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THE COMPOSITION OF ORGANOCADMIUM COMPOUNDS IN DIETHYL ETHER SOLVENT
II. THE ORGANOCADMIUM REAGENT*

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SUMMARY

The reactions of Grignard reagents with $CdCl_2$, $CdBr_2$ and CdI_2 in 1/1 and 2/1 ratios in diethyl ether have been studied in an attempt to define the composition of the so called organocadmium reagent in solution. The studies involved elemental analyses and IR examination of both the soluble and insoluble reaction products. In 1/1 ratio the reaction proceeds as expected to yield magnesium halide and an equilibrium mixture of R_2Cd and CdX_2. The IR spectra support the conclusion that both CdX_2 and MgX_2 are coordinated with R_2Cd in either a single or double halogen bridge arrangement. In 2/1 ratio the reaction between a Grignard reagent and CdX_2 produces only R_2Cd and MgX_2. Interaction between these two compounds was demonstrated from IR spectra and from enhanced solubility of the MgX_2. Pure compounds of empirical formula $RCdX \cdot MgX_2$ have been isolated when the Grignard reagent and CdX_2 were allowed to react in 1/1 ratio. Evidence for RCdX in solution is also presented.

INTRODUCTION

The importance of the organocadmium reagent in organic synthesis is well known[1-3]. This reagent, generated by the addition of two moles of Grignard reagent to one mole of cadmium halide is represented by eqn. (1), which is the familiar

$$2\,RMgX + CdX_2 \rightarrow R_2Cd + 2\,MgX_2 \qquad (1)$$

description of the species involved. Synthetically, this reagent is commonly used *in situ* and will alkylate an acid halide to produce a ketone, with no further reaction of the ketone to produce a tertiary alcohol as would be the case with the Grignard reagent alone. Thus, the organocadmium reagent is, in general, less reactive toward ketones than the Grignard reagent. For some time it was assumed that the difference in alkylating ability of these two reagents was simply the difference in reactivity

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between RMgX and R_2Cd; R_2Cd being reactive toward acid chlorides, but relatively inert toward ketones.

Subsequent work has proven this interpretation to be an oversimplification. It has been shown[4] that magnesium salts are in part responsible for the alkylating ability of the organocadmium reagent since dialkylcadmium compounds alone react little or not at all with acid halides. Subsequent work has contributed additional support to this observation[5-7]. IR studies have produced evidence for magnesium halide complexes with both the dialkylcadmium compound (R_2Cd)[8] and acid halides[9]. The reaction between dialkylcadmium compounds and acid halides has been shown to be first order in both reactants[10].

It is clear that an unambiguous description of the organocadmium reagent is is far from complete. It has been established that halides "activate" the reagent, but it has not been established if this is the result of halide being associated with the organocadmium species or if the halide functions solely as an independent Lewis acid by interacting with the acyl halides, rendering them more susceptible to attack by the organocadmium compound. At this time we wish to report additional studies of the organocadmium reagent in diethylether solvent.

EXPERIMENTAL

Solvents

Just prior to use, diethyl ether was distilled from $LiAlH_4$ at atmospheric pressure in a nitrogen atmosphere. Hexane (concd. H_2SO_4 wash, dried over Linde 4A Molecular sieve), 1,4-dioxane, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED) were distilled from $NaAlH_4$ in a nitrogen atmosphere.

Reagents

Triply sublimed magnesium (Dow Chemical Co.) was used in the form of chips, freshly machined from bulk metal. Cadmium chloride and iodide were anhydrous, high purity reagents used without further purification, but subjected to a final drying step at 115° for 2 h at reduced pressure. n-BuCl and n-BuI were distilled prior to use through a one foot packed column.

