Infrared Matrix Isolation Study of Magnesium Metal Atom Reactions. Spectra of an Unsolvated Grignard Species

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Abstract: Reactions of magnesium atoms with methyl halides in argon matrices have given rise to four product bands which can be assigned to a new chemical species, at 543, 1305, 2800, and 2892 cm^{-1}. All four are hydrogenic in nature, and are assigned to the four vibrations of a C_{3v} methyl group in the reaction product. Evidence is presented for insertion of the magnesium atom into the carbon–halogen bond of the methyl halide to form a species H_3CMgX, for X = Cl, Br, I. Similar reactions were observed with calcium and strontium atoms, while zinc atoms did not react with methyl halides under these conditions. No evidence was detected for a strong polar covalent carbon–magnesium bond, suggesting that the unsolvated Grignard reagent formed here has a structure other than that of the solvated solution species.

Introduction

Grignard reagents, alkylmagnesium halides, have been a very important synthetic tool for organic chemists since their discovery in the early 1900s.[1-4] Grignard reactions have been carried out in a number of solvent systems; ether and THF are the most common solvents. The state of aggregation of a Grignard reagent has been shown to be sensitive to the solvent; in THF the monomeric form is favored at all concentrations,[5] while in ether the monomer is present at only very low concentrations (0.05 M) and dimeric forms predominate at higher concentrations.[6] Several attempts have been made to obtain spectra of Grignard reagents in these solvents, but these attempts have been relatively unsuccessful, owing to the variety of species present.[7-8]

The complexity of the solution studies of Grignard reagents has led to interest in the unsolvated Grignard reagent. In 1972, Skell and Girard condensed magnesium atoms and a variety of alkyl halides at 77K, and reported that a black matrix was formed. This was not directly assigned to a Grignard reagent, but upon warming this matrix a new chemical species was formed, which was characterized as an unsolvated Grignard reagent.[9] However, no spectroscopic data was obtained for either the 77 K black matrix or the product formed upon warming. In one preliminary reaction, Knight investigated the reaction products of magnesium atoms and ethyl bromide at 15 K, and observed a complex spectrum, with an implication of a possible reaction product, but did not continue this study.[10]

Magnesium atoms are readily vaporized and deposited into argon matrices, and have been shown to undergo a number of different reactions. Mg atoms can undergo abstraction reactions[11] with O_3 to form $MgO + O_2$, and with[12] CCl_4 to form $MgCl + CCl_3$ as well as insertion reactions, such as with Cl_2 to form $MgCl_2$.[12] In addition, Andrews and Pimentel[13] attempted to form the methyl radical CH_3 via the abstraction of an iodine atom from CH_3I by a Li atom. It was subsequently shown that the product species was in fact a methyl alkali halide species, $CH_3\cdots LiI$, indicating that rupture of the C–I bond can occur.[14] These previous experimental results suggest that a magnesium atom might insert into the C–I bond of CH_3I to form an unsolvated Grignard reagent. With the continuing interest in Grignard reagents, and the possibility of matrix synthesis in this fashion, a study was undertaken to investigate the reaction of magnesium atoms with methyl halides in inert matrices.

Experimental Section

All of the experiments performed here were carried out using a conventional matrix isolation apparatus, the details of which have been described previously.[15] Magnesium (Alfa) was loaded in a stainless steel Knudsen cell and outgassed under vacuum behind a closed door before the start of experiment. Vaporization temperature was around 460 °C, which lead to deep red matrices indicative of the isolation of Mg atoms and Mg$_2$, after approximately 20 h deposition. Calcium (Alfa) and strontium (Alfa) were each used in several experiments and vaporized at slightly higher temperatures (550 °C for Ca and 525 °C for Sr). Zinc (Fisher) was used in one experiment and vaporized at a slightly lower temperature.

