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Metal Cluster vs. Atom Reactivities: Magnesium Cluster Grignard Reagents

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The reaction of Mg atoms, Mg_2 dimers, and Mg_3 trimers with CH_3Br has been studied under matrix-isolation conditions by UV–vis spectroscopy and matrix-gas-replacement techniques. Under the conditions of high dilution in argon, Mg atoms were found to be totally inert whereas clusters of Mg reacted by an oxidative-addition mode: $(Mg)_x + CH_3Br \rightarrow CH_3(Mg)_xBr$. We believe this is the first example where a σ-bond-breaking reaction took place on a cluster but not on an atom under the same experimental conditions. Greater thermodynamic stability of the cluster Grignard product, steric/orbital considerations, and a lower ionization potential of Mg clusters are likely reasons for the higher reactivity of the clusters. These results imply certain steps in the Grignard reagent formation, and similar experiments with other metals and substrates might yield substantially new understanding of reactions at metal surfaces.

Introduction

The notion that metal clusters might mimic metal surfaces is particularly relevant when the clusters are ligand free or "naked". To carry this thread of thought even further, in order to understand how and why metal clusters (surfaces) interact with organic molecules, a direct comparison with naked metal atoms would be quite instructive.[2,3]

Using matrix-isolation techniques, it is possible to study reactions of naked atoms and clusters in some instances. However, to date, reports comparing reactivities of metal atoms with clusters have been rare and controversial,[4,5] and there is apparently no example of a σ-bond cleavage taking place on a metal cluster but not on an atom (although the Fe/Fe_2 system with N_2 has been studied where Fe_2 showed greater complexing ability toward N_2).[6]

Recently we reported a matrix-isolation infrared spectroscopic study of the CH_3Br/M system, where M = Al, Ga, In, Mg, and other metals.[7] Metal/CH_3Br concentration studies indicated that Al, Ga, and In reacted as atoms (and perhaps clusters as well) but Mg apparently required higher clusters since only high concentrations of Mg in the matrix led to infrared bands due to product (CH_3Mg_xBr). Thus, we proposed that for magnesium perhaps Mg_2, Mg_3, or larger clusters were necessary so that C–Br bond cleavage could occur. Soon thereafter, Jasien and Dykstra lent theoretical support to our proposal in that their ab initio calculations indicated cluster Grignard reagents should be more thermodynamically stable than single-atom compounds, e.g. $R(Mg)_2X > RMgX$.[8] In this paper we report UV–visible spectroscopic evidence that indeed Mg_2 and $(Mg)_x$ ($x > 2$) are more reactive than Mg atoms in an oxidative-addition reaction with CH_3Br.

Results and Discussion

Table I. UV-Visible Absorption Assignments for Matrix-Isolated Magnesium and Calcium Species

wavelength, nm	species	assgnt	ref
243.7 (244.3)[a]	$(Mg)_x$		12b
265.3 (263.5)[a]	Mg_2	$^1\Sigma_g^+ \rightarrow \Pi_u$[d]	12b, 13b
279.5, 281.5, 283.6 (281.0, 284.5)[a]	Mg	$^1S \rightarrow {}^1P$	12a
305.0 (306.2)[a]	Mg_4[c]	$^1A_1 \rightarrow {}^1T_2$	12b
307			13
315 (318)[a]	unknown[b]		13
318			23
343.5 (345.3)[a]	Mg_3[c]	$^1A_1' \rightarrow {}^1E'$	12b
345			13
370 (370)[a]	Mg_2	$^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$	12b
367			13
410 (410)[a]	Ca	$^1S \rightarrow {}^1P$	13, 23
444	Mg_2	$^1\Sigma_g^+ \rightarrow {}^1\Pi_g$	13
484, 548	$(Ca)_x$		23
648	Ca_2	$^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$	23

[a] This work. [b] This band was also observed during the deposition of calcium atoms with Ar. [c] The specific assignments for Mg_3 and Mg_4, including the geometries, were discussed in ref 13b. [d] Andrews and co-workers have confirmed these spectroscopic assignments in ref 13b.

