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HYDROALUMINATION OF OLEFINS CATALYZED BY IMMOBILIZED TITANIUM COMPOUNDS

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Summary: SiO_2-supported titanium chloride (1) and polystyrene-supported titanocene dichloride (2) and (3) were synthesized. These heterogenized titanium compounds are excellent catalysts for hydroalumination of olefins.

The recently developed hydroalumination reaction of olefins catalyzed by titanium compounds makes many organoaluminum compounds readily available[1] and investigations hitherto revealed that this new hydroalumination reaction is potentially useful for organic chemists.[2] One disadvantage in this reaction is the difficulty of removing the catalyst from the organoaluminum compounds prepared. To overcome this difficulty, we commenced a study to heterogenize the catalyst.

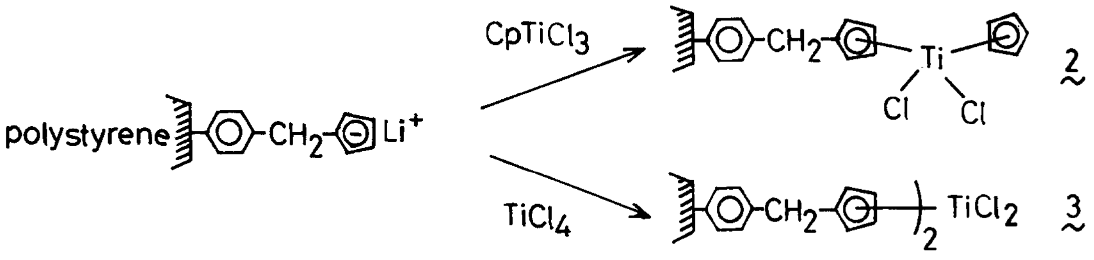
Preparation of Heterogenized Titanium Compounds

Heterogenization of $TiCl_4$ and $(\eta^5\text{-}C_5H_5)_2TiCl_2$, which are excellent catalysts for the hydroalumination reaction, was undertaken. $TiCl_4$ was supported on silica gel through the siloxy group on the support as shown below.[3,4]

$$SiO_2\text{-}OH + TiCl_4 \longrightarrow SiO_2\text{-}O)_nTiCl_{4-n}$$

1

$(\eta^5\text{-}C_5H_5)_2TiCl_2$ was attached to a divinylbenzene cross-linked polystyrene by the following two procedures shown in the scheme below. One procedure was the same as that previously outlined by Grubbs, et. al.[5], and compound 2 was prepared using a 0.9% cross-linked polystyrene support. The other procedure is a newly developed one; 0.9% cross-linked polystyrene support containing cyclopentadienyl anion attached to 6.6% of the aromatic rings produced enough mobility to allow the anion to act as a chelate[6] and gave compound **3** by treatment with $TiCl_4$[7] in contrast to the result obtained when using 20% cross-linked polystyrene support which gave polymer attached η^5-$C_5H_5TiCl_3$.[5,8]



Hydroalumination Reaction Catalyzed by Immobilized Titanium Compounds

The immobilized titanium compounds **1**,**2** and **3** synthesized as above showed catalytic activity in the reaction of $LiAlH_4$ and olefins.[9] Thus reaction of $LiAlH_4$ and olefin in the presence of **1**,**2** or **3** followed by hydrolysis or halogenolysis gave the corresponding alkanes or alkyl halides as shown in the Table.

The catalysts were easily recovered from the reagents by filtration and could be reused many times without any observable change of activity, whereas the colorless filtrate showed no catalytic activity. These results indicated that the titanium compound did not elute into solution, and that the catalyst site is bound to the support. It is noteworthy that though the reaction of 1-hexene and $LiAlH_4$ by catalysis of **2** or **3** afforded tetrahexylaluminate, the reaction with 1-hexene in the presence of **1** and the reaction with 4-vinyl-1-cyclohexene by catalysis of **3** proceeded to the dialkylaluminum stage but not beyond. This is apparently due to the difficulty of diffusion of $LiAlR_2H_2$ into the support because the reactants must diffuse into a channel of silica gel or polymer matrix to reach a bound catalyst site. The degree of hydroalumination may be dependent on kinds of support and bulkiness of the olefin. In the previous report it was revealed that the reaction of $LiAlH_4$ with 4 equiv of α,ω-dienes gave either monohydroaluminated and dihydroaluminated products and that the latter was produced via the former.[10]

$$CH_2{=}CH(CH_2)_nCH{=}CH_2 \xrightarrow{+\ \text{al-H}} \text{al}CH_2(CH_2)_{n+1}CH{=}CH_2 \xrightarrow{+\ \text{al-H}} \text{al}\left(CH_2\right)_{n+4}\text{al}$$

It was therefore expected that the hydroalumination of α,ω-dienes could be stopped at monohydroaluminated stage more selectively by using immobilized titanium catalyst because the monohydroaluminated product is more bulky than the diene. As shown in the Table, this expectation was realized. For example, the ratio of mono- and di-hydroaluminated product from 1,5-hexadiene increased by a factor of 2.2 compared to homogeneous reaction. Noteworthy here is that the present reaction provides a satisfactory synthetic route to ω-halo-1-alkenes.