Analytical

Halogens were determined titrimetrically using the standard Volhard procedure. Cadmium and magnesium were measured complexometrically using EDTA at pH 10, with Eriochrome Black T as the indicator. When magnesium and cadmium were present simultaneously, the total metal content was determined by adding excess EDTA and back titrating with standard Mg^{2+}. Potassium cyanide was then added, masking the Cd^{2+} by forming the cyano complex and releasing an equivalent amount of EDTA corresponding to the amount of Cd present. The amount of released EDTA was determined by titration again with standard Mg^{2+}. The magnesium content was found by subtracting the Cd equivalent from the total.

Spectra

IR spectra were recorded on a Perking–Elmer 621 grating Infrared spectrometer. Windows for solution cells and mull cells were CsI to enable acquisition of spectra from 1600 cm^{-1} to 200 cm^{-1}.

NMR spectra were recorded on a Varian Associates A-60 nuclear magnetic resonance spectrometer (60 MHz).

Sample cells were flushed with nitrogen prior to use and were filled in the dry box or against a countercurrent stream of dry nitrogen.

Grignard reagents

Grignard reagents were prepared by adding an alkyl halide (neat or in an ether solution) dropwise to a stirred excess of triply sublimed magnesium in diethyl ether. The halide was added slowly in order to minimize side reactions. The products were clear, colorless solutions, stable indefinitely when stoppered well, and exhibited a Mg/X ratio of 1/1 in all cases.

n-Bu_2Cd

Two moles of a standardized solution of Grignard reagent were added dropwise to one mole of $CdCl_2$ suspended in diethyl ether. The $CdCl_2$ suspension was cooled in dry ice during the addition and the reactor was protected from light with aluminum foil. After the addition was complete, the reaction vessel was allowed to warm to room temperature with continual stirring. The product mixture was a white or light gray suspension of $MgCl_2$ in a clear colorless solution of n-Bu_2Cd. Exposure of this mixture to light caused darkening of the solid in the mixture, presumably due to decomposition of the dialkylcadmium compound to hydrocarbon and black metallic cadmium. The solution containing the product was separated from the by-product $MgCl_2$ by filtration, followed by washing of the solid. The clear, colorless filtrate (which contains some magnesium halide) was stored in the refrigerator to prevent decomposition.

Isolation of the dialkylcadmium compound was accomplished by solvent removal under reduced pressure followed by fractional distillation of the n-Bu_2Cd at 0.5 mm and a pot temperature to 80–85°. The product was a clear colorless liquid which was frozen to a white crystalline solid as it dripped into a receiver cooled in liquid nitrogen.

Gravimetric analysis of the pure liquid n-Bu_2Cd indicated a purity of 98.7% by cadmium analysis. IR spectra of the neat liquid (Fig. 1) indicated no residual ether. The NMR spectrum of the product showed a triplet associated with the α-methylene protons at 401 Hz upfield from an internal benzene standard in diethyl ether solution (*vs.* 249 Hz for α-CH_2 in n-BuI). The remainder of the spectrum consisted of a triplet due to the terminal methyl and a complex multiplet composed of a quintet and a sextet arising from the β and α methylene protons. Satellite peaks arising from ^{111}Cd and ^{113}Cd nuclei were also observed.

n-Bu_2Cd is stable when stored frozen or in the refrigerator protected from light. If the compound is exposed to light or warmed to room temperature, darkening occurs. For this reason, transfers were made in the dark and in the cold whenever possible.

n-$C_4H_9MgCl+CdCl_2$ (1/1) in diethyl ether

A portion of standardized Grignard solution was added dropwise to a stirred suspension of $CdCl_2$ in diethyl ether, cooled to dry ice temperature. The reactor was protected from light by a covering of aluminum foil. After the addition was complete, the dry ice was allowed to evaporate and the reactor warmed slowly to room temperature with continual stirring. The product mixture consisted of a white solid suspended in a clear, colorless solution. The mixture darkened very slowly when stored protected from light at room temperature; however, rapid discoloration (gray) occurred when the mixture was left exposed to room light.

