derivatives.—The vinyl region of the n.m.r. spectrum of triisopropenylgallium–TMA is shown in Fig. 2a. The spectrum is of the ABX_3 type as are all the tripropenylgallium derivatives. The spectrum of the methyl protons is a triplet centered at $\delta_x = -1.947$ p.p.m. The center line of the triplet on careful examination can be seen to be slightly split into two lines. This indicates J_{BX} is almost equal to J_{CX}.[24]

The vinyl region consists of two groups of lines arising from protons B and C. Each group consists of a pair of overlapping quadruplets. The chemical shift difference between protons B and C is large enough to allow the use of first-order perturbation rules in analysis of this spectrum. The eigenfunctions used in computing the relative line intensities were obtained directly from second-order perturbation theory.[21] To check the results, the Hamiltonian, composed from the

(23) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution, Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., (1959), Chapter 6.

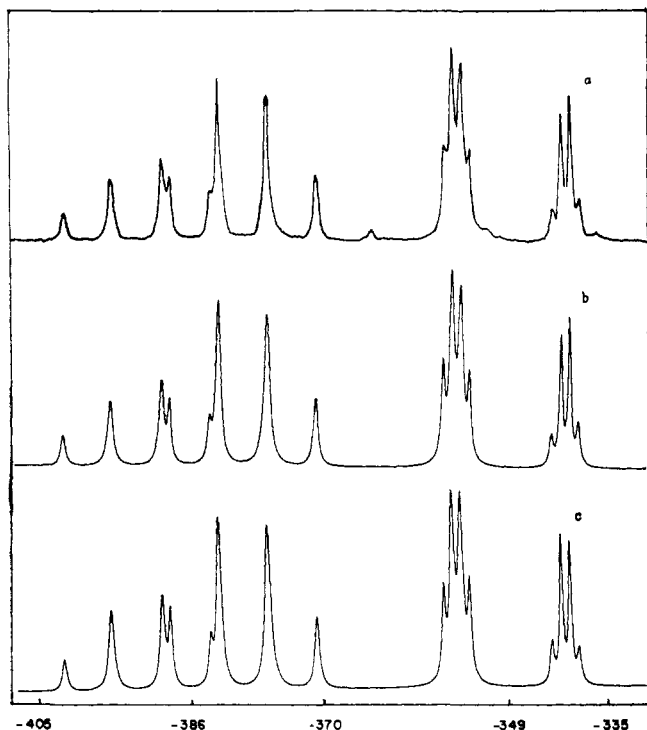(24) The classification of the A, B, and C protons is consistent with assignment given above for the vinyl derivative.

Fig. 3.—(A) The experimental n.m.r. spectrum of tri-*cis*-propenylgallium·TMA. (B) The calculated spectrum plotted using the line shape function G(ν) with opposite signs for the coupling constants. (C) The calculated spectrum plotted using the line shape function G(ν) with the same signs for the coupling constants.

first-order perturbation parameters, was solved exactly. The resulting calculated spectrum is shown in Fig. 2b. The parameters which reproduce the spectrum are listed in Table IV.

The methyl region of tri-*cis*-propenylgallium·TMA consists of a pair of doublets centered at $\delta_x = -1.755$. The vinyl region is shown in Fig. 3a. Four groups of quadruplets appear as well resolved lines as is expected from the geometry. Initial parameters were obtained *via* perturbation theory. However, these required one iteration cycle to obtain close agreement between the theoretical and experimental spectra. In this iteration, eq. 7 was used. A sufficient number of equations were generated by working only with the $F = \pm^3/_2$ blocks of the Hamiltonian.

Various combinations of signs of the three coupling constants generated the same line positions. However, slightly different intensities were obtained when using either like or opposite signs[25] for J_{AX} and J_{BX}. Figure 3b shows the theoretical spectrum obtained when J_{AX} and J_{BX} have opposite signs while Fig. 3c shows the spectrum produced by the like sign combinations. Comparison with the experimental spectrum shows that opposite signs reproduce the proper intensities. Thus, the signs of J_{AX} and J_{BX} are either $+, -$ or $-, +$, respectively.

