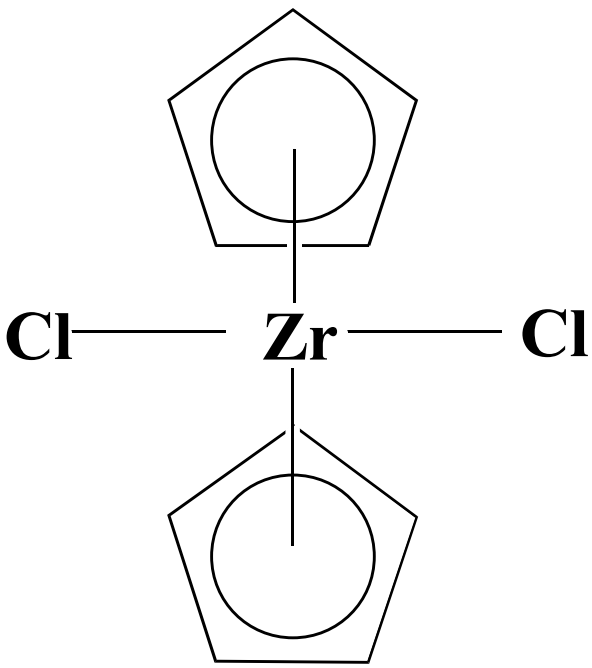
Zirconocene Dichloride

Technical Data



NICHIA CORPORATION

Contents:

1. General Features:

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

2) The product can be used as a raw material for various derivatives that become high-function materials.
Examples: Schwartz Reagent, Negishi Reagent

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

2. Product Guide

Physical and Chemical Properties:

Chemical Name: Bis-Cyclopentadienyl Zirconium Dichloride

Molecular Formula: $(C_5H_5)_2ZrCl_2$

Molecular Weight: 292.32

Appearance: White needle crystal

Melting Point: 242~245°C

Sublimation Point: 150~180°C (29.1 kPa)

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

Decomposability: Zirconocene Dichloride gradually decomposes from the moisture and oxygen in air if left in the open air. (Forming Hydrochloride and $[ZrCl(C_5H_5)_2]_2O$)

Assay and Impurities:

Analytical data of Zirconocene Dichloride:

	Specifications	Typical Data	Theoretical Value
Zr	≥30.60%	31.16%	31.21%
Cl	≥23.80%	24.20%	24.26%

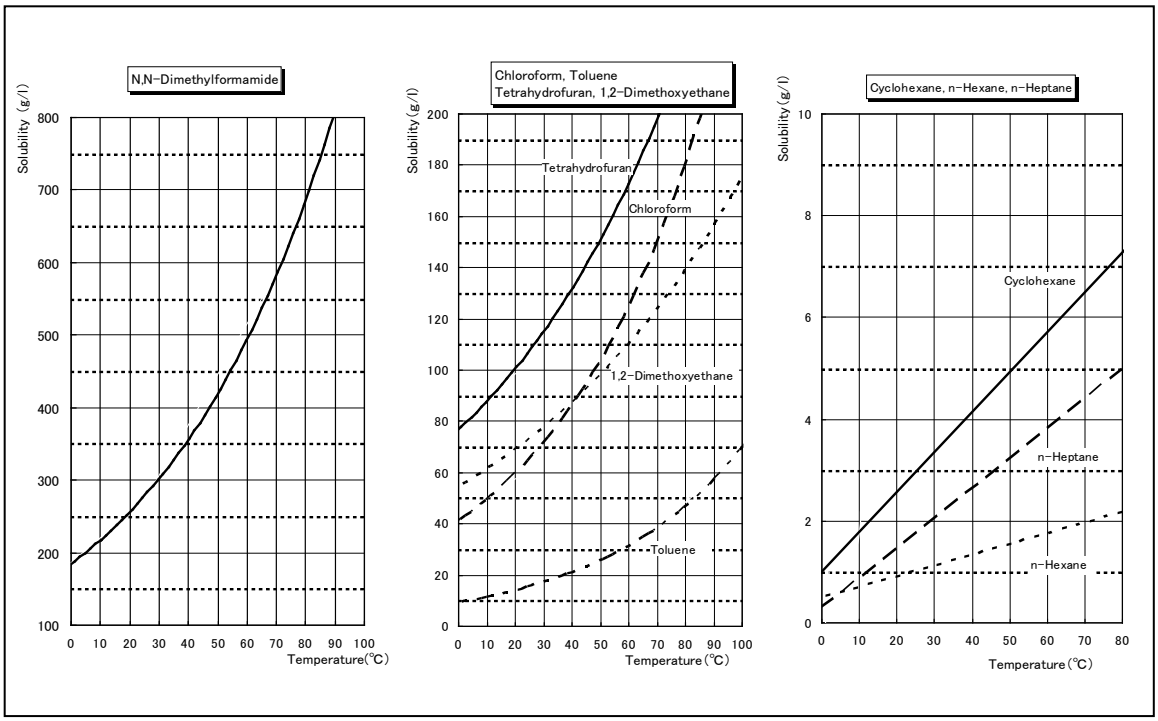
Comparison with reagent products:

Suppliers		Zr(%)[1]	Cl(%)[1]	Cl/Zr (Molar Ratio)	Notes
Nichia		31.16	24.20	2.00	White Needle Crystal
Reagent	A	31.19	24.22	2.00	Colored Crystal
	B	31.09	24.24	2.01	
	C	31.18	24.20	2.00	
	D	31.20	24.21	2.00	

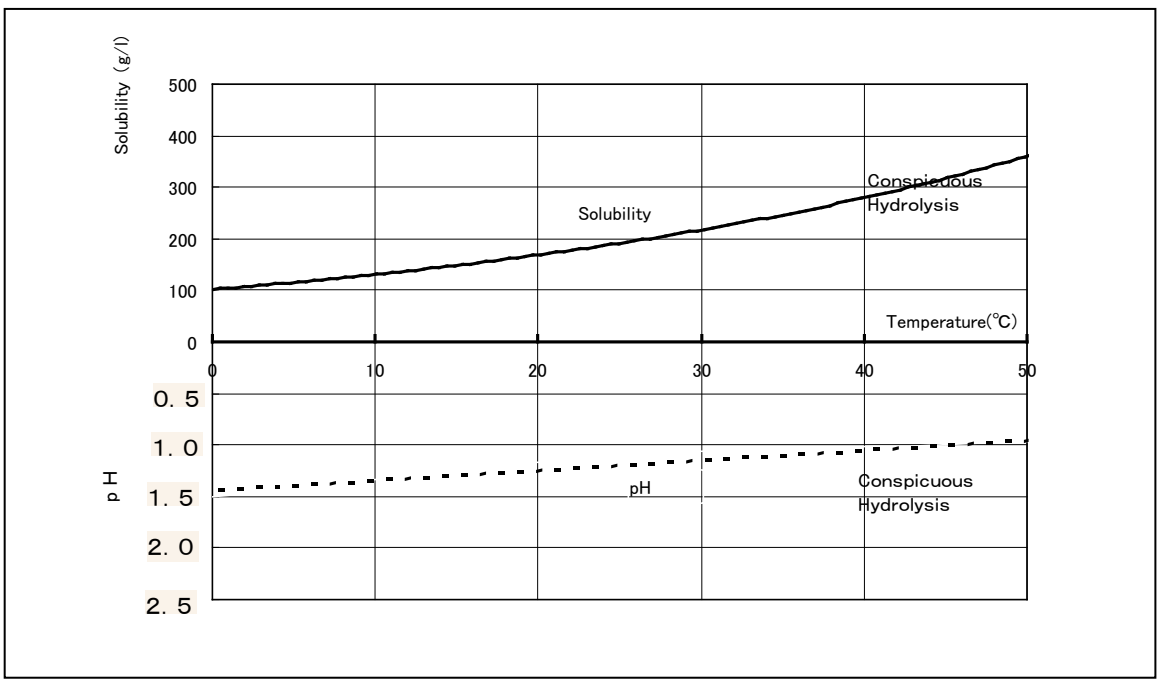
[1] Zr and Cl contents were analyzed by Nichia.

