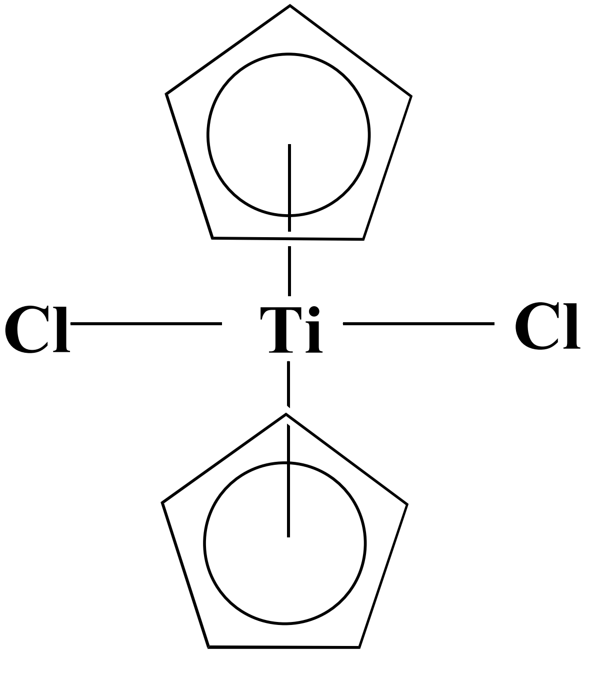
Titanocene Dichloride

Technical Data



NICHIA CORPORATION

Contents:

1. General Features:

1) Titanocene Dichloride is highly active in unsaturated compounds and shows excellent effects as an active homogeneous hydrogenation catalyst under moderate conditions.

2) Titanocene Dichloride improves stereoregularity due to the effect of the cyclopentadienyl group.

3) Titanocene Dichloride can be widely used for various derivatives which become the basic materials for high performance chemical products.

4) Consistently uniform and high quality as the product is manufactured under strict process/quality controls.

Nichia has its own technical service system.
Nichia can also provide consultation on other Titanocene derivatives.

2. Product Guide

Packaging: Packing units/formats are available upon request.

2. Product Guide (Continued)

Physical and Chemical Properties:

Chemical Name: Bis-Cyclopentadienyl Titanium Dichloride

Molecular Formula: $(C_5H_5)_2TiCl_2$

Molecular Weight: 248.99

Appearance: Red~Reddish-brown crystalline powder

Melting Point: 287~293°C

Sublimation Point: 160°C (13Pa)

Solubility: Soluble in halogenated hydrocarbon, aromatic hydrocarbon and polar solvents. Slightly soluble in aliphatic hydrocarbon.

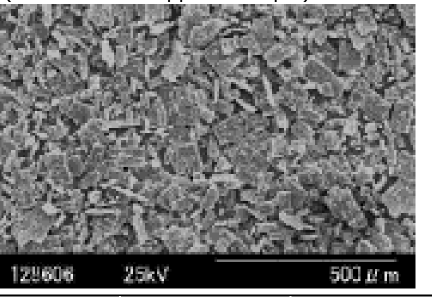
Decomposability: Titanocene Dichloride gradually decomposes from the moisture and oxygen in air if left in the open air. Titanocene Dichloride is relatively stable against heat.

Assay and Impurities:

Analytical data of Titanocene Dichloride:

	Specifications	Typical Data	Theoretical Value
Ti	≥19.00%	19.18%	19.23%
Cl	≥28.20%	28.40%	28.48%
Fe	≤0.05%	0.0005%	–

SEM (Particle Size: Approx. 100µm)

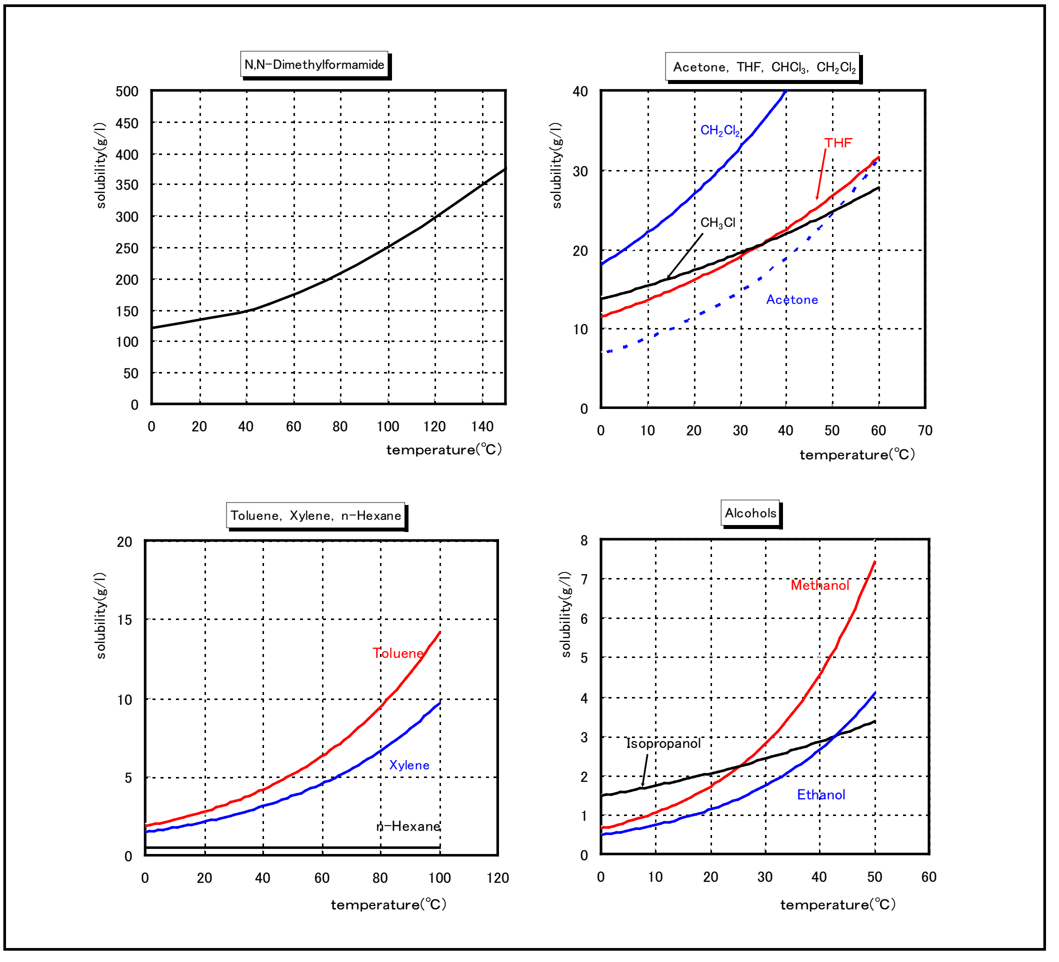


Comparison with reagent products:

