In summary, a new molybdenum $\eta^4$-trimethylene cation has been synthesized and fully characterized. A novel cyclization involving this cationic intermediate has been demonstrated.[18] Further expansion of this cyclization involving the use of dienophiles such as ketones and $\alpha,\beta$-unsaturated ketones will be the focus of future studies.

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[18] We have placed **5** and **9** under CO (2 atm), which does not produce their $\eta^1$-allyl compounds. Therefore, the cyclization described in this paper cannot be attributed to a Diels-Alder reaction between $\eta^1$-allyl and dienophiles.

**Acknowledgment.** We thank the National Science Council of the Republic of China for financial support of this work; special funds (1990-1993) from National Tsing Hua University are also acknowledged.

**Supplementary Material Available:** Spectral data and satisfactory elemental analyses of **1**-**7**, **9**, and **10**, tables of atomic coordinates, thermal parameters, bond lengths and angles, and crystal data for **10**, and a drawing of molecule B of **10** (11 pages); a listing of structure factors for **10** (19 pages). Ordering information is given on any current masthead page.

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# A New Catalyst for the Epimerization of Secondary Alcohols: Carbon-Hydrogen Bond Activation in the Rhenium Alkoxide Complexes ($\eta^5$-$C_5R_5$)Re(NO)($PPh_3$)(OCHRR')

Isabel Saura-Llamas, Charles M. Garner, and J. A. Gladysz*

*Department of Chemistry, University of Utah, Salt Lake City, Utah 84112*

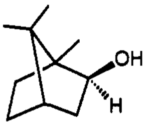
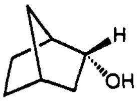
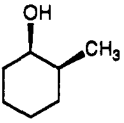
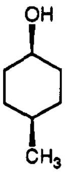
*Received April 9, 1991*

*Summary:* The methoxide complexes ($\eta^5$-$C_5R_5$)Re(NO)($PPh_3$)($OCH_3$) (R = H, Me) catalyze the title reaction (65-90 °C, $C_6H_5R$ solvent); intermediate secondary alkoxide complexes undergo $PPh_3$ dissociation and sequential epimerization at rhenium and carbon.

Unsymmetrical secondary alcohols, RR'CHOH, constitute ubiquitous stereogenic units in organic molecules. Accordingly, the need to manipulate configuration frequently arises. For example, considerable attention has been directed at methods for the catalytic epimerization of secondary alcohols.[1,2] In this communication, we disclose an efficient and mechanistically novel epimerization catalyst that operates in aromatic hydrocarbon solvents at 65-90 °C.

The diastereomerically pure alcohols shown in Table I were dissolved in deuterated benzene or toluene. Then 10 mol % of the racemic chiral rhenium methoxide complex ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($OCH_3$) (**1**)[3] was added. The samples were heated, and the organic products were assayed by $^1H$ NMR spectroscopy and in some cases GLC. In each case, the alcohols epimerized to a mixture of diastereomers. Small amounts of the corresponding ketones were usually produced (3-5%).[4] Also, *endo*-borneol gave a product distribution identical with that obtained from *exo*-borneol.

**Table I. Data for the Catalytic Epimerization of Secondary Alcohols by ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($OCH_3$) (1)**

| Starting alcohol | time (h) | temp (°C) | isomer ratio found[a] | literature ratio[b] |
|---|---|---|---|---|
| <br>((±)-exo-borneol) | 48 | 65[c] | 67:33<br>(endo/exo) | 71:29 |
| <br>((±)-endo-norborneol) | 180 | 70[c] | 76:24<br>(exo/endo) | 80:20 |
| (±)- | 80 | 80[c] | 70:30<br>(trans/cis) | 77:23 |
|  | 40 | 90[d] | 70:30<br>(trans/cis) | 70:30 |

[a] Assayed by $^1H$ NMR spectroscopy. The *endo*/*exo*-borneol and -norborneol ratios were confirmed by GLC. [b] These ratios were obtained in benzene with use of Raney Ni or in 2-propanol with use of Al(O-*i*-Pr)$_3$/acetone.[2] Equilibrium ratios in benzene sometimes differ significantly from those in 2-propanol. [c] In benzene-$d_6$. [d] In toluene-$d_8$.

Parallel reactions were conducted with the *pentamethyl*cyclopentadienyl complex ($\eta^5$-$C_5Me_5$)Re(NO)($PPh_3$)($OCH_3$) (**1**-Me$_5$).[5] Rates were 2-5 times faster. In

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[1] (a) Feghouli, G.; Vanderesse, R.; Fort, Y.; Caubere, P. *Tetrahedron Lett.* **1988**, *29*, 1383. (b) Vanderesse, R.; Feghouli, G.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1990**, *55*, 5916. (c) Choudary, B. M. *Polyhedron* **1986**, *5*, 2117. (d) Nugent, W. A.; Zubyk, R. M. *Inorg. Chem.* **1986**, *25*, 4604.