Elemental analysis of the supernatant solution indicated the following: Mg/Cd/Cl = 1.0/1.81/3.36, Cd/Cl($-MgCl_2$) = 1.33/1.0. These ratios were constant after stirring for one week (±0.1). A Gilman test was negative for both supernatant and precipitate, indicating that the Grignard reagent was completely consumed. The concentrations of the species present in the supernatant were as follows: M(Cd) = 0.093 (82% total Cd), M(Mg) = 0.052 (46% total Mg), M(Cl) = 0.17 (50% total Cl). Cooling of the supernatant in dry ice produced a slow-forming precipitate which, when isolated by filtration in the cold, gave the analysis: Mg/Cd/Cl = 1.0/1.06/2.98.

The insoluble portion of the reaction mixture yielded elemental ratios as follows: Mg/Cd/Cl = 2.19/1.0/5.88, Cd/Cl($-MgCl_2$) = 1.0/1.50. Cadmium species account for 31% of the insoluble portion. Fractional precipitation of the supernatant solution resulted in the isolation of mixtures of magnesium and cadmium species in no specific molar ratio.

n-BuMgCl + $CdCl_2$ (2/1) in diethyl ether

The addition of the Grignard reagent was made according to the procedure outlined for the (1/1) reaction. Again, the product was a white solid suspended in a clear, colorless solution. Exposure of the product mixture to light induced darkening of the product. A Gilman test was negative for both soluble and insoluble fractions of the product.

In a reaction between 30.6 mmoles of n-BuMgCl and 15.3 mmoles of $CdCl_2$ in 240 ml of diethyl ether, the supernatant solution gave the following analysis: Mg/Cd/Cl = 1.0/3.71/2.14, Cd/Cl($-MgCl_2$) = 26.5/1.0. M(Cd) = 0.070 (100% total Cd), M(Mg) = 0.019 (15% total Mg), M(Cl) = 0.041 (16% total Cl). The insoluble portion of the reaction mixture gave the analysis: Mg/Cd/Cl = 78.7/1.0/152.7, Mg/Cl = 1.0/1.93. (Found: Cl, 41; Mg, 14.5. $MgCl_2 \cdot Et_2O$ calcd.: Cl, 41.8; Mg, 14.35%.)

n-BuMgI + CdI_2 (1/) in diethyl ether

The same addition procedure was used as outlined above for the (1/1) and (2/1) chloride analogs. The reaction between 88 mmoles of n-BuMgI and 88 mmoles of CdI_2 in 1000 ml of diethyl ether, after 24 h of stirring, protected from light, produced a mixture consisting of a light gray solid suspended in a clear, colorless supernatant solution. Analysis of the supernatant solution gave the elemental ratios: Mg/Cd/Cl = 1.28/1.0/2.99, Cd/I($-MgI_2$) = 2.32/1.0. M(Mg) = 0.081 (98% total Mg), M(Cd) = 0.063 (71% total Cd), M(I) = 0.19 (72% total I). The residue from filtering the reaction mixture was very photosensitive and turned black at the surface in spite of precautions to keep it well covered. Analysis of this solid produced the ratios: Mg/Cd/I = 1.0/1.70/5.04, Cd/I($-MgI_2$) = 1.0/1.79. A Gilman test was negative for both supernatant and residue from this reaction. This reaction was performed under conditions such that the solubility limit of MgI_2 would not be exceeded (ca. 0.26 M). Fractional precipitation of the supernatant solution of this reaction produced mixtures of cadmium and magnesium species of indefinite composition.

Cooling of the (1/1) supernatant in dry ice initiated the slow precipitation of a white solid, isolated by filtration in the cold, which had the elemental ratio: Mg/Cd/I = 1.0/1.10/2.85, similar to the substance isolated from the analogous chloride system.

n-BuMgI + CdI_2 (2/1) in diethyl ether

The mode of addition was similar to that described above. A white precipitate was evident immediately after addition of the Grignard solution was complete; this precipitate dissolved completely after 40 h of stirring. The product was a homogeneous, clear, colorless solution. A minute amount of black precipitate was evident on standing at room temperature for one week. Analysis of the solution resulting from the reaction between 44.1 mmoles of n-BuMgI and 22.06 mmoles of CdI_2 indicated: Mg/Cd/I = 1.95/1.0/3.77, Mg/I = 1.0/1.93, M(Mg) = 0.202. A Gilman test was negative for the reaction mixture. Fractional precipitation of this mixture using hexane resulted in the separation of two phases; the lower phase was $MgI_2 \cdot Et_2O$ and the upper phase was predominantly n-Bu_2Cd.

