

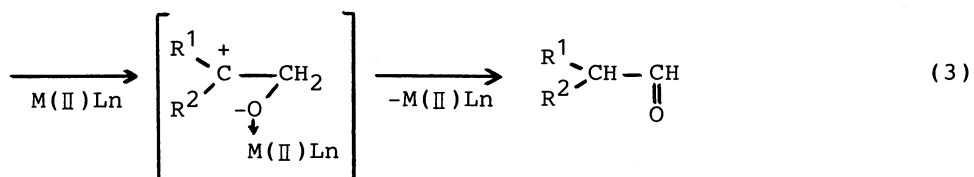
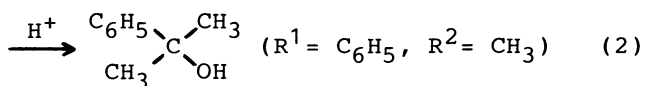
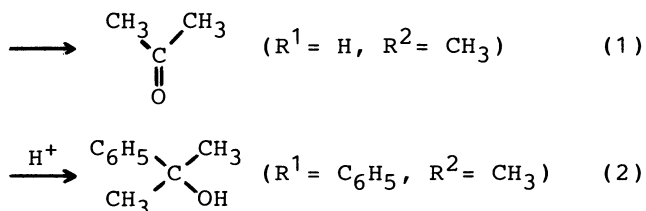
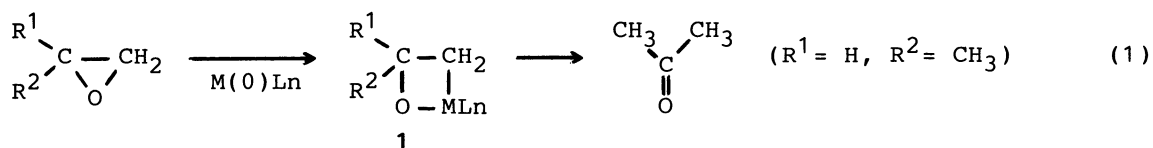
Regioselective Methylation of Epoxides Using Transition Metal Complexes

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$M(PPh_3)_4$ ($M = Ni, Pd, Pt$) promoted regioselective methylation of 1,2-epoxy-2-methylpropane with methyl iodide affording 2,2-dimethylpropanol. In the course of the reaction, $trans-CH_3MI(PPh_3)_2$, initially formed from the reaction of $M(PPh_3)_4$ with CH_3I , attacked the epoxide electrophilically resulting regioselective cleavage of the C-O bond of the epoxide, followed by the formation of the isolable 2,2-dimethylpropoxymetal complexes.

Transition metal-catalyzed ring-opening reactions of epoxides are current topics in transition metal chemistry.¹⁾ In particular, metal-assisted carbon-carbon bond formation reactions using various epoxides as the starting materials attract much attention for synthetic chemistry.²⁾ Despite the ubiquitous use of various epoxides in organic synthesis, transition metal-promoted reactions of epoxides and particularly their detailed study on reaction mechanisms remain unexplored.

Previously, we reported that in ring-opening isomerization of epoxides catalyzed by nickel phosphine complexes, the regioselectivity and the reaction mode were largely affected by the electronic state of metal center, and these reactions were well explained by taking account of a mechanism involving oxanickellacyclobutane complexes (1) as active intermediates.³⁾



It remains to be answered, however, how the isomerization of epoxides takes place using transition metal catalysts in high-oxidation state which are presumed to behave as Lewis acids. In this paper, we report regioselective ring-opening addition reactions of 1,2-epoxy-2-methylpropane (2) with methyl iodide using Ni, Pd, and Pt complexes, and describe the possible mechanism involving the formation of 2,2-dimethylpropoxymetal complexes.

Into a toluene solution of $M(PPh_3)_4$ ($M = Ni, Pd, \text{ or } Pt$) (0.07 mmol) was added epoxides (0.70 mmol) and CH_3I (0.70 mmol) at room temperature under N_2 . The solution was then placed in a constant temperature bath for the prescribed time. The products obtained by quenching with HCl were determined by GLC, and identified by NMR spectroscopy. The results are summarized in Table 1.