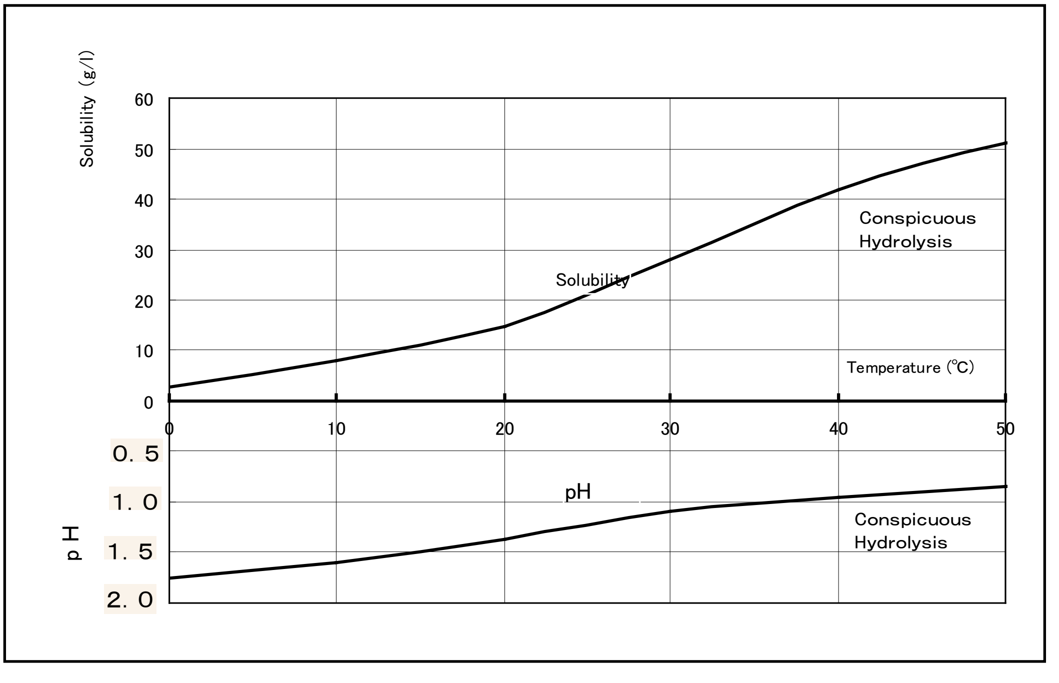
Suppliers		Ti(%)[1]	Cl(%)[1]	Cl/Zr (Molar ratio)	Notes
Nichia		19.18	28.40	2.00	Crystalline Powder, Narrow Particle Size Distribution Fe: 5ppm
Reagent	A	19.26	28.32	1.99	Crystalline Powder, Broad Particle Size Distribution
	B	18.50	27.82	2.03	Powder
	C	18.88	28.11	2.01	Crystalline Powder, Broad Particle Size Distribution
	D	19.19	28.16	1.98	Crystalline Powder, Broad Particle Size Distribution Fe: 154ppm
	E	18.83	28.34	2.03	Crystalline Powder, Broad Particle Size Distribution Fe: 25ppm
	F	18.83	27.82	2.00	Crystalline Powder, Broad Particle Size Distribution Fe: 32ppm

[1] Ti and Cl contents were analyzed by Nichia.

3. Solubility in Various Solvents

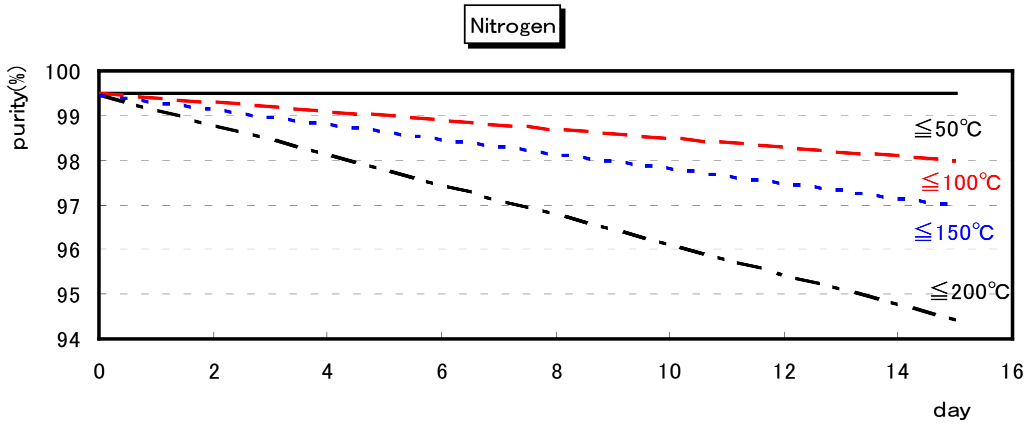


4. Solubility in Water and pH



5. Stability

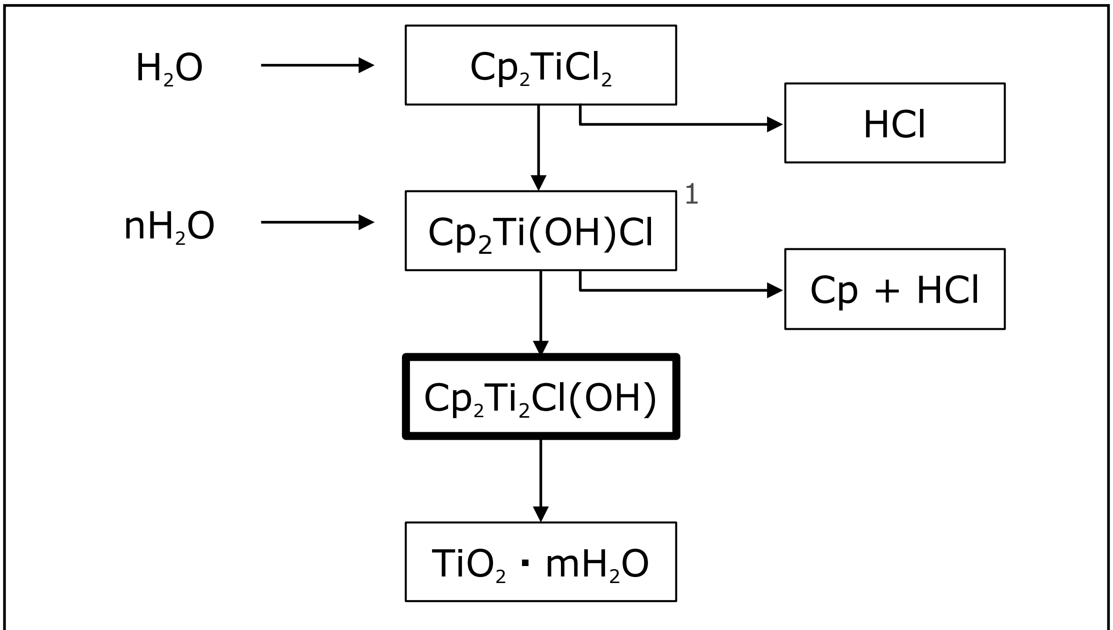
1) Titanocene Dichloride is stable in a nitrogen atmosphere at ≤50°C and its purity will not deteriorate.



2) Its quality will deteriorate under the influence of ultraviolet rays.