Cooling of a portion of the reaction mixture caused the precipitation of a large amount of white solid which gave the analysis: Mg/Cd/I = 3.66/1.0/7.84, Mg/I = 1.0/2.14.

RESULTS AND DISCUSSION

The results of this work indicate that eqns. (2), (3) and (4) describe the equilibria involved when a Grignard reagent is added to a cadmium halide.

$$RMgX + CdX_2 \rightarrow RCdX + MgX_2 \rightleftarrows RCdX \cdot MgX_2 \qquad (2)$$

$$R_2Cd + CdX_2 \rightleftarrows 2\,RCdX \qquad (3)$$

$$2\,RMgX + CdX_2 \rightarrow R_2Cd + 2\,MgX_2 \rightleftarrows R_2Cd \cdot MgX_2 + MgX_2 \qquad (4)$$

The nature of the solvent is most important in the consideration of the equilibria, since the solvation of the species present affects the solubility, association, and the position of the equilibria. Diethyl ether was chosen for use in this study because it is the solvent used in the preparation of organocadmium reagents. All of the reports concerning the presence of RCdX in mixtures of R_2Cd and CdX_2 have been in tetrahydrofuran solvent only. Very little information is available concerning the composition of organocadmium compounds in diethyl ether solvent. We have chosen the alkyl group, n-butyl, to gain sufficient solubility in ether for IR studies.

Of particular interest is the interaction between the magnesium halides produced in reactions (2) and (4) and the organocadmium species present in the mixture. It is the nature of this interaction, if any, which is important to the understanding of the role of magnesium halides in "activating" a pure dialkylcadmium species toward reaction with an acid halide. Important aspects of this mixture include competing acid–base equilibria involving interactions such as: solvent–MgX_2, MgX_2–MgX_2, MgX_2–RCdX, and MgX_2–R_2Cd.

Fig. 1 shows the IR spectrum which we obtained for neat n-Bu_2Cd as a liquid film. Two strong absorption bands at 644 cm^{-1} and 501 cm^{-1} dominate the spectrum below 700 cm^{-1}. A tentative assignment may be made by assigning the 644 cm^{-1}

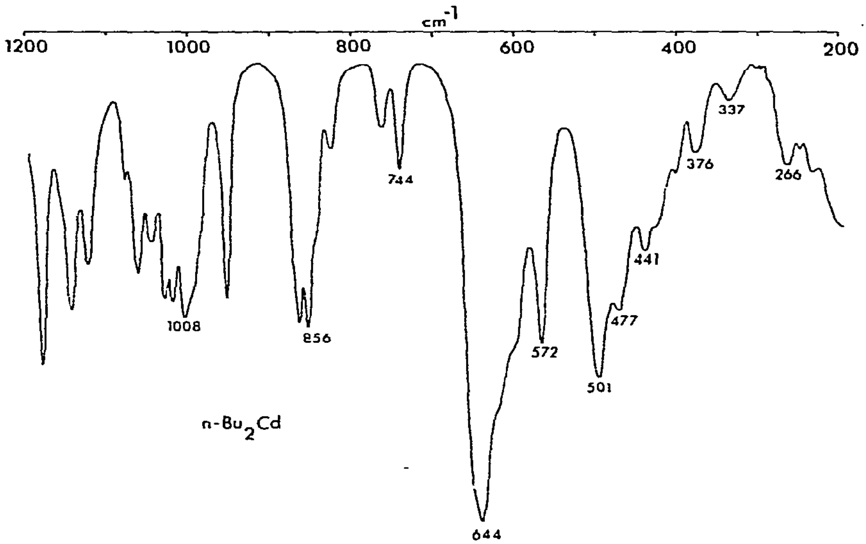


Fig. 1. IR Spectrum: Neat $(n\text{-}C_4H_9)_2Cd$, liquid film.