Although the spectrum of the *trans* derivative belongs to the ABX_3 classification, there is a considerable difference between it and the spectra of the iso and *cis* derivatives. The strong coupling of the *trans* protons introduces a large intensity perturbation which causes the intensities of the A and C proton lines to pile up toward the center of the AC portion of the spectrum. Thus, the low-field portion of the vinyl lines is barely visible because of its low intensity and multiple splittings. The measured line positions of the vinyl protons

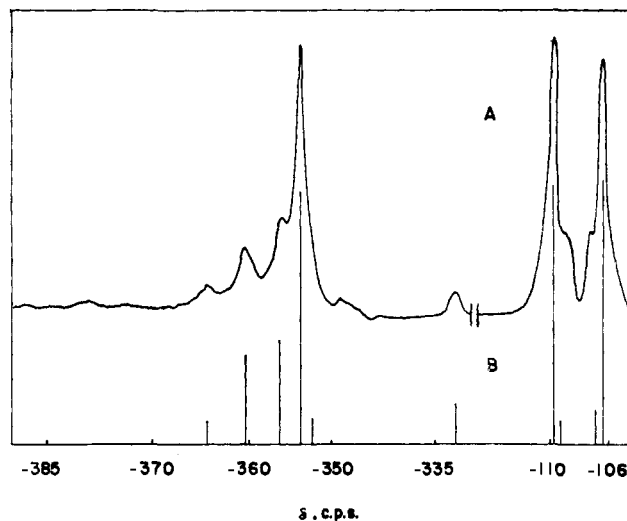(25) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **33**, 1794 (1960).

Fig. 4.—(A) The experimental n.m.r. spectrum of tri-*trans*-propenylgallium·TMA. (B) The calculated line spectrum of tri-*trans*-propenylgallium·TMA.

are listed in Table V. The characteristic quartets are observed only for proton C, lines 4, 5, 6, and 7, and the low-field group of lines of low intensity. This leaves lines 3 and 4 as the A lines (line 4 is actually a result of a partial superposition of an A and a C line). This suggests immediately that $J_{AX} = 0$. The values of δ_A and δ_C could not be obtained directly from the spectrum because of strong coupling of the A and C protons. These were computed, neglecting the X couplings, by averaging out the two C quartets. This results in a hypothetical two-spin system which is easily solved for δ_A and δ_C.

TABLE V

FREQUENCIES AND RELATIVE INTENSITIES FOR THE VINYL PROTONS OF TRI-*trans*-PROPENYLGALLIUM–TMA

Line no.	$\nu_{exptl}{}^a$ (c.p.s.)	$\nu_{calcd}{}^a$ (c.p.s.)	I
1	-105.55 ± 0.15	-105.35	20.51
2		-105.89	2.95
3	$-109.89 \pm .15$	-109.84	2.04
4		-110.09	19.89
5	$-334.59 \pm .20$	-334.59	2.36
6	$-353.71 \pm .27$	-353.71	12.98
7		-351.82	1.95
8	$-355.78 \pm .34$	-355.78	6.23
9	$-360.25 \pm .20$	-360.25	5.73
10	$-364.77 \pm .16$	-364.77	1.53
11		-371.14	0.01
12		-375.01	.37
13		-379.51	.66
14		-383.83	.04

^{a} All line frequencies are measured relative to TMS, which was used as the internal standard. Negative signs indicate a downfield shift.

The calculated spectrum obtained from the first trial parameters showed considerable deviations from the experimental spectrum and iteration of these parameters (always keeping $J_{AX} = 0$) failed to converge to the observed spectrum. Thus, it became apparent that J_{AX} was not zero.[26] On inclusion of this parameter in the iterations convergence to the observed spectrum was obtained after two cycles. The final constants are shown in Table IV. The resulting calculated spectrum is shown in Fig. 4b. The agreement with the experimental spectrum is sufficient to verify the final assignments. Sign combinations of $+, -$

