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ROLES OF TITANIUM COMPLEX IN THE CATALYTIC HYDROMETALATION AND ISOMERIZATION OF OLEFINS

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The reaction of Cp_2TiCl_2 with $LiAlH_4$ forms the complex $Cp_2Ti(AlH_3)_2$ [1] with the evolution of H_2. Treatment of [1] with 1-octene gave the isolable titanium complex which was characterized as $[Cp_2Ti(AlH_3)_2][C_6H_{13}CH{=}CH_2]$ [2a]. The roles of [1] and [2a] in the catalytic hydrometalation and the catalytic isomerization of olefins are discussed.

The hydrometalation and the isomerization of olefins proceed catalytically by use of the reagent system Cp_2TiCl_2-$LiAlH_4$.$^{1)}$ These two catalytic reactions in the presence of excess olefins can be discriminated from one another by the composition of two reagents in the reagent system: the reagent system composed of $LiAlH_4/Cp_2TiCl_2 \leq 2$ in the molar ratio preferentially promotes the catalytic isomerization and that composed of $LiAlH_4/Cp_2TiCl_2 > 2$ preferentially promotes the catalytic hydrometalation which occurs in the anti-Markownikoff fashion.

We report here the probable pathways of these two catalytic reactions from the stoichiometry of the reaction of Cp_2TiCl_2 with $LiAlH_4$, and also from the characterization and chemical properties of the isolated titanium complex coordinated with an olefin.

The reaction of Cp_2TiCl_2 with $LiAlH_4$ in ether proceeded smoothly at room temperature with the evolution of H_2.$^{2)}$ The evolved H_2 was collected in a sealed vessel and analyzed by the method of Brown and Yoon.$^{3)}$ The volume of H_2 varied with the molar ratio $Cp_2TiCl_2/LiAlH_4$. The results shown in Table 1 indicate that, if $LiAlH_4$ is present in large excess, one molar quantity of Cp_2TiCl_2 reacts with two molar quantities of $LiAlH_4$ with the evolution of one molar quantity of H_2. The

Table 1. Amounts of the Hydrogen Evolved During the Reaction of Cp_2TiCl_2 with $LiAlH_4$

Cp_2TiCl_2 (mmol)	$LiAlH_4$ (mmol)	Evolved H_2 (mmol)	Molar Ratio H_2/Cp_2TiCl_2
2.0	2.0	1.0	0.50
2.0	4.0	1.9	0.95
1.9	5.7	1.8	0.95
1.3	26.0	1.3	1.00

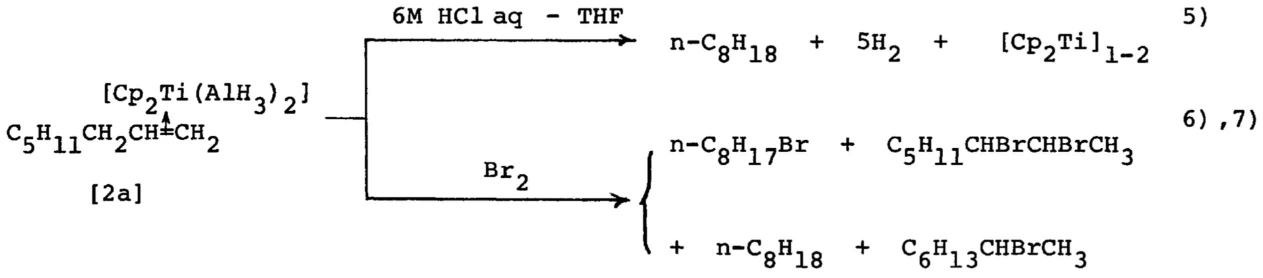
stoichiometry suggests that the complex [1], which is formulated as $Cp_2Ti(AlH_3)_2$, is formed by the reaction of one molar quantity of Cp_2TiCl_2 with two molar quantities of $LiAlH_4$. Furthermore, the UV spectrum of the reaction mixture displayed that the absorbance at 320 and 390 nm (absorption maxima of Cp_2TiCl_2) diminished as the reaction proceeded. This result implies the formation of a low valent titanium complex.$^{4)}$ Although [1] was unable to isolate in a pure state, it gave a complex

$$Cp_2TiCl_2 + 2LiAlH_4 \longrightarrow \underset{[1]}{Cp_2Ti(AlH_3)_2} + H_2 + 2LiCl$$

which permitted isolation and characterization upon treatment with 1-octene.

