

Infrared and nuclear magnetic resonance spectroscopic studies of the structure and dynamics of allylic magnesium compounds ¹

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Abstract

The infrared spectra of allyl- and methallyl-d₂-magnesium bromides have two double bond stretching bands, corresponding to C=CH₂ and C=CD₂ groups in equilibrating allylic isomers. The methylene resonances in the ¹³C NMR spectra of allylmagnesium bromide and chloride and methallylmagnesium bromide are broadened at low temperatures by an exchange process which appears to be the interconversion between the classical unsymmetrical allylic structures. Analogous changes are seen in the spectrum of 1,3-dimethylallylmagnesium chloride and in the proton NMR spectrum of allylmagnesium bromide. Rate constants and activation parameters for the exchange have been determined from the line broadenings. Unlike the Grignard reagent, the methylene resonances of diallylmagnesium in tetrahydrofuran are not significantly broadened at reduced temperature, and the deuterated reagent does not have two distinct double bond stretching bands in the IR spectrum.

Keywords: Magnesium; Allyls; Nuclear magnetic resonance spectra; Infrared spectra; Fluxionality; Carbon-13

1. Introduction

The structure of allylic Grignard compounds has been a subject of considerable uncertainty and some controversy. It was recognized early that two covalent structures related by allylic rearrangement may be drawn for an allylic organometallic compound, and that their existence carries implications for the mechanisms of reaction of these reagents [1]. In 1959, Nordlander and Roberts [2a] observed that the ¹H NMR spectrum of allylmagnesium bromide in ethyl ether consists of only two resonances, a doublet and a pentuplet. This spectrum, formally an AX₄ pattern, implies that all four methylene hydrogens are equivalent on the NMR time scale. The spectrum remained simple to the lowest temperatures studied (–80 °C [2b,c]; –80 °C for allyl-

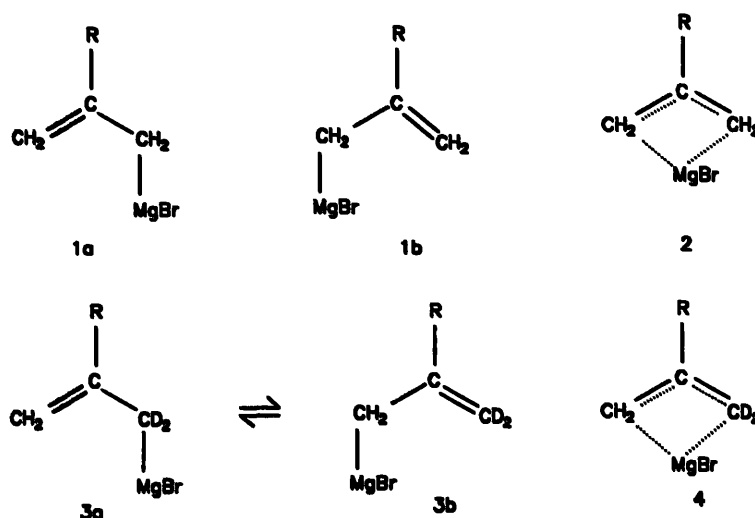
magnesium chloride in ether [2e]; –120 °C for diallylmagnesium in tetrahydrofuran (THF) [2b,d]). Subsequently, Leibfritz et al. [3] and Stähle and Schlosser [4] reported that the ¹³C NMR spectrum of allylmagnesium bromide also has only two resonances.

Two 'families' of structures are consistent with the NMR result. First (structure 1), the allyl group may be unsymmetrically bonded to the metal, so that the two methylene groups are inherently nonequivalent. Such structures are characteristic of covalently-bonded allyl groups in organic compounds, and normally lead to the more complex ABCX₂ NMR spectrum. However, rapid interconversion of the allylic isomers (1a ⇌ 1b; a 'permanent allylic rearrangement') makes the methylene groups equivalent; rapid rotation about the formal single bond in each structure completes the averaging of all four methylene hydrogens. The second alternative is a symmetrical bridged or ion-pair structure (represented in simplified form by structure 2). In this formulation, the methylene groups are equivalent, but their rapid rotation is necessary to make all four methylene hydrogens equivalent (unless they should be accidentally degenerate in shift). A number of variables within these structures might be imagined: the degree of ionic character of the C–Mg bond, and partial delocalization of

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the C–Mg bond electrons or secondary coordination of the magnesium to the double bond in 1. Still, a basic distinction between the symmetrical and the equilibrating unsymmetrical structures remains. Spectra of substituted allylic Grignard reagents [2c,e,5] are subject to similar interpretations.

Allyl compounds of other metals have structures which span the range of possibilities discussed above. The static covalent structure (analogous to 1) is preferred by the less electropositive main-group metals, including silicon, germanium and tin [6], and mercury [6,7]. Boron [8], aluminum [9], and zinc [10] compounds have NMR spectra corresponding to the unsymmetrical structure at low temperatures, but average to give spectra similar to the Grignard reagent at higher temperatures, while diallylcadmium has an AX_4 spectrum as low as $-100\text{ }^\circ\text{C}$ [11]. Alkali-metal allyl compounds [2d,12] appear to have bridged or ion-pair structures with hindered methylene rotation. Transition-metal allyl

compounds [13] are also varied in structure and dynamics.

Infrared C=C stretching frequencies of allylmagnesium compounds (1560 to 1588 cm^{-1}) [2d,14,15] are intermediate between those of the more covalent diallylmercury or diallylzinc (about 1620 cm^{-1}) and the more ionic allylsodium (1535 cm^{-1} ; more correctly identified as the asymmetric stretch of the allyl anion) [15]. In the solid state [16], lower frequencies are reported for allylmagnesium compounds (1510 – 1540 cm^{-1}). However, the stretching frequency does not distinguish in principle between the structures on the basis of their symmetries.

