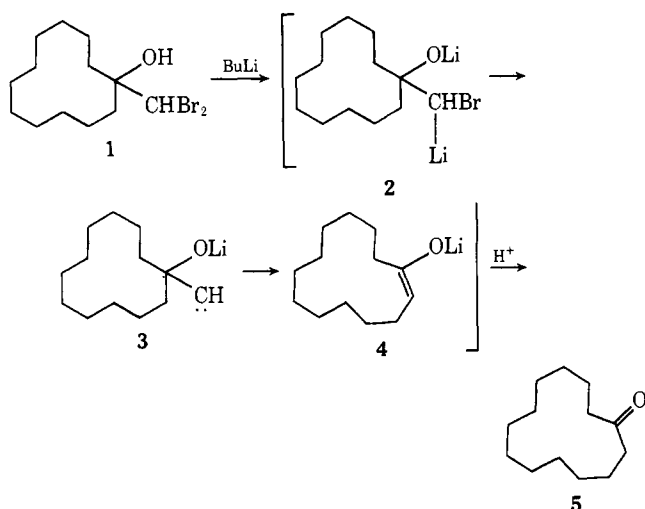


Scheme I



found to be a halogen–lithium exchange rather than a hydrogen–lithium exchange process,¹² since no more than 5% impurities could be detected in the unpurified ketonic products.

This approach depends crucially on the recently developed method for the *in situ* generation of dibromomethyl lithium from methylene bromide in the presence of carbonyl compounds using lithium dicyclohexylamide as the base.^{13,14} Thus, the over-all transformation is a two-step sequence, both of which are easy to operate and also highly efficient.

The following procedure is illustrative of the new reaction. The dibromide **1** (356 mg, 1.00 mmol) was dissolved in dry tetrahydrofuran (3 ml) under nitrogen and cooled to -78° . To the stirred solution was added *n*-butyllithium (1.35 ml of a 1.55 *M* hexane solution, 2.10 mmol) dropwise over a period of 30 min.¹⁵ The resulting pale yellow solution was stirred for 30 min at -78° and 5 min at 0° , quenched by pouring into ice cold 1 *N* hydrochloric acid, and extracted with ether repeatedly. The ethereal layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo* to afford cyclotridecanone in 89% yield after preparative layer chromatography on silica gel (benzene, $R_f = 0.44$).¹¹

(13) H. Taguchi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **96**, 3010 (1974).

(14) Depending on the structure of the cyclic ketone, the dibromomethyl lithium carbonyl adduct may rapidly form epoxide, even at low temperature. The reaction should be performed at -100° , with vigorous stirring, to minimize that pathway.

(15) The addition of *n*-butyllithium was carried out rather slowly to minimize the epoxide formation, see ref 14.

Hiroaki Taguchi, Hisashi Yamamoto,* Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan
Received June 24, 1974

Stereospecific Photochemical Reactions of Group VIb Metal Tetracarbonyl Norbornadiene Complexes with ^{13}C O

Sir:

Chromium tetracarbonyl norbornadiene has been implicated as an intermediate in the photoassisted

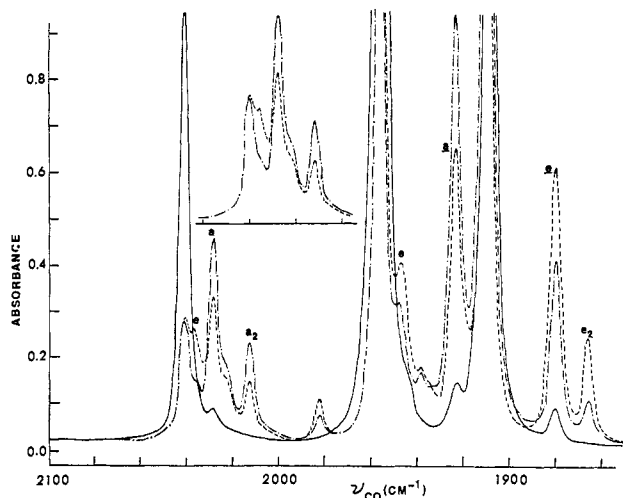


Figure 1. Infrared spectra in $\nu(\text{CO})$ region of $\text{W}(\text{CO})_4(\text{NBD})$: (a) —, ^{13}C O natural abundance; (b) ---, after photolysis with 92% ^{13}C O for 2 min; (c) ·····, after standing in the dark at 37° for 45 min. The a and e designations correspond to bands of axially and equatorially mono- ^{13}C O substituted species, respectively, whereas, a_2 and e_2 correspond to exclusively di- ^{13}C O substituted axially and equatorially, respectively.