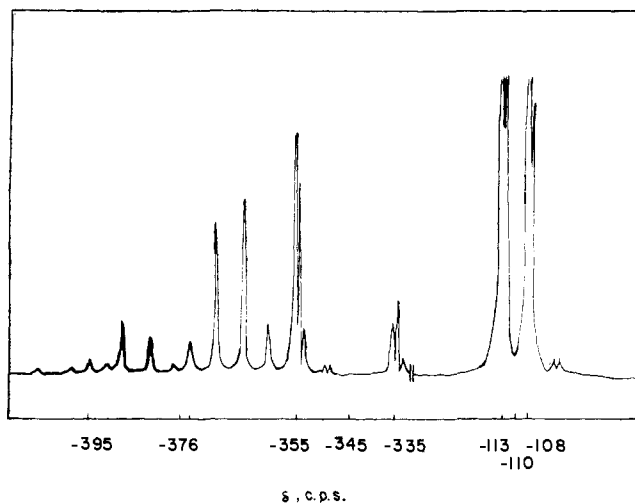(26) R. W. Fessenden and J. S. Waugh, *ibid.*, **30**, 944 (1959).

Fig. 5.—The experimental n.m.r. spectrum of tri-*trans*-propenyl-
gallium.

or −, + for J_{AX} and J_{CX} reproduce the experimental
relative intensities. It should be noted that the line
appearing at −346 c.p.s. is unaccounted for in this
analysis and must be assigned to an impurity.

(3) **Tri-*trans*-propenylgallium.**—The experimental
spectrum of tri-*trans*-propenylgallium is shown in
Fig. 5. A complete analysis of this spectrum was not
attempted. However, it appears that the propenyl
groups are equivalent, but quite distinct from the
propenyl groups in the TMA adduct. From first-
order splitting rules, approximations of the chemical
shifts were obtained and are shown in Table IV.
The coupling constants appear to be nearly the same
as those in the TMA adduct. From Fig. 5, the relative
intensities of the vinyl lines show the contour character-
istic[25] of sign combinations of +, − or −, + for J_{AX}
and J_{BX}.

Discussion

Isomeric derivatives of tripropenylgallium have
been prepared by the metal exchange reaction

$$2Ga + 3HgR_2 \longrightarrow 2GaR_3 + 3Hg$$
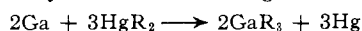
This reaction was found to proceed with dipropenyl
mercury derivatives under conditions similar to those
previously reported for divinylmercury.[15] Addition
of a nonpolar solvent did not appear to reduce the re-
action rate appreciably but did reduce the side reaction
including polymerization. In all cases the reactions
with di-*cis*-, di-*trans*-, and diisopropenylmercury were
found to proceed with complete retention of configura-
tion. The structural assignments followed directly
from the n.m.r. spectra.

The assignment of the vinyl proton bands was easily
accomplished for the *cis*- and *trans*-propenyl derivatives
by comparing the magnitude of the coupling constants
of the methyl group. The proton attached to the same
carbon as the methyl group will be more strongly
coupled to the methyl group than a proton on the op-
posite end of the vinyl group. Therefore, the well re-
solved quadruplet is assigned, in both cases, as the
proton *gem* to the methyl group. For the isopropenyl
derivative the assignment of the B and C proton lines
was made by comparing the relative chemical shifts
with those of the corresponding mercury compound
where an unambiguous assignment is possible by using
the magnitude of the Hg^{199}–H coupling constants.[14]
The observed variations in the chemical shifts of the
vinyl- and propenylgallium derivatives listed in Table
IV can be explained qualitatively by considering the
shift of electrons induced by substituting an electro-

positive gallium atom or methyl group. One would
expect that the highly electropositive gallium would
push extra electrons into the vinyl system which would
then redistribute electrons in the vicinity of protons
B and C. It is assumed that because of its proximity
to the gallium atom, the electrons will be pushed away
from the A proton position. Since an increase in elec-
tron density at the site of a proton displaces its chemical
shift upfield, the relative order of the shifts would be
$\delta_A < \delta_B < \delta_C$. Proton C is expected to be influenced
more by the gallium because it is nearer than B.