Packaging: Packing units/formats are available upon request.

3. Solubility in Various Solvents

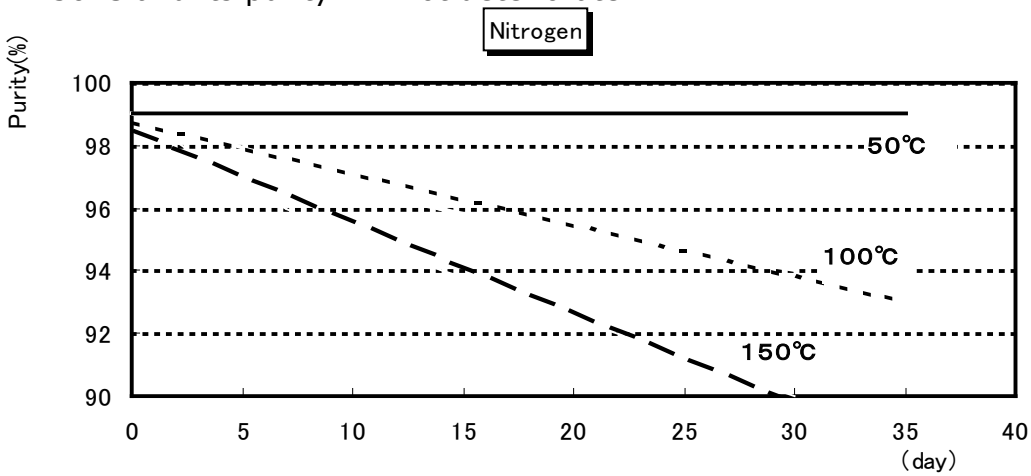


4. Solubility in Water and pH

