however, a solution of **1** in MeOH generates the orange adduct, **1**·2HQ.[8] Reflux of either a solution of this adduct in MeOH or an equimolar solution of **1** and HQ in MeOH for 3–4 h results in the formation of the methoxide cluster **2**. The composition of **2**·MeOH, established by X-ray study, is consistent with other data.[8]

The crystal structure consists of well-separated **2** and MeOH. The molecular structure of **2**, displayed in Figure 1a along with selected metrical data, contains an 11-vertex $Rh_2Mo_3O_6$ framework which can be viewed as an inorganic analogue of organic trishomocubanes.[7] The $Rh_2Mo_2O_4$ cubic fragment is similar to, but more distorted than, that observed in **1**. Another intriguing structural feature of **2** is the spatial arrangement of the four methoxy groups. Three groups engaged in bridging interactions encompass the vacant vertex. One terminal methoxy group is situated in such a way that C_1 molecular symmetry results. The overall methoxy conformation leads to close proximities (3.05–3.12 Å) between doubly bridged methoxy carbons and terminal Mo═O oxygens (O(13), O(14), and O(17)), indicating possibly short C—H···O intramolecular contacts.[9] Similar close proximities (3.13–3.21 Å) are also found between one of the doubly bridging methoxy oxygens (O(7) and O(10)) and a methoxy carbon of a triply bridged or terminal methoxy group. These indicate a possible path for nonredox methyl transfers between methoxy groups involved in the MeOH/MoO_3 reaction system.[6a,b]

The solid-state trishomocubane framework of **2** is quite stable in air at room temperature, but its integrity does not remain intact upon dissolution in most organic solvents such as CH_2Cl_2, MeCN, $MeNO_2$, etc. A 20-min-old solution of **2**·MeOH in CD_2Cl_2 reveals extra peaks in addition to signals[8] assigned to **2** in the ^1H NMR spectrum. Over a period of 12 h, orange microcrystals precipitate and the ^1H NMR spectrum does not contain any features of **2** but mainly reveals peaks ascribable to **1** and MeOH. In a separate experiment, a solution of **2** (100 mg) in 5 cm^3 of CH_2Cl_2 was kept at room temperature for 2–3 days, affording orange crystalline **3**·4CH_2Cl_2, whose structure and composition were established by a single-crystal X-ray diffraction study.[8] Consistent with the ^1H NMR observation is the isolation of **1** from the filtrate obtained by removing crystalline **3**·4CH_2Cl_2.

The linear quadruple cubane type of **3** is depicted in Figure 1b. Two trishomocubane-type $Rh_2Mo_3O_6$ framework share two oxygen vertices, forming an unprecedented organometallic oxide cluster with a center of symmetry at the centroid of a planar Mo_2O_2 rhombus. The overall molecular symmetry of **3** deviates from the ideal D_{2h}. Because of the linearly extended Mo_4O_4 cubic unit in **3** relative to the triple cubane-type cluster **1**, the former might be a better congruent representation of the infinite layer lattice[5] of MoO_3 recovered in the catalytic cycle of oxidation of MeOH. The structure of **3** also can be viewed as four Cp*Rh^{2+} cations being bound to a central $Mo_6O_{22}{}^{8-}$ anion which constitutes a new member to the family of Mo(VI) hexametalates[10] along with $Mo_6O_{19}{}^{2-}$.[11] The Mo_6 core forms a rather regular octahedron whose four peripherally situated Mo_3 triangular faces are capped with oxygens. Two other oxygens in the Mo_6O_6 polyhedral core of the $Mo_6O_{22}{}^{8-}$ anion are located at the extremely distorted tetrahedral interstices defined by two sets of two equatorial and two axial Mo atoms.

The clusters described here provide a novel synthetic example of extending the topological equivalent of a recognizable unit in the infinite lattice. The stoichiometric expressions for the conversions outlined in Scheme I remain to be established. Currently, other chemical products associated with the formation of **2** and **3**, as well as the reactivities of these clusters, are under investigation.

