

Attempted preparation of 1,3-diphenoxy-2-propene. A suspension of 19.9 g. (0.05 mole) I and 4.2 g. (0.05 mole) sodium bicarbonate in 75 ml. dimethyl sulfoxide was stirred vigorously and warmed slowly, so that it reached 90° in 63 min. and 100° in 140 min. Carbon dioxide evolution was fairly brisk beginning at the former temperature. After 4 hr. at 100° the reaction mixture was poured onto ice. The gummy solid was broken up, washed thoroughly with water and dried *in vacuo*, wt. 17.3 g. Recrystallization from 2-propanol yielded unchanged I, melting point and mixture m.p. 121–122°.

Oxidation of I by dimethyl sulfoxide. The reaction mixture was prepared as in the experiment above and heated more strongly so that it remained in the range 138–150° for 2 hr. It was then poured onto ice. The precipitated tar was dissolved in benzene and the solution washed several times with water, dried over sodium sulfate and filtered. Evaporation of the benzene at room temperature left 11.6 g. of a brown semisolid residue. Trituration with 2-propanol at room temperature followed by filtration removed 1.2 g. of solid which, after purification, was found to be identical with II. After removal of the propanol from the filtrate, the residual liquid was distilled, b.p. 158–163°/0.30–0.36 mm. Trituration of the distillate with Skellysolve F induced crystallization. The solid after two recrystallizations from 50% 2-propanol melted at 57° (reported² 59–60°). The infrared spectrum showed strong absorption at 5.90 μ .

The 2,4-dinitrophenylhydrazone after recrystallization from ethanol containing a little ethyl acetate melted at 128° (reported² 125–126°).

Anal. Calcd. for C₂₁H₁₇N₃O₆: N, 13.30. Found: N, 13.96.

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Crystalline Racemic Bornyl Acetate

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Although optically pure bornyl acetate has long been known to be a low melting solid with a tendency to supercool, nothing is known about the melting behavior of mixtures of the two optical antipodes. A search of the literature uncovered only a statement by Haller¹ that racemic bornyl acetate did not crystallize, even at -17°. Having samples of pure *d*-bornyl acetate and *l*-bornyl acetate available, the melting point behavior of mixtures of the two was investigated.

When a mixture of equal parts of the dextro and laevo isomers was stored in a freezing chest for a week, crystallization occurred to give a solid mass which had a melting point of 7.0°. With this assurance, a series of mixtures was prepared and the melting points taken: % levo isomer (m.p.); 100%, m.p. 27°; 75%, 18.5°; 62.5%, m.p. 12°; 50%, m.p. 7°; 37.5%, m.p. 12°; 25%, m.p. 17.5°; 0% (i.e. 100% dextro isomer), m.p. 26.5°.

A plot of these melting point data gives a symmetrical fusion curve with a single eutectic point

(1) M. A. Haller, *Comp. rend.*, **109**, 29 (1889).

demonstrating² the formation of a simple conglomerate or racemic mixture. This behavior is to be contrasted with the much more common occurrence of a racemic compound, or, rarely, a solid solution.

EXPERIMENTAL³

The *d*-bornyl acetate, $[\alpha] + 41.2^\circ$, used in this study had a melting point of 26.5° (lit.¹ $[\alpha] + 44.38^\circ$; m.p. 24°). The *l*-bornyl acetate, $[\alpha] - 42.0^\circ$, had a melting point of 27.0° (lit.¹ $[\alpha] - 44.45^\circ$; m.p. 24°). Each sample, and mixture, was originally crystallized by storage in a freezing chest (-10°) for periods up to one week. Thereafter recourse was had to seeding when necessary.

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(2) A. Findlay (ed. Campbell and Smith), *The Phase Rule and Its Applications*, 9th Ed., Dover, New York, 1951, p. 190.

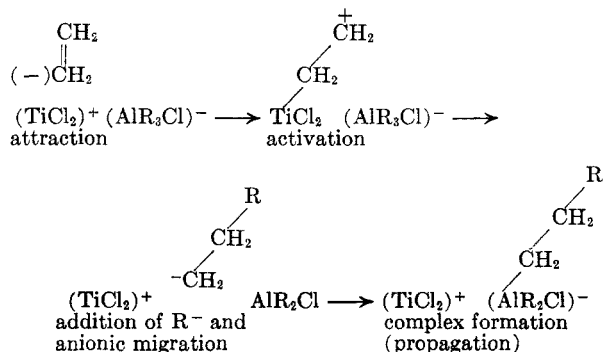
(3) All melting points are uncorrected and rotations (D line) are determined on the supercooled liquid at ambient temperatures. The temperature at which the last crystal disappeared was recorded as the melting point.