TABLE

YIELDS AND PRODUCTS OF ADDITION REACTION OF OLEFINS

Olefin	Catalyst	Reaction[a] conditions	Hydrolysis or Halogenolysis	Product (yield,%)[b]
1-Hexene	**1**	A	H_2O	n-Hexane (54) 2-Hexene[c] (46)
	1	B	H_2O	n-Hexane (98)
	2	C	H_2O	n-Hexane (98)
	3	C	H_2O	n-Hexane (99)
4-Vinyl-1-cyclohexene	**3**	C	H_2O	4-Ethyl-1-cyclohexene (54)[d]
1,4-Pentadiene	**3**	D	H_2O	n-Pentane (11) 1-Pentene (77) 1,4-Pentadiene (12)
			NBS	5-Bromo-1-pentene (63)[e]
1,5-Hexadiene	**3**	D	H_2O	n-Hexane (12) 1-Hexene (76) 1,5-Hexadiene (12)
			NBS	6-Bromo-1-hexene (54)[e,f]
	$TiCl_4$	E	H_2O	n-Hexane (20) 1-Hexene (57) 1,5-Hexadiene (23)
	Cp_2TiCl_2	E	H_2O	n-Hexane (36)[g]
1,7-Octadiene	**2**	D	H_2O	n-Octane (18) 1-Octene (64) 1,7-Octadiene (18)
	3	D	H_2O	n-Octane (15) 1-Octene (68) 1,7-Octadiene (17)
			NBS	8-Bromo-1-octene (50)[e,f]

[a] A,B; 2 g of **1** (1.8×10^{-4} g-atom of Ti), Olefin; 13 mmol, $LiAlH_4$; 3.6 mmol for A or 6.7 mmol for B. C; 0.5 g of **2** (3.1×10^{-4} g-atom of Ti) or **3** (9.7×10^{-5} g-atom of Ti), Olefin; 13 mmol, $LiAlH_4$; 3.6 mmol. D; 0.5 g of **2** or **3**, Diene; 12 mmol, $LiAlH_4$; 3 mmol. E; 0.14 mmol of $TiCl_4$ or 0.8 mmol of Cp_2TiCl_2, Diene; 12 mmol, $LiAlH_4$; 3 mmol. Reaction Temp.; 25°C. Reaction Time; 1.5h for A,B and E or 15h for C and D. Solvent; THF (15 ml for A,B and E or 20 ml for C and D). [b] Yields determined by GLC and based on olefin. [c] Isomerized product of unreacted olefin. [d] Longer reaction time did not improve yield. [e] Based on reacted diene. [f] Isolated yield. [g] Other products are mixture of hexenes presumably due to the isomerization of monohydroaluminated product.

References and Notes

1. F. Sato, "Fundamental Reserch in Homogeneous Catalysis" vol 2, Y. Ishii and M. Tsutsui (Eds.), Plenum Press, New York, 1978, p81.
2. F. Sato, Y. Mori, and M. Sato, Tetrahedron Lett., 1405 (1979). F. Sato, H. Kodama, Y. Tomuro, and M. Sato, Chem. Lett., 623 (1979) and references cited therein.
3. Homogeneous catalysts absorbed on silica gel through the reaction of metal halide with surface silanol have been reported; see R.H. Grubbs, Chemtech, 512 (1977).
4. Preparation of complex **1** was carried out as follows: silica gel (Wako, 100 mesh, 2 g) calcined at 220°C for 3h in vacuo before use was impregnated with a THF solution of $TiCl_4$ (0.18 mmol) for 12h at room temperature followed by evacuation at 200°C (4 Torr) after decantation.
5. W.D. Bonds,Jr, C.H. Brubaker,Jr, E.S. Chandrasekaran, C. Gibbons, R.H. Grubbs, and L.C. Kroll, J. Am. Chem. Soc., 97,2128 (1975).
6. Content of the cyclopentadienyl anion was controlled by the extent of chloromethylation of the aromatic ring. From the supports having a high content of cyclopentadienyl anion, a mixture of polymer-attached Cp_2TiCl_2 and $CpTiCl_3$ was produced (Analytical result of molar ratio of Cl/Ti was 2~3), because the support becomes rigid through cross-linking by $TiCl_2$ with progress of the reaction.
7. The reaction.was carried out as follows: 0.9% cross-linked polystyrene was chloromethylated with chloromethyl ethyl ether (Anal. Found, Cl;0.62 mequiv/g) and then allowed to react with sodium cyclopentadienide to afford cyclopentadiene substituted polymer (Anal. Found, Cl;0%). This polymer was treated with a threefold excess of methyllithium in THF overnight with stirring, then the solution was removed and the residue was washed with THF four times. The beads were allowed to react with a twofold excess of $TiCl_4$ in THF and stirred overnight, then separated by filtration and washed with THF in a Soxlet extractor until excess chloride had been removed. The resulting orange-red beads had the following analytical data and UV spectrum; Anal. Found. Cl; 0.38 mequiv/g, Ti; 0.193 mequiv/g (Cl/Ti ratio; 1.97), Calcd. Cl/Ti ratio; 2, UV[5], 250, 285, and 425 nm.
8. It has been reported that cross-linking makes supports rigid and their chelating nature weak: see for example, Y. Chimura, M. Beppu, S. Yoshida, and K. Tarama, Bull. Chem. Soc. Jpn., 50, 691 (1977).
9. It is difficult to compare catalytic activity with that of the homogeneous system because it is dependent on the support particle diameter. However, it is evident that the activity per equiv of Ti is not decreased by a significant extent.
10. F. Sato, S. Sato, H. Kodama, and M. Sato, J. Organometal. Chem., 142, 71 (1977).

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