Although matrix-isolated metal atoms have been studied spectroscopically by several groups, comparatively less has been reported regarding the spectroscopy of the clusters.[9] However, the useful work of Schnepp,[10] Brewer,[11] Knight,[12] and Andrews[13] and their co-workers with Mg, Ca, Sr, and Ba allowed us to carry out the present study. These workers established that Mg atoms, Mg_2, and $(Mg)_x$ could be prepared in an argon matrix; cf. Table I. Bands for Mg atoms were observed at 281.0 and 284.5 nm corresponding to the $3s3p(^1P) \leftarrow 3s^2(^1S)$ transition.[10-12] The bands for the Mg_2 dimer appeared at 370.0[11-13] and 263.5 nm.[12b,13b] The absorptions at 345.3 and 306.2 nm can be assigned to Mg_3 and Mg_4, respectively.[13b]

Turning to our results, Figure 1 illustrates a total UV–visible spectrum after 79 min of deposition of Mg vapor with a 10^4–10^5-fold excess of argon at 9 K. The series of spectra of

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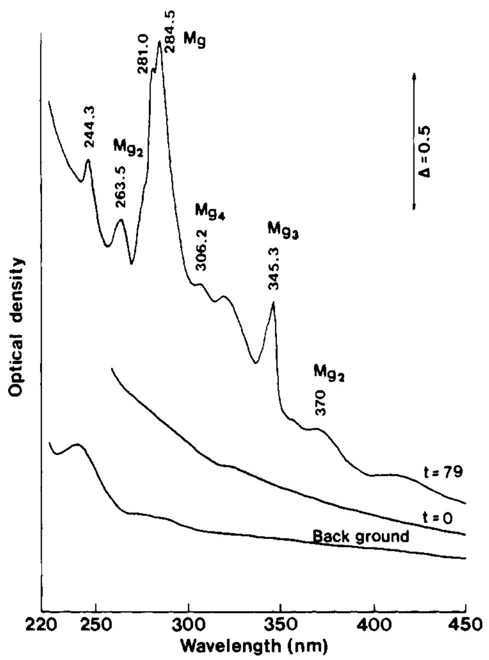

Figure 1. UV–visible spectrum of magnesium species isolated in an Ar matrix at 9 K after 79-min deposition.

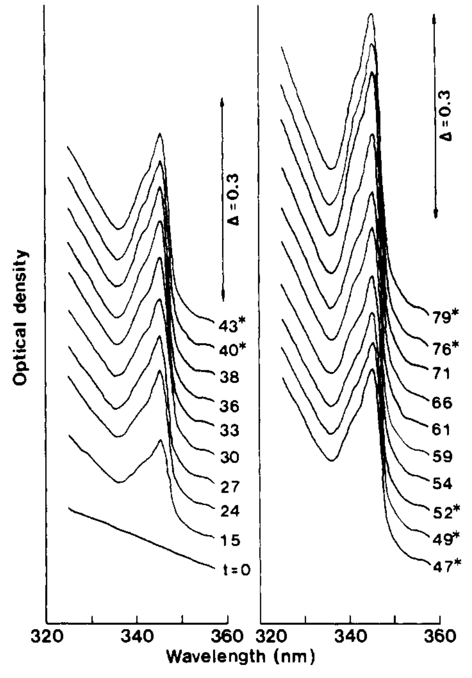

Figure 2. UV–visible spectra of Mg_3 at 345 nm in an Ar matrix at 9 K. *t* indicates deposition time, in minutes at constant deposition rate after an initial 24-min deposition period. Numbers marked with an asterisk are ascribed to deposition with a CH_3Br/Ar mixture.