More recently, several additional techniques have yielded evidence favoring unsymmetrical structures for allylmagnesium compounds. Schlosser and Stähle [4] reported that the technique of deuterium perturbation of the ^{13}C NMR shift (as developed by Saunders and co-workers [17]) implies the unsymmetrical structure for

Table 1
Double bond stretching frequencies (cm^{-1}) of undeuterated and dideuterated allyl and methallyl compounds $\text{CH}_2=\text{C}(\text{R})-\text{CH}_2\text{X}$

Allyl compounds, R=H					Methallyl compounds, R=CH ₃				
X	d ₀	=CD ₂	-CD ₂ X	Reference	X	d ₀	=CD ₂	-CD ₂ X	Reference
H	1653	1614	1645	24a	H	1661	1620 ^b	1640 ⁱ	25a,24b
OH	1654	1603	1652,1638 ^a	26b	OH	1661	1629	1656	— ^b
	1646	1607	1651,1640	— ^b	Br ^j	1648	1622	1643.5	— ^b
Cl ^d	1642	1575 ^c	1637	26e,f	SnMe ₃	1631.5	1600	1627	— ^b
Br ^e	1637	1596	1631	— ^b	SnPh ₃	1631	— ^f	1629	— ^b
CPh ₂ OH	1641.5	≈ 1600 ^f	1631	— ^b	CEt ₂ OH	1642.5	1611 ^k	1640.5	— ^b
SiMe ₃	1632	1589.5	1626 ^g	— ^b	C ₄ H ₇ ^l	1650	1616.5	1647	— ^b

^a Assigned in Raman spectrum for gauche and *cis* isomers. ^b This work; spectra of deuterated compounds from mixture of allylic isomers. ^c Allyl chloride-d₃. ^d Minors peaks assigned to *cis* isomer: 1647, 1587, and 1657 respectively. ^e Weaker peaks at 1645.5, 1604, and 1646 respectively. ^f Partly obscured by aromatic absorption. ^g Shoulder at 1633.5. ^h Isobutylene-d₈. ⁱ Isobutylene-d₆. ^j 1630(sh), very broad, and 1653(sh) respectively. ^k Additional weaker peak 1594. ^l Dimeric hydrocarbon, 2,5-dimethyl-1,5-hexadiene, accompanying Grignard reagent formation.

allylmagnesium bromide, whereas a more symmetrical bridged or ion-pair structure is favored for allyllithium and the other allylic alkali-metal compounds [4,18]. The proton and carbon NMR spectra of cyclopentadienyl-(2-methylallyl)magnesium [19], unlike those of allylmagnesium bromide and diallyl-magnesium, change at low temperature to the pattern of an unsymmetrical allyl group. The X-ray structure of a crystalline allylmagnesium chloride-TMEDA dimer has allyl groups with quite normal 'covalent' structures [20]. Other data in best accord with the unsymmetrical allyl structure are ^{25}Mg NMR shifts [21] and ^{13}C - ^{13}C coupling constants [22]. Finally, theoretical calculations support an unsymmetrical structure with a significant barrier to either the allylic shift or rotation about the C-C 'single' bond [23].

The present study was undertaken in an attempt to provide additional evidence for the nature of allylmagnesium compounds in solution, utilizing IR and NMR spectroscopy.

2. Infrared spectra

As noted above, the 'NMR time scale' appeared from earlier literature to be too slow to observe the unsymmetrical isomers of allylmagnesium bromide. We therefore explored infrared spectroscopy, which has, with its higher frequencies, the capability of observing species of shorter lifetimes. Our approach was to distinguish by deuterium substitution between the two otherwise identical isomers 3a and 3b. The mass effect of deuterium directly substituted on a double bond lowers the double bond stretching frequency, while more remote deuteration has a smaller influence. Several examples from the literature and the current work which illustrate this effect are collected in Table 1. If the allyl Grignard reagent exists as interconverting structures, then a pair of bands should be observed corresponding to 3a and 3b. Symmetrical structure 4 should only have a single band in this frequency range—the asymmetric stretch of the allyl group—at somewhat lower frequency than in the undeuterated compound. The symmetrical allyl stretching frequency appears in a lower-frequency range.

Solutions of the Grignard reagent from allyl bromide in ethyl ether had an infrared absorption at 1587.5 cm^{-1} (Fig. 1(a)). The frequency was invariant ($\pm 1\text{ cm}^{-1}$) over the concentration range from about 0.3 to 3 M, or with partial destruction of the reagent by oxygenation or protolysis; the band was also quite constant in width. The Grignard reagent from allyl-1,1- d_2 bromide had two peaks, at 1559 and 1577.5 cm^{-1} (Fig. 1(b)). Similar spectra were observed with the Grignard reagent from methallyl bromide; the band at 1584 cm^{-1} in the undeuterated Grignard reagent was transformed to a pair

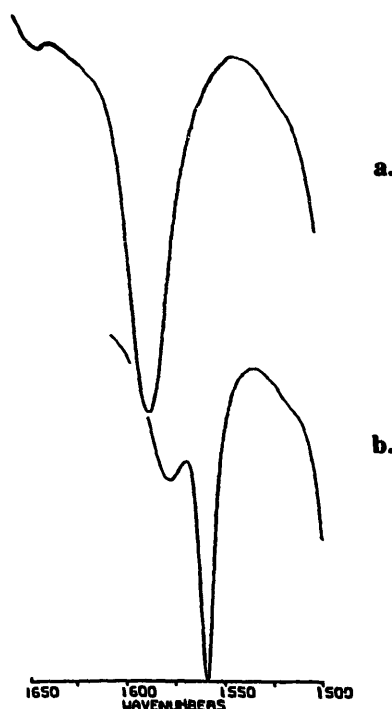


Fig. 1. Infrared spectra of 1 M solution of allylmagnesium bromide in diethyl ether: (a) undeuterated, (b) 1,1- and 3,3-dideuterated.

of bands at 1566 and 1582 cm^{-1} on deuteration. In contrast, the band at 1528.5 cm^{-1} in methallyllithium was shifted to 1508.5 cm^{-1} by similar deuteration; there was no apparent splitting, but its broadness might have obscured a small separation. The foregoing results are consistent with the interpretation that the allyl and methallyl Grignard reagents consist of rapidly-equilibrating mixtures of unsymmetrical allylic isomers, while the lithium reagent is a bridged ion-pair species.