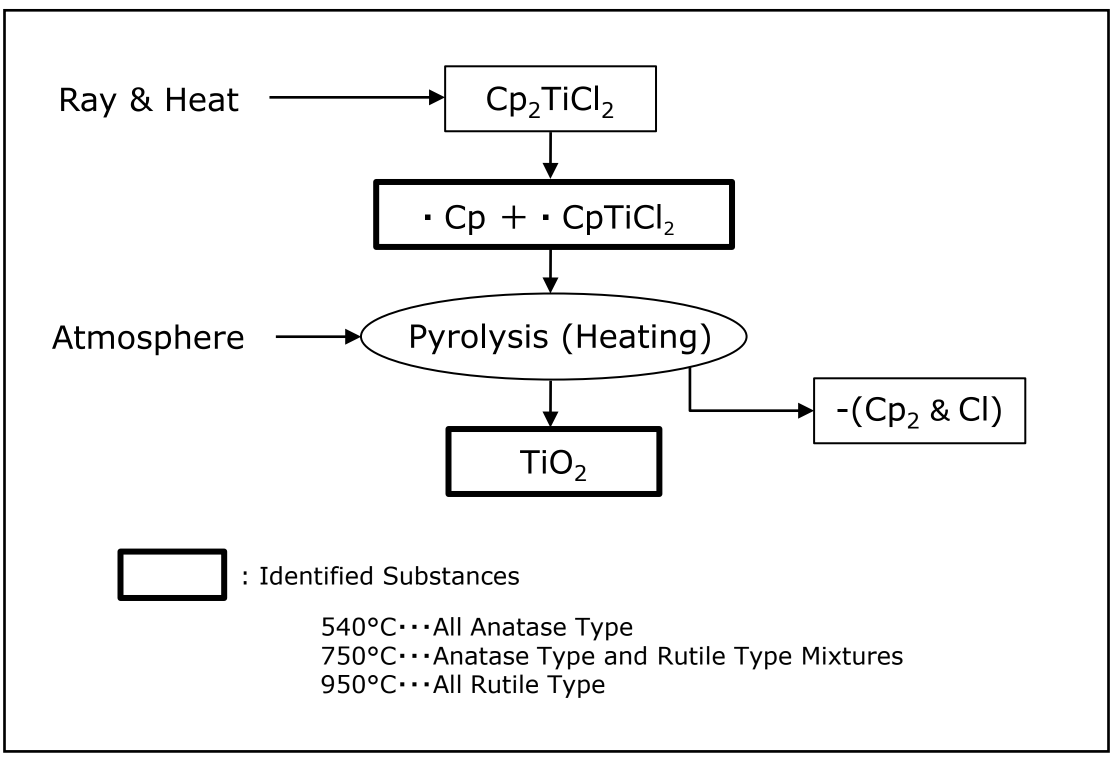
6. Decomposition Mechanism

A. Hydrolysis

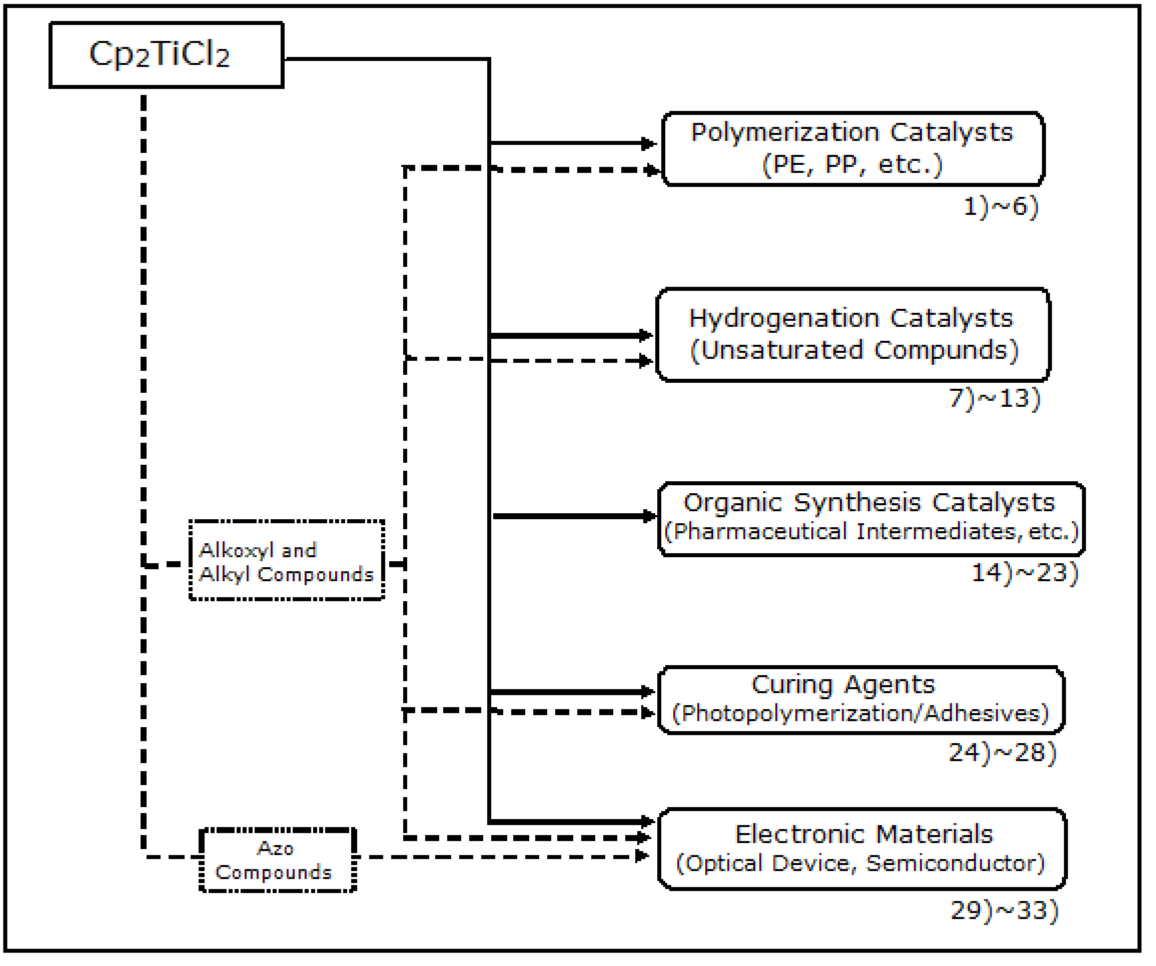


[1] G. Wilkinson, F. A. Cotton, *Progress in Inorganic Chemistry*, 1, 1-124 (1959)

B. Photolysis and Pyrolysis



7. Applications (Examples)



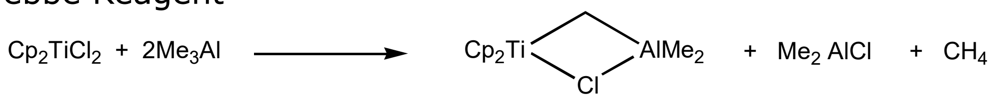
References for Applications:

1) *J. Polym. Sci.*, 3, 1729 (1965)
2) *Polym. Sci. Technol.*, 37, 239 (1988)
3) JP 01282214 A
4) DD 237671 A1
5) DD 282013 A5
6) JPH 8-12716 A
7) *Am. Chem. Soc. Div. Pet. Chem.*, 27, 816 (1982)
8) *J. Am. Chem. Soc.* 85, 4014 (1965)
9) JPH 7-90017 A
10) JPH 11-071426 A
11) *J. Organomet. Chem.*, 382, 69 (1990)
12) *J. Organomet. Chem.*, 384, C17-20 (1990)
13) USP-529807 (1990)
14) *Angew. Chem. Int Ed Eng.*, 18, 477 (1979)
15) *J. Organomet. Chem.*, 302, 281 (1986)
16) *Huaxua Xuebao*, 46, 703 (1988)
17) *J. Am. Chem. Soc.*, 110, 8561 (1988)
18) *Tetrahedron Lett.*, 31, 3105 (1990)
19) *Can. J. Chem.*, 68, 471 (1990)
20) *J. Am. Chem. Soc.*, 113, 5093 (1991)
21) *J. Chem. Soc. Chem. Commun.*, 13, 941 (1992)
22) *J. Am. Chem. Soc.*, 114, 2276 (1992)
23) EP 407804 A1
24) *Proceedings of Conference on Radiation Curing Asia* 461 (1988)
25) JPS 63-41484 A (or CHP 3101/86-2)
26) JPH 4-47680 B
27) JPH 6-65549 A
28) EP 401166 A2
29) *J. Organometal Chem.*, 111, 297 (1976)
30) *Appl. Phys. Lett.*, 43, 992 (1983)
31) *Proc Int Conf Chem Vapor Deposition.*, 11, 703 (1990)
32) JPH 6-65549 A
33) JPH 4-235994A