Acknowledgment. We gladly acknowledge the award of a JSPS fellowship (to X.-Z.Y.), and we appreciate the kind editing of this manuscript by Professor J. R. Kincaid (a visting professor of IMS).

Supplementary Material Available: ORTEP diagrams, crystallographic data, bond distances and angles, listings of fractional coordinates with equivalent isotropic thermal parameters, and anisotropic thermal parameters for **2** and **3** and selected analytical, spectroscopic, and other data to characterize **1**·2HQ, **2**, and **3** (16 pages); listings of observed and calculated structure factors for **2** and **3** (58 pages). Ordering information is given on any current masthead page.

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(8) Selected data (analytical, spectroscopic, and other data) to characterize new clusters have been deposited as supplementary material.

(9) The similar close C–H···O contact with H···O distance of 2.5 Å was observed in $[Mo_8O_{24}(OCH_3)_4]^{4-}$: McCarron, E. M., III; Harlow, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 6179. In this case, C···O proximity was calculated as 3.004 Å. In **2**, no intermolecular close C···O contact is observed.

(10) The other hexametalates $Mo_6O_{20}{}^{4-}$ and $Mo_6O_{21}{}^{6-}$ have been found in solution with dilatometric titrations, but have not been well characterized. Wiese, G.; Böse, D. *Z. Naturforsch.* **1974**, *29b*, 630.

(11) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, Heidelberg, New York, Tokyo, 1983.

Direct Insertion of Alkali (Alkaline-Earth) Metals into Allylic Carbon–Halogen Bonds Avoiding Stereorandomization

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An allylmetal is one of the most useful reagents in organic synthesis.[1] The reason for its synthetic importance is that there exist a straightforward way of generating it and regio- and stereoselective methods for controlling its subsequent reactions. In the realm of stereoselectivity, however, one great challenge that had not previously been met was the preparation of stereochemically homogeneous alkali allylmetals directly from allylic halides.[2] This is not a simple problem, since γ-substituted allylmetal, crotylmagnesium bromide, for example, is known to isomerize rapidly between the *Z* and *E* isomers even at −80 °C.[3] Our interest in the structural and mechanistic aspects of these species has led us to undertake a careful investigation of these well-known organometallics.

Our initial assumption was that stereoisomerization of the allylmetal was due to the rapid isomerization through metallotropic rearrangements that were temperature dependent. Thus geranyl or neryl chloride[4] was transformed to the corresponding Grignard reagent at low temperature, advantage being taken of the pioneering work of Rieke.[5] The mixture was stirred for 30 min at each temperature[6] and quenched by methanol. The isomerization

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(1) Reviews: (a) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. (b) Biellmann, J. F.; Ducep, J. B. *Org. React.* (*N.Y.*) **1982**, *27*, 1. Reviews of allylic Grignard reagents: (c) Benkeser, R. A. *Synthesis* **1971**, 347. (d) Nützel, K. In *Houben-Weyl*: *Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1973; Vol. 13/2a, p 88. See also: (e) Wakefield, B. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, Chapter 44. (f) Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988. (g) Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627.

(2) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 2.

(3) Hutchinson, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075.

(4) All allylic chlorides were prepared by treatment of the corresponding allylic alcohols with a mixture of *N*-chlorosuccinimide and dimethyl sulfide in CH_2Cl_2; see: Davisson, V. J.; Woodside, A. B.; Neal, T. R.; Stremler, K. E.; Muehlbacher, M.; Poulter, C. D. *J. Org. Chem.* **1986**, *51*, 4768.

(5) Reactive magnesium powder was prepared by Rieke's method in which anhydrous magnesium chloride was reduced by lithium in the presence of naphthalene: Burns, T. P.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 3674.

(6) A digital thermometer (Model HH81, OMEGA Engineering, Inc.) was used to measure the internal reaction temperatures.