Mg atoms and Mg_3 (at 345.3 nm) recorded during alternate depositions of Mg/Ar and $Mg/Ar/CH_3Br$ are shown in Figures 2 and 3. After determination of peak areas, absorption vs. time of deposition was plotted, and the constructed graph is shown in Figure 4.

The plots in Figure 4 reveal four breaks at certain times during the deposition (15, 38, 52, and 71 min). The first break results from changing the inlet rate of Ar matrix gas, and the last three breaks are due to switching matrix-gas composition. During deposition without CH_3Br (only pure Ar), each absorption band continually grew at constant rates. When the matrix-gas composition was switched from pure Ar to a 0.65% CH_3Br/Ar mixture, the band growth rate for Mg atoms was enhanced by a factor of 5–6! On the other hand, the band for Mg_3 actually decreased during this same time period when CH_3Br was being inlet. Similar results were obtained for the Mg_2 bands.[14]

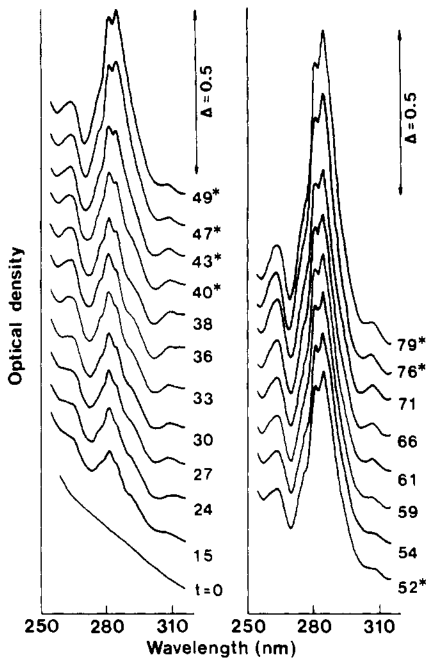

Figure 3. UV–visible spectra of Mg atoms at 281 and 285 nm in an Ar matrix at 9 K. *t* indicates deposition time, in minutes, at constant deposition rate after an initial 24-min deposition period. Numbers marked with an asterisk are ascribed to deposition with a CH_3Br/Ar mixture.

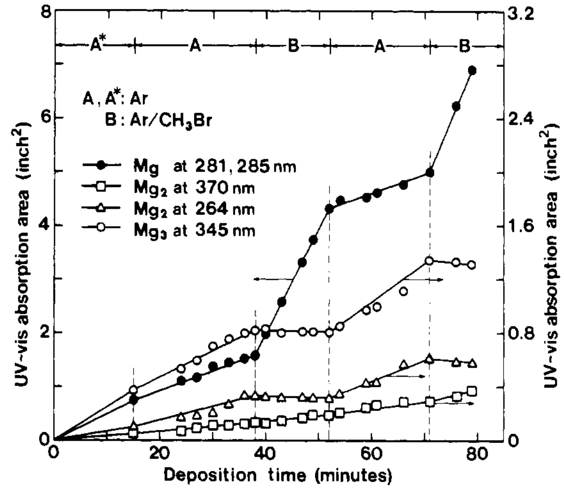

Figure 4. UV–visible spectra band intensity vs. time plots of Mg atoms, Mg_2, and Mg_3 in an Ar matrix at 9 K. An asterisk indicates a higher inlet rate of Ar matrix gas than that of A under the conditions of constant Mg atom vaporization rate.

In order to reconcile these results we must deal with several pieces of data. First, extensive earlier work[10–13] has shown that it is virtually impossible to isolate only Mg atoms in frozen argon. Our results confirm this idea in that even the lowest concentrations of Mg atoms in Ar led to Mg, Mg_2, and Mg_3. In fact, our matrices were essentially still transparent when these species were detected. Thus, Mg_2 and Mg_3 are easily formed in a frozen Ar matrix in spite of the fact that Mg_2 and Mg_3 are van der Waals molecules (in the gas phase) and Mg_4 is the smallest non van der Waals cluster.[15] So, we conclude

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(14) The only way to ensure identical and unchanging metal-evaporation rates and matrix-gas-deposition rates was to gather each full set of data during extended experiments where the settings for the evaporation furnace and gas-inlet valves were not changed.

that Mg_2 and Mg_3 formation is purely a kinetic phenomenon and that Mg is very mobile in cold argon, especially just before solidification occurs.