8. Application of Cp_2TiCl_2 in Organic Synthesis

A. Synthesis of Methylenation Reagent

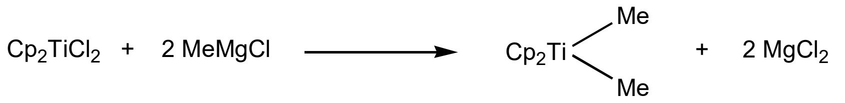
- Tebbe Reagent



Tebbe Reagent

J. Am. Chem. Soc., 100, 3611 (1978)

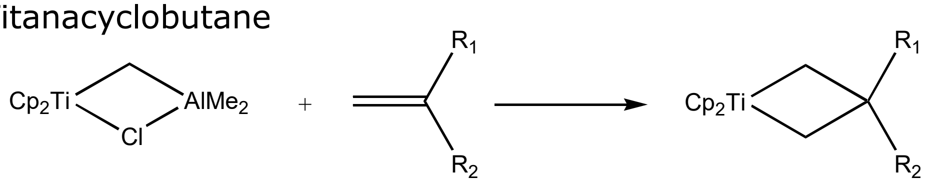
- Petasis Reagent



Petasis Reagent

J. Am. Chem. Soc., 112, 6392 (1990)

- Titanacyclobutane

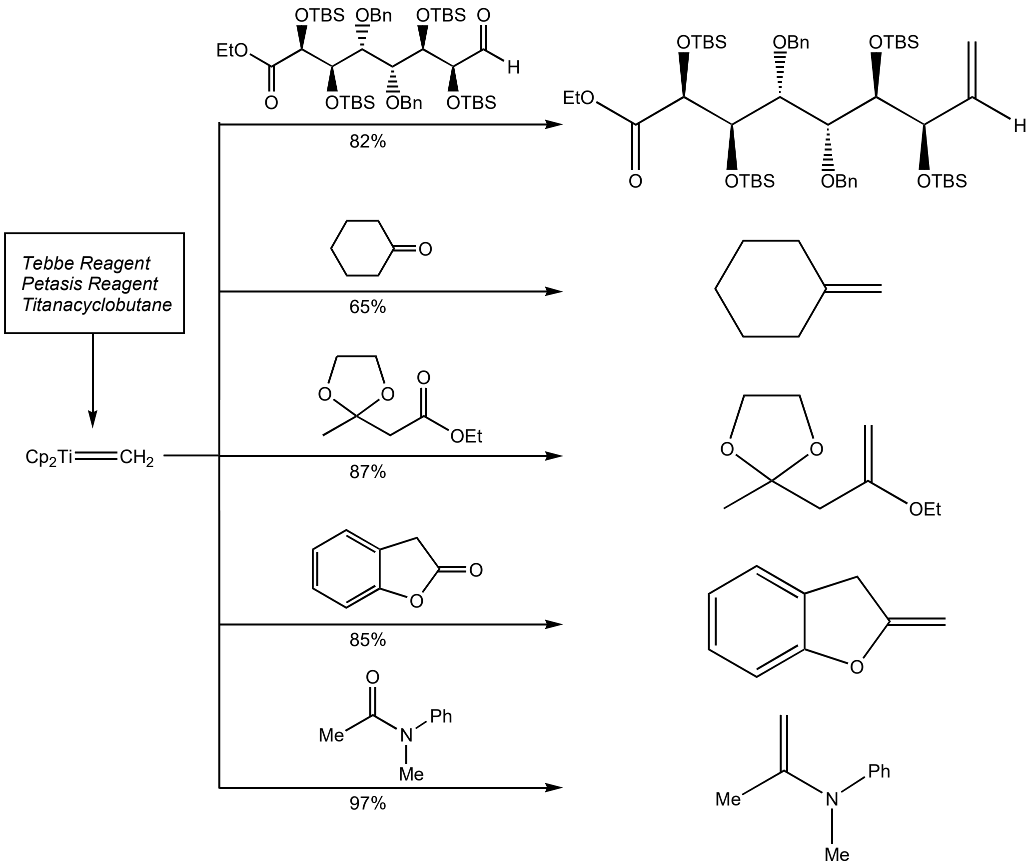


Tebbe reagent

Titanacyclobutane

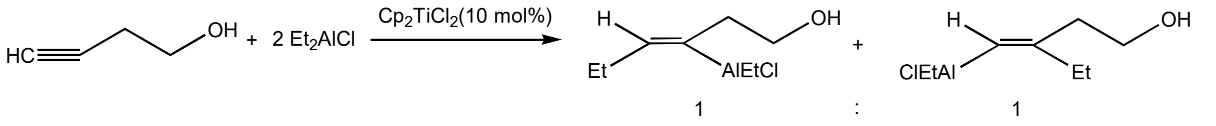
J. Am. Chem. Soc., 102, 6876 (1980)

B. Methylenation of Aldehydes, Ketones, Esters, Lactones, and Amides



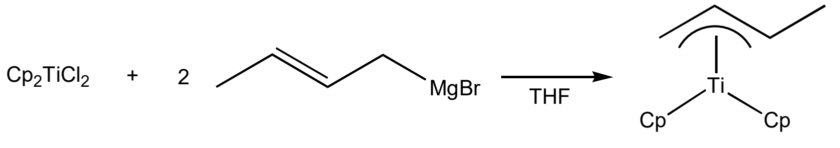
J. Am. Chem. Soc., 114, 2524 (1992)
J. Am. Chem. Soc., 100, 3611 (1978)
J. Am. Chem. Soc., 102, 3270 (1980)
J. Org. Chem., 50, 1212 (1985)