0002-7863/91/1513-5893$02.50/0

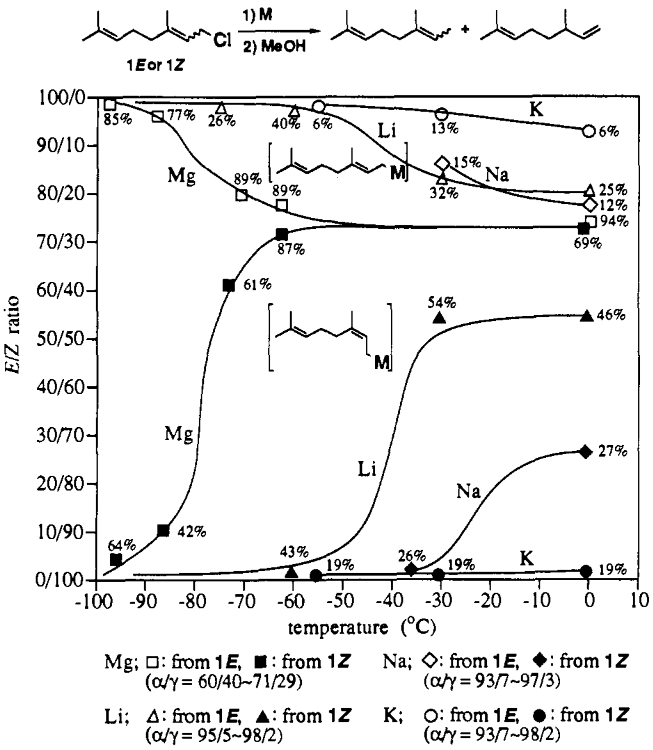


Figure 1. Temperature dependence of the E/Z ratio of the allylic metals (Mg, Li, Na, and K) derived from geranyl chloride (**1E**; $E/Z > 99/1$) and neryl chloride (**1Z**; $E/Z < 1/99$).

ratio was measured by analyzing protonated E and Z isomers, to produce Figure 1. Similarly, lithium, sodium, and potassium derivatives were prepared with the corresponding metal diphenylide[7] and quenched as above. The implications of Figure 1 are apparent. There are five variables: the E/Z ratio of the olefins produced, the temperature of the system, the choice of metal, the yield (%), and the α/γ ratio of the protonation products. Although there was no remarkable E/Z selectivity obtained by protonation on magnesium derivatives above −60 °C, *extremely high stereoretention was observed below −95 °C*. In contrast, the double-bond geometry of the alkali allylmetals was retained even at higher temperature: the allylic potassium compounds underwent isomerization only very slowly at 0 °C.[9] The superiority of potassium metal is thus apparent for stereoselectivity. However, it should be noted that the yields of the derived olefins were significantly reduced because of the accompanying Wurtz coupling process.[2]

The temperature dependence of the E/Z ratio of 2-decenylmetals was also investigated, and the results are summarized in Figure 2. In contrast to the disubstituted allylmetals, a significant isomerization rate enhancement was observed for these monosubstituted allylmetals and rapid stereoisomerization of magnesium derivatives was observed even at −100 °C. Although the cause of this enhancement was not immediately apparent, it does indicate that lithium at below −90 °C rather than magnesium should be chosen for the effective generation of configurationally homogeneous monosubstituted allylmetals. Finally, it is noteworthy that, at the extreme configurational equilibrium of allyllithium[10] or allylsodium, significantly more Z form seems to be produced. This probably comes from the theory of Schlosser's "endo preference" using electropositive metals.[9b,11,12]

