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THE ^{1}H NMR SPECTRA OF Zn, Cd, Hg, Al, Ga AND In VINYL DERIVATIVES

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SUMMARY

The ^{1}H NMR spectra of $(C_2H_3)_2Zn$, $(C_2H_3)_2Cd$, $(C_2H_3)_2Hg$, $(C_2H_3)_3Al \cdot N(CH_3)_3$, $(C_2H_3)_3Ga \cdot N(CH_3)_3$, and $(C_2H_3)_3In \cdot N(CH_3)_3$ are reported. The change in the chemical shifts and coupling constants are discussed as a function of the central metal atom. The temperature dependences of exchange between the gallium and indium derivatives and their trimethylamine adducts are reported.

INTRODUCTION

NMR studies have been useful in providing information concerning the structure, bonding, and reactivity of organometallic compounds. NMR has often been used to study electron-deficient bonding and the exchange phenomena often associated with compounds which contain this type of bonding. ^{1}H and ^{7}Li resonance spectroscopy have been extremely helpful in defining the degree of association and type of bonding found in organolithium compounds[1]. Variable temperature NMR has been particularly useful in the study of the kinetics and mechanism of methyl group exchange in the $(CH_3)_6Al_2$ system[2] and also in the various exchange processes that occur upon the addition of a Lewis base to the Group IIIB methyl derivatives[3].

Of the many NMR studies of organometallic compounds, very few have dealt with the vinylmetallic species. In the past several years we have been engaged in the study of these compounds to ascertain the effects of the unsaturation upon the bonding, exchange parameters, and stability of these organometallic systems. We have previously observed that these vinyl compounds exhibit a greater tendency toward association than the comparable alkyl derivatives[4]. This increased tendency toward association is thought to arise from the interaction of the π orbitals of the vinyl group with the non-bonding orbitals associated with the 3-centered molecular orbital[5]. Alternately the effect may result from the greater electronegativity of the sp^2 orbital of the vinyl group. In addition to the tendency for the vinyl group to appear in the bridging position, the Lewis acidity of the compound is increased as demonstrated by the increased heat of formation of adducts over that observed for simple alkyl derivatives[6].

In this paper the analysis of the ^{1}H NMR spectra of a series of metal vinyl

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compounds will be reported and a number of these factors will be discussed in view of these results.

EXPERIMENTAL

$(C_2H_3)_2Zn^7$, $(C_2H_3)_2Cd^8$, $(C_2H_3)_2Hg^9$, $(C_2H_3)_3Al^{10}$, $(C_2H_3)_3Ga^4$, LiC_2H_3, and $C_2H_3MgX^{12}$ were prepared by the methods previously described in the literature.

$(C_2H_3)_3In$ was prepared by a method similar to that used for the $(C_2H_3)_3Ga$ synthesis[4]. Indium metal was stirred with an excess of $(C_2H_3)_2Hg$. After stirring for two days at room temperature the indium metal became amalgamated, however the reaction was continued for a week. The excess $(C_2H_3)_2Hg$ was distilled from the reaction vessel leaving a viscous yellow oil. When this oil was heated to 80° at 10^{-6} mmHg a crystalline white solid (m.p. $27.0 \pm 0.5°$) was sublimed. The NMR spectrum of this compound did not exhibit the metal–proton coupling which is typical of vinylmercury compounds. When reacted with $N(CH_3)_3$ a 1/1 addition compound was obtained. $(C_2H_3)_3In$ resembled $(CH_3)_3In$ in possessing only limited solubility in hydrocarbon solvents such as hexane and cyclopentane.

Sample preparation was performed using standard vacuum and dry box techniques. Hydrocarbon and ether solvents were distilled from sodium metal and thoroughly degassed prior to use. NMR spectra were recorded on either a Varian A–60A or a Jeolco JNM–4H–100 spectrometer. The spectra were calibrated using linear interpolation between audio frequency sidebands for each experimentally observable line. $(CH_3)_4Si$ was used as an internal standard. The spectra were analyzed using the method of Castellano and Waugh[13]. In most cases the results were checked using LAOCN3 method[14]. Since these two methods differ mathematically in their mode of analysis they constitute an effective check on the accuracy of the spectral parameters. In all cases the agreement between the two methods was within 0.1 Hz for all parameters.