Methyl chloride (Matheson), methyl bromide (Matheson), and methyl iodide (Baker) were frozen at 77 K and volatile impurities pumped off prior to sample preparation. CD$_3$I (Merck, 99%) and CD$_3$Br (Merck, 99%) were handled in a similar fashion. Argon was used as a matrix material in most experiments, and was used without further purification. Nitrogen was used as a matrix material in one experiment, and was passed through a trap immersed in liquid nitrogen prior to sample preparation.

Matrix samples were deposited for 20–24 h before final scans were recorded on a Beckman IR-12 infrared spectrophotometer, both standard and expanded-scale scans. In several experiments, the sample was then irradiated with a 200-W high-pressure Hg arc lamp, using a 10-cm water filter to remove infrared radiation. In one experiment, the matrix was warmed to 45 K to allow diffusion in the matrix and then recooled to 15 K, and more spectra were recorded.

Results

Before the reaction products of magnesium atoms with the methyl halides were investigated, blank spectra were run with each of the methyl halides in argon, at both high and low dilution (M/R ranging from 1000/1 to 200/1). The resulting spectra in each of these blank runs resembled very closely the literature gas-phase values, for both fundamentals, and overtones.[16] Bands were sharp in all of these spectra, and no indication of aggregation of the methyl halides was present.

Mg + CH$_3$I. Mg was codeposited with samples of Ar/CH$_3$I in six experiments, with M/R values ranging from 100/1 to 1000/1. In each case, four distinct product bands were observed, at 543, 1305, 2800, and 2892 cm^{-1}. The 543-cm^{-1} band was particularly distinctive, being very intense and also quite broad, while the 1305-cm^{-1} band was moderately intense and relatively sharp, and the two upper bands were both quite weak. As the concentration of the sample was varied, these four bands maintained a constant intensity ratio, within the limits of accuracy in measuring the intensity of the 543-cm^{-1} band, whose bandwidth varied somewhat from experiment to experiment.[17] Mg was also codeposited with CH$_3$I in one experiment into a nitrogen matrix, and again four product bands were observed. The upper three bands remained unshifted with the change in matrix material, while the 543-cm^{-1} band broadened further and split into two components. As a result of this broadening, no further nitrogen matrix experiments were conducted.
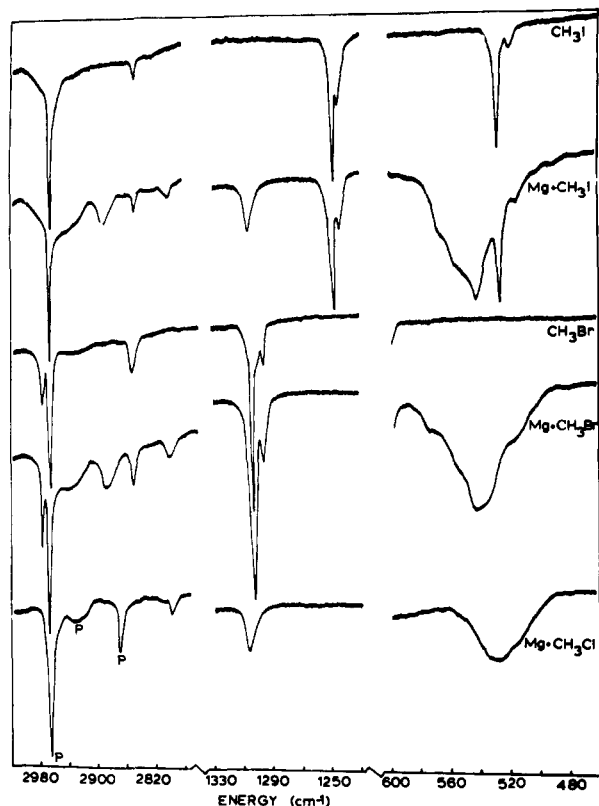
Figure 1. Infrared spectra, over selected spectral regions, of the reaction products of magnesium atoms with methyl halides, along with spectra of CH₃I and CH₃Br deposited in argon without magnesium present. In the bottom trace, "P" denotes a parent band of CH₃Cl.