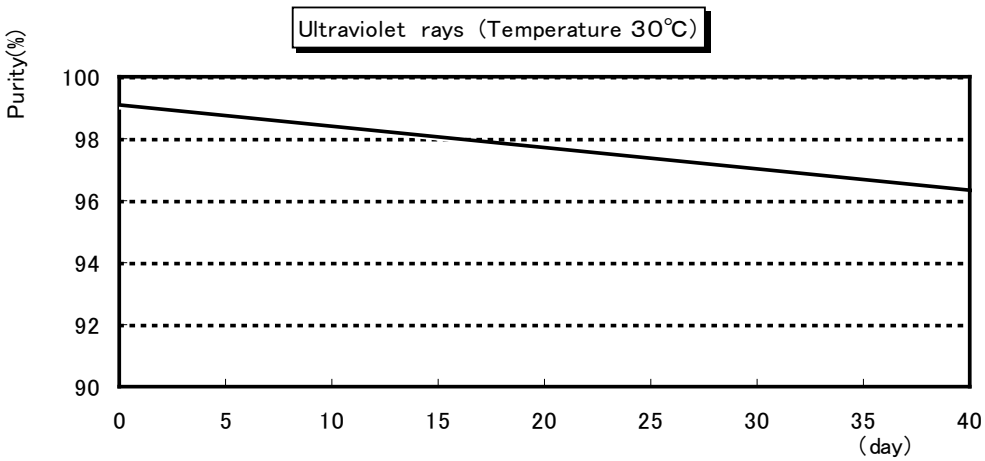


5. Stability

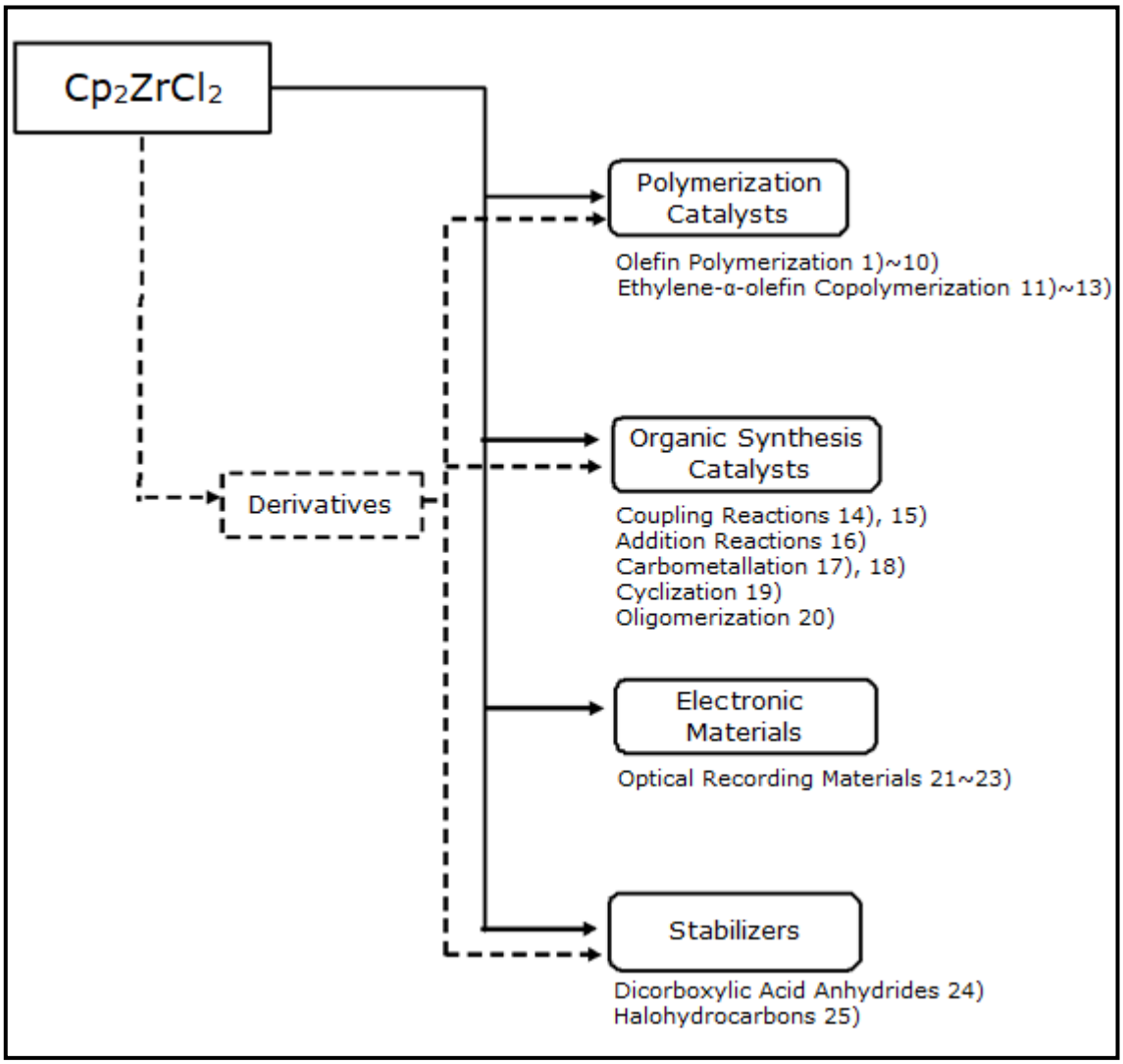
1) Zirconocene Dichloride is stable in a nitrogen atmosphere at ≤50°C and its purity will not deteriorate.