Interpretation of Some Reactions on Complex Ionic Bonds^{1a}

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The mechanism of olefin polymerization with Ziegler catalysts has been considered to occur on complex ions, such as $(\text{TiCl}_2)^+(\text{AlR}_3\text{Cl})^-$ from $\text{TiCl}_3/\text{AlR}_3$, with the direct participation of the cation metal and anion metal.^{1b} The initiating step of the polymerization is the activation of the monomer on a cation of a transition element. The second step is the migration of the activated monomer to the anion metal (aluminum for instance, or titanium) which occurs at the moment when the propagation starter (R^- , H^-) neutralizes the cationic transition state of the monomer. The migration can be compared with the addition of a metal alkyl to a Lewis type metal alkyl with the formation of more stable complex ions. The polymerization mechanism of ethylene on $(\text{TiCl}_2)^+(\text{AlR}_3\text{Cl})^-$ complex is formulated below.



The addition of the propagation starter and the migration of the monomer are concerted reactions.

The principal reasons why this mechanism proceeds are the following:

1. Special activity of transition metal cations for the activation of the monomer (low temperature initiation) can be based on the fact that inner orbitals ($3d$) participate in resonance stabilization of the electrons accepted from the monomer.

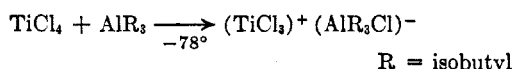
2. Migration of the monomer from titanium to aluminum is explained by the formation of a more stable aluminum carbon bond.

3. The addition of the carbanion chain end of the polymer to the cationically activated monomer (propagation) occurs continuously because it is still activated (excited) from the previous migration.

4. Very high molecular weight polymers are obtained because the growing chain end is resonance-stabilized in the complex anion, thus diminishing termination reactions.

The cation can be blocked by electron donors (ethers, amines, etc.) which form more stable coordination complexes with the cation than the monomer does.

The formation of a four valent titanium cation can be expected when titanium tetrachloride and aluminum triisobutyl are allowed to react at -78° . The ionic structure below has been proposed for the red, soluble complex formed under these conditions.^{1b,2}

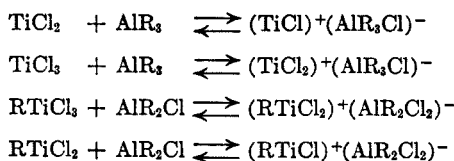


This complex decomposes above -30° yielding TiCl_3R and AlR_2Cl which can form another complex. The driving force for the decomposition in this direction is the formation of a more stable aluminum-chlorine bond.²

(1a) This treatise is based on a paper presented at the Symposium on Stereoregulated Polymerizations at the Polytechnic Institute of Brooklyn, Brooklyn, N. Y., Nov. 22, 1958.

(1b) H. Uelzmann, *J. Polymer Sci.* **32**, 457 (1958).

(2) H. Uelzmann, *J. Polymer Sci.* **37**, 561 (1959). The heat of formation for the aluminum-chlorine bond (based on aluminum chloride) is 55.6 kcal., and for the titanium chlorine bond 44.8 kcal. (based on titanium tetrachloride). However, the heat of formation of titanium-chlorine in titanium trichloride is 55 kcal. and in titanium dichloride 57 kcal. which is close to the aluminum-chlorine value. Weak addition complexes can be expected to be formed, and an equilibrium according to

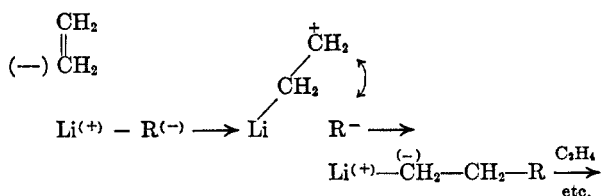


is possible. The nature of the R group, its stability, polarity, and steric factor is not accounted for in these formulations and will influence the complex formations.

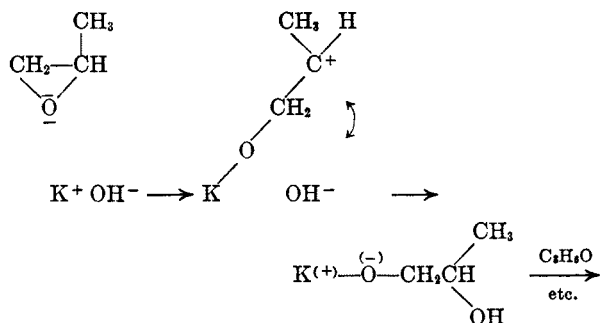
The ionic nature of the complex solution at -78° has been proven by A. Malatesta³ in conductivity measurements.