C. Cp_2TiCl_2-Catalyzed Carbometalation of Alkynols

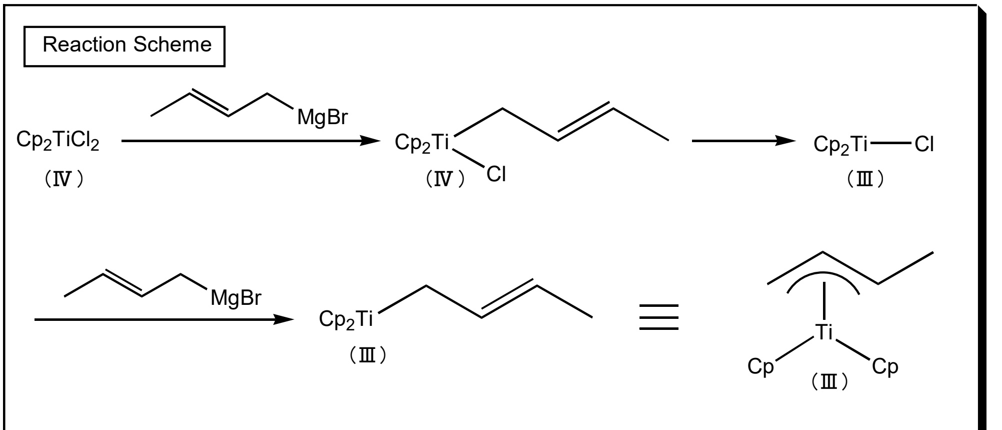


J. Org. Chem., 44, 3457 (1979)

D. π-Allyltitanium Compounds in Organic Synthesis



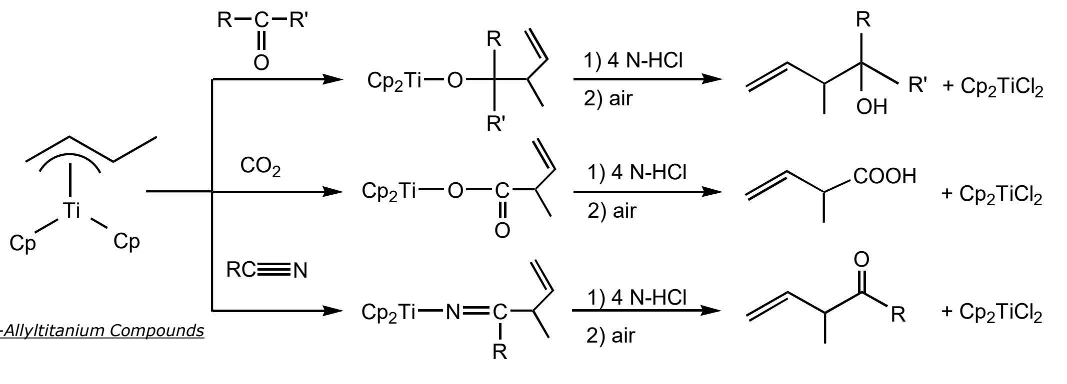
π-Allyltitanium Compounds



π-Allyltitanium Compounds

J. Organometal. Chem., 8, 115 (1967)

- Insertion Reactions



π-Allyltitanium Compounds

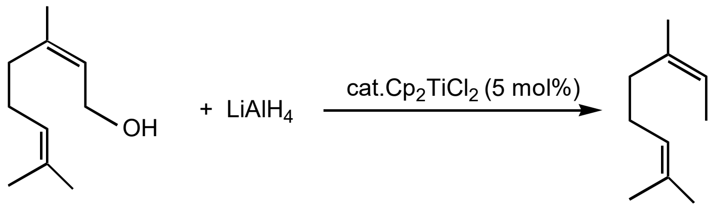
J. Chem. Soc., Chem. Commun., 342 (1981)
Tetrahedron Lett., 22, 243 (1981)
J. Chem. Soc., Chem. Commun., 180 (1981)

E. Hydroalumination of Olefins Catalyzed by Cp_2TiCl_2

$$NaAlH_4 + 4RCH{=}CH_2 \xrightarrow{\text{cat.}Cp_2TiCl_2\ (5\ \text{mol\%})} NaAl(CH_2CH_2R)_4$$

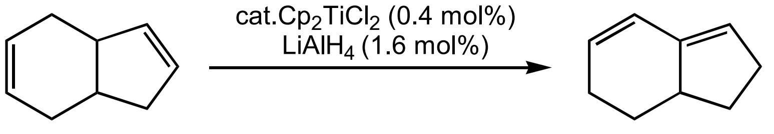
J. Org. Chem., 45, 1035 (1980)

F. Hydrogenolysis of Allyl Alcohols Catalyzed by Cp_2TiCl_2



Chem. Lett., 103 (1980)

G. Isomerization Catalyzed by Cp_2TiCl_2



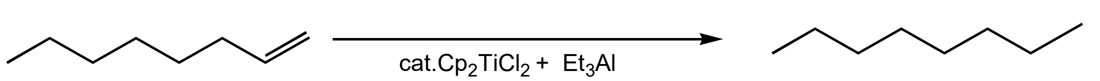
Tetrahedron Lett., 21, 637 (1980)

H. Olefin Metathesis Catalyzed by Cp_2TiCl_2

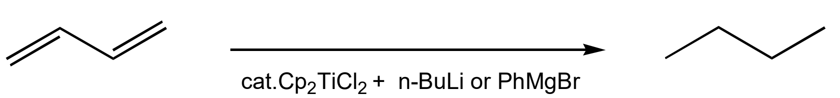
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOEt \underset{Cp_2TiMe_2\ (12\ \text{mol\%})}{\overset{WCl_6\ (10\ \text{mol\%})}{\rightleftharpoons}} EtO_2C(CH_2)_7CH{=}CH(CH_2)_7COOEt + CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3$$

Tetrahedron Lett., 21, 2955 (1980)

I. Hydrogenation of Olefins and Conjugated Diolefins Catalyzed by Cp_2TiCl_2



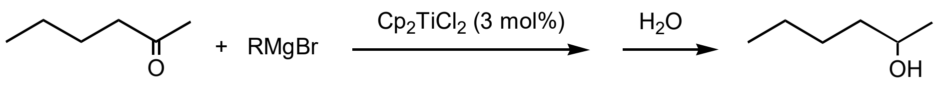
J. Am. Chem. Soc., 85, 4014 (1963)



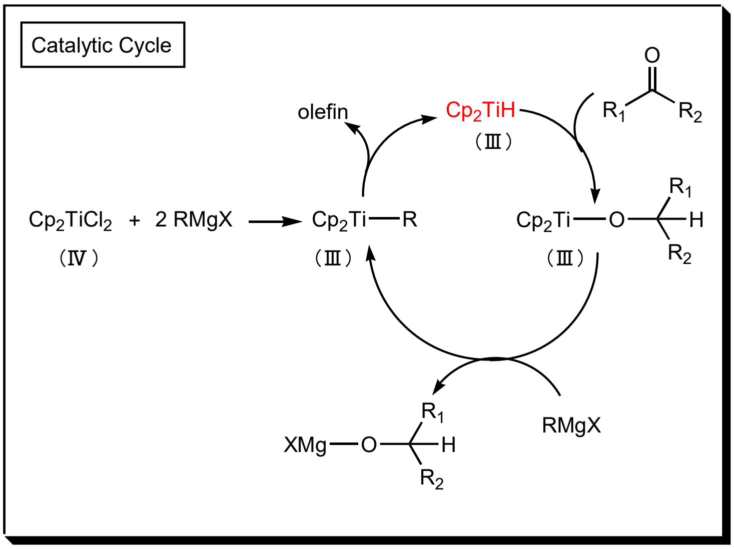
J. Org. Chem., 33, 1689 (1968)

J. Cp_2TiCl_2-Catalyzed Reduction Using Grignard Reagent

- Cp_2TiCl_2-Catalyzed Reduction of Ketones and Aldehydes

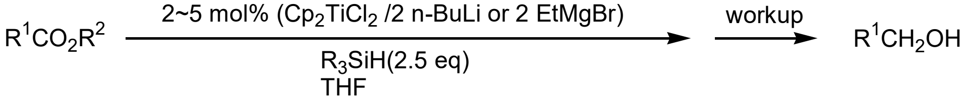


(R=propyl, iso-propyl,2-methylbutyl, hexyl etc.)