hydrogenation of norbornadiene with chromium hexacarbonyl.^{1,2} In addition, the intermediacy of $\text{Cr}(\text{CO})_4(\text{NBD})$ has been demonstrated in the photochemical dimerization of norbornadiene with $\text{Cr}(\text{CO})_6$.³ We have, therefore, undertaken a study to establish the nature of the species produced from the photochemical reactions of group VIb $(\text{NBD})\text{M}(\text{CO})_4$ complexes. We wish to report in this communication initial results on the photochemical production of ^{13}C O labeled complexes of $(\text{NBD})\text{M}(\text{CO})_4$. This study has as well allowed for an unambiguous assignment of the CO stretching vibrations in these molecules.

Irradiation of the $\text{M}(\text{CO})_4(\text{NBD})$ complexes was carried out in a water-jacketed 25-ml Pyrex cell employing a 450-W Hanovia Mercury lamp ($\lambda > 2800 \text{ \AA}$) for $\text{M} = \text{Cr}$ and W , and a 100-W lamp for the less stable species where $\text{M} = \text{Mo}$. A 20.9% or a 92.0% ^{13}C O enriched carbon monoxide atmosphere was continuously recirculated within the closed system by a variable speed Masterflex tubing pump. The course of the enrichment reaction was followed by withdrawing samples with a hypodermic syringe at approximately 1-min time intervals. Infrared spectral measurements were used to follow the extent of enrichment. All three samples were rapidly enriched with ^{13}C O producing various mono- and disubstituted species with ^{13}C O as well as small quantities of $\text{M}(\text{CO})_6$. Figure 1 illustrates the ^{13}C O enriched spectra observed for $\text{W}(\text{CO})_4(\text{NBD})$ in hexane solution employing 92% ^{13}C O. It was possible to assign all the bands in the spectra by computing their positions using a restricted CO force field.⁴ Table I contains the calculated and observed $\nu(\text{CO})$ bands for the ^{13}C O enriched species of $\text{W}(\text{CO})_4(\text{NBD})$.

(1) L. Wilputte-Steinert, International Conference on Organometallic Chemistry, Moscow, 1971.

(2) G. Platbrood and L. Wilputte-Steinert, *J. Organometal. Chem.*, **70**, 393 (1974).

(3) W. Jennings and B. Hill, *J. Amer. Chem. Soc.*, **92**, 3199 (1970).

(4) Frequencies were calculated with an iterative computer program using an energy-factored block matrix for the carbonyl stretching vibrations as described elsewhere; see, e.g., C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1075 (1973). Agreements between calculated and observed frequencies were generally with $\pm 0.5 \text{ cm}^{-1}$.

Table I. Calculated and Observed CO Stretching Frequencies in (NBD)W(CO)₄ Species^a

	A ₁ (²)	A ₁ (¹)	B ₁	B ₂
All ¹² CO species	2042.0 (2042.2)	1956.0 (1956.0)	1956.0 (1955.7)	1909.2 (1908.9)
Mono- ¹³ CO, ax substituted	2029.0 (2029.9)		1924.5 (1923.8)	(1908.9)
Mono- ¹³ CO, eq substituted	2038.5 (s) (2037.9)	1948.0 (s) (1945.4)	(1955.7)	1879.6 (1880.5)
Di- ¹³ CO, eq substituted			(1955.7)	1866.5 (1866.4)
Di- ¹³ CO, ax substituted	2015.5 (2014.0)		(1912.0)	(1908.9)
Di- ¹³ CO, ax-eq substituted	2024.7 (s) (2024.4)		(1923.0)	(1880.3)

^a The 11 frequencies were calculated with an average error of 0.6 cm⁻¹; calculated frequencies are listed in parentheses. Force constants calculated were: $k_1 = 15.260$, $k_2 = 15.960$, $k_c = 0.305$, $k_c' = 0.548$, and $k_t = 0.51$ g, where k_1 and k_2 are equatorial and axial CO stretching force constants, respectively, whereas, k_c (CO_{ax}-CO_{eq}), k_c' (CO_{eq}-CO_{eq}), and k_t (CO_{ax}-CO_{ax}) are the CO interaction force constants. The symmetry labels describe vibrations for the all ¹²CO species as well symmetrically di-¹³CO substituted species.