Polymerization on simple and complex ionic bonds. The catalytic site in ionic polymerizations can be a simple or a complex ionic bond.

When a simple ionic bond is involved the polymerization takes place on one metal atom only. Catalysts with simple ionic bonds are, for instance, $\text{Li}^{(+)}-\text{R}^{(-)}$ or $\text{R}_2\text{Al}^{(+)}-\text{R}^{(-)}$ for ethylene poly-



merization or K^+OH^- , $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{H}_2\text{O}$,⁴ and strontium carbonate⁵ for epoxides



No migration of the monomer, therefore, is likely to occur in a simple ionic mechanism and it can be expected that both activation and propagation proceed on the same metal-oxygen bond ($\text{K}-\text{O}$, $\text{Zn}-\text{O}$, $\text{Sr}-\text{O}$, etc.).

The active site can also be a complex ionic bond which can be represented by a complex acid, such as $\text{H}^+(\text{AlBr}_4)^-$ for α -olefins (cationic propagation), $\text{H}^+(\text{FeCl}_2\text{OR})^-$, $\text{H}^+(\text{BF}_4)^-$ for cyclic ethers, or a complex salt, such as a Ziegler catalyst from $\text{TiCl}_3/\text{AlR}_3$ for olefins or Price's catalyst $\text{ZnCl}_2/\text{Al}(\text{OR})_3$ for epoxides.⁶ The increase in reactivity by complex formation is generally known⁷ and is due to a strong ionic or polarized complex bond on which monomers or other reactive molecules are activated according to their polarization.

In olefin polymerization reactions complex ionic bonds generally offer better control of propagation than simple ionic bonds. The growing chain is more effectively resonance-stabilized as a member of a complex ion than as a simple ion. Therefore, complex catalysts allow the chain to grow longer yield-

(3) A. Malatesta, paper presented at the Ninth Canadian Polymer Forum, Oct. 26-28, 1959, Toronto, Ontario, Canada.

(4) Junji Furukawa *et al.*, *J. Polymer Sci.*, **36**, 541 (1959).

(5) F. N. Hill, F. E. Bailey, Jr., and J. T. Fitzpatrick, *Ind. Eng. Chem.*, **50**, 5 (1958). Belgian Patent No. 557,766.

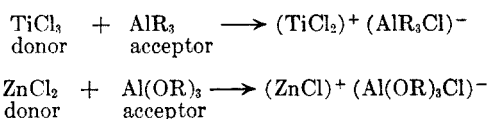
(6) C. C. Price and Maseh Osgan, *J. Polymer Sci.*, **34**, 153 (1959). Belgian Patent No. 566,583.

(7) G. Wittig, *Angew. Chem.*, **70**, 65 (1958).

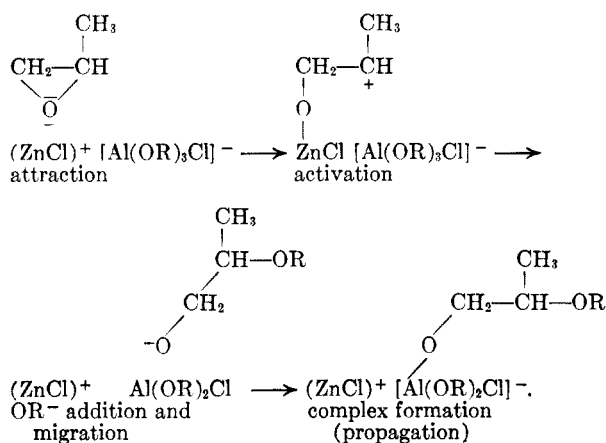
ing high degrees of polymerization. This is particularly true in anionic propagations where the cation or the anion portion of the catalytic bond can be efficiently complexed and where termination reactions by hydride ion abstraction require higher activation energies. In cationic propagations low temperatures are usually required for the formation of long chains in order to avoid proton eliminations or hydride shifts.

K. Ziegler and co-workers⁸ obtained only low molecular weight polyethylenes with aluminum alkyls, but polymers of high molecular weight resulted when these metal alkyls were complexed with compounds of transition elements.