The major product in these stoichiometric reactions on the basis of ML_4 was found to be 2,2-dimethylpropanol (3) while no C_5 -alcohol was yielded without using $M(PPh_3)_4$. At 70 °C, competitive ring-opening isomerization of the starting epoxide appeared to be in favor with Ni complex giving 2-methylpropionaldehyde (Run 2; 87% per Ni). In other cases (Runs 1,3,4, and 5), the starting epoxide remained unchanged.

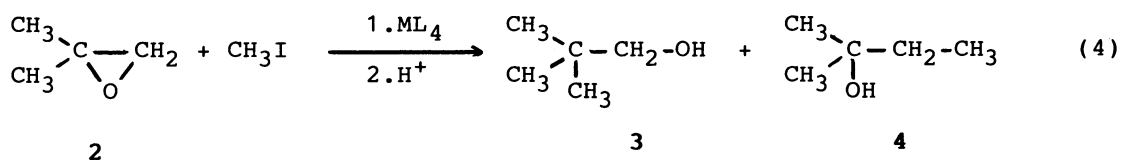
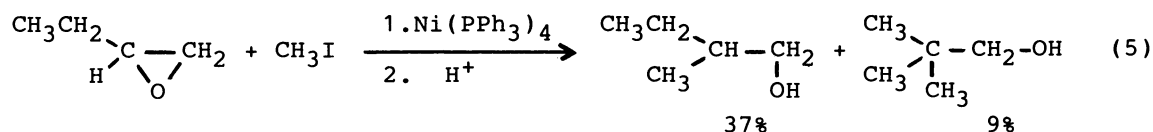


Table 1. Formation of 2,2-dimethylpropanol from the reaction of 1,2-epoxy-2-methylpropane with methyl iodide a)

Run	$M(PPh_3)_4$	Temp/ °C	Products (%/M)	
			3	4
1	Ni	20	72	-
2	Ni	70	14	-
3	Pd	70	42	0.2
4	Pt	70	65	-
5	-	70	-	-

a) Epoxide/ CH_3I / ML_4 = 10/ 10/ 1 (molar ratio), in toluene, for 120 h.

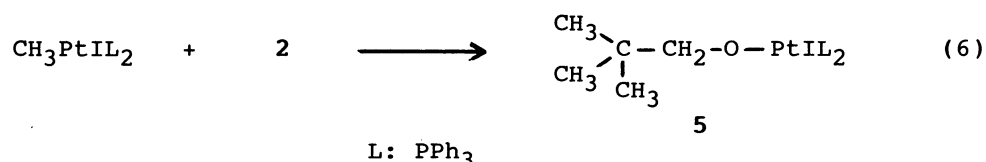
Using $Ni(PPh_3)_4$, 1,2-epoxybutane was also converted to 2-methyl-1-butanol in 37% yield in addition to 2,2-dimethylpropanol (9%) at room temperature for 50 hours, as in Eq. 5. The origin of 2,2-dimethylpropanol is not clear so far.



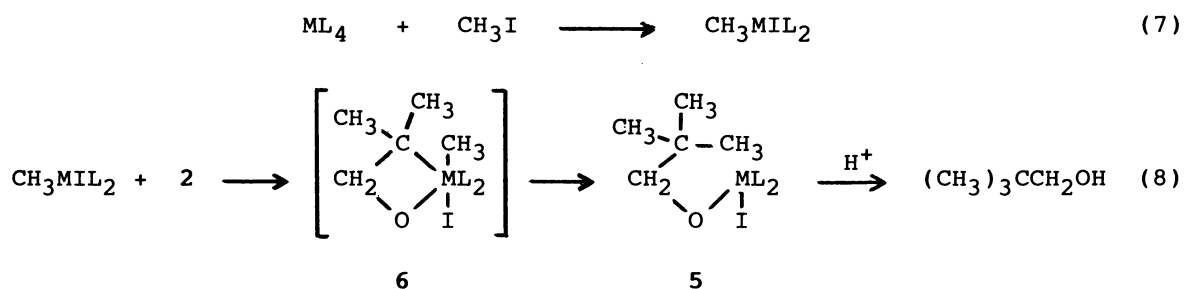
Basic to the understanding of these reactions are the mechanism of the initial regioselective C-O bond cleavage of epoxides. We reported previously the regioselectivity of the metal-catalyzed ring-opening reaction of the epoxides largely affected by the electronic state of the metal center.³⁾ In these reactions, therefore, 2-oxametallacyclobutane complexes (1), which are considered to be derived from the nucleophilic attack of ML_4 to less hindered carbon of the epoxide during the course of the reaction, are expected to be conceivable intermediates.⁴⁾

We thought it most likely, however, that these regioselectivity of the methylation reactions in Eq. 4 should be ascribed to $M(II)L_4$, and $M(0)L_4$ might not be responsible in these particular reactions.

