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SYNTHESIS AND PROTON NUCLEAR MAGNETIC RESONANCE STUDIES ON DIVINYL- AND METHYLVINYLCADMIUM AND METHYL-VINYLMERCURY*

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SUMMARY

Divinylcadmium was synthesized by group exchange between $Hg(CH=CH_2)_2$ and $Cd(CH_3)_2$. Pure divinylcadmium is a colorless, crystalline solid which can be sublimed under high vacuum. It is soluble in ethers but is sparcely soluble in hydrocarbons.

The proton NMR spectra of ether and hydrocarbon solutions of $Cd(CH=CH_2)_2$ do not show [111]Cd or [113]Cd coupling. This has been interpreted as indicating rapid vinyl group exchange. Investigation of mixtures of $Cd(CH=CH_2)_2/Cd(CH_3)_2$ show slow methyl group exchange between $Cd(CH=CH_2)(CH_3)$ and $Cd(CH_3)_2$, while vinyl group exchange appears to remain rapid since no Cd–H coupling is observed.

INTRODUCTION

Organocadmium compounds have been widely used in synthetic organic chemistry and as a result, considerable information has been reported about the reactivity of the dialkyl and diaryl derivatives. Until very recently, however, almost no information existed concerning the non-cyclic unsaturated organocadmium derivatives. Current interest in this latter area centers around the structure and bonding present in these compounds and the exchange phenomena exhibited by them. Some acetylenic derivatives, namely, bis(phenylethynyl)cadmium and bis-(1-octynyl)cadmium, have been prepared and were found to be polymeric[1]. Diallylcadmium has been synthesized and similar to diallylzinc it is believed to possess an "ionic" structure[2,3], whereas diallylmercury is thought to contain a σ bonded allyl group. Variable temperature NMR studies indicates that some of these structures are temperature dependent. These temperature dependent "allylic exchanges" have been and still are the subject of study by several research groups[4].

At this time we would like to report the synthesis of $Cd(CH=CH_2)_2$, compare

its physical properties with other Group IIB vinyl compounds, and describe some of the exchange phenomena exhibited by these Group IIB vinyl species.
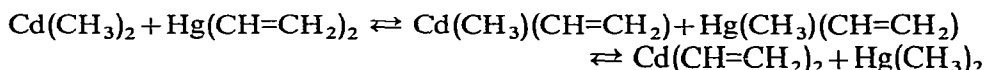
EXPERIMENTAL

Preparation of compounds

The $Cd(CH_3)_2$ and $Hg(CH=CH_2)_2$[5] were prepared by the standard Grignard methods and were purified by trap to trap distillation in a high-vacuum line. $CH_3Hg-CH=CH_2$ was prepared[6] by heating $Hg(CH_3)_2$ and $Hg(CH=CH_2)_2$ together for one week at 100°. $Zn(CH=CH_2)_2$ was synthesized both by the Grignard method[7] and by the metal exchange reaction[8] of zinc metal with $Hg(CH=CH_2)_2$.

Synthesis of divinylcadmium

Several different techniques were tried to obtain divinylcadmium. Direct reaction between vinyl Grignard and $CdCl_2$ gave a variety of decomposition products including cadmium metal, but no vinylcadmium species were detected in accord with the previously reported result[9]. Reaction of $LiCH=CH_2$ with $CdCl_2$ in THF appeared to yield vinylcadmium derivatives, but no pure product was obtained.

The successful synthesis was accomplished by mixing $Cd(CH_3)_2$ with $Hg-(CH=CH_2)_2$. The equilibrium:

$$Cd(CH_3)_2 + Hg(CH=CH_2)_2 \rightleftarrows Cd(CH_3)(CH=CH_2) + Hg(CH_3)(CH=CH_2)$$
$$\rightleftarrows Cd(CH=CH_2)_2 + Hg(CH_3)_2$$

reactions occurred with production of a variety of products discussed below. The equilibrium appears to lie far to the right, thus allowing recovery of $Cd(CH=CH_2)_2$.