Alternative explanations for the appearance of two bands in the deuterated Grignard reagent spectra should be considered. These might arise from conformational isomers [26], from the Schlenk-equilibrium species RMgBr and R_2Mg , or from species of different aggregation. However, there is no obvious reason why these same factors should not double the peak in the undeuterated compound as well. Furthermore, both theoretical calculations [23] and analogy with other allylic metal derivatives [27] indicate a strong preference for one conformation in which the C-Mg bond lies out of the plane of the allyl group. It is also likely that the allylic reagents should be mostly in the RMgBr form, since (a) this species generally predominates in ethyl ether solutions of Grignard reagents [28], (b) an excess of magnesium bromide from the formation of the reagent should shift the equilibrium further in that direction, (c) RMgBr appears to be more strongly favored in the more 'ionic' or delocalized organomagnesium compounds [29], and (d) addition of dioxane to precipitate magnesium bromide did not produce a simple alteration of

intensities of the peaks. The appearance of the spectrum was not dependent on concentration.

The appearance of the spectra, nevertheless, suggests some caution in their interpretation. The pair of bands in the deuterated Grignard reagents differ significantly in width. Approximate resolution of the partly overlapping pair led to a higher-frequency band similar in width to that of the undeuterated reagent (about 20–25 cm^{-1}) and a lower-frequency one (deuterated double bond) about half as wide but similar in area. However, the variation in band width is not unique to the Grignard reagents. In spectra of other allyl and methallyl compounds in this study, the double bond stretch varied in width from less than 10 cm^{-1} to more than 20 cm^{-1} , with no consistent pattern relating the widths in deuterated and undeuterated compounds. Some of the broader bands had a shoulder or separation into two peaks. Multiple overlapping bands in this region have been attributed to conformational isomers [26]. Combination, or overtone, bands are reported for some molecules [25], and vibrational analyses imply that the 'double bond stretch' also contains substantial contributions from other internal coordinates [24,26a,b]. While we do not have evidence supporting a specific rationalization for the difference in widths of the Grignard reagent 'double bond stretches', it seems more reasonable to consider them a 'spectroscopic' complication than to attach distinct structural significance to them. (One possibility is that a large out-of-plane vibrational amplitude about the double bond, as a consequence of partial delocalization of the C–Mg electrons, leads to broadening of the double bond stretch. The smaller amplitude of the CD distortion would produce less broadening.)

3. Variable-temperature NMR studies

Although previously noted proton NMR studies of allyl Grignard reagents had failed to produce evidence for slowing of the allylic rearrangement process at even the lowest temperatures of observation [2], there was reason to hope that modern ^{13}C NMR might be more successful. For a symmetrical two-site exchange, three approximate equations relating the rate constant, the line width, and the chemical shift difference between sites are shown in Eqs. (1)–(3) [30].

$$k = \pi(\delta\nu)^2/2(W - W_0) \quad (1)$$

$$k = \pi(\delta\nu)/\sqrt{2} \quad (2)$$

$$k = \pi(W - W_0) \quad (3)$$

where ($\delta\nu$) is the shift difference between exchanging sites, and ($W - W_0$) is the line broadening resulting from exchange.

The line shape depends on the square of the chemical

shift difference between the two environments near fast exchange (Eq. (1)), but only on the first power at the coalescence point (Eq. (2)), and not at all near the slow exchange limit (Eq. (3)). Hence, it is much easier to detect exchange broadening of an averaged resonance when there is a large shift difference between the exchanging nuclei, but the advantage diminishes and eventually disappears as the spectrum passes into the slow exchange regime at lower temperature. Combining the inherently larger shift range of ^{13}C (about five-fold in hertz at constant field) with the higher field/frequency operation of modern superconducting NMR spectrometers, exchange broadening of an averaged ^{13}C resonance observed on a '250 MHz spectrometer' might typically be 400 times greater than for a ^1H resonance at 60 MHz with the same exchange rate.

The ^{13}C NMR spectrum of allylmagnesium bromide in ethyl ether at room temperature consisted of only two lines of similar width, the methylene carbons at 58.7 and the methine carbon at 148.1 ppm (reported previously as 58.7 and 148.2 ppm [3,4]). As the temperature was reduced, the methylene resonance broadened and eventually disappeared into baseline noise, while the methine signal remained relatively constant in width. Similar results were observed at concentrations of 0.1 and 1.0 M in ethyl ether, at spectrometer frequencies of 62.9, 90.6 and 125.76 MHz, and for Grignard reagents prepared using different grades of magnesium. At the lowest temperatures studied (about 180 K at 62.9 MHz), there was no indication of the appearance of separate high- and lowfield methylene resonances. Similar behavior was also noted in less extensive studies of methallylmagnesium bromide, allylmagnesium chloride, and the 'secondary-secondary' allylic Grignard reagent, 3-penten-2-ylmagnesium chloride (1,3-dimethylallyl).