RESULTS AND DISCUSSION

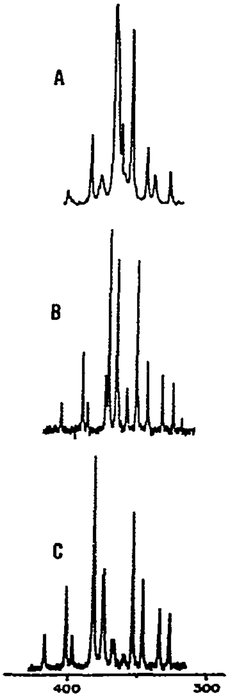
The most convenient laboratory method for preparing adduct-free organo aluminum, gallium and indium compounds is through the reaction between a diorganomercury derivative and the appropriate metal. The trisubstituted vinyl derivatives of these metals are more difficult to prepare than either the aryl or alkyl analogues, since they tend to polymerize. We prepared $(C_2H_3)_3In$ by reaction of $(C_2H_3)_2Hg$ with In metal. As in the case of the $(C_2H_3)_3Al^{10}$ and $(C_2H_3)_3Ga^4$, the crude reaction product was a viscous yellow oil [a mixture of polymerized and unpolymerized $(C_2H_3)_3In$]. Once $(C_2H_3)_3In$ was purified it was stable at room temperature toward further polymerization. $(C_2H_3)_3Ga$ polymerizes at room temperature but can be stored for months below 0° without any evidence of polymerization. $(C_2H_3)_3Al$ is difficult to prepare and characterize at any temperature and polymerizes at temperatures below 0°. Thus there exists a trend in the stability of these Group III compounds toward polymerization: $(C_2H_3)_3In > (C_2H_3)_3Ga > (C_2H_3)_3Al$.

Fig. 1 shows the NMR spectra of $(C_2H_3)_3Al \cdot N(CH_3)_3$, $(C_2H_3)_3Ga \cdot N(CH_3)_3$ and $(C_2H_3)_3In \cdot N(CH_3)_3$. The amine adducts were chosen for comparison because of the inability to isolate pure $(C_2H_3)_3Al$. In addition these adducts eliminate consideration of the effects of monomer–dimer equilibrium $[(C_2H_3)_6M_2 \rightleftarrows 2(C_2H_3)_3M]$, discussed previously for $(C_2H_3)_3Ga^5$. The spectral parameters of several Group III vinyl compounds as discussed in this study are listed in Table 1 along with some of the values which have appeared in the literature.

The NMR spectrum of $(C_2H_3)_3B$ has been reported[17] to be an 8 line multiplet broadened by nuclear quadrupole effects. The lines observed in the spectrum $(C_2H_3)_3$-$Al \cdot N(CH_3)_3$ were also very broad, presumably due to quadrupole and coupling effects, so the spectrum could not be accurately calibrated and therefore an accurate analysis could not be obtained. It has been reported previously that the intensities of the calculated and experimental spectrum of $(C_2H_3)_3Ga \cdot N(CH_3)_3$ could not be matched until the difference in half width ($\nu_{\frac{1}{2}}$) of various lines was taken into account[16]. No explanation was given at that time why the $\nu_{\frac{1}{2}}$ of the lines assigned to the *trans* proton were broader than those of the *cis* and *gem* protons. Similar line broadening was observed for the other addition compound of $(C_2H_3)_3Ga$.

This line broadening might be explained on the basis of exchange with trace quantities of excess base or trivinylgallium. However, Fig. 2 shows that the portion of spectrum assigned to the *cis* proton, not that of the *trans* proton, is the most sensitive to exchange phenomena in the $(C_2H_3)_3Ga$–$(C_2H_3)_3Ga \cdot N(CH_3)_3$ systems, thus ruling out exchange broadening. In addition the broadening in the $(C_2H_3)_3Ga \cdot N(CH_3)_3$ spectrum is not particularly sensitive to temperature. This latter factor also points to quadrupole effects.

Theoretical calculations have shown that, when quadrupole relaxation has



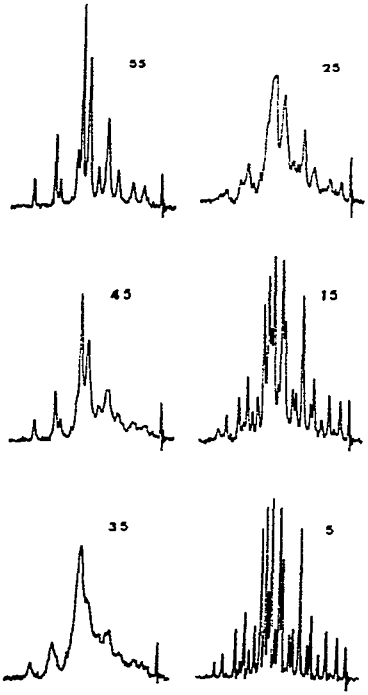


Fig. 1. The 60 MHz NMR spectra of the addition compounds of $(C_2H_3)_3Al \cdot N(C_2H_3)_3$ (A), $(C_2H_3)_3Ga \cdot N$-$(CH_3)_3$ (B) and $(C_2H_3)_3In \cdot N(CH_3)_3$ (C).

