Table I. Results of Transformations Shown in Scheme I

series	acetal 8, % yield^{8b,9}	ether 9		ketone 10, % yield^{8a,9}	alcohol 11	
		% yield^{9}	ratio^{10}		% yield^{8b}	$[\alpha]^{25}_{D}$, deg (c), CCl_4
a	96	90^{8b}	88:12	91	72^{9a}	+8.4 (2.5)
b	95	98^{8a}	87:13	98	98^{9}	+7.9 (2.5)
c	95	92^{8b}	82:18	98	73^{9}	+8.3 (4.1)
d	94	96^{8b}	82:18	98	88^{9a}	−0.5 (4.3)

The procedure is typified by the following example. Equimolar amounts of *n*-nonaldehyde and (2*R*,4*R*)-pentanediol[6b] were condensed (C_6H_6, trace of *p*-TsOH, reflux 2 h) to give the acetal **8b**[8b,9] in 95% yield. Titanium tetrachloride (0.19 mL, 1.7 mmol) was added rapidly to a stirred solution of 273 mg (1.2 mmol) of acetal **8b** and 0.7 mL (4.4 mmol) of allyltrimethylsilane in 25 mL of dichloromethane at −78 °C under argon. After 20 min, 1 mL of methanol was added, and then the mixture was warmed to above 0 °C and partitioned between 1 M hydrochloric acid and dichloromethane. The crude product, which amounted to 318 mg (98% yield), was homogeneous by TLC, and the ^1H NMR spectrum was consistent with the formula **9b**. GC analysis[10] showed two cleanly separated peaks in the ratio of 87:13 corresponding to the two diastereomeric forms of **9b**. It is noteworthy that in this case a single rapid chromatography on silica gel[8b] gave a 78% yield of **9b** with a diastereomeric ratio of 94:6. Crude **9b** was oxidized[11] to the ketone **10b** (98% yield), which underwent base-catalyzed[15] β-elimination to give the homoallylic alcohol **11b**[8b,9] (98% yield) $[\alpha]^{25}_{D}$ +7.9° (c 2.5, CCl_4).

Proof of Constitution of the Homoallylic Alcohols. The constitution of **11b** was confirmed by its transformation[16] into the natural product γ-dodecanolactone (**12**), which has been shown by a stereorational synthesis[7] to have the *R* configuration. The structure and *R* configuration of the dienol **11c**, which has been used as an intermediate in the synthesis of nonactic acid,[19] were confirmed by comparison with an authentic specimen of (4*S*)-octa-1,7-dien-4-ol (enantio-**11c**) derived from (*S*)-(−)-malic acid.[20] The GC (co-injection) and spectral properties (^1H NMR, IR, MS) of the two specimens were identical. The $[\alpha]^{25}_{D}$ (c 4.1, CCl_4) for the *S* isomer was −12.6° while that of our specimen was +8.3°, corresponding to 65% ee, which is in agreement with the diastereomeric composition of the precursor **9c**.

The product **11d** exhibited a very low $[\alpha]_D$ in carbon tetrachloride solution; however, in ethanol the value was −7°. The configuration of this alcohol is presumed to be as shown in **11d** by analogy to the established cases (see above).

Conclusions. The diastereoselectivity of the Lewis acid catalyxed reaction of the chiral acetals **8a–d** is consistent with the hypothesis outlined at the outset, which may be reasonably extended to include six-membered-ring acetals. This process, coupled with removal of the chiral auxiliary, provides a facile enantioselective synthesis of some homoallylic alcohols (65–74% ee), which promises to be generally useful for either the *R* or *S* forms.[21]

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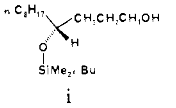
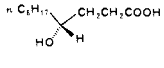
(15) Except for the case **10a** → **11a**, the side-chain-elimination procedure involved stirring with 4:2:1 THF/MeOH/7.5 M KOH at 26 °C for 5 h.