Next we must deal with the fact that Mg atom isolation is greatly enhanced by the presence of a small amount of CH_3Br in the Ar stream. There are three plausible explanations: (1) CH_3Br scavenges Mg atoms, forming a weak $CH_3Br\text{---}Mg$ complex that completely inhibits cluster growth; (2) as in a kinetic steady-state analysis,[16] if Mg_2 were reacting with CH_3Br very rapidly, Mg_2 could not exist long enough for further reaction with Mg (or more Mg_2) to form higher magnesium aggregates $(Mg)_x$ ($x > 2$), which would allow a more rapid growth of Mg atoms with the same Mg atom flux; (3) when Mg_3 reacts, a Mg atom is ejected:

$$Mg_3 + CH_3Br \rightarrow [CH_3Mg_3Br] \xrightarrow{?} CH_3Mg_2Br + Mg$$

The weakness of explanation 1 is that, upon $CH_3Br\text{---}Mg$ complex formation, it would be expected that some change in the atomic absorption spectrum for the Mg atoms would be observed. No change whatever is observed, however, for either the atoms or the clusters when CH_3Br is present. This indicates that in the presence of CH_3Br, the Mg, Mg_2, and Mg_3 that still remain and are observable by UV–visible spectroscopy are isolated in argon and not complexed to CH_3Br.

Explanations 2 and 3 cannot be differentiated at this time. They are both supported by our earlier infrared work showing that with the CH_3Br/Mg system reaction *does* occur.[7] They are also supported by annealing experiments. Thus, when a $Mg/Mg_2/Mg_3/Ar$ matrix was warmed in the absence of CH_3Br, even below 35 K all atoms and clusters combined to form a film (spectrum disappeared); however, the same annealing experiment, except that a coating of CH_3Br had been deposited on top of the $Mg/Mg_2/Mg_3/Ar$ matrix, showed *that Mg_2 and Mg_3 were consumed but Mg atoms were not.* In a sense this is like "titrating" the Mg_2 and Mg_3 species with CH_3Br and is very strong evidence that Mg_2 and Mg_3 are indeed reactive in the 10–30 K range, but Mg atoms are not.

Unfortunately the spectra were broadened during annealing, and we could not tell if Mg atom concentration *increased* during Mg_2 and Mg_3 consumption, which would support explanation 3.

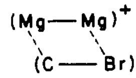
$$\begin{array}{c} Mg/Mg_2/Mg_3 \\ \text{isolated in} \\ \text{argon at 9 K} \\ (CH_3Br\ \text{layered} \\ \text{on top)} \end{array} \xrightarrow[\text{the argon layer}]{\text{upon warming}\atop CH_3Br\ \text{permeates}} \begin{array}{c} Mg \\ \text{isolated} \\ \text{in argon} \\ (Mg_2/Mg_3 \\ \text{consumed)} \end{array}$$

Further support is found in Figure 4, showing a *decrease* in Mg_2 and Mg_3 when CH_3Br was present, which again suggests that Mg_2 and Mg_3 are consumed as rapidly as they are formed along with some already formed (presumably CH_3Br permeates the argon layer slightly and Mg_2 and Mg_3 are attacked).