Figure 2. Infrared spectra of the analogous deuterium reactions to Figure 1, over the appropriate spectral regions.

In one experiment in which Mg was codeposited with Ar/ CH₃I, the matrix sample was irradiated for 3 h after deposition, and all four of the product bands grew slightly in intensity and in the same ratio. In one of the most productive Mg + CH₃I experiments, the sample was annealed thoroughly in several stages. The matrix temperature was cycled from 15 to 29 K, recooled and scanned from 15 to 37 K, recooled and scanned, finally from 15 to 45 K, then recooled and scanned. The four product bands described above were not affected at all by this annealing; there was no measurable decrease in intensity. At the same time, no new bands grew, including in the 820-cm⁻¹ region where C₂H₆ is known to have an intense band.

Mg + CD₃I. Magnesium atoms were codeposited with samples of Ar/CD₃I in three experiments, and the resulting spectra indicated that there was no detectable hydrogen counterpart remaining. In these experiments, four product bands were detected, each an apparent counterpart to the four bands observed above, and were located at 418, 990, 2048, and 2102 cm⁻¹, showing deuterium shift of 1.30, 1.32, 1.37, and 1.38, respectively. These bands showed a constant intensity ratio to one another in the three experiments, and the 418-cm⁻¹ band was broader than the remaining three bands, but not nearly as broad as the 543-cm⁻¹ band in the analogous hydrogen experiments. There was *no* residual intensity in the 540-cm⁻¹ region.

Mg + CH₃Br. Magnesium atoms were codeposited with samples of Ar/CH₃Br in two experiments, with M/R = 200 and 400. In both cases, three product bands were observed, at 541, 2800, and 2886 cm⁻¹, each shifted only slightly from the CH₃I experiments. Also analogous to the CH₃I experiments, the 541-cm⁻¹ band was very intense, and much broader than the remaining product bands. Unfortunately, the 1295–1310-cm⁻¹ spectral region was obscured by an intense band
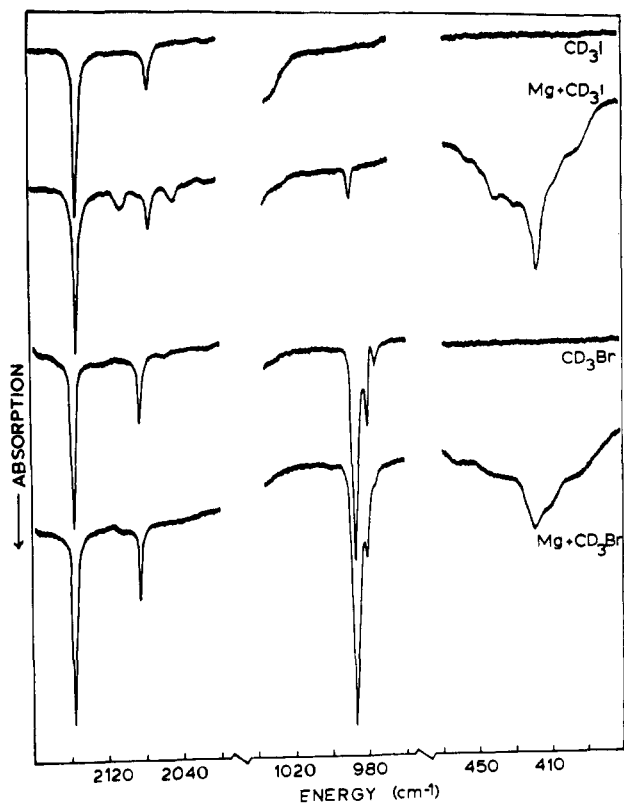
of the parent CH₃Br, so that the fourth anticipated product band was not detected. It is noteworthy that the overall yield in these experiments was slightly less than in the CH₃I experiments, despite roughly equal concentrations of each reactant.