The optimum reaction conditions so far found are to distill equimolar amounts of $Cd(CH_3)_2$ and $Hg(CH=CH_2)_2$ into a tube attached to the vacuum system and seal this off, then heat this mixture for approximately 5 days at 60° to allow the reaction to approach equilibrium, reattach it to the vacuum system, and pump off the liquid portion which consists mostly of $Hg(CH_3)_2$ and a small amount of $Cd(CH_3)_2$ and $Hg(CH_3)(CH=CH_2)$. This leaves a grayish-white solid which is principally $Cd-(CH=CH_2)_2$. This crude product was then sublimed at 70° and 10^{-6} mm to give a clear crystalline material. Acid hydrolysis of a 41.4 mg sample gave the results indicated in Table 1. The amount of ethylene produced was determined by its gas

TABLE 1

RESULTS FOR THE HYDROLYSIS OF $Cd(CH=CH_2)_2$

	Cd (g-atoms)	C_2H_4 (mmoles)
Calculated	0.249	0.498
Found	0.222	0.483
% theoretical	94.4%	96.6%

volume and identified by its IR spectrum. The cadmium analysis was performed by a polarographic method.

Further identification of divinylcadmium was obtained by examination of its

mass spectrum obtained at 70 eV on an Atlas CH-4 mass spectrometer. This showed the molecular ion $Cd(CH=CH_2)_2^+$, with the correct ratio of cadmium isotopes, the ion $CdCH=CH_2^+$ and Cd^+ as well as other fragments.
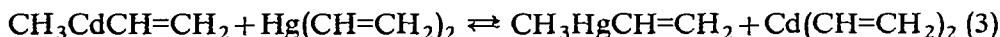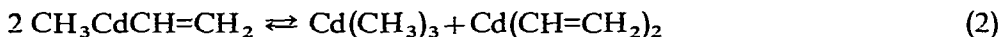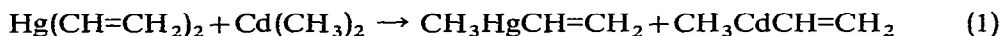
NMR spectra

The NMR spectra were recorded on a Varian A-60A spectrometer and a Jeolco JNM 4H-100 spectrometer which was equipped with a JRA-5 computer to perform the time average spectra. The spectra were calibrated by the audio-frequency side band method using internal $Si(CH_3)_4$ in the case of the zinc and cadmium compounds and internal cyclopentane in the case of the mercury compounds.

RESULTS AND DISCUSSION

A literature search produced two references concerning $Cd(CH=CH_2)_2$. One reports that the attempted synthesis of $Cd(CH=CH_2)_2$ by the reaction between $LiCH=CH_2$ or $CH_2=CHMgX$ and CdX_2 did not yield any vinylcadmium species[9]. Similar attempts in our laboratory failed to produce any significant amounts of $Cd(CH=CH_2)_2$. The patent literature reports the synthesis of $Cd(CH=CH_2)_2$ by the reaction of $Hg(CH=CH_2)_2$ with cadmium metal; however, no analytical data was supplied to verify this belief[8]. Efforts to duplicate these results were unsuccessful even when attempted under far more vigorous conditions. Furthermore, the product originally claimed to be $Cd(CH=CH_2)_2$ was a liquid, whereas the substance we eventually identified as $Cd(CH=CH_2)_2$ was a crystalline solid.

In an attempt to gain information about vinylcadmium species, we conducted a detailed investigation of the redistribution reaction between $Cd(CH_3)_2$ and $Hg(CH=CH_2)_2$. The progress of this reaction was monitored by NMR in a series of samples containing different relative amounts of $Cd(CH_3)_2$ and $Hg(CH=CH_2)_2$ (no solvent). The reaction mixture was heated to 65° and monitored periodically for one week. This study indicates that the reaction sequence must be:

$$Hg(CH=CH_2)_2 + Cd(CH_3)_2 \rightarrow CH_3HgCH=CH_2 + CH_3CdCH=CH_2 \qquad (1)$$

$$2\,CH_3CdCH=CH_2 \rightleftharpoons Cd(CH_3)_3 + Cd(CH=CH_2)_2 \qquad (2)$$

$$CH_3CdCH=CH_2 + Hg(CH=CH_2)_2 \rightleftharpoons CH_3HgCH=CH_2 + Cd(CH=CH_2)_2 \;(3)$$

The first reaction of this sequence was identified by the early build-up of CH_3Hg-$CH=CH_2$. The NMR spectrum of this species has not been previously reported. Its spectrum was identical with the NMR spectrum of an authentic sample of CH_3Hg-$CH=CH_2$ which was prepared by the prescribed literature route[6].