For the iso derivative, where a methyl group re-
places proton A, the partial positive charge is increased
in that position because of the inductive effect of the
slightly electropositive methyl. The result should be
a general enhancement of the dispersed charges of the
vinyl group leading to an upfield shift in δ_B and δ_C
relative to the vinyl. In the *cis* derivative, a methyl
group in position C results in a partial neutralization of
the negative charge in that position, leading to an up-
field shift in δ_A and a downfield shift in δ_B relative to the
vinyl. In the *trans* derivative, putting the methyl
group in position B again results in a partial neutrali-
zation of the negative charge in that position leading
to an upfield shift in δ_A and a downfield shift in δ_C
relative to the vinyl. These trends are observed in
the spectra of the four compounds.

The magnitudes of the coupling constants of the
vinyl derivative agree well with those of the three pro-
penyl derivatives. Those of the propenyl compounds
tend to be slightly less than those of the vinyl com-
pound. Besides confirming the stereochemistry of the
propenyl group, the agreement shows the consistency
of the analysis and supports the assumptions made
earlier concerning the dependence of coupling constants
on electronegativity of the group attached to the organic
moiety.

The absolute signs of the coupling constants cannot
be determined experimentally, however, in the case of
trivinylgallium–TMA, the di-*cis*-, and the di-*trans*-
propenylgallium–TMA, relative signs were obtained.
Coupling across the double bond is usually assigned a
positive sign, as indicated by valence-bond calcula-
tions.[13] For long-range couplings, the signs apparently
alternate as the number of bonds between the coupled
nuclei increases. If one takes the vinyl coupling con-
stants as positive, then J_{AX} is negative and J_{BX} and
J_{CX} are positive in the *cis* and *trans* isomers. On this
basis one would expect that J_{BX} and J_{CX} are negative in
the iso derivative. Although in these systems the
valence-bond calculations are unable to assign the posi-
tive or negative signs distinctly, the sign combinations
given appear to be reasonable.[25]

A comparison of the spectra of the two *trans* deriva-
tives (Fig. 4 and 5) shows that the C proton lines have
been shifted considerably downfield in tri-*trans*-
propenylgallium. This has simplified the spectrum
somewhat by decreasing $J_{AC}/(\delta_A - \delta_C)$. The remain-
ing five parameters in the two systems coincide closely.

The chemistry of these systems is of particular in-
terest because the complete retention of configuration
implies that the metal exchange reaction takes place *via*
a concerted mechanism in which the gallium atom
attacks the mercury–carbon bond. Furthermore,
it would appear that polarity of this bond is the pri-
mary factor in determining the rate of metal exchange
as cited earlier—the rate of reaction increases with in-
creasing bond polarity. However, one cannot rule out
the possibility that the double bond participates in
the metal exchange until further work is carried out.
Steric factors do not appear to effect the reaction
markedly since all of the propenyl derivatives appear

to be formed at approximately the same rate. These factors, however, are under further investigation.

The resulting tripropenylgallium compounds undergo slow isomerization reactions at room temperature. This precludes the possibility that the isomerization proceeds by the same path as exchange of propenyl groups because it has been shown that this exchange is rapid for trivinylgallium and can be shown to be rapid for tri-*trans*-propenylgallium in the same way. It should be pointed out that a factor which complicates this picture is that upon formation of the TMA adducts of the tripropenylgallium derivatives, the rate of isomerization is greatly reduced since the resulting ad-

ducts can be distilled at 40–80° without isomerization and, in fact, can stand for some time without noticeable change in this form. Thus, it would appear that the bridge bond participates in some way in the isomerization reaction. Both this phenomenon and the "rapid exchange" of the bridge and terminal vinyl groups are under investigation in this laboratory at the present time.

[Contribution from the Department of Chemistry, University of California, Riverside, California]

The Proton Magnetic Resonance Spectra and Structures of Ethylenediaminetetraacetic Acid, Methyliminodiacetic Acid, and Nitrilotriacetic Acid Chelates of Molybdenum(VI)[1]

By Sunney I. Chan, Richard J. Kula, and Donald T. Sawyer

The molybdenum(VI) chelates of ethylenediaminetetraacetic acid (EDTA), methyliminodiacetic acid (MIDA), and nitrilotriacetic acid (NTA) have been studied in aqueous solution as a function of pH (12 to 3) in varying metal–ligand ratios using proton magnetic resonance at 56.4 and 100 Mc. The combining ratios for Mo(VI)–ligand are 1:1 for NTA and MIDA, and 2:1 for EDTA. In the low pH region the methylene protons of the MIDA and EDTA chelates exhibit AB-type splitting which indicates that these protons are nonequivalent. The structures of the chelate molecules are established by interpretation of the spectra. The spectra also indicate that there is nonlabile bonding between Mo(VI) and the carboxylate groups in these chelates.