band as the C–Cd asymmetric stretching vibration and the 501 cm^{-1} absorption as the symmetric stretching vibration, which is allowed in the IR because of the low symmetry of the butyl group attached to cadmium. As expected, ν_s is of diminished intensity compared to ν_{as}. This assignment is analogous to the $n\text{-}Bu_2Hg$ case[11] where both ν_s and ν_{as} are observed in the IR, ν_s being at 519 cm^{-1} and ν_{as} at 602 cm^{-1} (Raman ν_s at 505 and ν_{as} at 596). The spectrum of $n\text{-}Bu_2Cd$ dissolved in diethyl ether is identical to a superposition of the two independent spectra, indicating no solute–solvent interaction. IR spectra of nujol mulls of anhydrous $CdCl_2$ and CdI_2 show no absorption down to 200 cm^{-1}. Spectra of the etherates of $MgCl_2$ and MgI_2, as nujol mulls, are rich in strong bands and are readily identified in product mixtures.

The reactions of Grignard compounds with cadmium halides

A. $RMgX/CdX_2 = 2/1$. On the basis of the Gilman test, the Grignard reagent reacts quickly and quantitatively with cadmium halides in diethyl ether. The products are unstable at room temperature in the presence of light and cannot be stored for long periods except when kept cold in the dark.

The (2/1) mixture is the common *in situ* reagent which is used in organic synthesis (X is usually Cl). Happily, this stoichiometry is also the most straightforward in explanation. Elemental analysis, Gilman test, and IR spectra indicate that the products are $n\text{-}Bu_2Cd$ and MgX_2 alone.

$$2\,(n\text{-}BuMgX) + CdX_2 \xrightarrow{Et_2O} n\text{-}Bu_2Cd + MgX_2 \tag{5}$$

Where X = I, the halide has high solubility and no solid residue is present; but when X = Cl, the halide is insoluble and is isolated as very pure $MgCl_2 \cdot Et_2O$. $MgI_2 \cdot nEt_2O$ can be isolated by cooling the (2/1) solution. The IR spectrum of the product compares with the spectrum of $MgI_2 \cdot nEt_2O$ prepared by independent methods.

Interaction between $n\text{-}Bu_2Cd$ and magnesium halide is evident for X = Cl and

I. For X = Cl, it is found that $MgCl_2$ is soluble in ethereal n-Bu_2Cd to give a solution ca. 0.02 *M* in $MgCl_2$, whereas the halide is normally insoluble in diethyl ether. The Cd/Mg ratio of this solution, 3.7/1.0, did not imply strong interaction; however, the IR spectrum shows evidence of coordination of $MgCl_2$ by n-Bu_2Cd. A shoulder was observed at 618 cm^{-1}; the same position as that found for mixtures of n-Bu_2Cd and $CdCl_2$ in diethyl ether[12].

When X = I, a solution is obtained containing the dialkylcadmium compound and magnesium halide in the molar ratio 1/2, respectively. Removal of the solvent produces no solid $MgX_2 \cdot nEt_2O$, indicating solubility or interaction of the halide etherate in n-Bu_2Cd. The IR spectrum of a solution of the reaction product exhibits several bands characteristic of MgI_2 in ether (308, 460, 504, 773, 833, 894 cm^{-1}) plus the familiar pattern of di-n-butylcadmium. The band assigned to ν_{as}(C–Cd) is shifted slightly to 641 cm^{-1}, and again a shoulder at 614 cm^{-1} is suggestive of that observed for the n-Bu_2Cd–CdI_2 redistribution reaction (615 cm^{-1})[12].