(16) Conversion of **11b** (74% ee) into the silyl ether[8b,9] (99% yield) followed by hydroboration[17] (2.5 mol equiv of 9-BBN,[6b] THF, reflux, 5 h) and oxidation (0.5:2:1, 6 M KOH, EtOH, 30% H_2O_2) gave the alcohol i[8b,9] (81% yield). Further oxidation[18] of i (3.8 mol equiv of pyridinium dichromate,[6b] DMF, 26 °C, 10 h), followed by desilylation (n-Bu_4NF, THF, 25 °C, 12 h), and then lactonization (trace of *p*-TsOH, C_6H_6, reflux, 1 h) of the acid ii afforded the lactone **12**[8b,9] (60% yield from i), $[\alpha]^{25}_{D}$ +29° (c 1.1, MeOH) corresponding to an optical purity of 70% on the basis of the reported value of $[\alpha]^{25}_{D}$ +41.1° (c 5, MeOH).[7] The overall yield from nonaldehyde was 43%.



i



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(21) **Note Added in Proof**: Recently S. Natarajan of our laboratory (Stanford) showed that the diastereoselectivity of the reaction **8** → **9** is dramatically improved by the use of a premixed solution of $TiCl_4$ and Ti(O-*i*-Pr)$_4$ (4 mol equiv of each) in CH_2Cl_2 (cf. Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817–826). Thus the diastereomeric ratio[10] was 96:4 for **9b** (90% yield after 4 h, −78 °C), 97:3 for **9c** (92%, 3.5 h, −78 °C), and 95.5:4.5 for **9d** (>85%, 3 h, −40 °C), corresponding to >90% ee for each of the homoallylic alcohols **11**.

Simplest Magnesium Cluster Grignard. Theoretical Evidence for Strong Metal–Metal Stabilization of RMg_2X Species

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Grignard reagents, RMgX, have a long history of study,[1] yet clearly there is certain knowledge about these molecules that is still lacking. In part, this is a consequence of the fact that Grignards are generally formed and used synthetically in solution. The characterization of an isolated RMgX molecule then is not so forthcoming. However, recent experimental studies[2-4] where magnesium atoms and alkyl halides are codeposited in a matrix have provided some fascinating insights into the process of forming Grignards. In particular, Klabunde and co-workers[4] have suggested that it is clusters of magnesium atoms that may be necessary for reaction with alkyl halides.

We have carried out ab initio electronic structure calculations that support Klabunde's contention because they show at least comparable stability of CH_3MgX and $CH_3(Mg)_2X$ (X = F, Cl). The existence of these dimagnesium Grignards is predicted not only by these stabilities but also by what we find to be a strong magnesium–magnesium bond that places an activation barrier in the way of unimolecular dissociation to a monomagnesium Grignard.

Formation of an RMg_2X molecule in a matrix deposition experiment would seem possible in several ways. Mg_2 is a fleeting, van der Waals molecule[5] in the gas phase, but deposition of

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Table I. Properties of Simple Magnesium Molecules

	bond lengths, Å				atomic partial charges		
	R-Mg	Mg-X	Mg-Mg	dipole, D	halogen	Mg (near halogen)	second Mg
HMgH	1.720			0.0		0.16	
HMgMgH	1.742		2.916	0.0		0.08	0.08
HMgF	1.702	1.783		1.98	−0.63	0.67	
HMgMgF	1.733	1.793	2.880	2.48	−0.63	0.58	0.10
CH_3MgF	2.081	1.786		2.46	−0.60	0.95	
CH_3MgMgF	2.100	1.795	2.888	3.10	−0.63	0.56	0.46
CH_3MgCl	2.080	2.234		2.50	−0.34	0.68	
$CH_3MgMgCl$	2.099	2.255	2.889	3.34	−0.35	0.22	0.51

Table II. Relative Energetics

comparative species	ΔE, kcal[a]
$Mg + HF \rightarrow HMgF$	29.0
$Mg + CH_3F \rightarrow CH_3MgF$	57.8
$Mg + CH_3Cl \rightarrow CH_3MgCl$	53.8
$Mg + HMgH \rightarrow HMgMgH$	2.8
$Mg + CH_3MgH \rightarrow CH_3MgMgH$	2.6
$Mg + HMgF \rightarrow HMgMgF$	5.8
$Mg + CH_3MgF \rightarrow CH_3MgMgF$	5.7
$Mg + CH_3MgCl \rightarrow CH_3MgMgCl$	5.4
$CH_3F + CH_3MgMgF \rightarrow 2CH_3MgF$	52.0