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



6. Applications (Examples)

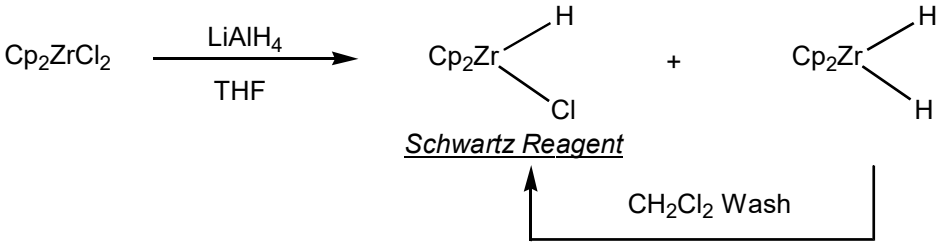


References for Applications:

1) *Inorganica Chimica Acta*., 270, 20 (1995)
2) *Acta Polytech. Scand. Chem. Technol. Ser*., 227, 1-50 (1995)
3) *J. Polym. Sci., part A :Polym. Chem*., 26,(11), 3089 (1988)
4) JPH 11-035617A
5) JPH 11-001511A
6) JPH 5-331219A
7) JPH 9-302017A
8) JPH 10-316695A
9) JPH 10-130316A
10) JPH 9-328508A
11) JPH 10-182749A
12) JPH 9-241326A
13) JPH 10-254094A
14) *J. Am. Chem. Soc*., 109, 2393 (1987)
15) *J. Am. Chem. Soc*., 108, 7411 (1986)
16) *J. Am. Chem. Soc*., 102, 1333 (1980)
17) *J. Am. Chem. Soc*., 108, 6639 (1985)
18) *J. Organometal. Chem*., 304, 17 (1956)
19) *Tetrahedron Lett*., 28, 917 (1987)
20) *Inorganica Chimica Acta*., 270, 20 (1998)
21) JPS 63-165181A
22) JPS 63-165182A
23) JPS 63-168393A
24) JPS 48-028405A
25) JPH 5-156062A