So, the increase in Mg atom concentration and the decrease in Mg_2 and Mg_3 when CH_3Br is present can be explained by the higher reactivity of Mg_2 and Mg_3 under the reaction conditions (explanation 2 or 3 above). Further work is needed before explanations 2 and 3 can be differentiated, but the important point is that Mg_2 and Mg_3 are more reactive. Why should this be so? Most likely, it is due to more favorable reaction energetics as pointed out by Dykstra.[8] This is apparently the result of the Mg–Mg bond being very weak in Mg_2 but relatively strong in R–Mg–Mg–X; thereby *three* bonds are made while only one is broken in the sequence $Mg_2 + CH_3Br \rightarrow CH_3MgMgBr$. Ionization potential probably also plays a role. Clusters generally have lower IP than metal atoms,[17,18] and our earlier work supported an electron transfer from M to CH_3Br to initiate the reaction.[7] This primary step should be more favorable for a cluster, and in the process of ionization a considerably stronger Mg–Mg bond would form.[18] Lastly, we should consider symmetry and steric factors.

$$Mg_2 + CH_3Br \rightarrow Mg_2{}^+CH_3Br^- \rightarrow CH_3Mg_2Br$$

Although cleavage of C–Br on Mg_2 would involve moving C and Br further apart in the final product, the initial bond-breaking act may be facilitated by a four-centered approach:



The implications of this work on understanding Grignard reagent formation[19,20] on bulk magnesium are that small clusters of magnesium may be removed from the surface and that cluster Grignard reagents $R(Mg)_xX$ may be stable species. We are currently initiating the next major phase of this work where we hope laser-Raman and other techniques, coupled with kinetic analyses,[16b] will allow structure elucidation of the $CH_3(Mg)_xBr$ species. We are also attempting large-scale preparation and isolation of cluster Grignard reagents.

Experimental Section

The general design of our matrix-isolation (MI) unit is modeled after that of Hauge, Kauffman, and Margrave.[21] It is mounted so that both reflectance (with the proper mirror setup) and absorption/transmission IR studies using a Beckman IR-12 are possible. The MI unit can also be pushed into position for UV–visible absorption/transmission experiments on a Cary 14 spectrophotometer. The MI unit is fitted with an Air Products Displex closed-cycle helium refrigerator, Model CSW202, an Air Products APD-E temperature indicator/controller, and an in-house-constructed quartz-crystal microbalance for monitoring metal evaporation/deposition rates (although this work did not require use of this microbalance). For magnesium evaporation an Al_2O_3 tubular furnace[21] wrapped with tantalum foil was used. A 1.7-mm opening was available for escape of Mg vapor toward the cold window, which was a 4-mil KBr (25 mm × 4 mm) window cooled to 9 K.

Materials used were Mg chips m4N (99.99%) resublimed (Alfa Products) and argon 99.99% (Linde). Argon and CH_3Br were mixed in an ~3.5-L gas bulb by using convection heating. The ratio of Ar

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to CH_3Br was 152.5:1 and the Mg to Ar ratio was 1:(10^4–10^5).

Before an experiment the background pressure was below 2×10^{-6} torr, and during an experiment it was 2×10^{-5} to 1.5×10^{-5} torr. Vaporization periods were long, perhaps 14 h, but during spectroscopic observations a shutter covered the KBr cold window, thereby not allowing any Mg vapor or Ar/CH_3Br to contact it. During the observation times the window was rotated 90° into the UV–visible source path and was rotated back during deposition periods.

During observation by UV–visible spectroscopy, a 5-mil KBr (25 mm × 5 mm) clean window served as a reference sample. A scan from 650 to 230 nm (usually 450–240 nm) was obtained at a scan speed of 0.25 nm/s. A black cloth was used to block out all room light around the entrance of the MI unit into the spectrometer. Peak areas were determined by using an Apple computer graphic tablet.

Direct comparisons of UV–visible spectra with IR spectra were attempted but were not successful due to the very low concentrations of magnesium species in the UV–visible experiments but rather high concentrations needed for IR studies. The UV–visible spectra were the highest quality when the matrix was almost completely clear and transparent whereas good IR spectra required a deep red to black matrix, which has also been reported by Ault.[22] Table I summarizes UV–visible data for the Mg and Ca systems.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Program support from the National Science Foundation is also greatly appreciated.