Cp_2TiCl_2 (957.7 mg, 3.85 mmol) was added to a stirred suspension of $LiAlH_4$ (295.1 mg, 7.78 mmol) in 20 ml of ether at room temperature under argon. The dark violet mixture gradually turned black, accompanying the evolution of H_2. The mixture was stirred for 1 h, and then 1-octene (8.79 g, 78.3 mmol) was added over 10 min. After the addition, stirring was continued for 24 h. The dark-red reaction mixture was filtered under an argon atmosphere, and the filtrate was evaporated to dryness. The solidified residue was dried under reduced pressure and then washed thoroughly with hexane and ether, giving 391 mg of an orange solid which was found to be the 1-octene-coordinated titanium complex [2a]; Found: Al, 15.01; Ti, 12.75 %. Calcd for $C_{18}H_{32}Al_2Ti$: Al, 15.40; Ti, 13.67 %. MS m/e (rel intensity): 352 (M^++2, 5), 351 (M^++1, 30), and 350 (M^+, 100). Calcd rel intensity for $C_{18}H_{32}Al_2Ti$: (M^++2, 7), (M^++1, 26), and (M^+, 100). IR (KBr): 1600 cm^{-1} (νC=C).

The complex [2a] was stable under argon at room temperature, but unstable in air. The hydrolysis of 0.037 mmol of [2a] in THF with an aqueous 6M HCl at 35°C yielded 0.033 mmol of octane and 0.165 mmol of H_2. Treatment of 0.100 mmol of [2a] in ether with bromine at 0°C gave 0.042 mmol of 1-bromooctane, 0.019 mmol of 2,3-dibromooctane,



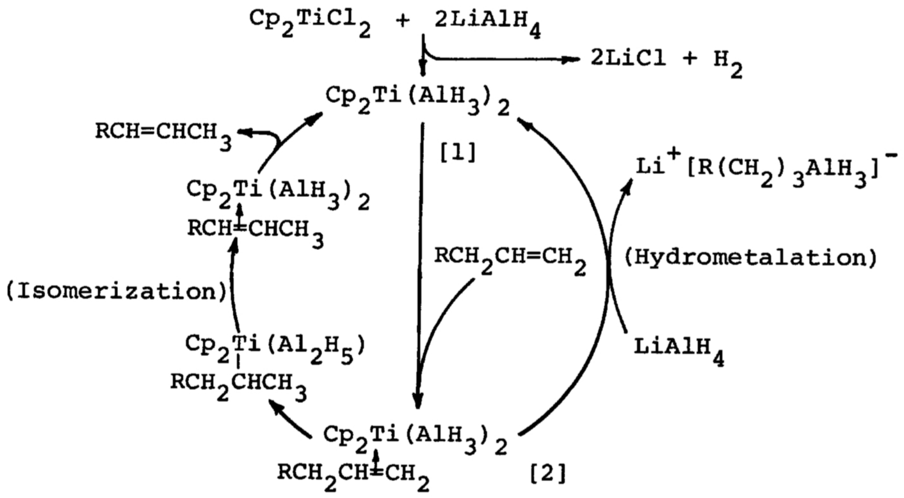
Scheme 1.

0.030 mmol of octane, and a trace amount of 2-bromooctane. The stoichiometry of these reactions (Scheme 1) is consistent with the view that [2a] has the molecular formula $[Cp_2Ti(AlH_3)_2][C_6H_{13}CH{=}CH_2]$.