The shoulder observed for both n-Bu_2Cd/CdX_2 and n-Bu_2Cd/MgX_2 mixtures suggests that the interaction is of the type $R_2Cd \cdot MX_2$, where the halide is coordinated by halogen bridge bonds. The assignment of the shoulder absorption would thus become a vibration associated with n-Bu_2Cd adduct, where cadmium has a higher coordination number, and would reasonably be found at lower energy.

B. RMgX/CdX₂ = 1/1. Assuming stepwise alkylation of CdX_2 by the Grignard reagent, the 1/1 reaction mixture would yield initially equimolar quantities of RCdX and MgX_2. However, it has been demonstrated that disproportionation processes, as represented in eqn. (3), are important under the conditions of the experiment[12]. Thus, the description of this mixture requires a combination of arguments from other systems described earlier.

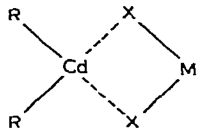
Where X = Cl, $MgCl_2$ is solubilized to some extent by the cadmium species which are present. Also, the solubility of $MgCl_2$ in this product mixture is higher than the solubility of $MgCl_2$ in ether solutions of n-Bu_2Cd (0.05 *M* *vs.* 0.02 *M*). The Cd/Cl ratio of the soluble fraction is approximately the same as that found from mixtures of n-Bu_2Cd and $CdCl_2$ in diethyl ether, indicating that the disproportionation equilibria [eqn. (3)] are unchanged by the interaction with $MgCl_2$.

IR spectra of the soluble portion of the 1/1 mixture where X = Cl show only minor differences from the spectrum of the 2/1 reaction. The pattern of absorption due to n-$Bu_2Cd/CdCl_2$ mixtures is evident, along with two new bands at 895 cm^{-1} and 782 cm^{-1} which may be ascribed to the presence of $MgCl_2$.

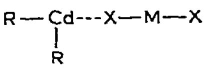
For the mixtures where X = I, the results are similar to the case above except that the by-product halide, MgI_2, is soluble. The presence of a large amount of soluble magnesium halide causes an apparent shift in the n-Bu_2Cd–CdI_2 interaction equilibrium from Cd/I = 1.1/1.0 in the absence of MgI_2 to Cd/I = 2.3/1.0 when MgI_2 is present. The IR spectrum of the soluble portion of the reaction mixture exhibits absorptions arising from n-Bu_2Cd–CdI_2 interaction with additional bands at 325, 775, and 895 cm^{-1}. These three latter absorptions are found also in ethereal solutions of MgI_2 alone and cannot be said to be the result of interaction with cadmium species. They are more plausibly described as halide–solvent interactions.

Spectra of the insoluble material from the 1/1 reactions indicate that $MgCl_2 \cdot Et_2O$ (Fig. 2) and $MgI_2 \cdot nEt_2O$ are the predominant absorbing species in these residues. Elemental analysis supports the conclusion that the solid residues are, for the most part, mixtures of magnesium and cadmium halides. Little absorption is noted in the region 600–650 cm^{-1} where R–Cd vibrations are expected.

In summary, the 1/1 reaction proceeds as expected, to yield magnesium halide and an equilibrium mixture of n-Bu_2Cd and CdX_2. From the increased solubility of $MgCl_2$, it may be said that interaction with the soluble cadmium species is responsible. The IR spectra support the conclusion that both CdX_2 and MgX_2 are coordinated by n-Bu_2Cd in the same manner. A good model for this interaction might be a structure such as (III), where cadmium may assume a coordination number of four. Alternatively, a singly-bridged species, (IV), is possible. Although coordination of the halides to dialkylcadmium species is pictured above, it is possible that a finite concentration of RCdX species is present, and that this also may coordinate additional cadmium or magnesium halide. The IR solution spectra do not distinguish this latter possibility from the predominant interactions with dialkyl cadmium.