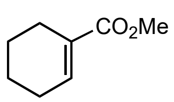
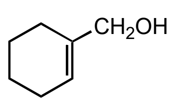
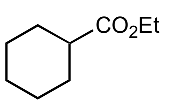
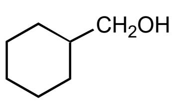
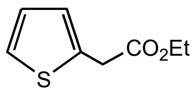
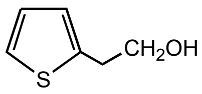


Tetrahedron Lett., 21, 2171 (1980)

- Cp_2TiCl_2-Catalyzed Reduction of Esters Using Polymethylhydrosiloxane as the Stoichiometoric Reductant

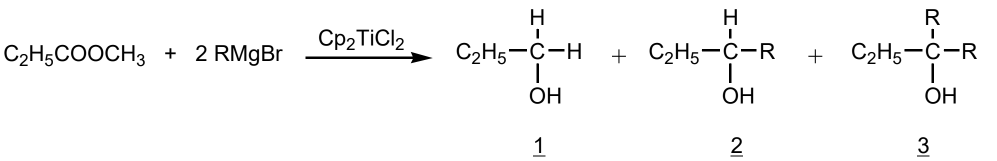


R_3SiH ; poly-(methylhydrosiloxane)

Ester	Product	mol% Cat	n-BuLi or EtMgBr	Time(h)	Yield(%)
$PhCO_2Me$	$PhCH_2OH$	2	EtMgBr	1.5	94
		5	n-BuLi	1	65
		5	EtMgBr	5	88
		5	EtMgBr	17.5	92

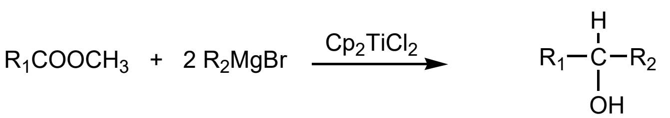
J. Org. Chem., 59, 4323 (1994)

- Distribution of The Cp_2TiCl_2-Catalyzed Grignard Reaction Products



R in RMgBr	mol% of Cp_2TiCl_2	Product Distribution(%) 1	2	3	Total Yield(%)
$CH_3CH_2CH_2$	0	4	0	96	99
	1	9	90	1	97
	4	50	50	0	96
	8	78	22	0	98
$(CH_3)_2CHCH_2$	0	0	60	36	86
	0.13	4	96	0	92
	1	73	27	0	99
	2	96	4	0	94

- The Yields of Secondary Alcohols from The Cp_2TiCl_2-Catalyzed Grignard Reactions with Esters



Secondary Alcohol

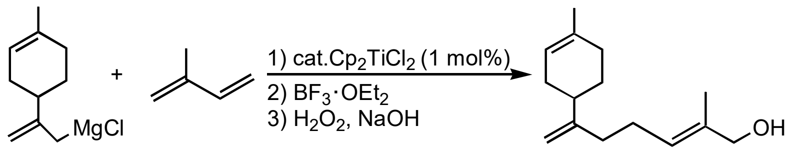
Starting Material: Ester R_1 in R_1COOCH_3	Grignard Reagent R_2 in R_2MgBr	Catalyst Content (mol%)	Yield of R_1R_2CHOH (%)
C_6H_{13}	CH_3	1	*
C_6H_{13}	CH_3CH_2	1	*
C_2H_5	$CH_3CH_2CH_2$	1	83
C_6H_{13}		1	81
$(CH_3)_2CH$		1	75
$C_6H_5CH_2$		1	88
C_2H_5	$(CH_3)_2CH$	0.4	74
C_2H_5	$(CH_3)_2CHCH_2$	0.13	85
CH_3	C_6H_{13}	1	91
C_2H_5	C_6H_5	1	*

* No secondary alcohol was obtained.

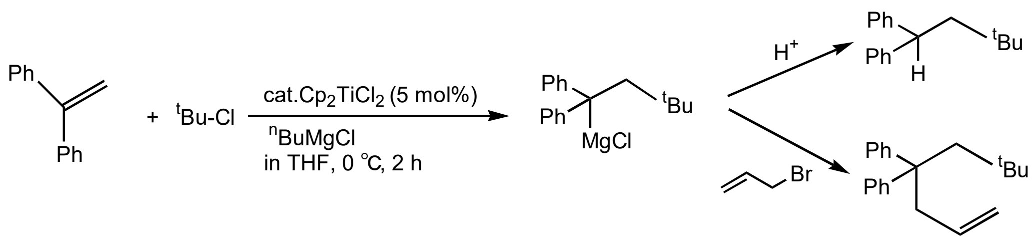
Tetrahedron Lett., 21, 2175 (1980)

K. Grignard Exchange Reactions of Alkenes, Dienes, and Alkynes

- Cp_2TiCl_2-Catalyzed Carbomagnesation

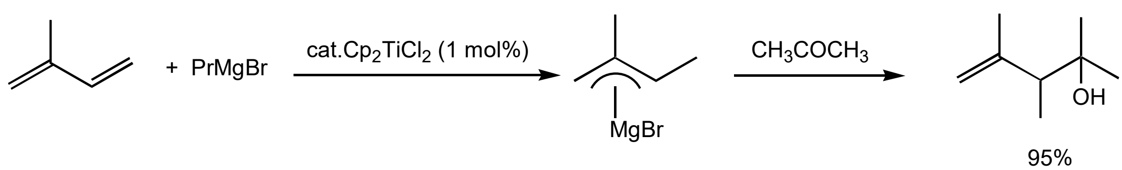


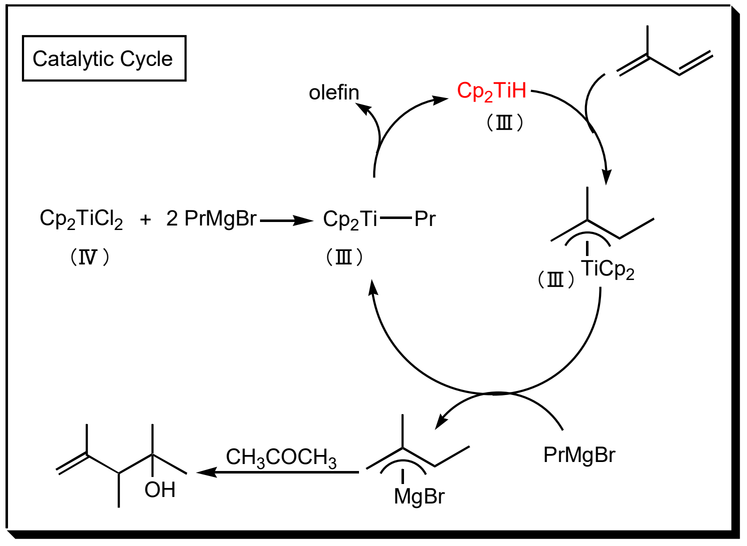
J. Am. Chem. Soc., 97, 6870 (1975)



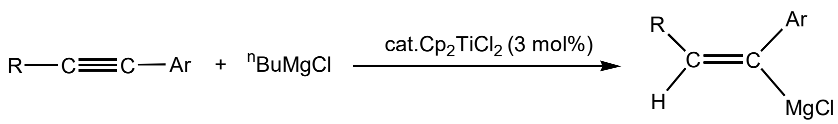
J. Org. Chem., 69, 573 (2004)

- Cp_2TiCl_2-Catalyzed Hydromagnesation





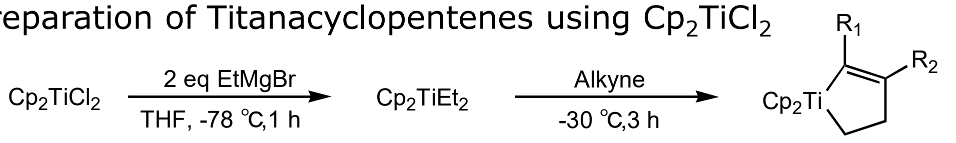
Tetrahedron Lett., 21, 365 (1980)