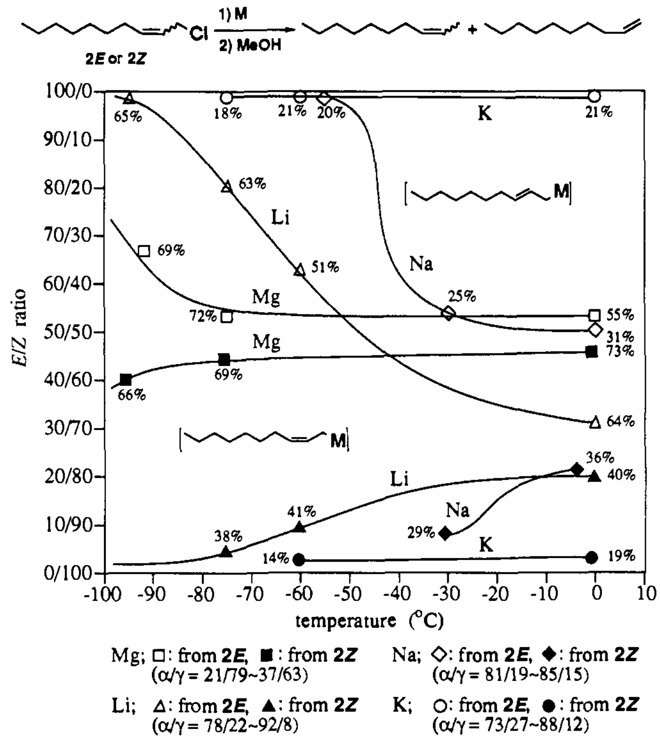
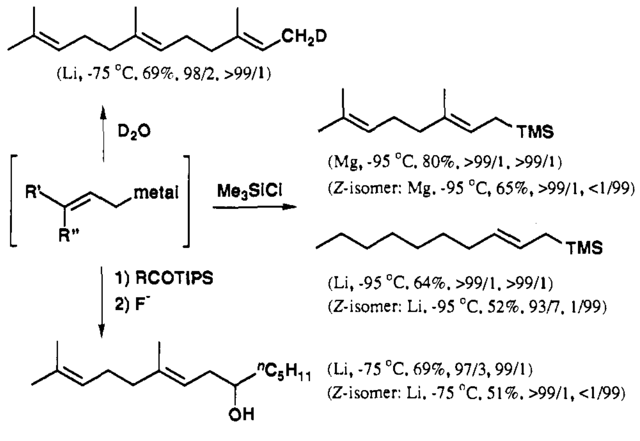


Figure 2. Temperature dependence of the E/Z ratio of the allylic metals (Mg, Li, Na, and K) derived from (E)-2-decenyl chloride (**2E**; $E/Z > 99/1$) and (Z)-2-decenyl chloride (**2Z**; $E/Z = 2/98$).

Scheme I[a] (Metal, temp, Yield, α/γ, E/Z)



[a] The following information is included within the parentheses: metal, temperature, yield, α/γ, E/Z. TMS = trimethylsilyl; TIPS = triisopropylsilyl.

The versatility of stereochemically homogeneous mono- and disubstituted allylmetals in synthesis is noteworthy,[13] as is their complementary relationship to other key functional groups. The transformations in Scheme I illustrate the broad range of applications that follow from the present studies. Stereochemically pure allylic silanes[14] can be prepared easily from the corresponding

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(7) For a review of aromatic radical anions, see: (a) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243. (b) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152. Lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[8] also was effective in this case.

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(9) (a) Schlosser, M.; Hartmann, J.; David, V. *Helv. Chim. Acta* **1974**, *57*, 1567. (b) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674. (c) Stähle, M.; Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1977**, *60*, 1730. (d) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *Tetrahedron Lett.* **1976**, 37.

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(12) For the Z/E-isomerization mechanisms; (i) rapid torsional isomerization via an intermediary radical (Root, K. S.; Hill, C. L.; Lawrence, L. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 5405) and (ii) at the organometallic stage; for an excellent discussion, see: Schlosser, M.; Stähle, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 487.

(13) For producing E- and Z-monosubstituted allylmetals by a deprotonation process, see refs 9a,c.

Grignard or lithium derivatives.[15] Deuteriation can be accomplished smoothly and selectively. Reaction of carbonyl derivatives selectively produced the stereochemically homogeneous homoallylic alcohols.[16]

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(14) A representative experimental procedure for the synthesis of geranyltrimethylsilane is as follows: A mixture of freshly cut lithium (79 mg, 11.4 mmol), anhydrous magnesium chloride (543 mg, 5.70 mmol), and naphthalene (120 mg, 0.94 mmol) in 15 mL of THF was stirred at room temperature for 14 h. To the resulting black suspension of magnesium powder in THF was slowly added a solution of geranyl chloride (350 mg, 2.03 mmol) in THF (2 mL) below -95 °C (internal temperature[6]). After 20 min of stirring, the mixture was treated with a solution of chlorotrimethylsilane (0.25 mL, 2.0 mmol) in THF (1 mL) at -95 °C and stirred for an additional 1 h at this temperature. To the mixture was added a saturated NH_4Cl aqueous solution, and the organic material was extracted with ether. The combined extracts were dried and concentrated, and the product was purified by column chromatography on silica gel (hexane) to give geranyltrimethylsilane (0.033 g, 80% yield); the ratio of both α/γ and E/Z was determined to be >99:1 by GLC analysis.