[2] (a) Eliel, E. L.; Schroeter, S. H.; Brett, T. J.; Biros, F. J.; Richer, J.-C. *J. Am. Chem. Soc.* **1966**, *88*, 3327 and references therein. (b) Wilcox, C. F., Jr.; Sexton, M.; Wilcox, M. F. *J. Org. Chem.* **1963**, *28*, 1079.

[3] (a) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. (b) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293.

[4] Ketone byproducts are also observed with other epimerization catalysts.[1b] A $C_6D_6$ solution of camphor (formed in the borneol epimerizations) and the hydride complex ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)(H) was kept at 65 °C for 48 h. No reaction occurred. Also, the epimerization of *exo*-borneol was repeated in the presence of camphor-*d* (1.0 equiv). No deuterium was incorporated in the product borneol, as assayed by $^1H$ NMR spectroscopy and mass spectrometry. Thus, the ketone byproducts form irreversibly.

[5] This compound was prepared by a procedure analogous to that reported for **1** in ref 2a.

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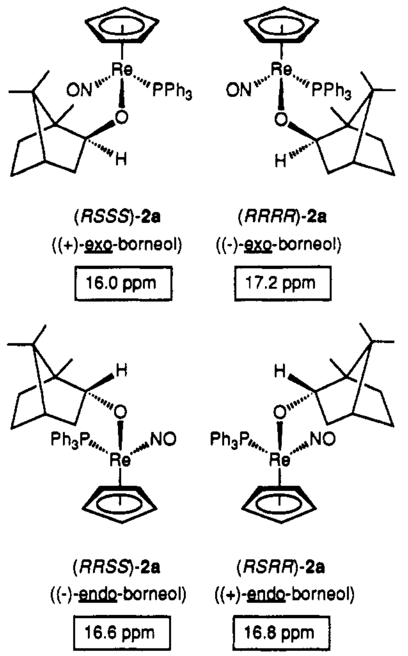
**Chart I. Structures and $^{31}P$ NMR Data ($C_6D_6$, 23 °C) for Diastereomeric Alkoxide Complexes Derived from Borneol**



all cases, $^1H$ and $^{31}P$ NMR spectra showed that the methoxide ligand of 1-$Me_x$ first exchanged with the alcohol substrate to give alkoxide complexes $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(OCHRR')$ (2). In order to help define the epimerization mechanism, samples of diastereomerically and enantiomerically pure 2 were sought. Toward this objective, a recently reported protocol was employed.[3b]

First, the optically active methyl complex $(+)\text{-}(S)\text{-}(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$[6] was dissolved in dichloromethane and treated with $HBF_4{\cdot}OEt_2$ (−78 °C). Then, authentic samples of (+)-*exo*-borneol, (−)-*exo*-borneol, (−)-*endo*-borneol, and (+)-*endo*-borneol were added. Subsequent reaction with $Et_3N$, and workup, gave the four diastereomeric alkoxide complexes **2a** shown in Chart I. The absolute configuration at rhenium is specified first, and that of the alkoxide carbon is given second.

The epimerization of (*RRRR*)-**2a** was followed by $^{31}P$ NMR spectroscopy as shown in Figure 1. A diastereomer with a chemical shift (16.0 ppm) corresponding to that of (*RSSS*)-**2a** (Chart I) formed first. However, any process that simultaneously inverts all three carbon stereocenters can be rejected. Hence, the resonance was assigned to the enantiomer (*SRRR*)-**2a**, derived from epimerization at *rhenium*. At higher temperatures, resonances appeared at 16.8 and 16.6 ppm. These were assigned, on the basis of the data in Chart I and similar reasoning, to diastereomers derived from *carbon* epimerization, (*RSRR*)- and (*SSRR*)-**2a**.