Since only the broadening of the averaged signal in the 'fast-exchange' regime could be observed, it is important to be confident that the line-broadening process is indeed the allylic rearrangement. Potential alternatives, including the exchange of allyl groups between RMgBr and R_2Mg species, between species of different aggregation, or between locations within an aggregate, should involve sites only slightly different in shift (e.g. methylene resonances differ by only 0.8 ppm between ethyl ether solutions of composition R_2Mg and $\text{RMgBr} + 0.1 \text{MgBr}_2$, and chemical shifts of R_2Mg differ by less than 1 ppm between ether and THF). Complete line shapes were calculated for a series of two-site exchanges with a variety of shift separations and rate constants. With small assumed shift differences of only 1 or 2 ppm, the signal split into two peaks without ever broadening to the observed extent. With larger shift separations (5–10 ppm) the observed width could be duplicated, but incipient approach to coalescence led to obvious distortion from Lorentzian line shape. Allylic rearrangement seems to be the only reasonable process

with a large enough shift difference to produce the observed broadening. Further support comes from the similarity in behavior among the four allylic magnesium compounds reported here. We also observe qualitatively similar spectral changes with cycloalkenyl Grignard reagents, except that slower rearrangement allows detection of the unsymmetrical species [31]. In the ^{13}C spectra of crotylmagnesium bromide, spectral changes occur as expected for 'freezing' of the equilibrium between *cis* and *trans* isomers, but the extreme broadening observed here was not seen [32].

Rate constants for the allylic rearrangement were calculated from the broadening of the averaged methylene signal using Eq. (1). The unbroadened line width was taken as that of the C_2 resonance. Chemical shifts of the allylic and olefinic methylene signals of allylmagnesium bromide in the absence of exchange were estimated as 21 and 94 ppm, based on comparisons of the shift differences between several allylic Grignard reagents and corresponding hydrocarbons [4,32,33]. The resulting shift difference of 73 ppm was used in subsequent calculations. (A difference of 70 ppm was estimated by Schlosser and Stähle [4], based upon slightly different assumptions. Use of the smaller shift difference would yield rate constants lower by about 8% and an insignificant change in activation parameters.) Similar shift differences between allylic and vinyl methylene groups were assumed for allylmagnesium chloride and methallylmagnesium bromide, and an analogous value of 79 ppm was used for dimethylallylmagnesium chloride. Complete line-shape calculations confirmed the accuracy of Eq. (1) throughout the range of observed line widths.

Activation parameters were calculated using the Eyring equation from individual sets of data and from

various combinations of the data for allylmagnesium bromide (including the total body of 105 individual rate constants). No obvious systematic deviation was apparent. Further details are included in the experimental section. Activation parameters and rate constants extrapolated to 200 and 298 K for all of the substrates are summarized in Table 2.

A limited ^1H NMR study of allylmagnesium bromide was also undertaken. Spectra at 250 and 500 MHz were recorded at 287, 257, 237, and 217 K, and at 233 and 223 K respectively. The components of the methylene doublet were broadened, and in the 500 MHz spectrum at 223 K they had merged into a single broadened line. Using the line widths of the methine pentuplet to represent the unbroadened line width and estimating the exchanging methylene shifts as 0.87 and 4.51 ppm, rate constants were calculated from the broadening of the doublet. These rate constants were quite comparable with the ^{13}C data. Eyring parameters and extrapolated rate constants for the correlation of proton data at 250 and 500 MHz combined are included in Table 2. The current ^1H observations appear to be consistent with the absence of exchange broadening in the earlier 60 MHz ^1H NMR studies of allyl Grignard reagents [2]. The extrapolated rate constant of $4.8 \times 10^4 \text{ s}^{-1}$ for allylmagnesium bromide at 200 K would predict a line broadening of only 1.5 Hz in a 60 MHz spectrum, probably not discernible in the presence of the considerable general spectral broadening also observed at this temperature.

In several of the spectra at lowest temperatures it was also observed that the central carbon resonance of the Grignard reagent was accompanied by a smaller peak of about 1/10 of its intensity. It is likely that at these temperatures the Schlenk equilibrium between RMgBr

Table 2
Eyring equation correlation of rate constants for allylic exchange of symmetrical allylic Grignard reagents ^a

Substrate	No. of points	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	k_{calcd} (s ⁻¹)	
				200 K	298 K
AllylMgBr ^b	6	5.8 ± 0.2	-7.7 ± 0.7	4.0 × 10 ⁴	7.2 × 10 ⁶
AllylMgBr ^c	5	5.5 ± 0.3	-8.4 ± 1.2	5.4 × 10 ⁴	7.8 × 10 ⁶
AllylMgBr ^d	28	6.4 ± 0.2	-5.4 ± 0.9	2.9 × 10 ⁴	8.5 × 10 ⁶
AllylMgBr ^e	20	5.8 ± 0.5	-7.4 ± 1.8	4.5 × 10 ⁴	8.2 × 10 ⁶
AllylMgBr ^f	105	5.88 ± 0.11	-7.3 ± 0.5	4.0 × 10 ⁴	7.7 × 10 ⁶
AllylMgBr ^g	6	6.0 ± 0.2	-6.2 ± 0.7	4.8 × 10 ⁴	10.6 × 10 ⁶
AllylMgBr ^h	4	5.4 ± 0.2	-9.2 ± 0.6	5.3 × 10 ⁴	6.7 × 10 ⁶
AllylMgCl ⁱ	8	5.5 ± 0.3	-6.0 ± 1.3	20 × 10 ⁴	28 × 10 ⁶
2-MethylallylMgBr ^j	5	9.7 ± 0.6	7.0 ± 2.3	0.35 × 10 ⁴	16 × 10 ⁶
1,3-DimethylallylMgCl ^k	5	6.6 ± 0.4	-4.7 ± 1.3	2.4 × 10 ⁴	8.4 × 10 ⁶