Either step 2 or 3 is essential for the production of divinylcadmium and both may be operative. Step 2 is, however, probably the predominant path for formation of $Cd(CH=CH_2)_2$ early in the reaction since rapid Cd–C bond breaking is indicated by the line broadening and disappearance of the $^{111}Cd-^1H$ and $^{113}Cd-^1H$ satellites. The eventual appearance of $Hg(CH_3)_2$ in this reaction mixture implies the following reaction also occurs:

$$CH_3HgCH=CH_2 + RCdCH_3 \rightarrow RCdCH=CH_2 + Hg(CH_3)_2 . \qquad (4)$$

$Hg(CH_3)_2$ could arise from the redistribution of $CH_3HgCH=CH_2$; however, this

reaction is slow under our reaction conditions. No direct evidence was obtained for the existence of $CH_3CdCH=CH_2$ in these reaction mixtures. Vacuum distillation of these mixtures gave only five products: $Hg(CH_3)_2$, $CH_3HgCH=CH_2$, $Hg(CH=CH_2)_2$, and $Cd(CH=CH_2)_2$.

The physical properties of $Cd(CH=CH_2)_2$ are especially noteworthy since they differ markedly from those of $Zn(CH=CH_2)_2$ and $Hg(CH=CH_2)_2$. $Cd(CH=CH_2)_2$ is a colorless, air and water sensitive crystalline solid, which can be readily sublimed in a vacuum system. When this solid is left undisturbed in an evacuated vessel it grows into square pyramidal shaped crystals. $Cd(CH=CH_2)_2$ is virtually insoluble in non-polar hydrocarbon solvents, but is readily soluble in basic solvents, such as ethers and amines. In contrast, $Zn(CH=CH_2)_2$ and $Hg(CH=CH_2)_2$ are relatively non-volatile liquids which at room temperature are miscible with hydrocarbon solvents. In the past the insolubility of Group IIB compounds in hydrocarbon solvents has been taken as evidence for the association of these compounds into a polymeric structure[1,10], thus, the solubility behavior of $Cd(CH=CH_2)_2$ raises the question as to its associative properties. Cryoscopic molecular weight determination were unsuccessful when benzene was used as a solvent because of limited solubility and unexplained decomposition. Similar attempts failed for cyclohexane solutions because of insufficient solubility. The solubility behavior and the ease of crystal growth for $Cd(CH=CH_2)_2$ closely resemble that of $In(CH_3)_3$, which is "pseudo associated" in the solid state[11] but monomeric in solution[12].

$Cd(CH=CH_2)_2$ is very stable when pure with only very slight decomposition observed after several months of storage at room temperature under vacuum. In solution, however, it is less stable especially when the solutions contain additional organometallic derivatives which may interact with the cadmium. This could be the reason that the $LiCH=CH_2$ and $CH_2=CHMgX$ preparative methods failed to produce any significant yield of $Cd(CH=CH_2)_2$; that is, these reagents catalyze the decomposition of the vinylcadmium species which are formed. This decomposition is shown by the fact that these reactions generate large amounts of colloidal cadmium metal[9]. A similar catalyzed decomposition occurs in solutions of $Zn(CH=CH_2)_2$ which contain additional salts or organometallic compounds[7].

In the mechanism described earlier, we postulated the existence of CH_3Cd-$CH=CH_2$ as an intermediate. The species, however, was never isolated from or directly observed in the reaction mixture. This apparent absence was the subject of further investigation. Circumstantial evidence for its existence was obtained by the observation that the addition of $Cd(CH_3)_2$ to a saturated solution of $Cd(CH=CH_2)_2$ in cyclopentane [$Cd(CH=CH_2)_2$ itself is only very slightly soluble in cyclopentane] greatly increased the solubility of the vinyl species. Similar solubility data were observed in methylene chloride solutions at low temperatures (-30 to $50°$). This indicates the reaction