Mg + CD₃Br. The analogous deuterium experiment was conducted two times as well, and in this case yet lower overall intensity was observed, yielding two product bands, at 418 and 2102 cm⁻¹. Again the 990-cm⁻¹ region, where a product band was anticipated, was obscured by a band of the parent CD₃Br, and no deuterium counterpart to the 2800-cm⁻¹ band was observed, presumably owing to low intensity. The deuterium shift for the two observed hydrogen and deuterium product bands were 1.29 and 1.37, from the 541- and 2886-cm⁻¹ hydrogen product band positions.

Mg + CH₃Cl. Magnesium atoms were codeposited with samples of Ar/CH₃Cl in several experiments at M/R = 200, and again three product bands were detected. The overall yield in these experiments was considerably less than in the CH₃I and CH₃Br experiments. Product bands were located at 530 (medium, broad), 1306, and 2805 cm⁻¹, while the 2890-cm⁻¹ region was obscured by an overtone band of the parent CH₃Cl. Owing to the relatively low intensities, no deuterium substitution was attempted with the chloride system. The spectra of the reaction products of Mg with CH₃I, CH₃Br, and CH₃Cl, along with blank spectra of CH₃I and CH₃Br, are shown in the five traces of Figure 1, while the analogous deuterium spectra are shown in Figure 2. All product band positions are listed in Table I.

Ca + CH₃I. Calcium atoms were codeposited with samples of Ar/CH₃I = 200 in several experiments, and product bands obtained. The overall yields in these experiments were quite low; the concentration of Ca atoms was low as a consequence of the high temperature necessary to vaporize calcium. A broad doublet was observed in each experiment, centered at 380 and 420 cm⁻¹, as well as a weaker but sharper band around 1305 cm⁻¹.
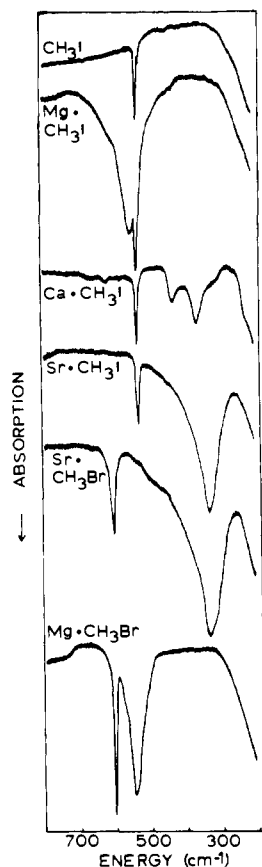
Figure 3. Infrared spectra, over the low-energy spectral region, of the reaction products of magnesium atoms, calcium atoms, and strontium atoms with methyl halides.

Table I. Product Band Positions (cm^{-1}) and Assignments[a] in Alkaline Earth Metal Atom/Methyl Halide Reactions

reactants	ν_1	ν_2	ν_3	ν_4
Mg + CH$_3$I	2800	543	2892	1305
Mg + CD$_3$I	2048	418	2102	990
(ν_H/ν_D)	(1.37)	(1.30)	(1.38)	(1.32)
Mg + CH$_3$Br	2800	541	2886	
Mg + CD$_3$Br		418	2102	
(ν_H/ν_D)		(1.29)	(1.37)	
Mg + CH$_3$Cl	2805	530		1306
Ca + CH$_3$I		380,420		1305
Sr + CH$_3$I		320		1305
Sr + CH$_3$Br		320		

[a] Band assignments assuming a C_{3v} geometry for the methyl group in the reaction product; vibrational numbering taking into account methyl group only.