^a Concentration about 1 M in ethyl ether, 62.9 MHz ^{13}C spectra, and temperatures corrected from thermocouple measurements, unless otherwise indicated; uncertainties are standard deviations. ^b Single run, 90 MHz, chemical thermometer, 222.5 to 247.5 K. ^c Single data set, 125.76 MHz, Waltz decoupling, 233 to 298 K. ^d All chemical thermometer data combined, 62.9 and 90 MHz, 222.5 to 299 K. ^e Five data sets combined, 236 to 265 K. ^f All ^{13}C data at 62.9, 90.6, and 125.76 MHz combined, ca. 0.6 to 1.1 M, 222 to 312 K. ^g Proton NMR data, 250 and 500 MHz, 217 to 287 K. ^h Concentration 0.1 M, 250 to 307 K. ⁱ Data combined from two sets, concentration about 0.2 M, 205 to 258 K. ^j 232.5 to 270.5 K. ^k THF solution, 250 to 290 K.

and R_2Mg is no longer rapid, so that a small concentration of the latter is observable [2e]. Absence of the minor peak in higher temperature spectra may be a consequence of either exchange broadening or a low equilibrium concentration.

As noted in the introduction, Schlosser and Stähle [4] reported that application of Saunders' 'isotopic perturbation' criterion [17,34] to (allyl- d_1)magnesium bromide supports the equilibrating unsymmetrical structure. In the present work, similar observations with (allyl- d_2)magnesium bromide (3) led to quantitatively identical results on a 'per deuterium' basis.

4. Diallylmagnesium

Diallylmagnesium solutions were prepared by precipitation of magnesium bromide from the Grignard reagent or by reaction of diallylmercury with magnesium. In the spectrum of the undeuterated reagent in ether, the 'double bond stretch' was shifted from 1587.5 cm^{-1} in the Grignard reagent to 1577 cm^{-1} . Di(allyl- d_2)magnesium absorbed at 1555 cm^{-1} in ether (vs. 1577 and 1560 cm^{-1} for the corresponding Grignard reagent) and splitting into two bands was not evident.

Variable-temperature ^{13}C NMR spectra of the diallylmagnesium solutions did not lead to useful estimates of an allylic rearrangement rate. In ether, both resonances (particularly C_2) were quite broad, and not very sensitive to temperature. Solutions of diallylmagnesium in THF had narrow resonances which broadened only minimally at lower temperatures, implying either a symmetrical structure or equilibration rates at least one or two orders of magnitude greater than the Grignard reagent. With less complete precipitation of magnesium bromide, some broadening at low temperature was seen. Although definitive conclusions cannot be drawn, it is likely that the allyl groups in diallylmagnesium are more extensively delocalized than in the Grignard reagent, particularly in THF solution, leading to more ionic allyl-metal bonding. Association in solution may lead to a variety of more complex structural alternatives, and both covalent and ion-pair structures could be present in rapid equilibrium. (It may be recalled that in the solid state allylmagnesium compounds are reported to have IR frequencies [16] similar to the alkali metal compounds.)

5. Experimental

Melting and boiling points are uncorrected. Tetrahydrofuran (THF) and ethyl ether were dried by distillation under nitrogen from sodium benzophenone or lithium aluminum hydride, and used immediately. Dioxane was purified by stirring for 18 h with sodium

borohydride (3 wt.%), distillation, and redistillation under nitrogen from sodium metal. Magnesium metal was commercial 'Grignard-grade' turnings, or in some cases, magnesium powder (gift from Magnesium Elektron Ltd.) or chips of sublimed magnesium (gift from the Dow Metal Products Company).

Operations with organometallic compounds were carried out under a slight positive pressure of nitrogen or argon, in glassware which had been dried for several hours at $120\text{ }^\circ\text{C}$, assembled hot, and cooled while purging. Transfers were made by syringe in a counter-flow of the inert gas. Organomagnesium solutions which were not to be used immediately were sealed in dry glass ampules; when needed, they were opened under nitrogen in a glove bag. Sealed samples of Grignard reagents were prepared as follows: the NMR or storage tube was connected with a short length of Tygon tubing to a manifold, flamed briefly and cooled under vacuum; nitrogen was readmitted, and the tube was filled by syringe through an opening on the top of the manifold in a counter-flow of nitrogen and sealed after partial evacuation. Occasionally, spectra were run in an NMR tube with a septum screw-cap.

Organomagnesium solutions were analyzed by titration [35]. A measured sample (syringe or pipette) was added to water, warmed to evaporate the ether solvent, and an excess of standard sulfuric acid was added. Aliquots were analyzed for base (organometallic alkyl groups), magnesium, and bromide. The base was determined by back-titration with standard NaOH. The solutions so obtained were then titrated for either magnesium with EDTA [36] using Eriochrome Black T or 'Calmagite' indicator, or for bromide by the Volhard method [37]. Analyses reported are normalized to Mg as 1.00. Titrations were internally consistent, with the total for base and halide equal to twice the magnesium titer, within error limits of ± 0.03 for each component in $R_xMg_yBr_z$.

Infrared spectra were recorded on a Nicolet MX-1 FTIR spectrometer, operating with 2 cm^{-1} resolution. Sealed liquid cells with KBr or NaCl windows and path lengths of 0.015, 0.025, or 0.1 mm were used. They were loaded using a dry syringe (within a dry box or a glove bag for organometallic solutions). Gas chromatograms were obtained using Varian A90-P3 instruments with the following columns: 8 ft \times 1/4 in, 25% 'UCON Polar' on 60/80 mesh firebrick; 10 ft \times 1/4 in, 5% Carbowax 20 M on Chromosorb T; 10 ft \times 1/4 in, 25% tricresylphosphate on 60/80 mesh Chromosorb P.