In a recent study of various aqueous metal–ethylenediaminetetraacetic acid (EDTA) chelate systems using p.m.r.,[2] the spectrum for the molybdenum(VI)–chelate appeared more complex than the simple two-resonance spectra obtained for the other metal ions. Previous work has shown that the combining ratio of molybdenum(VI) EDTA is 2:1,[3] in contrast to the combining ratio of 1:1 exhibited by most of the other chelates of EDTA.

To help elucidate the [Mo(VI)]₂–EDTA n.m.r. spectrum two model chelating agents, methyliminodiacetic acid (MIDA) and nitrilotriacetic acid (NTA), have been studied as well as their molybdenum(VI) chelates. By varying the metal–ligand ratio and the solution pH, the stoichiometry and the ranges of stability can be determined for these chelates.

Experimental

The p.m.r. spectra were recorded at room temperature using a Varian DP-60 high resolution spectrometer, equipped with a 56.4 Mc. oscillator. Chemical shifts were measured in p.p.m. from an external reference of benzene using the conventional side-band technique. No corrections were made for bulk susceptibility. Sample solutions were prepared determinately and normally had a ligand concentration of 0.5 M. The ethylenediaminetetraacetic acid (reagent grade) was obtained from J. T. Baker and Co., the nitrilotriacetic acid was obtained from Matheson, Coleman and Bell, and the methyliminodiacetic acid was obtained from the Aldrich Chemical Co. Molybdic acid (anhydride, reagent grade) was supplied by Baker and Adamson and was used without further purification.

pH measurements were made with a line-operated Leeds and Northrup pH meter employing high range glass electrodes. The pH of a chelate solution was raised initially to some high value with NaOH or KOH and then lowered with HNO₃; n.m.r. samples were taken as the pH decreased.

The 100-Mc. p.m.r. spectra were recorded by Varian Associates, Palo Alto, California.

(1) This work was supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-34, Project No. 45, and by the National Science Foundation with a predoctoral Fellowship to R. J. K.

(2) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963).

(3) R. L. Pecsok and D. T. Sawyer, *ibid.*, **78**, 5496 (1956).

Results

In a previous paper[2] the changes in chemical shift as a function of pH have been shown for ethylenediaminetetraacetic acid and methyliminodiacetic acid; the positions of protonation of these ligands also have been deduced. A similar study for nitrilotriacetic acid is illustrated in Fig. 1. The first break of the δ vs. pH curve at high pH corresponds to the protonation of the N atom, and the break at lower pH represents the successive protonations of the carboxylate groups.

The n.m.r. resonances obtained for the molybdenum(VI) chelates of EDTA and of MIDA above pH 8, and of NTA above pH 9, are pH dependent and correspond to the spectra for the "free" ligand (that is, for the ligand associated with K⁺ or Na⁺ according to whether KOH or NaOH has been used to raise the pH). Below these threshold pH values the free ligand resonances diminish in intensity and new resonances appear at lower fields. These low-field resonances are independent of pH to the lowest values studied (approximately pH 3). By varying the ratio of metal to ligand and observing the two sets of resonances below the threshold pH values given above, some indication of the stoichiometry of the chelates can be found. Thus, when excess ligand is present a resonance due to the free ligand is observed. However, when the stoichiometric metal–ligand ratio is reached this resonance disappears. Thus, it has been established there are two molybdenum(VI) ions to one ligand for EDTA and one molybdenum ion to one ligand for NTA and MIDA. Henceforth, the results discussed are for solutions containing stoichiometric ratios of molybdenum(VI) and ligand.

The spectrum obtained for Mo(VI)–NTA (Fig. 2) consists of only a single sharp resonance for the methylenic protons. The spectra obtained for Mo(VI)–MIDA (Fig. 3A) and Mo(VI)–EDTA (Fig. 4A) consist of one resonance which can be assigned to the methyl protons or the ethylenic protons, respectively, and a