The absorbances of bands a and e, which were assigned to mono-¹³CO axially and equatorially substituted species, respectively, allowed for a quantitative determination of the relative enrichment of axial (cis to both olefinic bonds) *vs.* equatorial CO ligands. This is accomplished with the aid of the natural abundance ¹³CO spectrum (which contains 2% of each species). As noted in Figure 1a (natural abundance spectrum of W(CO)₄(NBD)) the ratio of absorbances or extinction coefficients for these two bands, a:e, is 1.1. Unfortunately in the case of Cr(CO)₄(NBD) the band due to the axially enriched species is buried beneath one of the intense bands in the all ¹²CO molecule (~1915 cm⁻¹). It was possible in the molybdenum and tungsten derivatives to observe that initially the bands due to the axially substituted species (labeled a and a₂ in Figure 1b) were greatly enhanced over those due to the equatorially substituted species (labeled e and e₂ in Figure 1b).⁵ However, upon standing in the dark⁶ a secondary process leads to a decrease in the quantities of mono- and di-¹³CO axially substituted species with a concomitant increase in the quantities of equatorially substituted mono- or di-¹³CO species (Figure 1c).

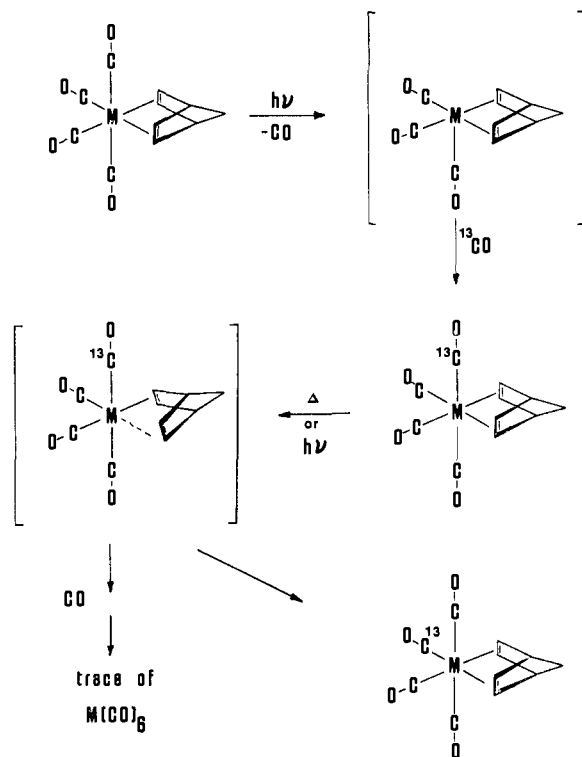
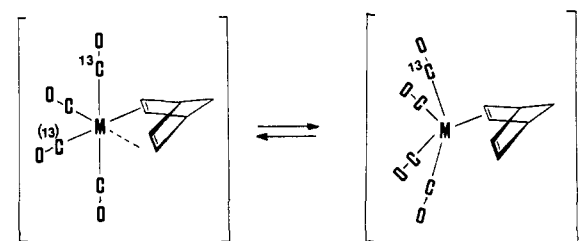
We propose Scheme I to explain our results which adhere to the principle of microscopic reversibility⁸ and provide for the added feature of axial-equatorial CO equilibration *via* a chelate ring opening mechanism. This equilibration of axial and equatorial CO ligands could occur as elaborated in Scheme II. An additional

(5) Previously a difference in the axial and equatorial rate constants for the thermal CO exchange reaction of Cr(CO)₄(*o*-phen) has been reported: M. Dokiya, R. D. Johnston, and F. Basolo, *Inorg. Chem.*, **9**, 996 (1970).

(6) This reaction was found to have a thermal half-life of about 11 min at 37° (k_1 for dissociation of one metal-olefin bond is 1.1×10^{-3} sec⁻¹). The kinetics of this reaction are presently being investigated in detail. The reaction is enhanced in the presence of the light source. It is assumed at this time that the barrier to olefin rotation which is necessarily associated with the Berry rearrangement of carbonyl groups is smaller than the barrier to ring opening.⁷

(7) L. Kruczynski, L. K. K. LiShingMan, and J. Takats, *J. Amer. Chem. Soc.*, **96**, 4006 (1974); S. T. Wilson, N. J. Coville, J. R. Shapely, and J. A. Osborn, *ibid.*, **96**, 4038 (1974).