A similarity in structure can be expected between Ziegler catalysts, such as $\text{TiCl}_3/\text{AlR}_3$, and Price's catalyst $\text{ZnCl}_2/\text{Al}(\text{OR})_3$. In both cases an electron donor reacts with a Lewis acid to form complex ions with two metal atoms:



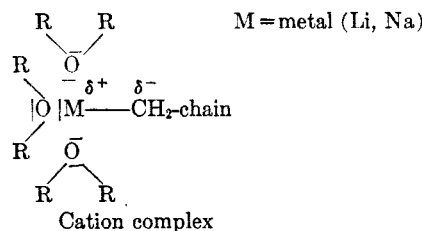
Therefore, it is likely that propylene oxide polymerizes similarly to ethylene when Price's catalyst is used:



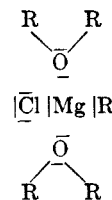
The migration of the monomer is comparable to the addition of an alcoholate anion to a Lewis type alcoholate. Other epoxides would polymerize similarly.

The ionic bond on which the polymerization proceeds offers two possibilities for complexing: the cationic or the anionic part. The mechanism of polymerization and consequently the properties of the resulting polymers can be strongly influenced by either kind of complexing.

Cation complexes. Electron donors, such as ethers or tertiary amines, will react with the cation to form association complexes. The complexing could go so far that the cation completes its outer electron shell to form an octet:

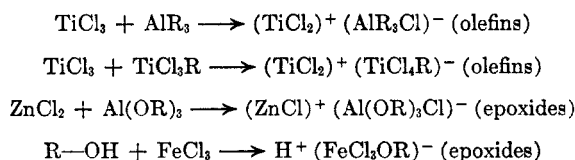


Similar complexes are generally known to be formed by the interaction of Grignard compounds and ethers:



Cation complexes are also formed from lithium or sodium cations and ethers [Szwarc catalysts,⁹ Dainton catalysts], or alcoholate and chlorine anions [Alfin catalysts¹⁰]. The differences in the polymerization of butadiene (or styrene) in the presence or absence of these cation complexes (ether solvents) are generally known. Propagation on an ether-complexed or salt-complexed sodium cation gives usually high molecular weight polymers and promotes stereo-preserving polymerizations [formation of *trans*-1,4-polybutadiene from *trans* conformational monomeric butadiene^{1b}]. However, when the energy level of the complexed cation is lower than the energy level required for the activation of the monomer no polymerization will occur. This is possibly the reason why conjugated dienes or styrene but not ethylene or α -olefins can be polymerized with Szwarc-type or Alfin-type catalysts. Since less energy is required for the activation of a conjugated system the complexed cations can activate dienes but not mono-olefins. The same seems to be true for lithium alkyls which normally polymerize ethylene to a certain degree. In the presence of ethers no polymerization of ethylene is observed.

Anion complexes. If the propagation starter (R^- , H^- , OR^- , OH^-) is a member of a Lewis acid it can become a member of a complex anion by adding a negative ion.



The activation would be cationic, followed by a migration and anionic propagation of the monomer.

Prerequisites for this type of anionic propagation are:

(8) K. Ziegler *et al.*, *Angew. Chem.*, **68**, 721 (1956).

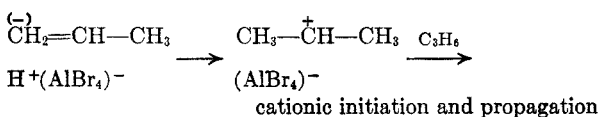
(9) M. Szwarc *et al.*, *J. Am. Chem. Soc.*, **78**, 2656 (1956).
(10) A. A. Morton, *Ind. Eng. Chem.* **42**, 1488 (1950).

1. The cation must always be reformed for the activation of new monomers.

2. The complex anion must contain a propagation starter which neutralizes the cationically activated monomer.

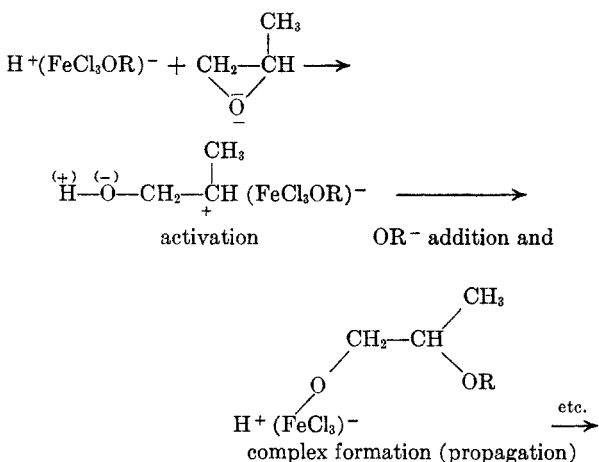
3. The bond of the polymer chain to the metal of the complex anion must be more stable than the bond to the activating cation to assure migration and propagation.