Sr + CH$_3$I. Strontium atoms were codeposited with samples of Ar/CH$_3$I = 200 in several experiments. In each case, an extremely intense, broad band was observed near 320 cm^{-1}, very similar in overall structure and intensity to the 543-cm^{-1} band observed in the Mg + CH$_3$I experiments. In addition, a band near 1305 cm^{-1} was also observed in each of the these experiments, analogous to the Mg-atom experiments, while the C–H stretching region was too opaque to obtain spectra.

Sr + CH$_3$Br. This pair of reactants was studied in two experiments, with M/R = 200 and 400, and in each experiment a very intense, broad band was observed, again at 320 cm^{-1}, almost identical with the band observed in the Sr + CH$_3$I experiments. Unfortunately, the 1300-cm^{-1} region was obscured by a parent band of CH$_3$Br, so that a product band in this region could not be detected. Finally, a blank experiment was conducted in which Sr atoms were codeposited into an argon matrix with no reactant present, and no bands were observed in the spectrum. A comparison of the reaction products of Mg, Ca, and Sr atoms with CH$_3$I and CH$_3$Br is shown in Figure 3.

Zn + CH$_3$I. Zinc atoms were codeposited in two experiments with samples of Ar/CH$_3$I = 200; in neither experiment was a reaction product detected, although physical evidence of zinc atom vaporization was present.

Discussion

Vibrational Assignments. The codeposition of magnesium atoms with the methyl halides led to a distinct reaction, with four product bands detected, not assignable to the parent methyl halide. These four product bands all maintained a constant intensity ratio from one experiment to the next, within the accuracy of the measurement of the 543-cm^{-1} band, suggesting only a single reaction product. This reaction product persisted at high dilution, M/R = 1000, suggesting a 1:1 re-

action complex. While magnesium is known to exist[18] in part as Mg$_2$, in the gas phase the predominant species at the oven temperature is Mg atoms, and these are most likely the reacting species. The fact that the four bands were nearly identical when CH$_3$I, CH$_3$Br, and CH$_3$Cl were used suggests that the complex is more than a perturbed methyl halide species, but rather a distinct 1:1 product.

All four of the product bands showed large deuterium isotope shifts, indicating that all four are hydrogenic in character. Using the reaction of Mg with CH$_3$I as a prototype, the four bands were located at 543, 1305, 2800, and 2892 cm^{-1} with deuterium counterparts at 418, 990, 2048, and 2102 cm^{-1}, for ν_H/ν_D = 1.30, 1.32, 1.37, and 1.38. If one assumes that in the reaction product the methyl group of the methyl halide remains intact and with a C_{3v} symmetry, then four infrared bands are expected with hydrogenic character.[19] Two are C–H stretching vibrations, analogous to the bands at 2970 and 3060 cm^{-1} for parent CH$_3$I, and two are deformation modes. Two bands were observed consistently in the C–H stretching region, at 2800 and 2892 cm^{-1} for Mg + CH$_3$I, and are assigned to the two C–H stretches of the methyl group in the reaction product. Following the analogy with the parent CH$_3$I, the upper is assigned to the doubly degenerate antisymmetric stretch, and the lower to the symmetric C–H stretch, although this ordering is neither definitive nor essential to the structure of the reaction product.

The antisymmetric deformation mode of CH$_3$I occurs at 1440 cm^{-1}, and shows very little shift with halogen substitution. It is likely that this antisymmetric deformation will not shift a large amount in whatever complex is formed with magnesium; the product band at 1305 cm^{-1} showed virtually no shift with either halogen or metal, and thus is assigned to the antisymmetric deformation. Unfortunately, this band position is very near that of isolated CH$_4$, which might be a possible product in these experiments. However, the antisymmetric C–H stretching mode of CH$_4$ at 3018 cm^{-1} was not observed in any of these experiments. Previous matrix studies have shown that ν_3 and ν_4 of CH$_4$ have about a 3:4 intensity ratio, and in the more productive experiments ν_3 of CH$_4$ should have been easily observable, but was not detected. Consequently, assignment of the 1305-cm^{-1} band observed here is made to the antisymmetric bending mode of the CH$_3$ unit. For comparison, the antisymmetric deformation of the isolated CH$_3$ radical has been located at 1396 cm^{-1}.[20]