$$Cd(CH=CH_2)_2 + Cd(CH_3)_2 \rightarrow 2\ CH_3CdCH=CH_2 \qquad (5)$$
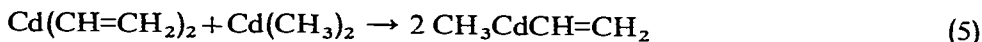
takes place and that $CH_3CdCH=CH_2$ has substantially greater solubility in hydrocarbon solvents than $Cd(CH_3)_2$. An analogous situation appears to be true for the reaction

$$CdR_2 + CdX_2 \rightleftharpoons 2\ RCdX \qquad (6)$$

as reported by Paleeva et al.[13] and more recently discussed by Cavanagh and Evans[14] and by Roberts et al.[15] in which the solubility of RCdX is substantially greater than that of CdX_2 in ethers.

Further evidence for the formation of the mixed species $CH_3CdCH=CH_2$ was found by examination of the NMR spectrum. If small amounts of $Cd(CH=CH_2)_2$ are added to a solution of $Cd(CH_3)_2$ in hydrocarbon, line broadening or collapse of the satellite spectrum is observed. In dilute methylene chloride solutions containing equal concentrations of $Cd(CH=CH_2)_2$ and $Cd(CH_3)_2$ more definitive evidence was obtained. Two resonances in the methyl region were observed each with a satellite pattern typical of a methylcadmium species (see Fig. 1). The upfield spectrum was
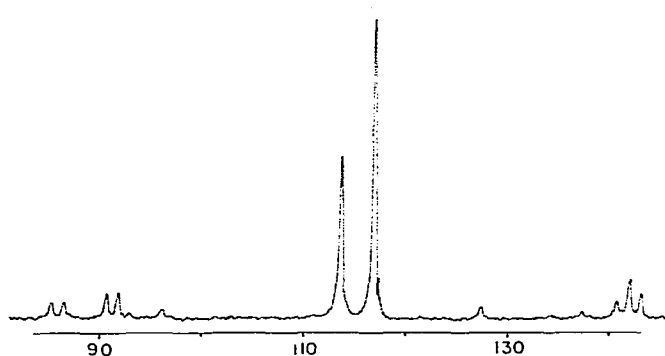

Fig. 1. The 60 MHz spectrum of the methyl region of a mixture containing $Cd(CH_3)_2$ (δ 1.95 ppm) and $CH_3CdC_2H_3$ (δ 1.89 ppm) showing [111]Cd and [113]Cd satellites. The line positions are relative to internal cyclopentane (solvent) in Hz and the sample was at 40°.

assigned to $Cd(CH_3)_2$ and lowfield spectrum was assigned to $CH_3CdCH=CH_2$. Table 2 lists the chemical shifts and coupling constants of these species along with

TABLE 2

CHEMICAL SHIFTS AND COUPLING CONSTANTS IN THE METHYL SPECTRUM OF THE $M(CH_3)_2$ AND $CH_3MCH=CH_2$ DERIVATIVES OF THE GROUP IIB METALS

	$\delta(CH_3)$ (ppm)[a]	$J(M-CH_3)$ (Hz)		
$Zn(CH_3)_2$	2.0			
$Cd(CH_3)_2$	1.95	50.0([111]Cd)[b]	52.2([113]Cd)[b]	
$CH_3CdCH=CH_2$	1.89	540([111]Cd)	56.6([113]Cd)	
$Hg(CH_3)_2$	1.20	102.5		
$CH_3HgCH=CH_2$	1.07	106.7		
$Cd(CH=CH_2)_2$	$\delta_A = -6.454^c$	$J_{AB}=15.2$		A B \C=C/ Cd C
	$\delta_B = -6.121^c$	$J_{AC}=21.7$		
	$\delta_C = -5.600^c$	$J_{BC}=4.93$		

[a] Upfield relative to internal cyclopentane. [b] Klein and Waugh[29] report [111]Cd–[1]H as 47.83 and [113]Cd–[1]H as 49.90 Hz. The somewhat different experimental conditions may have given to the ~2 Hz increase in Cd–[1]H coupling. [c] Relative to internal TMS, approximately 0.1 M in ether solvent at 38°, calculated by the method of Castellano and Waugh[30].