NMR spectra were recorded on Bruker WM-250 and WH-360 and General Electric GN-500 spectrometers. ^{13}C spectra were obtained in broad band and ^1H - ^{13}C dual frequency probes. In organometallic solutions, internal C_6D_6 (ca. 10%), ethyl ether- d_{10} , or an external chemical thermometer (see below) were used for the

lock signal. Shifts are relative to tetramethylsilane (TMS) at 0.00 ppm. The high-field THF or ethyl ether signals (consistently at 26.20 and 15.48 ± 0.05 ppm) or C_6D_6 (128.3 ppm) were used as secondary references in the absence of TMS. Other samples were run in $CDCl_3$ with internal TMS. Carbon NMR assignments were based on analogous compounds, shift correlations [33], and on off-resonance decoupling.

5.1. Allylmagnesium bromide (2-propen-1-ylmagnesium bromide)

In a typical preparation, allyl bromide (12.1 g, 0.10 mol) in 90 ml of ether was added dropwise to 9 g (0.37 mol) of magnesium turnings stirred initially in 10 ml of ether. Reaction initiated promptly, and the addition extended over a period of 2 h. In most preparations, the volatiles were distilled to a cold trap under vacuum, nitrogen was admitted, and fresh ether was added to produce a solution of about 1 M (or other desired concentration). The 1H NMR spectrum had a pentuplet (1H, $J = 11.3$ Hz) at 6.45 ppm and a doublet (4H, $J = 11.3$ Hz) at 2.69 ppm; coupling product, if present, had multiplets at 5.76, 4.96, and 2.11 ppm. The ^{13}C NMR had peaks at 148.1 and 58.7 ppm, and coupling product at 138.57, 115.0, and 33.9 ppm. A typical composition from titration analysis was $R_{0.90}Mg_{1.00}Br_{1.14}$. On various occasions, the Grignard reagent was characterized by reaction of small samples with chlorotrimethylsilane, benzophenone, or chlorotriphenyltin. IR double bond frequencies of Grignard reagent and related products are collected in Table 1.

5.2. (Allyl- d_2)magnesium bromide

Allyl-1,1- d_2 alcohol was prepared by reduction of acryloyl chloride with $LiAlD_4$ according to the procedure of Schuetz and Millard [38]. The product was accompanied by substantial amounts of polymer; temperature and solvent for the reduction were varied with little improvement in yield. Proton NMR absorption for the allylic hydrogens at 4.05 ppm could not be detected. The alcohol (5.3 ml) was then added quickly to a mixture of 48% hydrobromic acid (13.7 ml) and 96% sulfuric acid (3.25 ml) in a flask equipped with a short-path still-head. The flask was immediately lowered into a heating bath maintained at 100 °C, and an additional 3.25 ml of sulfuric acid was added dropwise. Allyl- d_2 bromide distilled rapidly from the flask at a temperature of 65–67 °C; it was used after brief drying over calcium chloride (7.0 g, 75%). The proton NMR spectrum indicated that the bromide obtained was about 80% allyl-1,1- d_2 and 20% allyl-3,3- d_2 . Conversion to the Grignard reagent followed the procedure described for the undeuterated compounds. NMR spectra were consistent with expected structures and IR double bond

frequencies of the Grignard reagent and related compounds are collected in Table 1.

5.3. Diallylmagnesium and di(allyl- d_2)magnesium

Dioxane was added incrementally to a solution of allylmagnesium bromide in ether, precipitating magnesium bromide and a substantial fraction of the organometallic. The IR double bond frequency changed from 1587.5 cm^{-1} with no dioxane, to 1583.5 cm^{-1} with 3/4 equivalent, to 1577 cm^{-1} with a full equivalent; there was little further change with more than one equivalent. A typical solution obtained from addition of 1 mol of dioxane per equivalent of bromide had the composition $R_{1.86}Mg_{1.00}Br_{0.09}$. Solutions of diallylmagnesium in THF were obtained by removing the ether under vacuum and dissolving the residue in THF (or alternatively, by extracting the dioxane-precipitated magnesium salts with THF), centrifuging, removing volatiles from the clear solution, and again dissolving the residue in fresh THF. The ^{13}C NMR spectrum indicated the absence of ether and dioxane. The diallylmagnesium was sparingly soluble in ether. Extracting solid allylmagnesium bromide (from evaporation of an ether solution) with THF also led to a solution with an IR spectrum similar to the diallylmagnesium solution, but with broadened allyl ^{13}C NMR signals. Di(allyl- d_2)magnesium was prepared similarly. Solutions of the normal and deuterated diallylmagnesium in ether had an additional broad isotope-dependent band at about 1555–1550 and 1525 cm^{-1} respectively.

Halogen-free diallylmagnesium was also prepared via reaction of allylmagnesium bromide with mercuric bromide to form diallylmercury [39]; b.p. 58 °C, 2.5 Torr (Ref. [39] b.p. 58–58.5 °C 1.5 Torr); ^{13}C NMR (ether): δ 149.6, 57.2, 68.7 ppm. The product was dissolved in ether or THF and stirred with a 10% excess of magnesium chips for 24 h. The clear supernatant solution was removed by syringe after the suspension of mercury had settled. The ^{13}C NMR spectrum had peaks at 149.4 and 57.2 ppm in THF and 148.7 and 57.9 ppm in ethyl ether.