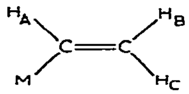
Fig. 2. The temperature dependence 60 MHz NMR spectra of a Freon 11 solution containing $(C_2H_3)_3Ga$ and $(C_2H_3)_3Ga \cdot N(CH_3)_3$ in approximately equal concentrations.

TABLE 1

PROTON NMR SPECTRAL PARAMETERS FOR VINYL METAL COMPOUNDS

Compound	δ_A[a]	δ_B	δ_C	J_{AB}	J_{AC}	J_{BC}	ΣJ	*Solvent*	*Ref.*
C_2H_3Li	0.0[b]	0.511	1.19	19.3±0.5	23.9±0.5	7.1±0.5	50.3	Diethyl ether	25
C_2H_3MgCl	6.68	6.13	5.57	17.6	23.0	7.5	48.1	THF	26
C_2H_3MgBr	6.48	5.98	5.66	17.2	22.1	7.4	46.7	THF	27
	6.66	6.148	5.57	17.70	23.30	7.60	48.60	THF	22
$(C_2H_3)_2Zn$	6.275	6.065	5.604	15.74	21.90	5.44	43.08	Diethyl ether	
				16.1	20.7	2.6	39.4		20
$(C_2H_3)_2Cd$	6.454	6.121	5.600	15.20	21.66	4.93	41.79	Diethyl ether	
$(C_2H_3)_2Hg$	5.87[c]	5.07	4.53	13.1	21.0	3.5	37.6		15
	6.637	5.881	5.314	13.83	20.72	3.28	37.83	Cyclopentane	
$(C_2H_3)_3Al$ etherate	4.79[c]	4.54	4.18	15.3	21.4	6.3	43.0		15
$(C_2H_3)_6Ga_2$	6.486	6.260	5.930	14.49	21.30	4.07	39.86	Freon 11	
$(C_2H_3)_3Ga\cdot N(CH_3)_3$	6.380	6.068	5.686	14.94	21.20	5.15	41.29	Freon 11	
	4.986[d]	4.665	4.273	14.92	21.16	5.03	41.11	Cyclohexane	16
$(C_2H_3)_3In$	6.631	6.130	5.881	14.40	21.47	4.13	40.00	Freon 11	

[a] Protons are labeled as indicated:



Chemical shift δ values are relative to $(CH_3)_4Si$ and all spectral parameters reported were obtained at ambient probe temperature of approximately 38°. [b] Internal chemical shifts are relative to H_A. [c] Chemical shifts (40 MHz spectra) are downfield relative to external cyclohexane ($\approx$1.42 ppm downfield from $(CH_3)_4$-Si), and have not been corrected for differences in magnetic susceptibility of the solvent. [d] δ relative to cyclohexane solvent.

caused collapse of a multiplet into a single line, $\nu_{\frac{1}{2}}$ depends upon the product $J^2 \cdot T_1$ (where T_1 is the spin–lattice relaxation time). Since the J term appears to the second power, the line width should be very sensitive to its value[18]. In all metal vinyl systems for which data are available, the metal atom is coupled to the *trans* proton to a greater extent than either of the other two protons. Hence, as is experimentally observed, the line shape of the *trans* proton should be more sensitive to quadrupole effect than the other two protons. Evidence for quadrupole broadening by gallium has been reported for the hydride derivatives in which the directly bonded hydrogen resonance is broadened to the point where it has not been experimentally observed[19].

Fig. 3 shows the NMR spectra of the three Group II metal vinyl compounds. The results of our analysis of these spectra, along with those reported previously, are listed in Table 1.