(8) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968). Assuming that the intermediate has thermalized, the principle of microscopic reversibility suggests that in the thermal dissociation reaction it is an axial CO group that is labile. We thank a referee for this comment.

Scheme I**Scheme II**

important observation obtainable from the spectra in Figure 1b and 1c is the initial preferential production of axially di-¹³CO substituted species. This indicates that the intermediate, [W(CO)₂(¹³CO)(NBD)], produced upon photolysis (substitute axially enriched W(CO)₃(¹³CO)(NBD) in Scheme I) does not intramolecularly scramble CO groups, *i.e.*, the axial and equatorial CO groups maintain their integrity in the transition state and in the intermediate. In other words, the chelating norbornadiene ligand stabilizes the square pyramidal geometry.

The intermediate involving bond cleavage of one end of the diene in the above scheme is the same as that proposed in the substitution reaction of M(CO)₄(diene) with Lewis bases (L) to give M(CO)₄L₂ species.⁹ Indeed this study lends strong support to the existence of intermediates of this type. It has been proposed that enrichment of (NBD)M(CO)₄ with ¹³CO could occur *via* initial metal-olefin bond cleavage with concomitant ¹³CO addition, followed by dissociation of CO and chelate ring closure.² The intermediate necessarily produced from dissociation of CO from a monoligated

(9) See, *e.g.*, H. Werner, *Angew. Chem., Int. Ed. Engl.*, **7**, 930 (1968); F. Zingales, F. Canziani, and F. Basolo, *J. Organometal. Chem.*, **7**, 461 (1967).

$M(\text{CO})_5(\text{diene})$ species should, however, lead to intramolecular CO scrambling.¹⁰ The observed stereospecificity of CO exchange in addition to the fact that under no conditions was the monoolefin pentacarbonyl species ever observed strongly suggests this alternative mechanism to be unlikely.

As indicated earlier this study has also afforded an assignment of the $\nu(\text{CO})$ vibrations in $(\text{NBD})\text{M}(\text{CO})_4$ complexes. Table I contains the calculated CO force constants obtained with the aid of ^{13}C O frequency data. The observation of the B_1 band occurring at higher frequency than the B_2 band in these complexes is in agreement with the assignment proposed in a recent Raman study by Butler and Barna.¹¹

Acknowledgment. We thank the Research Corporation for a grant for the purchase of the Perkin-Elmer 521 infrared spectrophotometer used in this study. In addition, one of us (D. J. D.) thanks the Senate Committee on Research, Tulane University, for a summer grant.

(10) (a) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971); (b) W. J. Knebel, R. J. Angelici, O. A. Gansow, and D. J. Darensbourg, *J. Organometal. Chem.*, **66**, C11 (1974).

(11) I. S. Butler and G. G. Barna, *J. Raman Spectrosc.*, **1**, 141 (1973).

D. J. Darensbourg,* H. H. Nelson, III
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received June 18, 1974

Organoaluminum Reagents of Type $\text{R}^1\text{R}^2\text{NAlEt}_2$ Which Allow Regiospecific Isomerization of Epoxides to Allylic Alcohols

Sir:

The reaction of epoxides with strong base constitutes a well known synthetic method for the preparation of allylic alcohols.¹ The best current method for this transformation discovered by Cope,² and thoroughly developed by Crandall³ and Rickborn,⁴ involves isomerization with lithium diethylamide. Because of our needs to carry out such transformation under very mild conditions,⁵ we developed a new method based upon diethylaluminum dialkylamide.⁶ The method takes advantage of the affinity of aluminum metal for oxygen.⁷

(1) A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 1-523; recently Sharpless and Lauer reported a unique method for the above transformation using organoselenium reagent: K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973).

(2) (a) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958); (b) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960); (c) A. C. Cope and J. K. Heeren, *ibid.*, **87**, 3125 (1965); (d) A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, **80**, 2855 (1958).

(3) (a) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964); (b) J. K. Crandall and L. Chang, *ibid.*, **32**, 435, 532 (1967); (c) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967).