Registry No. Mg, 7439-95-4; Mg_2, 29904-79-8; Mg_3, 72673-77-9; CH_3Br, 74-83-9; CH_3Mg_2Br, 92055-49-7; CH_3Mg_3Br, 92055-50-0.

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Reactions of S_4N_4 with Ph_2PCl, $PhPCl_2$, and PCl_3: Preparation of the Six-Membered Rings $(Ph_2PN)_2(NSX)$ (X = Cl, Br, I, Ph, NR_2) and the Related Cation $[(Ph_2PN)_2(SN)]^+$

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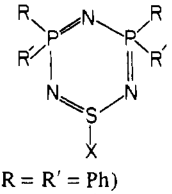
The reaction of S_4N_4 with Ph_2PCl (1:3 molar ratio) in boiling acetonitrile produces the six-membered ring $(Ph_2PN)_2(NSCl)$ in excellent yield. The salt $[Ph_2P(Cl)N(Cl)PPh_2]^+Cl^-$ is the major product when the molar ratio is increased to 1:12. The reactions of S_4N_4 with PCl_3 or $PhPCl_2$ (1:3 molar ratio) also give heterocycles containing the P_2SN_3 ring. Derivatives of the type $(Ph_2PN)_2(NSX)$ (X = I, Ph, NR_2 (R = Me, Et, $-(CH_2)_5-$)) are obtained by treatment of $(Ph_2PN)_2(NSCl)$ with KI, Ph_2Hg, Me_3SiNMe_2, Et_2NH, or $C_5H_{10}NH$, respectively, in acetonitrile. The cation $[(Ph_2PN)_2(SN)]^+$ is prepared as a trihalide salt by addition of halogens (Br_2 or I_2) to $(Ph_2PN)_2(NSCl)$. Thermolysis at 155 °C or treatment with Ph_3Sb converts $[(Ph_2PN)_2(SN)]^+Br_3^-$ to $(Ph_2PN)_2(NSBr)$. The halides $(Ph_2PN)_2(NSX)$ (X = Cl, Br, I) are readily hydrolyzed to $[Ph_2P(NH_2)N(NH_2)PPh_2]^+X^-$ in air.

Introduction

As part of our investigations of the reactions of S_4N_4 with trivalent phosphorus reagents, e.g. Ph_3P,[1] R_2PPR_2 (R = Me, Ph),[2] and Ph_2PH,[3] we have now studied the reaction of S_4N_4 and Ph_2PCl in detail. Although this reaction has not been reported previously, the reactions of S_4N_4 with PCl_3[4] and $PhPCl_2$[5] have been described. In both cases the only identified products were the salts $[RPCl_2NCl_2PR]^+Cl^-$ (R = Cl,[4] Ph[5]) and cyclophosphazenes, $(NPCl_2)_n$,[4] although the ^{31}P NMR spectrum of the $PhPCl_2$–S_4N_4 reaction mixture was very complex, suggesting the formation of additional products.

In this paper we report the full details of the preparation of the six-membered ring **1a** (X = Cl) from the reaction of S_4N_4 with Ph_2PCl.[6] We also describe the synthesis of derivatives of **1a** (X = I, Br, Ph, NR_2)[7] via simple substitution reactions and the formation of the cation $[(Ph_2PN)_2(SN)]^+$ by treatment of **1a** (X = Cl) with Br_2 or I_2. Finally, the reactions of S_4N_4 with PCl_3 and $PhPCl_2$ were briefly reinvestigated in the light of our results with the Ph_2PCl–S_4N_4 system.



1a (R = R′ = Ph)
b (R = Ph; R′ = Cl; X = Cl)
c (R = R′ = X = Cl)

Experimental Section

Reactions and General Procedures. Tetrasulfur tetranitride was prepared by the standard procedure and recrystallized from toluene before use.[8] The following reagents were commercial samples: Ph_2PCl

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