(III)



$$\underset{\displaystyle R}{\overset{}{R—Cd}}{-}{-}{-}X—M—X$$

(IV)

In comparison, the 2/1 reaction produces only R_2Cd and MgX_2. Interaction between these two species was demonstrated from IR spectra and from enhanced solubility of magnesium halides.

Evidence for RCdX

It has been demonstrated above that R_2Cd–CdX_2 interactions and R_2Cd–

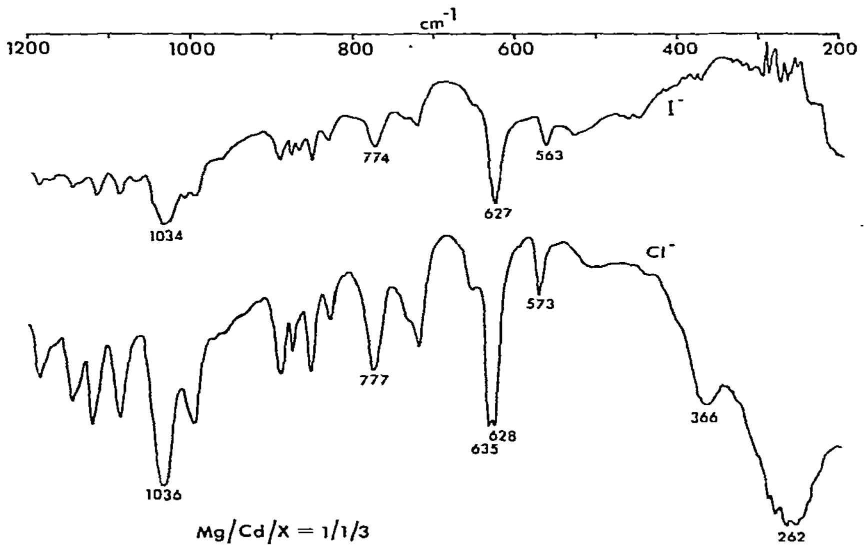


Fig. 2. IR Spectrum: Solids isolated from the soluble portion of the reaction mixture of n-C_4H_9MgX with CdX_2 in diethyl ether. Elemental ratios are Mg/Cd/X = 1/1/3. Upper curve: X = I; lower curve: X = Cl.

MgX_2 interactions are similar in terms of the IR spectrum of the soluble species, suggesting the interaction forms (III) and (IV) which do not involve alkyl–halogen exchange. When soluble fractions of the 1/1 $RMgX/CdX_2$ (R = n-Bu, X = Cl, I) are cooled in dry ice, white solids having the elemental ratios Cd/Mg/X = 1/1/3 are precipitated. The IR spectra of these solids are shown in Fig. 2. These spectra are remarkably similar to other spectra (Fig. 3) of crystalline solids of the empirical formula n-BuCdX (X = Cl, I) which have been isolated in other work[12] by cooling equimolar mixtures of $n\text{-}Bu_2Cd$ and CdX_2 (X = Cl, I) in ether and cyclohexane.

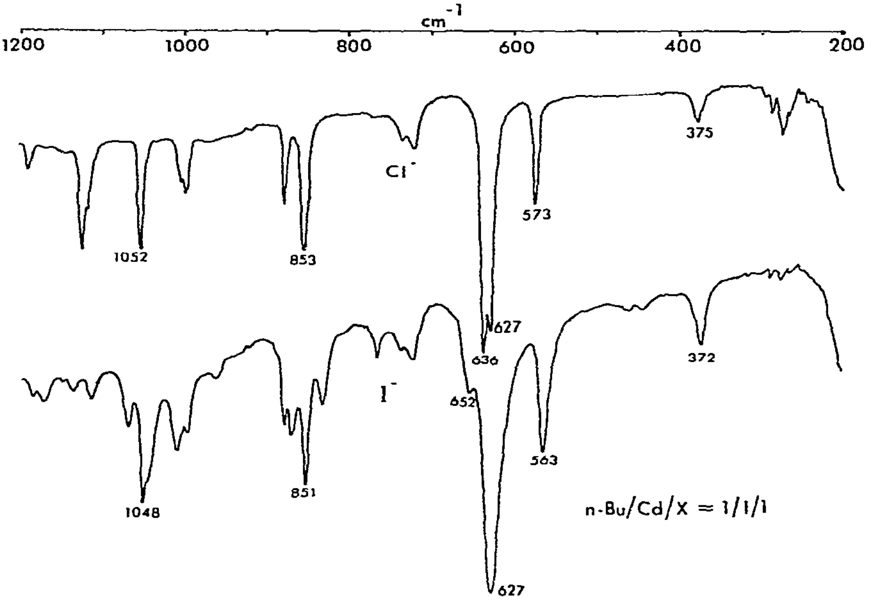
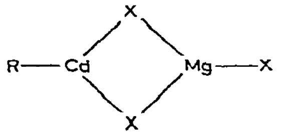