The symmetric deformation of the methyl group in CH$_3$I appears at 1250 cm^{-1} and has been shown to be very sensitive to the final substituent group on the carbon. This band ranges from 1450 cm^{-1} for CH$_3$F to 1250 cm^{-1} for CH$_3$I, and compares to a value of 611 cm^{-1} for the isolated methyl radical CH$_3$.[21] This vibration corresponds to the umbrella or breathing mode of NH$_3$, which is also extremely sensitive to its envi-

ronment;[22] moreover, this vibrational mode is the most intense mode in the spectra of both CH_3 and NH_3 and is by far the most intense band observed here. Consequently, the assignment of the 543-cm^{-1} band to the symmetric deformation of the methyl group in the reaction product is made. The proximity to the symmetric deformation mode of the methyl radical (611 cm^{-1}) supports this assignment as well, and all of these spectral observations appear to support the initial assumption that the methyl group remains intact as an entity during the formation of the reaction product.

The formation of a compound with a strong carbon-magnesium bond would have an infrared-active carbon-magnesium stretching vibration in the 500-cm^{-1} region,[23] by comparison to several dimethyl metal compounds (dimethylmagnesium shows an intense band near 550 cm^{-1} which has been assigned to the antisymmetric C-Mg-C stretch). Certainly, the 543-cm^{-1} band is an excellent candidate, until its deuterium shift is considered. ν_H/ν_D of the C-Mg stretch in $(CH_3)_2Mg$ is 1.11, compared to the 1.30 value observed here for the 543-cm^{-1} band. Moreover, codeposition of Mg with ethyl iodide did *not* show a strong band in this region, although a reaction product was observed, thus supporting the assignment of the 543-cm^{-1} band to the symmetric deformation mode, not a carbon-magnesium stretching vibration.

Structure and Geometry. The geometric arrangement of the methyl group, magnesium, and halogen atom may be inferred by the dependence of the symmetric deformation on the nature of the metal and the halogen. As can be seen in Table I, the nature of the halogen (Cl, Br, or I) in the complex has very little effect on this vibration, suggesting that the halogen is not directly bound to the carbon. Table I does show that there is a strong dependence on the nature of the metal atom, shifting from 543 cm^{-1} for Mg to near 400 cm^{-1} for Ca and 320 cm^{-1} for Sr. These data suggest that the magnesium atom has ruptured the carbon-halogen bond to yield a product of the general form H_3CMgX, the formal representation of a Grignard reagent. These results are in disagreement with those of Skell,[9] who codeposited magnesium and alkyl halides at 77 K and did not observe a reaction until the mixture was warmed above 77 K. There are several possible explanations for this discrepancy; Skell *did* observe a black matrix upon codeposition of these reactants, while deposition of magnesium atoms with a nonreactive partner such as neopentane gave colorless matrices. It is likely that the black matrix does indicate an initial reaction product (these samples were not monitored spectroscopically), and that warming gave rise to a more stable rearrangement product or aggregate, such as by the Schenk equilibrium. Also, Skell used larger alkyl halides, such as *n*-propyl iodide and *tert*-butyl bromide, and did not directly cocondense methyl iodide with magnesium atoms. The considerable differences in the experimental arrangement and means of monitoring the reaction may rationalize the apparent discrepancy in results. The one experiment of Knight also suggests that a reaction does occur at 15 K,[10] as does the work of Hauge et al.[17]

Ridge and co-workers[24] recently investigated the reactions of alkali and transition-metal cations with alkyl halides, and have observed that with the alkali metal cations halogen abstraction occurs, but with the transition-metal cations insertion to form a RMX^+ species occurs, supporting the notion that insertion into a carbon-halogen bond can occur.