those of the analogous mercury compounds. In both cases the chemical shift of the methyl group in the methylvinyl species occurs at lower field than that of the corresponding dimethyl species. This deshielding effect is what one would expect when a methyl group of the dimethyl species is replaced by a more electronegative group; namely, a vinyl group. The metal–proton coupling observed in the methyl spectra of $CH_3HgCH=CH_2$ is larger than that observed for the corresponding dimethyl species. This observation was anticipated based upon the previous study of a series of CH_3HgY compounds in which it was definitively shown that J(Hg–H) increases as the electronegativity of Y group increases[17]. On the other hand, replacing a vinyl group on $Hg(CH=CH_2)_2$ by a more electron donating methyl group causes a downfield shift or a deshielding effect on the vinyl protons. This is in the opposite direction from that expected based on electronegativity arguments. At this time we have no explanation for this observation other than possibly anisotropy effects.

Mixtures of $CH_3CdCH=CH_2$ and $Cd(CH=CH_2)_2$ gave a single sharp vinyl spectrum under all experimental conditions studied. The concentration dependence for the chemical shifts of the vinyl-protons in $Cd(CH=CH_2)_2$ made it difficult to obtain any reliable chemical shift information from a mixture of $CH_3CdCH=CH_2$. In addition no metal proton coupling was observed for this mixture or any other vinylcadmium species. Based on comparisons between a number of cadmium and mercury compounds J(Cd–H) in vinylcadmium system should be in the order of 50–100 Hz [in general J(Cd–H)$\simeq\frac{1}{2}J$(Hg–H)]. An effort was made to find this coupling for $Cd(CH=CH_2)_2$. Time average techniques did not give any evidence of cadmium proton coupling in a hydrocarbon solution of $Cd(CH=CH_2)_2$ in which solvent assisted vinyl group exchange would be minimal. An attempt was made to freeze the Cd atom in a tetrahedral environment by the use of a strong chelating agent such as dioxane or N,N,N',N'-tetramethylethylenediamine. The NMR spectrum did not show any metal proton coupling, but the vinyl spectrum was very broad. Low temperature failed to sharpen the spectrum sufficiently to ascertain the nature of the exchange phenomenon. These results are consistent with previous reports that alkylcadmium chelate complexes are partially dissociated in solution[18]. The fact that J(Cd–H) can be observed in the methyl region but is absent in the vinyl region means that vinyl group exchange is much more rapid than methyl group exchange in these cadmium systems. Similar results have been previously reported for the mixed methylvinyl-thallium system[19].

The exchange properties of $CH_3ZnCH=CH_2$ are of interest for comparison since $CH_3CdCH=CH_2$ and $CH_3HgCH=CH_2$ possess drastically different exchange properties, and because of the stability of some mixed dialkylzinc compounds[20]. Low temperature NMR studies failed to yield any direct evidence for the existence of $CH_3ZnCH=CH_2$ in equimolar mixture of $Zn(CH_3)_2$ and $Zn(CH=CH_2)_2$. In general the chemical shift of the methyl group in CH_3ZnY compounds is rather insensitive to the nature of the Y group. Thus, it is impossible to determine from a cursory examination of spectrum of a mixture of $Zn(CH_3)_2$ and $Zn(CH=CH_2)_2$ whether: (a) $Zn(CH_3)_2$ and $Zn(CH=CH_2)_2$ do not react, (b) the chemical shifts of $CH_3ZnCH=CH_2$ are identical to those of $Zn(CH_3)_2$ and $Zn(CH=CH_2)_2$, or (c) there is rapid exchange between all sites. Alternative (b) is possible, but highly unlikely. Alternative (c), which we believe to be correct, is consistent with the observation that all spectral lines, particularly those to the vinyl protons, are very sharp ($v_{\frac{1}{2}}=0.2$ Hz). This is in contrast to the lines

assigned to the *trans* and *cis* protons of $CH_3HgCH=CH_2$ and $Hg(CH=CH_2)_2$ which possess unusually large half-widths[21]. This line broadening has been shown to result from long-range "across metal" coupling. This coupling was never observed for the zinc system and it was suggested that the lack of observed coupling was due to intermolecular group exchange. A similar conclusion was obtained from a study of Group II methyl compounds. ^{13}C NMR spectra did not exhibit[22] any $^3J(^{13}C-H)$ for either $Cd(CH_3)_2$ or $Zn(CH_3)_2$.