We have previously established that diastereomeric rhenium amide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}HCHRR')$ undergo epimerization at *rhenium* (40–60 °C) in a process involving initial, rate-determining $PPh_3$ dissociation.[7] Evidence for anchimeric assistance by the amide ligand lone pair, directly giving an intermediate with a trigonal-planar rhenium, has been found. Experiments conducted to date suggest a similar epimerization mechanism for **2a**. For example, $k_{obs}$ for $PPh_3$ substitution in (*RRRR*)-**2a** by excess $P(p\text{-}tol)_3$ (28–35 °C) is a factor of 2.2–2.8 greater than $k_1$ for epimerization to (*SRRR*)-**2a**. In other words, every $PPh_3$ dissociation leads to substitution, but slightly less than half give inversion at rhenium.[8] Also, rhenium epimerization rates are not inhibited by added

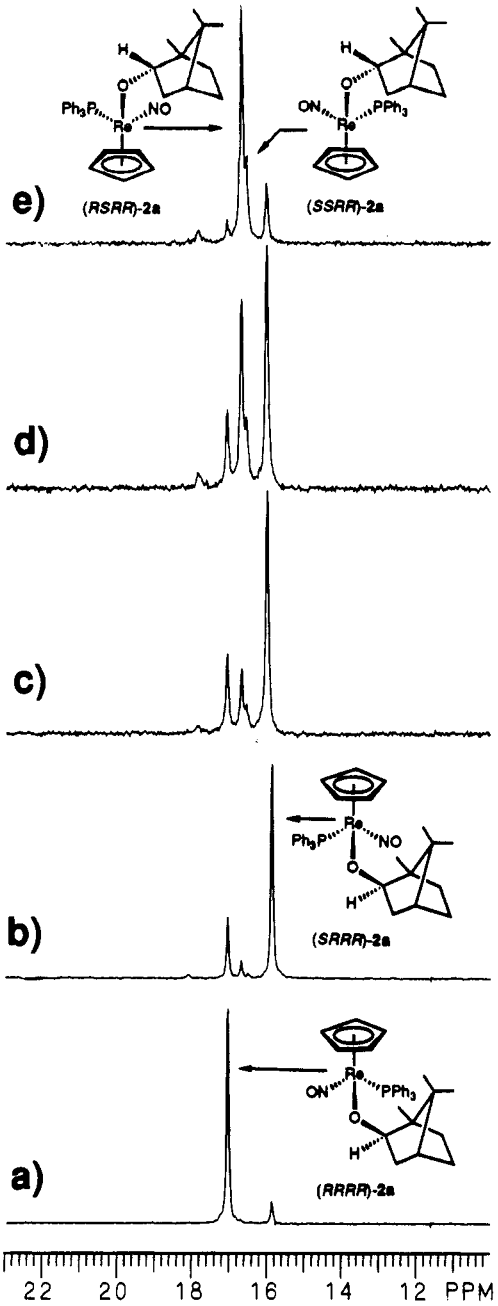
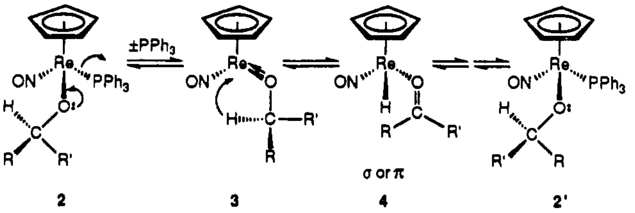


**Figure 1.** Epimerization of (*RRRR*)-**2a**: (a) $^{31}P\{^1H\}$ NMR spectrum of starting material at 35 °C; (b) spectrum after 9 h at 35 °C; (c–e) spectra after 0.2, 0.6, and 10 h at 65 °C.

**Scheme I. Proposed Key Steps in Alcohol Epimerization**



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(6) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(7) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.

(8) Since the transition states leading from the intermediate **3** (Scheme I) to (*RRRR*)- and (*SRRR*)-**2a** are diastereomeric, substitution and epimerization rates need not differ by a factor of exactly 2.

*Organometallics* 1991, *10*, 2535–2536

$PPh_3$, but the slower carbon epimerization rates are.

On the basis of the preceding observations, we propose that rhenium and carbon epimerization proceed via the key steps shown in Scheme I. The trigonal-planar intermediate **3** partitions between a return to **2** (accelerated by added $PPh_3$) and a slower $\beta$-hydride elimination to give the ketone complex **4**. Exchange of R and R′ in the ketone complex—a process known to be extremely facile in either $\sigma$ or $\pi$ coordination modes[9]—and reversal of the hydride elimination completes the carbon epimerization process. There is abundant precedent for the $\beta$-hydride elimination in alkoxide complexes,[10] although in most cases concomitant extrusion of a ketone or aldehyde appears to occur.[4] Finally, rate experiments with pentamethylcyclopentadienyl complexes establish a *much* faster $PPh_3$ dissociation, but apparently only slightly faster $\beta$-hydride elimination.