If the afore mentioned prerequisites are not fulfilled the following course of reactions for α -olefins could be concluded. The cation can not be reformed when a complex acid such as $H^+(AlBr_4)^-$ is used because of the elimination of the proton with the formation of a stable methyl group and a rather homopolar bond.



The carbonium ion formed allows cationic propagation only. If activated on a metal cation the bond of propylene to the cation is still ionic and allows migration, propagation, and reformation of the metal cation.

Contrary to olefins the anionic polymerization of epoxides by complex acids seems to be possible. The activating proton of the complex acid is not destroyed after the initiation of the monomer because of the formation of an ionizable hydroxyl group.

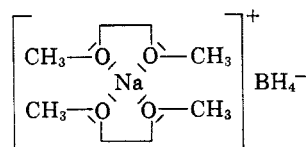


A cationic propagation would occur if the negative complex ion does not contain a propagation starter which would neutralize the cationically activated monomer. Such a complex acid could be $H^+BF_4^-$. On the other hand $H^+(BF_3OR)^-$ or $H^+(BF_3OH)^-$ could propagate anionically.

Cationic mechanisms with $H^+BF_4^-$ as a catalyst for the polymerization of cyclic ethers are generally known.

Reductions with complex metal hydrides. It can be deduced from the mechanisms discussed in the foregoing section that a similar migration of ionized groups or molecules from one metal to another is much more common in organic chemistry than hitherto expected.

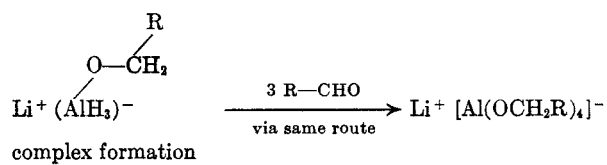
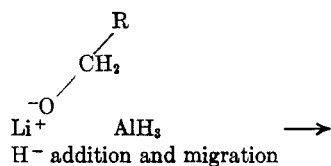
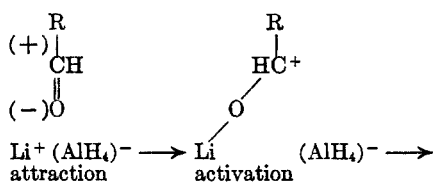
In reduction mechanisms of organic compounds with complex hydrides (lithium aluminum hydride, sodium aluminum hydride, sodium borohydrides, etc.) a direct participation of both the cation metal and anion metal would explain why there can be differences in reactivities when the cation metals are changed. H. C. Brown and co-workers¹¹ found that lithium borohydride reduces ester groups but sodium borohydride does not. Since different cations also differ in energy levels or steric factors their participation in the reduction mechanism as the initiating or activating site (attracting negatively polarized atoms, such as oxygen, nitrogen) explains their deviating behavior and selectivity in the above-mentioned complex ions. A reaction mechanism which proceeds solely on the complex anion allows no interpretation of this phenomenon. As already discussed the energy level of the cation can be modified additionally by the formation of coordination complexes with solvents which act as electron donors (ethers, amines). H. C. Brown *et al.*¹¹ have found that sodium borohydride in ethyleneglycol dimethylether reduces aldehydes but not ketones. It can be assumed that the sodium cation forms a coordination complex (octet formation) with the ether:



The activity of the sodium cation is decreased to such an extent that it can still activate aldehydes but not ketones. The latter apparently require higher activation energies than aldehydes and are more sterically hindered. The complete mechanism of the reduction of an aldehyde by lithium aluminum hydride is explained by the sequence of reactions shown below.

The negatively polarized oxygen atom, as the most exposed reactive atom of the aldehyde, is attracted and activated by the cation with the formation of a lithium-oxygen bond and a carbonium ion (cationic transition state). A hydride ion adds to the carbonium ion and the resulting alcoholate ion migrates and adds to the aluminum. The driving force is the reformation of stable complex ions. Here the migration compares with a simple addition of lithium alcoholate to AlH_3 :

(11) H. C. Brown, Lecture series "Frontiers in Chemistry," April 24, 1959, Western Reserve University, Cleveland, Ohio.



It can be expected that many other reactions of complex ionic bonds follow a similar mechanism, particularly in those cases where exposed reactive atoms are negatively polarized and, therefore, are subject to a cationic activation.

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