H_3CLiX is the formulation given to the methyl alkali halide species by Tan and Pimentel,[14] who viewed the species as a methyl radical perturbed by a neighboring lithium halide salt molecule, $H_3C\cdots LiX$. Several of the characteristics of the product observed here are suggestive of the perturbed methyl radical observed by Tan and Pimentel. The deuterium shift of the 543-cm^1 band is large, with a H/D frequency ratio of 1.30. This compares to a value of 1.29 for the methyl alkali halide species, which led to the conclusion that the CH_3 group in this

species was planar, but without the quartic anharmonicity observed for the isolated methyl radical ($\nu_H/\nu_D = 1.33$). The value here, 1.30, suggests a nearly planar methyl group as well, with little or no quartic anharmonicity, which is anticipated since the symmetry about the planar position is lost upon axial interaction with MgX.

If a structure with a strong Mg-X bond is correct, then one might expect to see a Mg-X stretching mode. These should lie somewhat below the position of the free MgX diatomic, which for MgI is 311 cm^{-1}.[19] The largest yield of product was observed for the reaction of Mg + CH_3I, so that this set of reactants would give the best opportunity to observe this mode. However, this should not be a particularly intense vibration, and lying below 300 cm^{-1} it would be difficult to detect. The vibration for MgCl should lie at higher energy, but a low yield was observed in this reaction, and such a vibration was not observed. In addition, Tan and Pimentel did not report a M-X stretching vibration for the methyl alkali halide species. So lack of observation of a MgX stretching mode does not decisively rule against a structure with a strong Mg-X bond.

A second possible structure would be the classical Grignard formulation, $H_3CMg^+\cdot X^-$, containing a strong polar covalent carbon-magnesium bond. No evidence for such a bond was obtained spectroscopically, suggesting that the unsolvated Grignard reagent does not contain such a bond. Nonetheless, since both the CH_3 unit and the MgX unit in the reaction product are free radicals, one would expect a strong interaction between the two and bond formation. Since solvation by the argon lattice will not occur, the resultant product should be less polar than its solution analogue, suggesting a relatively covalent structure. However, no definitive conclusions can be drawn on the basis of the infrared spectroscopic data.

Energetics. Consideration of the overall energetics of the reaction involves the rupture of the carbon-halogen bond, formation of a magnesium-halogen bond, and some interaction energy between the Mg-X unit and the CH_3 unit. The reaction is exothermic on the consideration of the first two factors alone; the Mg-I bond strength is 68 kcal/mol, while the C-I bond is on the order of 50 kcal/mol.[25] Similar energetic considerations hold for Ca and Sr, where a reaction was observed. The Zn-I bond strength is 33 kcal/mol, which is less than that of a C-I bond; no reaction was observed when Zn atoms were codeposited with CH_3I. Additional stabilization energy is gained through the interaction of the Mg-X unit with the methyl group in the reaction product.

Chemical Bonding. Tan and Pimentel[14] used a three-center molecular orbital scheme to describe the bonding of the methyl alkali halide species, employing the axial p orbitals on the carbon and halogen and the 2s orbital of the alkali metal, where the coefficients for the two terminal atoms are not constrained to be equal by symmetry, as is the case for FHF^-. Such a molecular orbital model is appropriate here, using the analogous set of orbitals, but with one additional electron, since an alkaline-earth metal was employed. This additional electron goes into a weakly bonding orbital, with most of the electron density residing on the terminal atoms (although not equally).[26] This provides for a somewhat more stable species than the methyl alkali halide species, and allows for somewhat more electron density on the methyl group than in either the methyl alkali halide species or the isolated methyl radical.