In summary, we have discovered a convenient and unusual new alcohol epimerization catalyst, the chirality of which allows a detailed probe of mechanism. Additional data pertaining to the nature of the reaction coordinates of these carbon–hydrogen bond activation processes will be described in our full paper.

**Acknowledgment**. We thank the DOE for support of this research and the Ministry of Education and Science of Spain and the Fulbright Commission for a postdoctoral fellowship (I.S.-L.).

**Supplementary Material Available:** Listings of characterization data for complexes 1-$Me_5$ and **2a** (7 pages). Ordering information is given on any current masthead page.

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[9] (a) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198. (b) Quirós Méndez, N.; Mayne, C. L.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1475.

[10] For particularly relevant examples, see: Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531 and references therein.

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# Activation of Organomagnesium Reagents by Crown Ethers: Unusual Ether Cleavage of (2-Methoxy-1,3-xylylene)-15-crown-4

Gert-Jan M. Gruter, Gerard P. M. van Klink, Georgios A. Heropoulos, Otto S. Akkerman, and Friedrich Bickelhaupt*

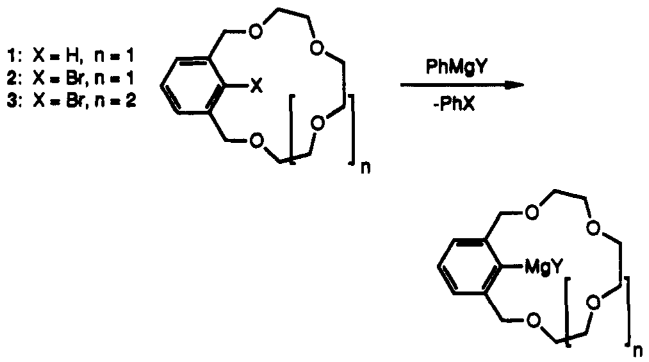
*Department of Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

*Received February 28, 1991*

*Summary:* The reaction of (2-methoxy-1,3-xylylene)-15-crown-4 (**4a**) with diphenylmagnesium *at room temperature* resulted in the cleavage of the methyl–oxygen bond with unprecedented ease, leading to (2-hydroxy-1,3-xylylene)-15-crown-4 (**10**) and toluene. In order to rationalize this unusually high reactivity, we suggest a transition state (**8** or **9**) with both an electrophilic and a nucleophilic component: the cationic magnesium atom is involved in an electrophilic attack on the oxygen, while the magnesate counterion attacks the methyl group in an $S_N2$ process.

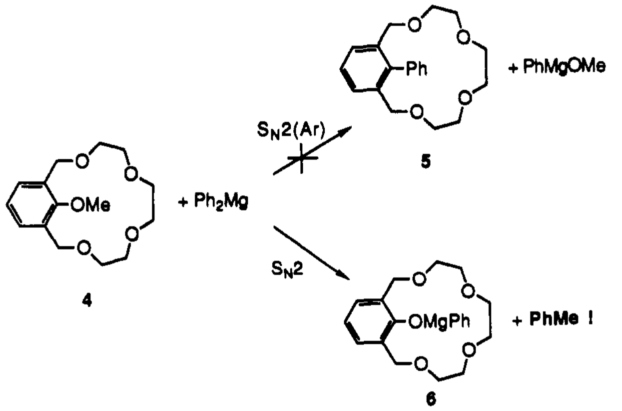
Crown ethers may exert a profound influence on organomagnesium reagents; unusual structures as well as unusual reactivities have been encountered.[1,2] In the present context, the strongly enhanced reactivity of diphenylmagnesium, and to a lesser extent that of phenylmagnesium bromide, toward (derivatives of) (1,3-xylylene)-15-crown-4 and (1,3-xylylene)-18-crown-5 is of relevance: metalation or halogen–metal exchange occurs, which is uncommon for organomagnesium compounds but reminiscent of the behavior of organolithium compounds (Scheme I).[1a,c]

Scheme I[a]



[a] Y = Ph, Br.

Scheme II



This unusual reactivity was tentatively explained[1c] by specific coordination of the organomagnesium species to the crown ether. As a result, the polarization of the

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[1] (a) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Angew. Chem.* **1988**, *100*, 1143. (b) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4845. (c) Markies, P. R. Thesis, Vrije Universiteit, 1990. (d) A similar "side-on" structure was tentatively identified for 1[1a] and for the rotaxane from (1,3-xylylene)-18-crown-5 and diphenylmagnesium[1b] by $^1H$ NMR spectroscopy; for the combination of 2 and 3 with the less reactive diphenylzinc, X-ray crystal structures confirm this assignment.[1c,e] (e) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L., submitted for publication.

[2] (a) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. (b) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.

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