The coupling constants previously reported for $(C_2H_3)_2Hg$ agree quite well with our results, but the chemical shifts do not. It is believed that the systematic difference in chemical shift is a result of the use of an external standard in the original

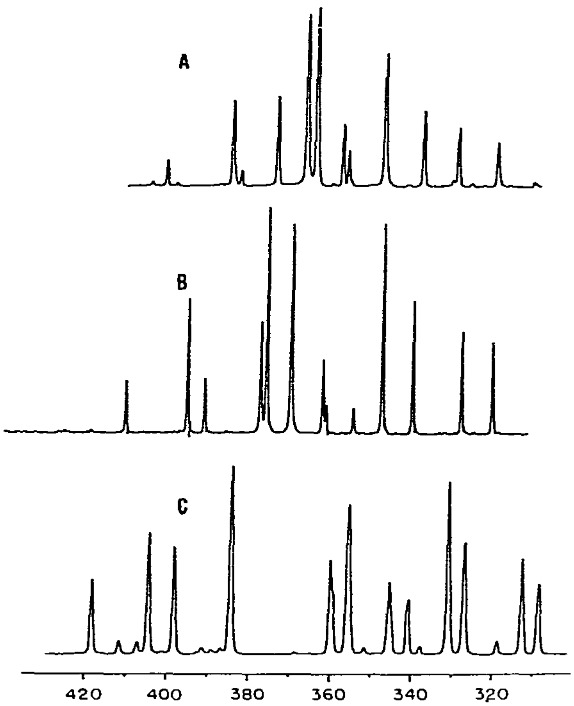


Fig. 3. The 60 MHz NMR spectra of A, $(C_2H_3)_2Zn$ (ether), B, $(C_2H_3)_2Cd$ (ether) and C, $(C_2H_3)_2Hg$ (cyclopentane).

report resulting in an apparent downfield shift[15]. No effort was made to correct these data for the differences in susceptibility resulting from the use of the external standard.

The literature contains a study of the relationship between electronegativity and the coupling constants in a series of vinyl compounds in which Muller references the exact analysis of the $(C_2H_3)_2Zn$ spectrum[20]. Close examination reveals, however, that the analysis assigned to $(C_2H_3)_2Zn$ in Muller's study is really that of $(C_2H_3)_4Sn$ in the original reference[21]. The fact that the electronegativities of zinc and tin are only slightly different (0.2 on the Pauling scale) enabled Muller to fit his electronegativity plots of $(C_2H_3)_2Zn$ quite well using the data for $(C_2H_3)_4Sn$. The same erroneous data were used subsequently in the correlation of the infrared data of several vinyl compounds with their respective NMR parameters[22]. In this study a linear relationship was obtained when $\Delta\nu(C{=}C)$ ($\Delta\nu(C{=}C)$ is the difference between double bond stretching frequency, $\nu(C{=}C)$, of the organometallic compound and that of propene) was plotted *versus* ΣJ (sum of the proton–proton coupling constants of vinyl group). In this plot, $(C_2H_3)_2Zn$ was one of the points which portrayed an especially large deviation from the linear relationship. Use of ΣJ 43.08, obtained from our analysis of the $(C_2H_3)_2Zn$ spectrum, rather than the incorrect ΣJ 39.4, does cause this point to fall within a standard deviation of the straight line in that plot.

From Fig. 1 and 3 it is readily apparent that the internal chemical shift increases as atomic number of the central metal atom increases. The trend in the internal chemical shifts of the Group III compounds is not as well defined as in Group II compounds. This is in part due to the fact that the amine addition compounds are being compared. The addition compounds generally have larger internal chemical shifts than the uncoordinated derivatives with the magnitude of this effect related to Lewis acidity of compound. Since Lewis acidity decreases as one goes down the periodic chart, this factor would tend to offset any trend in internal chemical shifts of these Group III metal vinyl compounds.

Apparently this trend in the chemical shifts for the Group III compounds can be extended through thallium. We, like several others, have been unable to isolate pure $(C_2H_3)_3Tl$[23], but the internal chemical shifts $(CH_3)_nTl(C_2H_3)_{(3-n)}$ species are larger than those of the analogous indium compounds.

Where sufficient data are available, this relationship between the magnitude of the internal chemical shift and the atomic number of the central element of the vinyl compound seems to be general. The trend has also been reported for the Group III compounds and was subjected to experimental and theoretical investigation by Cawley and Danyluk[24], who attributed the trend to diamagnetic anisotropy of the metal–carbon bond. Our observations agree with, and lend further credence to, their conclusions.

Considerable difficulty was encountered with the attempt to extend the relationship further in the periodic chart. Both C_2H_3Li[25] and C_2H_3MgX[21,26,27] (ether solvent) possess much larger chemical shifts than would be expected based on the preceding discussion. Lithium compounds and Grignard reagents are known to associate; and in the case of the lithium compounds, electron-deficient bonding in which the organic moiety participates is well documented. Electron-deficient bonding, however, normally causes a downfield shift in the resonance, as noted in $(C_2H_3)_6Ga_2$[5] and in organoaluminum compounds.