The alkyl groups which form stable mixed dialkylzinc compounds are the same ones which are the poorest bridging groups in the alkylaluminum systems[23]. The ability to isolate any stable mixed dialkylzinc compounds may be a result of the fact that these groups are such poor bridging groups that the activation energy for group exchange is extremely high. Methyl group exchange between $Zn(CH_3)_2$ and $Cd(CH_3)_2$ in methylene chloride proceeds[24] with an activation energy of 17 kcal/mole. The kinetics of this system were shown to be bimolecular by means of concentration studies at $+70°$. An equimolar solution of $Zn(CH=CH_2)_2$ and $Cd(CH=CH_2)_2$ in methylene chloride gave a single sharp vinyl spectrum even at $-40°$. This confirms our postulate that vinyl group exchange is much faster than methyl group exchange.

The mechanism most commonly used to account for exchange in these group II organometallic systems is the four center mechanism

$$R_2'M + R_2M \rightleftharpoons R'-M\underset{R}{\overset{R}{<>}}M-R \rightleftharpoons 2 R'MR \qquad (7)$$

Fig. 2 shows three possible energy profiles for systems which undergo this type of exchange. Case A is typified by uncatalyzed methyl group exchange in $Cd(CH_3)_2$ for which the activation energy is known to be[16] at least 16 kcals. Based on our observation of the temperature dependence for the catalysis of methyl group exchange by the
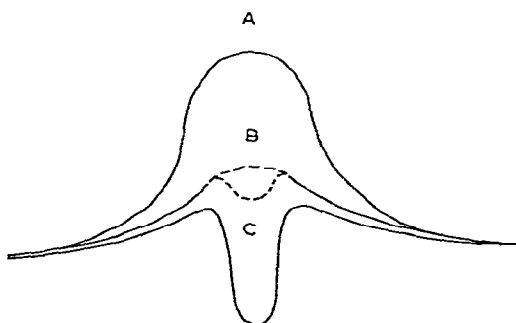

Fig. 2. The energy profile for the exchange of organic groups through four centered mechanism. Curve A is for the formation of the bridged transition state when bridging is difficult, Curve B for intermediate cases with or without intermediate complex formation, and Curve C for case in which dimer formation is favored.

vinyl group, we believe the vinyl group exchange must have a much lower activation energy than does methyl group exchange (case B in Fig. 2). The greater stability of the reaction intermediate or transition state containing bridging vinyl groups is consistent with our earlier studies of the $Ga(CH_3)_3/Ga(CH=CH_2)_2$ system, in which it was

shown that the vinyl group preferentially occupied the bridging position of the electron deficient dimeric species[25]. The utility of this four-center mechanism approaches its limit in case C where the dimeric or associated species becomes more stable than the monomeric species. An example of this behavior is acetylenic derivatives of cadmium and zinc. RCdOR compounds, many of which are tetrameric, do exhibit metal–proton coupling and therefore exchange, must be slow for these systems[26]. For these associated compounds the exchange rate should be governed by a dissociative process as proposed in some alkylaluminum systems[27]. Thus for the organocadmium systems the vinyl group seems to possess a unique position in the scheme of group exchange. It represents the case where the rate of group exchange is maximum. Poorer bridging groups, such as the methyl group, require a rather high activation energy to form the necessary transition state for exchange. Stronger bridging groups, such as the alkoxy and ethynyl groups, require considerable energy to break up the oligomer.

We believe the increased stability of the associated forms of these unsaturated Group IIB compounds is due to the donation of electron density from the double and triple bond into the electron deficient bridge bond. Rundle's simplified molecular orbital description[28] of a·three-center electron-deficient bond contains an empty non-bonding molecular orbital which has appropriate symmetry to overlap with a vinyl or ethynyl group. This reemphasizes the postulation that the terms electron-deficient and non-electron deficient are really classical descriptions of bonding, and' in reality there exists a whole series of compounds which traverse the range between these classical limits.

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