If this is the case, methylmetal(II) complexes which are certainly formed from oxidative addition reaction of CH_3I with ML_4 should electrophilically attack to the hindered carbon of the epoxide forming 4,4-dimethyl-2-oxaplatina-cyclobutane intermediate (6). To test this hypothesis, a divalent complex $trans-Pt(CH_3)I(PPh_3)_2$ was attempted to react with the epoxide (10 molar excess) in toluene at 50 °C for 48 hours until yellow crystalline solids precipitated. These complexes which were isolated by filtration and washed with ether, were identified as bis(triphenylphosphine)-2,2-dimethylpropoxyplatinum iodide (5) in 41% yield; 1H -NMR (CD_2Cl_2), δ 1.46 (s, 9H, CH_3 -C), 2.28 (s, 2H, CH_2 -O), 7.61 (m, 30H, Ph). The complex 5 afforded 2,2-dimethylpropanol stoichiometrically by protonolysis with HCl.



These reactions can be accounted for by the initial formation of methylmetal(II) complexes, which attacked the epoxide as Lewis acid leading presumably to unstable 4,4-dimethyl-2-oxametallacyclobutane intermediate (6). Then, this may be converted to isolable 2,2-dimethylpropoxymetal complex (5), which undergoes protonolysis to yield 2,2-dimethylpropanol.

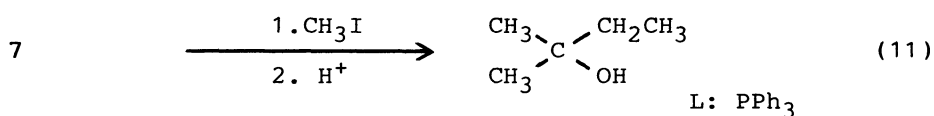
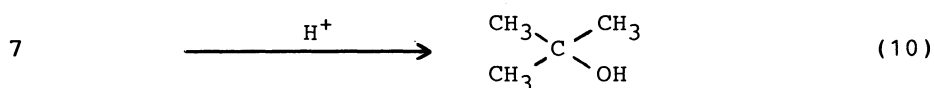
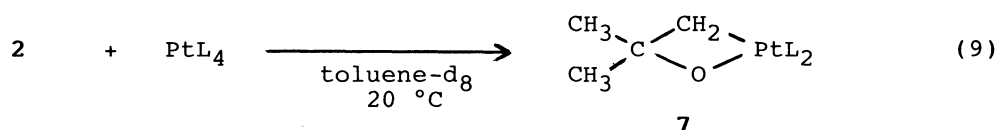


These results reflect that M(II) complexes virtually play key roles on the regioselective C-O bond cleavage by attacking the carbon center of the epoxide as electrophiles.

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References

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- 4) We substantially observed 3,3-dimethyl-2-oxaplatinacyclobutane species (**7**) in NMR spectrum of the solution which formed by the treatment of $\text{Pt}(\text{PPh}_3)_4$ with 1,2-epoxy-2-methylpropane (5 molar excess) in toluene- d_8 ; $^1\text{H-NMR}$, $\delta 1.17$ ppm (m, 2H, Pt-CH_2 , $J_{\text{Pt-H}}$ 69 Hz), 2.25 (s, 6H, CH_3).⁵⁾ After complete removal of the solvent and unreacted epoxide, protonolysis of the residual light yellow precipitates **7** with HCl resulted in the formation of 2-methyl-2-propanol with 58% yield based on $\text{Pt}(\text{PPh}_3)_4$ as in Eq. 10. On the other hand,



the treatment of **7** with excess of CH_3I in toluene afforded colorless precipitate which gave 2-methyl-2-butanol on protonolysis with HCl in 23% yield based on $\text{Pt}(\text{PPh}_3)_4$, while no 2,2-dimethylpropanol was obtained as in Eq. 11.

- 5) The alternative structure of platinum-oxirane complex, in which the oxirane remained intact could not be excluded, although the large coupling constant of $J_{\text{Pt-H}}$ was observed.

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