Fig. 3. IR Spectrum: Products having the empirical formula C_4H_9CdX isolated from equimolar mixtures of $(n\text{-}C_4H_9)_2Cd$ and CdX_2 in diethyl ether and cyclohexane. Upper curve: X = Cl; lower curve: X = I.

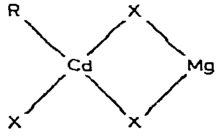
For each set of spectra it is noted that there are only minor changes in the absorption pattern when Cl is substituted for I. The only exception to this similarity is for the Mg/Cd/Cl = 1/1/3 species below 400 cm^{-1}. Of particular interest are the bands at 627 and 563 cm^{-1} for the 1/1/1 and 1/1/3 iodide species, and at 636, 627 and 573 cm^{-1} for the chloride species. These absorptions are in the region where the C–Cd stretching vibration is expected, the bands at 627 and 636 cm^{-1} having the greatest intensity and being the logical choices for a C–Cd stretching vibration. The absorptions at 573 and 563 cm^{-1} are always present for the n-butyl alkylcadmium species and show minor shifts of a few cm^{-1} for different situations; however, they have been excluded as C–Cd stretching absorptions because of their relatively lower intensities compared to the absorptions at ca. 630 cm^{-1}.

The IR spectra for these two products indicate that they probably have the same alkylcadmium arrangement since the band attributed to the C–Cd stretching vibration is unchanged for both materials. The empirical formula RCdX may be representative of three situations here: (a) monomer RCdX, (b) polymer $(RCdX)_n$, and (c) unsymmetrical dimer $R_2Cd \cdot CdX_2$. The isolation of a solid with elemental ratios Mg/Cd/X = 1/1/3 in addition to having characteristic IR bands at 627 and 636 cm^{-1} suggests that this material is the product $RCdX \cdot MgX_2$. This would seem to rule out $R_2Cd \cdot CdX_2$ as a likely form since the required empirical formula would then be $R_2Cd \cdot CdX_2 \cdot 2\ MgX_2$, a species without precedent.

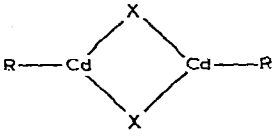
A preferred configuration for the 1/1/3 solid is thought to be that of structures (V) or (VI) and for the RCdX species structure (VII) is proposed. The 1/1/3 solid isolated in these systems is analogous to the RMg_2X_3 species isolated from tetrahydrofuran solutions of C_2H_5MgCl[13].



(V)



(VI)



(VII)

The structures represented above may be oversimplifications of the solid state arrangements; however, these forms do demonstrate the expected types of aggregation anticipated for these compounds in solution. For example, the solid state structures of $C_2H_5MgBr \cdot 2\,(C_2H_5)_2O$[14] and $C_6H_5MgBr \cdot 2\,(C_2H_5)_2O$[15] consist of discrete monomers in the solid state, association being prevented by the steric requirement of the solvating ether molecules. On the other hand, unsolvated ethylzinc iodide consists of polymeric chains with Zn–I bridges in the solid state[16].

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