[a] Reactions are written such that ΔE corresponds to an exothermicity.

magnesium atoms could well lead to Mg_2 molecules being held as reaction sites. Larger, more stable clusters might also be involved. Mg_4 is a possible species since calculations of Chiles et al.[6] have revealed that it is the smallest non van der Waals cluster, a result recently confirmed in other studies.[7] Its longer existence in a flux of magnesium atoms would make it more available than Mg_2. We have not carried out calculations on RMg_4X species, but what is significant from what has been done is that the simplest magnesium cluster Grignard is stable, and it could be that larger cluster Grignards are too. Therefore, the observations of Klabunde[4] of a deeply colored species that was presumed to be a magnesium cluster alkyl halide is surely plausible.

The ab initio calculations have been performed to provide structural and energetic comparisons between the simple Grignards and the dimagnesium Grignards. In addition, we have systematically studied simpler "model" species, some at quite detailed levels, in order to understand the magnesium–magnesium bonding and to assess the quality of our calculated results. Table I gives bond lengths and properties and Table II gives relative energetics.

The atomic basis function sets were Dunning-contracted,[8] Huzinaga[9] double-ζ (DZ) sets for methyl groups and hydrogens. The magnesium basis was a 13s8p1d/8s4p1d contracted set.[9,10] The fluorine basis was a DZ set supplemented by diffuse s and p functions, and the chlorine set was 11s7p1d/7s5p1d.[9,11,12] Various checks were performed, and these atomic sets seem to be reasonably balanced and flexible enough to describe the electronic wave functions accurately. Calculations were carried out at the self-consistent field (SCF) level and at the correlated approximate double-substitution coupled cluster[13] (ACCD) level. The ACCD wave functions, obtained using an electron-pair operator approach,[10] included into the wave function the directly interacting doubly substituted configurations, singly substituted configurations, and quadruple and hextuple substitutions, there being six bonding electrons in the dimagnesium systems that were correlated. For HMgMgH, correlation contracts the bonds somewhat but changes the energy relative to Mg + HMgH by only 0.3 kcal. For HMgMgF, the correlation effect on stability was also less than 1 kcal, indicating only a small importance of correlation in the energetic comparisons. Thus, all values in the tables have been taken from SCF calculations.

The energetic comparisons in Table II show that there is a consistent 5–6-kcal stabilization that arises from forming a dimagnesium Grignard instead of a simple Grignard (plus the unattached ground-state magnesium atom). At the same time, though, it is quite apparent that the dimagnesium Grignards will exist only in isolated conditions because addition of a second alkyl halide to produce two simple Grignards ($RX + RMg_2X \rightarrow 2RMgX$) is nearly as exothermic as the production of one simple Grignard from one magnesium atom and an alkyl halide. This is interesting because it means that while a cluster Grignard may be the most stable and thus may be a first product from the attack of an alkyl halide on solid magnesium, once formed the cluster Grignard would react with other alkyl halides to end up with simple Grignards. Should the activation barrier for reducing the cluster Grignard to simple Grignards be lower than for the initial reaction, then the magnesium in the Grignard cluster would in effect be activated relative to bulk metal atoms.

The last point considered in our calculations was the strength of the Mg–Mg bond. For the simplest system, HMgMgH, orbitals were localized by separation of charge centroids,[14] and the Mg–Mg bond orbital was improved[10] in the course of the ACCD calculations to be a two-electron natural orbital, thereby ensuring that the bond breaking was properly described. The bond strength obtained was about 50 kcal. The SCF potential curves for Mg–Mg stretching are comparable in HMgMgH and CH_3MgMgF, and so this strong metal–metal bonding appears to be responsible for the stabilization of CH_3MgMgF and $CH_3MgMgCl$ also. Previous ab initio calculations[15-17] of simple Grignards have provided structural parameters and charge distributions that are in line with those we have obtained.

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