(15) For a recent review of the synthesis of allylsilanes, see: Sarkar, T. K. *Synthesis* **1990**, *969*, 1101.

(16) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 5198.

Mechanism of Cis–Trans Isomerizations of Amide and Peptide Excited States

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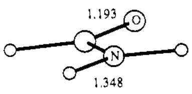
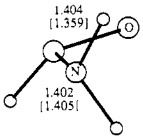
Peptides and simple amides such as *N*-methylacetamide (NMA) photoisomerize in aqueous solution to the less stable cis isomers during 220-nm ultraviolet resonance Raman (UVRR) experiments.[1,2] This observation has prompted us to reinvestigate the excited states of amides and peptides.[3] NMA in water has a weak $n-\pi^*$ transition at 210 nm and a strong $\pi-\pi^*$ transition at 188 nm.[2] Preresonance Raman enhancement of in-plane amide II and III modes and cis/trans isomerization led to the proposal that the amide $\pi-\pi^*$ excited state resembles the $\pi-\pi^*$ excited state of ethylene, which is known to have a single minimum, twisted 90° relative to the planar ground state.[4,6] However, we have found from ab initio calculations that the excited states of amides have pyramidal carbonyl and amine groups, as well as multiple energy minima.

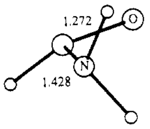
Geometry optimizations of the singlet and triplet excited states of formamide and NMA were performed with the 6-31G* basis set and the unrestricted Hartree–Fock (UHF) method for triplets or with configuration interaction between all singly excited configurations (CIS).[7a] The molecular orbitals of formamide relevant to this discussion are given in Figure 1.[7b] The three π orbitals are typical of allyl systems. π_2 is concentrated more heavily on N than on O. π_3^* is a slightly perturbed carbonyl π^* orbital. CIS calculations predict the lowest vertical singlet state of formamide to be primarily $n_O-\pi_3^*$ in character. The higher energy $\pi-\pi^*$ singlet is nearly degenerate with a Rydberg transition. These results compare well with experimental assignments[8a] and other calculations.[9]



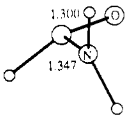
1 (Ground state)



2 (T_1)



3 (S_1)



4 (S_2)

Geometrical relaxation results in pyramidalization of both the carbonyl and amine groups. The T_1 and S_1 states (**2** and **3**) involve primarily excitation of the carbonyl. The pyramidal carbonyl group is a common feature of $n-\pi^*$ excited carbonyl compounds, and it results from the buildup of electron density on carbon.[10] The stabilizing interaction between the carbonyl and amine present in the ground state[11] now becomes repulsive. Consequently, the amine pyramidalizes, and the system resembles an aminomethyl anion, $R_2NCH_2^-$, in its conformational preferences.[12]

Both the S_1 and T_1 states have several staggered conformers, with rotational barriers of about 5 kcal/mol in S_1 and 3 kcal/mol in T_1. This is much lower than the ground-state barrier of 17–21 kcal/mol.[13] The most stable conformers of both T_1 and S_1 have the amine lone pair situated gauche to the carbonyl π^* orbital density on carbon and also directed away from oxygen, which is a region of high electron density.

The S_2 state, **4**, also has a pyramidal carbonyl group, but the amine group remains planar. The planarity of the amine in S_2 arises from the significant charge transfer from N to the carbonyl group. Consequently, the amine has some radical-cation character and the carbonyl group has some radical-anion character.[14]

[†] University of California, Los Angeles.

[‡] University of Pittsburgh; present address, University of California, Los Angeles.

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