The molecular orbital occupancy for the methyl radical in the D_{3h} point group is $(1s_c)^2(1a_1')^2(1e')^4(1a_2'')^1$, so that additional electron density enters the half-filled $1a_2''$ orbital.[27,28] This increased electron density without increased nuclear charge should serve to destabilize the methyl radical slightly and lower the vibrational frequencies below that of isolated methyl radical. In fact, Goddard calculates the electron affinity of CH_3 to be negative.[29] The observation here of the symmetry deformation below that of CH_3 supports this bonding scheme,

and for comparison the symmetric deformation of CH_3^+, where the $1a_2''$ electron has been removed, has been identified at 1380 cm^{-1}.[30] The shift of this mode to lower energies with Ca and Sr agrees as well, as these metals are less electronegative than Mg, so that there will be less electron density on the metal center and more on the terminal halogen and methyl group, leading to a shift to lower energy. A similar trend was observed for the methyl alkali halide species, using Li, Na, and K.

Conclusions

The codeposition of magnesium atoms with methyl halides in argon matrices does lead to a reaction product in which the carbon–halogen bond is ruptured. The spectra in each case was dominated by the symmetric deformation mode of the CH_3 unit in the reaction product, although the remaining vibrations of the CH_3 unit were also detected. However, since neither a C–Mg stretch nor a Mg–X stretch was observed, no definitive conclusions concerning the exact structure of the product can be made.

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Kinetics and Mechanisms of Substitution Reactions on Decacarbonylmanganeserhenium

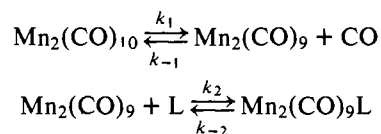**Dave Sonnenberger and Jim D. Atwood***

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Abstract: The kinetics of substitution reactions on decacarbonylmanganeserhenium, MnRe(CO)$_{10}$, are reported for the entering ligands P(C$_6$H$_5$)$_3$, P(C$_4$H$_9$)$_3$, and P(OC$_6$H$_5$)$_3$. Synthesis of all products and careful infrared analysis have allowed complete product assignment. For all three ligands the rhenium-substituted product, (CO)$_5$MnRe(CO)$_4$L, predominates, although formation of the bis-substituted product, L(CO)$_4$MnRe(CO)$_4$L, can be quite significant depending on the reaction conditions. A very small amount of the manganese isomer, L(CO)$_4$MnRe(CO)$_5$, was formed early in the reaction. In no case were the homodimetallic species (Mn$_2$(CO)$_{10}$ or Re$_2$(CO)$_{10}$) or substituted derivatives of the diatomics observed. The manganese isomer fails to rearrange to the rhenium isomer under the conditions of the kinetics reaction. The rate constants and activation parameters are nearly identical for the three ligands. These data strongly suggest that CO dissociation is the rate-determining step and are inconsistent with cleavage of the manganese–rhenium bond. Our proposed mechanism involves CO dissociation from the manganese center and an intermediate/transition state with carbon monoxide bridging the manganese and rhenium.

Introduction

Despite a very large number of reports on structures and reactivity of metal–metal bonded complexes, there have been relatively few studies of the kinetics of reactions of compounds containing metal-metal bonds.[1-11] Whether the metal–metal bond remains intact during reactions remains in question.[1,3,8] The substitution reactions of the dinuclear metal carbonyls, $M_2(CO)_{10}$, M = Mn, Tc, and Re, have been the most thoroughly explored mechanistically of the metal–metal bonded complexes.[12-21] Wawersik and Basolo reported kinetics studies

of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9L$ with L' (L,L' = P(C$_6$H$_5$)$_3$, P(OC$_6$H$_5$)$_3$, P(C$_4$H$_9$)$_3$, and As(C$_6$H$_5$)$_3$) and interpreted the rate data as being consistent with a CO dissociative process.[12]

$$Mn_2(CO)_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn_2(CO)_9 + CO$$

$$Mn_2(CO)_9 + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Mn_2(CO)_9L$$

The similarity in rates and activation parameters for the dif-