Finally, a suspension of 1-octene (3.35 mmol) and $LiAlH_4$ (3.35 mmol) in 15 ml of THF was refluxed for 4 h in the presence of a catalytic amount (0.196 mmol) of [2a], and then the mixture was treated with bromine at 0°C. Work-up of the reaction mixture gave a mixture consisting of 1-bromooctane (0.843 mmol), 2,3-dibromooctane (0.132 mmol), octane (0.906 mmol), and 1,2-dibromooctane (0.662 mmol). This result demonstrates that [2a] promotes the catalytic hydrometalation of 1-octene, accompanied by the hydrogenation of the olefinic double bond, in the presence of $LiAlH_4$.

All the results presented here suggest that the catalytic reactions proceed through the pathways outlined in Scheme 2.

The complex [1], which is formed by the reaction of Cp_2TiCl_2 with $LiAlH_4$ in the molar ratio of 1:2, promotes the catalytic isomerization of 1-olefins leading to



Scheme 2.

2-olefins, unless excess $LiAlH_4$ is present. However, in the presence of excess $LiAlH_4$, [1] promotes the catalytic hydrometalation of 1-olefins leading to lithium alkyl-1-trihydroaluminates. These two catalytic reactions proceed through the olefin-coordinated titanium complex [2] as an intermediate.[7] These catalytic reactions are always accompanied by the hydrogenation of olefins.

The preparation of alkyl-1-trihydroaluminates under mild conditions such as reported in this communication has a wide applicability for organic synthesis, which is now under study in this laboratory.

References and Notes

1) K. Isagawa, K. Tatsumi, and Y. Otsuji, Chem. Lett., 1976, 1145.

2) The reaction of Cp_2TiCl_2 with one molar equivalent of $LiAlH_4$ gave the complex $Cp_2TiH_2AlH_2$ which could not be isolated; G. Henrici-Olive and S. Olive, J. Organometal. Chem., 23, 155 (1970); J. G. Kenworthy, J. Myatt, and M. C. R. Symons, J. Chem. Soc. (A), 1971, 1020.

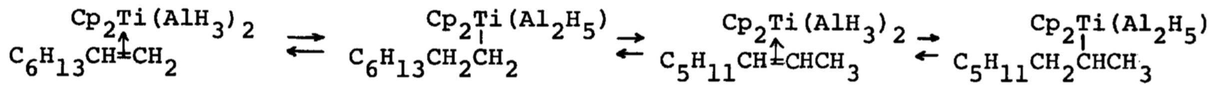
3) H. C. Brown and N. M. Yoon, J. Am. Chem. Soc., 88, 1464 (1966).

4) E. E. Van Tamelen, W. Cretney, N. Klentschi, and J. S. Miller, J. Chem. Soc., Chem. Commun., 1972, 481, and references cited therein.

5) The experimental result strongly suggests that upon treatment with 6M HCl, [2a] decomposes according to the stoichiometric equation indicated. The low valent titanium complex $[Cp_2Ti]_{1-2}$ thus produced is stable under the reaction conditions,[4] although it was not isolated.

6) The total amount (0.091 mmol) of 1-bromooctane, 2,3-dibromooctane, octane, and 2-bromooctane (trace) produced from 0.100 mmol of [2a] indicates that one molecule of 1-octene coordinates with one molecular unit of [1].

7) A low solubility of [2a] in organic solvents prevented recording of the NMR spectrum of the complex. Therefore, the detailed structure of [2a] is not clear at present. The IR spectrum ($\nu C{=}C$ at 1600 cm^{-1}) and the chemical properties strongly suggest that [2a] has chiefly the olefin-coordinated structure such as represented in Scheme 2. However, the experimental results also implies that the isolated complex is possible to be an equilibrium mixture of the following σ- and π-complexes:



$$\underset{C_6H_{13}CH{=}CH_2}{\overset{Cp_2Ti(AlH_3)_2}{\uparrow}} \rightleftarrows \underset{C_6H_{13}CH_2CH_2}{\overset{Cp_2Ti(Al_2H_5)}{|}} \rightleftarrows \underset{C_5H_{11}CH{=}CHCH_3}{\overset{Cp_2Ti(AlH_3)_2}{\uparrow}} \rightleftarrows \underset{C_5H_{11}CH_2CHCH_3}{\overset{Cp_2Ti(Al_2H_5)}{|}}$$

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