5.4. Allylmagnesium chloride

A Grignard reagent was prepared by dropwise addition of allyl chloride (Aldrich Chemical Co., 0.85 g, 11 mmol) in 12 ml ether to magnesium turnings (0.49 g, 20 mmol) in 4 ml ether, and stirred for an additional 16 h. The white suspension which resulted was diluted with an additional 16 ml of ether, allowed to settle, and the clear supernatant was transferred to an NMR tube. The base (allyl group) concentration was 0.30 M, and the approximate composition corresponded to $R_{1.1}Mg_{1.0}Cl_{1.0}$. The 1H NMR spectrum had a one-hydrogen pentuplet (δ 6.4 ppm) and a four-hydrogen doublet (δ 2.55

ppm, $J = 11.3$ Hz). The ^{13}C NMR spectrum had peaks at 149.8 and 57.8 ppm. The latter broadened at reduced temperature, and was not detectable at 210 K; at the lowest temperatures, two lowfield resonances were present at 148.6 and 149.5 ppm in a ratio of about 10:1.

5.5. Methallylmagnesium bromide (2-methyl-2-propen-1-ylmagnesium bromide)

Phosphorous tribromide (redistilled, 32.5 g, 0.12 mol) was added dropwise over 2 h to a stirred mixture of methallyl alcohol (2-methyl-2-propen-1-ol, Aldrich Chemical Co., 25.2 g, 0.35 mol) and pyridine (7.9 g, 0.10 mol) cooled to 0 °C. The mixture was warmed to room temperature over 2 h, and then evacuated with an aspirator through a trap cooled with dry ice; transfer of volatiles was completed by raising the pot temperature gradually to 80 °C. The product was redistilled at 91–92 °C. (Some samples were stabilized for storage over anhydrous K_2CO_3 .)

A Grignard reagent was prepared by dropwise addition of a solution of the bromide (10 g, 74 mmol) in 50 ml of ether over a period of 2 h to magnesium turnings (5.5 g, 230 mmol) in 25 ml of ether. Volatiles were distilled to a cold trap under vacuum and replaced by fresh ether. Titration analysis yielded a composition of $\text{R}_{0.81}\text{Mg}_{1.00}\text{Br}_{1.18}$. The ^1H and ^{13}C NMR spectra had resonances at 2.41 (CH_2) and 1.76 (CH_3), and 156.85, 59.5 and 27.2 ppm respectively; hydrocarbon dimer was at 145.8, 110.4, 36.8 and 22.5 ppm. At reduced temperatures, the 59.5 ppm ^{13}C resonance broadened; it was undetectable at 220 K. At the lowest temperature studied, about 190 K, the resonance at 156.8 ppm was accompanied by a smaller signal about 0.8 ppm to lower field.

Small samples of the Grignard reagent were allowed to react with a variety of reagents: chlorotrimethyltin, chlorotriphenyltin, 3-pentanone, and oxygen. A small amount of 2,5-dimethyl-1,5-hexadiene, the dimeric hydrocarbon by-product of Grignard reagent formation, was also isolated from the solvent recovered from the preparation. NMR spectra were consistent with expected structures, and IR double bond frequencies are collected in Table 1.

5.6. (Methallyl- d_2)magnesium bromide

Methacryloyl chloride was reduced by the same procedure as acryloyl chloride [38] with LiAlD_4 to methallyl- d_2 alcohol in 71% yield, and this was converted in turn to the bromide as described above. NMR spectra indicated essentially complete 1,1-dideuteration of the alcohol, and the bromide had only traces of allylic isomerization. Heating the neat bromide for several hours in a sealed NMR tube at 80–85 °C led to com-

plete equilibration. The Grignard reagent was formed as described above, and subjected to similar treatment.

5.7. Methallyllithium and methallyl- d_2 -lithium

Methallyltrimethyltin was prepared from methallylmagnesium bromide and chlorotrimethyltin; b.p. 140–144 °C (Ref. [40] b.p. 147 °C). Methylolithium (1.0 ml of a 1.2 M solution in ether) was added gradually via syringe to allyltrimethyltin (0.22 g, 1.0 mmol). The ^1H NMR spectrum of the solution had singlet resonances at 2.29 (CH_2) and 1.70 (CH_3) ppm. The same procedure was followed for the deuterated compound.

5.8. 1,3-Dimethylallylmagnesium chloride (3-penten-2-ylmagnesium chloride)

Magnesium shavings (sublimed grade, 0.20 g, 8.2 mmol) were activated by reaction with 2 mmol of 1,2-dibromoethane in ethyl ether, washed with THF, and covered with 13 ml of THF. 4-Chloro-2-pentene [41] (ca. 90% trans, 0.21 g, 2.0 mmol) in 7 ml of THF was added from an addition funnel provided with a jacket cooled by a dry ice–isopropyl alcohol mixture. After the first 5% of the chloride solution had been added, the reaction flask was irradiated in an ultrasonic bath for 10 min, and then cooled to –40 °C. This temperature was maintained while the remainder of the solution was added over a period of 2 h. After warming to room temperature, the volatiles were removed under vacuum (2–3 Torr), and the residue was dissolved in fresh THF to make up a solution of concentration approximately 0.6 M, which was centrifuged to remove a slight cloudiness before transfer to an NMR tube. The ^{13}C NMR spectrum had resonances at 147.6, 62.8, and 18.15 ppm. At reduced temperature, the 62.8 ppm band broadened; at 220 K it was only a shoulder on the nearby THF band, and it was undetectable at 190 K. Changes also appeared in the other Grignard reagent resonances: the methyl resonance appeared to split into a group of closely-spaced peaks, and weaker absorption at about 2 ppm to higher field accompanied the C_3 resonance.