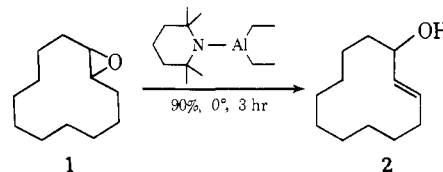
(4) (a) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969); (b) R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, **92**, 2064 (1970); (c) R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **36**, 1365 (1971); (d) C. L. Kissel and B. Rickborn, *ibid.*, **37**, 2060 (1972).

(5) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *J. Amer. Chem. Soc.*, in press.

(6) (a) J. K. Gilbert and J. D. Smith, *J. Chem. Soc. A*, 233 (1968); (b) R. Köster and P. Binger, *Advan. Inorg. Chem. Radiochem.*, **7**, 263 (1965); (c) see also, T. Mole and E. A. Jeffery, "Organoaluminium Compounds," Elsevier, Amsterdam, 1972.

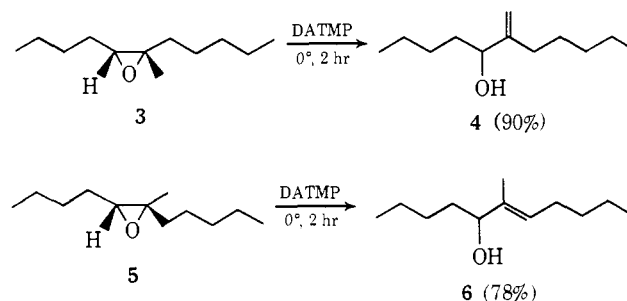
(7) For example, E. J. Corey and D. J. Beamer, *J. Amer. Chem. Soc.*, **95**, 5829 (1973).

Diethylaluminum 2,2,6,6-tetramethylpiperidide (DATMP) can be prepared *in situ*⁸ from diethylaluminum chloride and lithium 2,2,6,6-tetramethylpiperidide (LiTMP)⁹ (molar ratio 1:1) in benzene at 0° for 30 min. Reaction of DATMP (4 equiv) with (*E*)-cyclododecene oxide (**1**) in benzene was completed at 0° (external cooling) for 3 hr. The addition of 1 *N* hydrochloric acid, washing with water, and concentration *in vacuo* afforded (*E*)-2-cyclododecen-1-ol (**2**) in 90% yield after purification by plc (silica gel, $R_f = 0.23$ with 3:1 hexane-ether).¹⁰ The examples cited in Table I illustrate the synthesis of allylic alcohols using the indicated reactants and reaction conditions.



DATMP has proved to be most satisfactory for the isomerization, while some variation in the reagent was studied in detail. The yield of alcohol **2** with DATMP (4 equiv) used as the base in its production from the oxido **1** at 0° for 1 hr¹¹ is compared with the same data for several other $\text{R}^1\text{R}^2\text{NAlEt}_2$ species: diethylamide, <5%; dicyclohexylamide, 36%; diisopropylamide, 45%; TMP, 80%. It should be noted that LiTMP itself was an unsatisfactory reagent for this transformation under the same reaction conditions (<5% of **2** and >70% of the starting oxido **1** was recovered).

Regioselectivity was reported in the reaction of unsymmetrical epoxides with lithium diethylamide, leading to allylic alcohols.⁴ The preference for elimination is primary > secondary > tertiary in these systems and this has been attributed to a combination of steric effects and preferred geometry.^{4,12} It seemed logical to expect that the bulk of the extremely large TMP group might play an even more significant role in determining the course of reaction and a useful regiospecific route to allylic alcohols might thereby become available. Thus, the reaction of DATMP in benzene at 0° with *Z* epoxide **3**⁵ for 2 hr produced the disubstituted allylic alcohol **4** in 90% yield after work-up in the usual way. A dramatic alteration in the product distribution occurs when the same reaction with DATMP is conducted with *E* epoxide **5**⁵ (0° for 2 hr); although alcohol **4** was



(8) T. Hirabayashi, H. Imaeda, K. Itoh, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **19**, 299 (1969).

(9) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 583 (1973).

(10) The crude reaction mixtures are almost free of by-products, so that for most further applications purification is not necessary.

(11) The reaction was terminated at this point for comparison.

(12) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 5311 (1973); B. M. Trost and S. Kurozumi, *Tetrahedron Lett.*, 1929 (1974); see also ref 2c.