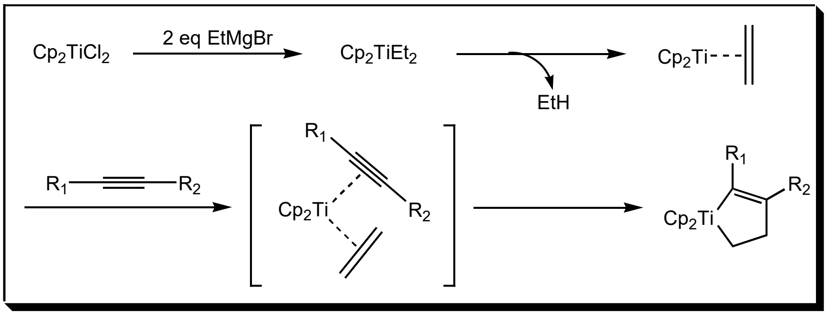


Tetrahedron Lett., 22, 85 (1981)

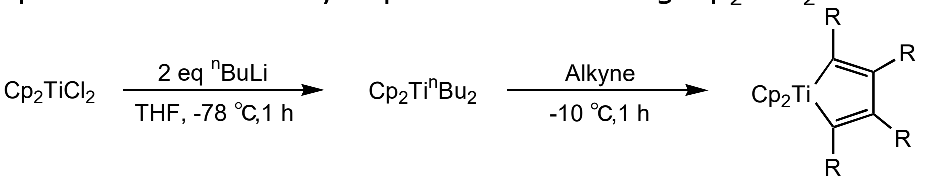
L. Preparation of Titanacyclopentenes and -pentadienes using Cp_2TiCl_2

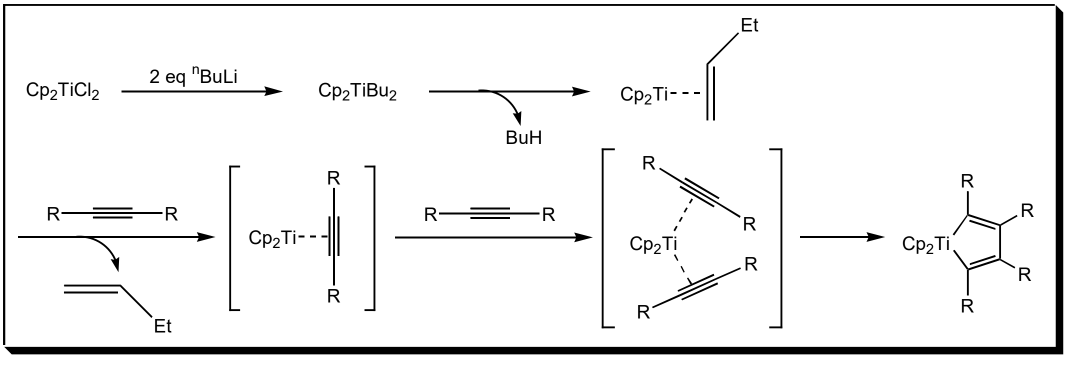
- Preparation of Titanacyclopentenes using Cp_2TiCl_2





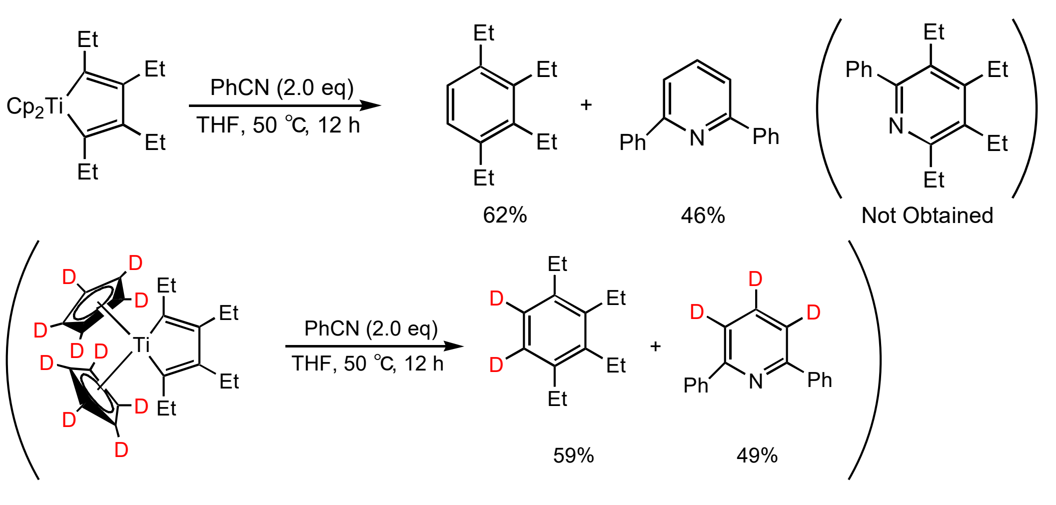
- Preparation of Titanacyclopentadienes using Cp_2TiCl_2





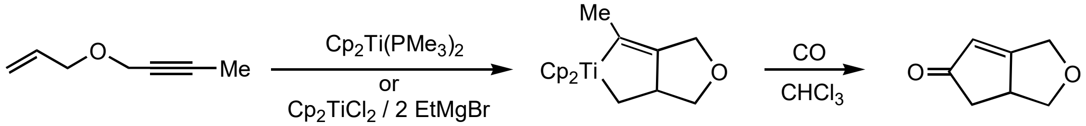
J. Organometal. Chem., 633, 18 (2001)

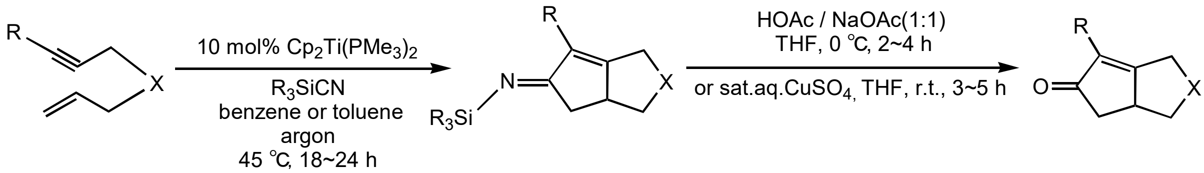
M. Double C-C Bond Cleavage of Cyclopentadienyl Ligand

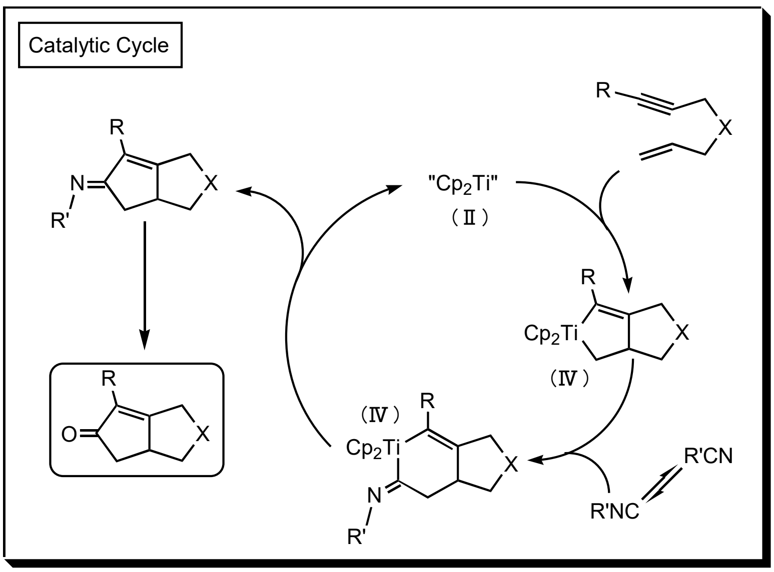


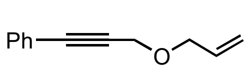
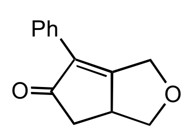
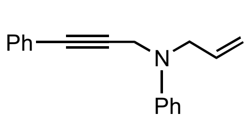
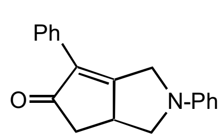
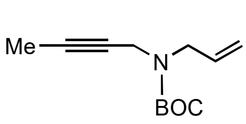
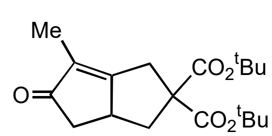
J. Am. Chem. Soc., 125, 9568 (2003)