5.9. NMR measurements

Temperature stability for low temperature ^{13}C NMR spectra was better than ± 1 °C with the spectrometer variable temperature unit. However, r.f. heating by the proton decoupling transmitter [42,43] led to sample temperatures higher than indicated by the spectrometer temperature read-out. A ^{13}C chemical thermometer [43], consisting of a 50/50 (v/v) mixture of CCl_4 and acetone- d_6 contained in a smaller concentric tube, was used to measure the temperature under spectrum conditions. The temperature dependence of the chemical shift

difference between CCl_4 and the acetone carbonyl resonance was calibrated against a thermocouple or platinum resistance thermometer. The calibration curve was similar, but not identical, to the published curve, and small differences were noted between batches of the chemical thermometer. Using a variety of controls with different arrangements of concentric tubes, it was confirmed that r.f. heating of the chemical thermometer itself was minimal and that radial temperature differences in the sample were small. R.f. heating was also reduced by gating the decoupler off during a delay between pulses, and in some spectra it was eliminated by using the WALTZ-16 composite pulse sequence for decoupling. At low power in a 5 mm tube, some spectra were nearly insensitive to the r.f. power level. A correction for 'typical' Grignard reagent solutions was based on the difference between the spectrometer readout and temperatures calibrated using the chemical thermometer or a thermocouple immersed in Grignard reagent solution during proton decoupling; this was applied to spectra run without the chemical thermometer. Variations in this calibration over longer time periods are possible (from changes in the probe configuration and nitrogen flow rate), but no attempt was made to individualize the standard corrections. R.f. sample heating with continuous decoupling was 17 ± 2 °C, depending somewhat on temperature. We estimate that sample temperatures from the chemical thermometer are accurate to about 1 °C, temperature-corrected results with gated decoupling to 2 °C, and with continuous broad-band decoupling to 4 °C.

Line broadening due to exchange was taken as the difference between the widths of the C_1/C_3 and C_2 resonances. Rate constants were calculated using Eq. (1). Overall consistency was confirmed by correlation of the temperature dependence of the rate using the Eyring equation. The activation enthalpy derived from 14 different sets of rate constants (each set run in a single spectrometer session with the same sample) varied from 5.11 to 6.29 kcal mol⁻¹. In Table 2, activation parameters derived from several representative combinations of the data are summarized, including the correlation of all available data—105 rate constants obtained on four different spectrometers from numerous sample preparations. Exclusion of several more deviant or otherwise questionable points would have further narrowed the uncertainty limits, with little change in parameters.

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Appendix A. Calculated conformation of allylmagnesium fluoride

Several molecular orbital studies of the structure of allyllithium, at varying levels of sophistication, have uniformly favored a symmetrical geometry in which the metal bridges the ends of the allyl group [23a,44]. In contrast, a lone calculation of an allylmagnesium compound, the hydride [23a], predicted that the most stable structure is an unsymmetrical one in which the metal lies over the 'plane' of the allyl group, most closely associated with one of the terminal carbons. We summarize here results of calculations for allylmagnesium fluoride. These have been reported in preliminary form [23b] and more extensive calculations will be published elsewhere, but a brief description is included at this point because of their limited accessibility and their pertinence to the foregoing experimental studies. Ab initio calculations were performed using the ALIS program (Iowa State University) [45]; s and p basis sets used were: carbon and fluorine [9s5p/3s2p] and hydrogen [4s/2s] from Van Duijneveldt [46] and magnesium [12s8p/4s3p] from Huizinaga [47]. Contracted basis sets were generated according to Raffanetti's generalized contracted scheme [48], and total energies were obtained from closed-shell SCFR runs converged to 0.0001 in the coefficients. Geometric parameters for the allyl group were taken from the earlier calculation of allylmagnesium hydride [23a]. The C–Mg and Mg–F distances and the C–C–Mg and C–Mg–F angles were optimized by varying the input values; the C–C–C angle in the bridged structure was also optimized since it interacted strongly with the C–Mg distance.

Calculations were performed for four geometries corresponding to those in the earlier study of allylmagnesium hydride: an unsymmetrical nonplanar 'gauche' structure with the magnesium in a plane perpendicular to the allyl plane (A), a structure with the magnesium symmetrically bridging (B), and planar structures with the magnesium cis (C) and trans (D) to the allyl group. The Mg–F bond length varied little from 1.78 Å; in the unbridged structures the C–Mg–F angle was about 180° and the total energy was quite insensitive to its distortion. By contrast, covalent character in the C–Mg bond was suggested by the variation of its length and the C–C–Mg angle with conformation, and the sensitivity of total energy to the values of these parameters.

The relative energies calculated for the four geome-

Table 3
Calculated relative energies of structures of allylmagnesium hydride and fluoride

Structure	Relative energy (kcal mol ⁻¹)	
	Hydride [23a]	Fluoride
Gauche (A)	(0.0)	(0.0)
Bridged (B)	2.8	8.2
Planar cis (C)	4.2	2.1
Planar trans (D)	7.9	4.9

tries of allylmagnesium hydride [23a] and allylmagnesium fluoride are summarized in Table 3. The two calculations agree that the unsymmetrical 'gauche' structure (A) should be the most stable. They do differ, in that the C–C–Mg angle predicted for allylmagnesium hydride (89.2°) is smaller than that for the fluoride (112°). The ordering of the other structures is not the same in the two calculations: the bridged one is next lowest in energy in the hydride calculation, but the planar trans and cis structures are lower for the fluoride. If the 'gauche' structure is the most stable form, then a bridged structure may represent the transition state for allylic rearrangement and the planar structures transition states for conformational rotation of the CH₂Mg group. Thus, calculations for the fluoride suggest that rotation is faster than allylic rearrangement, but those for the hydride imply the opposite. They agree that rotation of the CH₂Mg group 'inward' through the cis conformation should be preferred over an 'outward' rotation through the trans conformation. Owing to differences in the nature of the calculations, it is not profitable to pursue further comparisons. However, it does appear significant that the unsymmetrical, nonplanar structure is predicted in both instances to be the most stable.

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