This upfield shift possibly relates to the fact that both lithium and magnesium compounds are strongly coordinated in ether solvents. Generally speaking, coordination of the central metal atom causes a much larger upfield chemical shift change for the protons *cis* and *trans* to the metal than for the *geminal* proton; *i.e.*, the internal chemical shifts are increased by coordination. As stated earlier, the magnitude of these changes seems to be related to the Lewis acidity of these compounds. Solubility effects make it difficult to adequately test this hypothesis in the case of these Group I and II metal vinyl compounds.

It has been proposed that the proton–proton coupling constants of a vinyl group are linearly related to the electronegativity of substituent to which the vinyl group is attached[28]. More recently when the correlation was extended to include disubstituted ethylenes the coupling constants were related to the inverse of the sum of the substituent electronegativity[29]. In the electronegativity range under consideration in this study (*i.e.*, monosubstituted ethylenes with substitutions electronegativity < 2.5) the relationships are nearly identical. Including our data with those reported by others, the relationship appears to be fairly linear in nature.

Fig. 2 portrays the temperature dependence of the intermolecular group exchange in the $(C_2H_3)_3Ga$–$(C_2H_3)_3Ga \cdot N(CH_3)_3$ system, which is presumed to go through a rate determining dissociation of the Ga–N bond in $(C_2H_3)_3Ga \cdot N(CH_3)_3$. Above 50° the exchange is rapid so that only one average spectrum is observed. As the temperature is lowered the spectra lines begin to broaden and eventually split into two distinct spectra, that of $(C_2H_3)_3Ga$ and $(C_2H_3)_3Ga \cdot N(CH_3)_3$. As the tem-

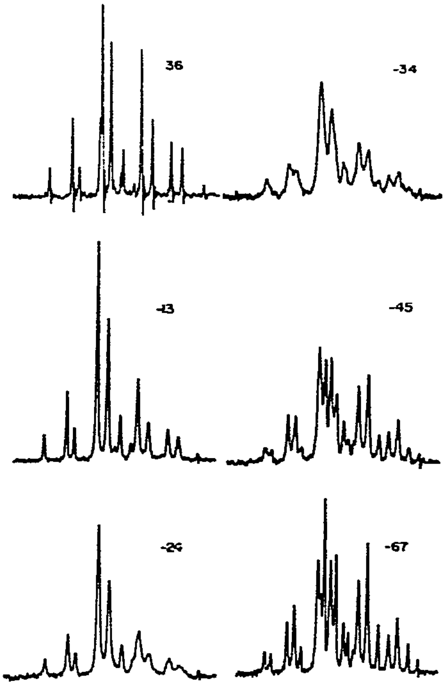


Fig. 4. The temperature dependence of the 60 MHz NMR spectrum of a Freon 11 solution containing $(C_2H_3)_3In$ and $(C_2H_3)_3In \cdot N(CH_3)_3$.

perature is lowered broadening is first observed in spectral lines assigned to the *cis* proton, then in those of the *trans* proton and eventually in the portion of the spectrum assigned to the *geminal* proton. Since all protons are undergoing the same exchange process we may assume that the temperature dependence of the collapse of various portions of the spectra will be related to $\Delta\delta$ (the difference in chemical shift between sets of lines arising from the same type of proton in the two species). Table 1 shows that the $\Delta\delta$ for the *cis*, *trans*, and *gem* protons are in the same relative order as the temperature dependence predicts:

$$\Delta\delta_c\ 0.24 > \Delta\delta_t\ 0.19 > \Delta\delta_g\ 0.11\ \text{ppm}.$$

Fig. 4 shows the temperature dependence of the exchange behavior for the $(C_2H_3)_3In$–$(C_2H_3)_3In \cdot N(CH_3)_3$ system. This indium system is similar to the gallium system except that the coalescence temperatures are considerably lower. This same observation was made for the analogous methyl indium and gallium systems[30]. Kinetic studies of these latter revealed that activation of the $(CH_3)_3Ga$–$(CH_3)_3Ga \cdot N(CH_3)_3$ systems was higher than $(CH_3)_3In$–$(CH_3)_3In \cdot N(CH_3)_3$ system. We are currently investigating methods for determining the kinetic parameter for the vinyl systems.

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