N. Enyne Cyclization by Cp_2TiCl_2



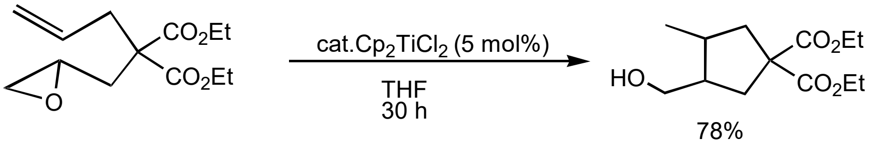


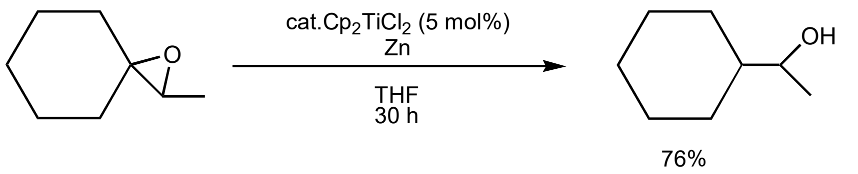


Starting Material	Cyanide	Product	Yield(%)
	Me_3SiCN		80
	Me_3SiCN		44
	Et_3SiCN		43

J. Am. Chem. Soc., 116, 8593 (1994)

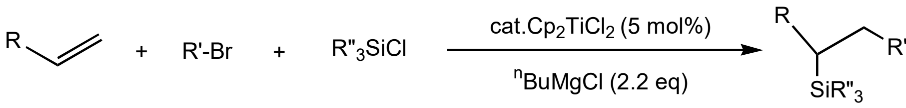
O. Reductive Opening of Epoxides

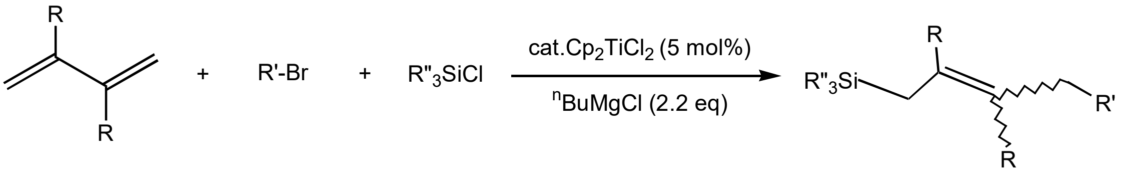


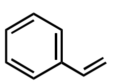
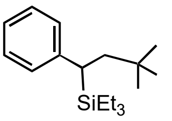
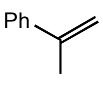
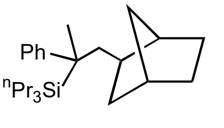
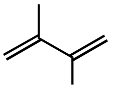
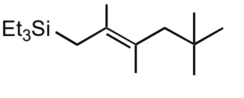


Angew. Chem. Int. Ed., 37, (1/2), 101 (1998)

P. Carbosilylation of Alkenes and Dienes Using Alkyl Halides and Chlorosilanes

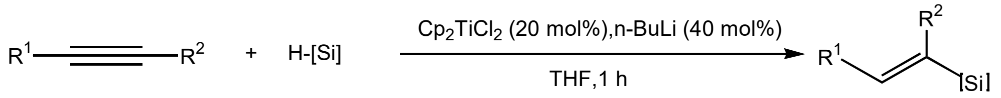




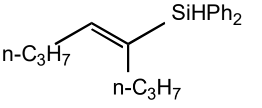
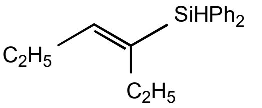
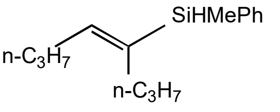
Starting Material	R-X	R'$_3$Si-Cl	Time(h)	Product	Yield(%)
	^{t}Bu-Br	Et_3Si-Cl	1		96
	2-Norbornyl-Br	^{n}Pr$_3$Si-Cl	6		85
	^{t}Bu-Br	Et_3Si-Cl	2		83 E/Z=96/4

J. Org. Chem., 65, (17), 5291 (2000)

Q. Regioselective Syn-Hydrosilation of Alkynes



([Si] = $SiHPh_2$, SiHMePh, SiH_2Ph)

Alkyne	Hydrosilane	Alkenylsilane	Yield(%)
$n\text{-}C_3H_7C\equiv C\,n\text{-}C_3H_7$	H-$SiHPh_2$		87
Et$C\equiv C$Et	H-$SiHPh_2$		96
$n\text{-}C_3H_7C\equiv C\,n\text{-}C_3H_7$	H-SiHMePh		97

Org. Lett., 5, (19), 3479 (2003)

9. Storage and Safety Handling Etc.

- Storage and Safety Handling:
  Storage:
  Store in a cool, dry, dark place with reasonable ventilation.
  Avoid direct sunlight to the container.

  Safety Handling:
  Open the product in a dry, inert gas atmosphere.
  Use dry utensils or dehydrated low-moisture solvents.
  After opening the container, displace the product with inert gas, then seal it and store it according to the storage method.

- First-aid Treatment:
  If Titanocene Dichloride adheres to the hands or face, it may cause allergic breakouts. It must be immediately washed off with an ample amount of clean water. For protection, use protective devices as follows：
  Rubber gloves
  Protective glasses
  Dust-protection masks
  Etc.

- Fire Fighting Procedure:
  Titanocene Dichloride is a flammable chemical.
  If a fire breaks out, move all the containers to a safe place where the fire cannot reach. In case this chemical catches fire, use plenty of water or a powder fire extinguisher to fight the fire.

- Waste Disposal:
  Waste disposal can be accomplished either by hydrolysis or by incineration.
  After dissolving the product in acid or an alkaline aqueous solution, separate the titanium hydroxide by a neutralization treatment.
  Or mix the product with a combustible solvent, incinerate, and dispose of the titanium oxide.
  For either disposal method, the resulting waste must then be disposed in accordance with industrial waste regulations.

- Toxicological Information:
  Acute Toxicity: ipr – rat LD_{50} 25mg/kg
  ivn – mus LD_{50} 180mg/kg

■ The information in this document is as of December 2023.

■ Contact:

(Manufacturing/Engineering Department)
NICHIA CORPORATION TOKUSHIMA PLANT
Metal Complex Manufacturing Dept.
224 Hiraishi Ebisuno, Kawauchi-Cho, Tokushima-Shi, TOKUSHIMA 771-0132, JAPAN
TEL: +81-88-665-2311

(Sales)
NICHIA CORPORATION TOKYO SALES OFFICE
13F Tamachi Center Building34-7, Shiba 5-Chome, Minato-Ku, TOKYO 108-0014, JAPAN
TEL : +81- 3-3456-3784