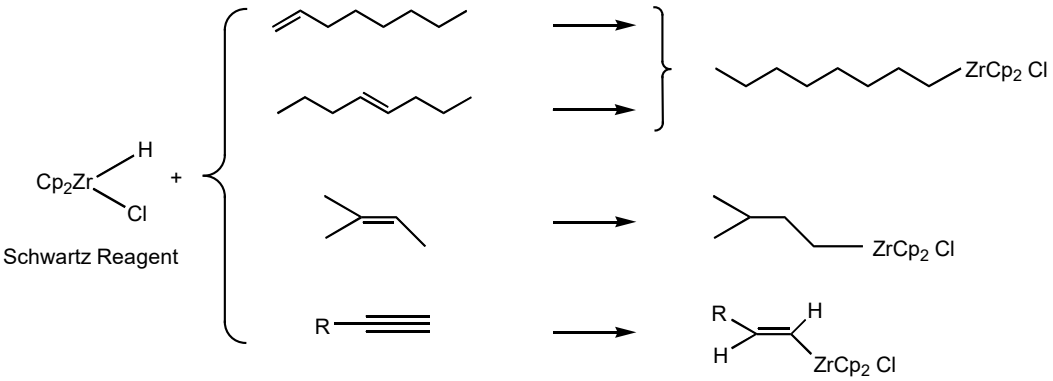
7. Application in Organic Synthesis

A. Schwartz Reagent



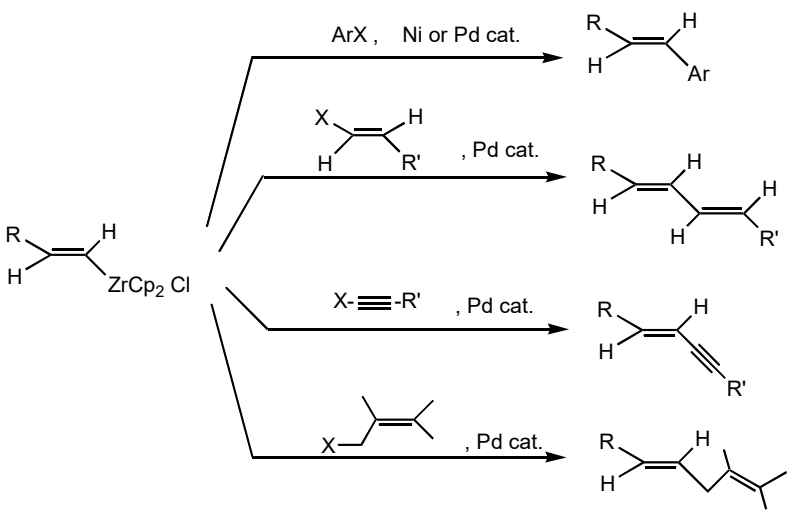
Tetrahedron Lett., 28, 3895 (1987)
J.Org.Chem., 56, 2590 (1991)
Tetrahedron Lett., 31, 7257 (1990)

- Hydrozirconation



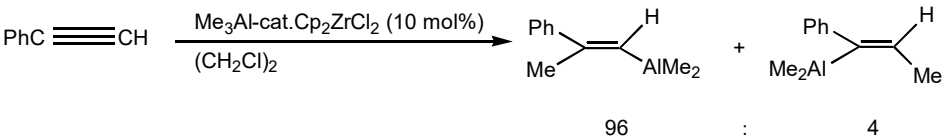
Angew.Chem.Int.Ed.Eng., 15, 333 (1976)

B. Cross-coupling Reaction of Alkenyl Zirconium Compounds

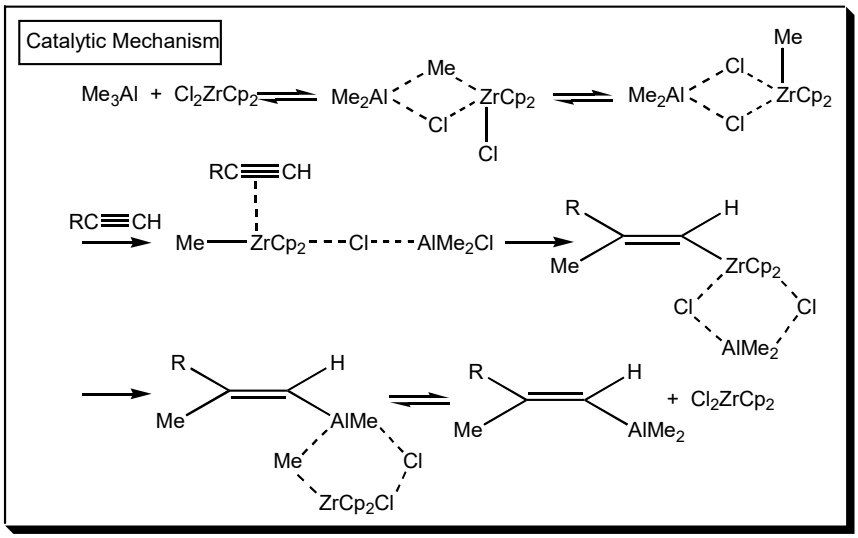


Journal of Synthetic Organic Chemistry Japan, 47, 2 (1989)
J.Am.Chem.Soc., 109, 2393 (1987)
Tetrahedron Lett., 30, 4299 (1989)

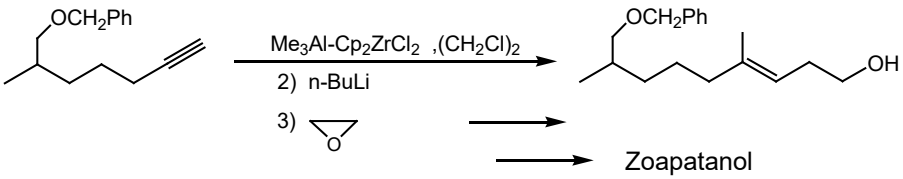
C. Cp_2ZrCl_2-Catalyzed Carbometalation



96 : 4

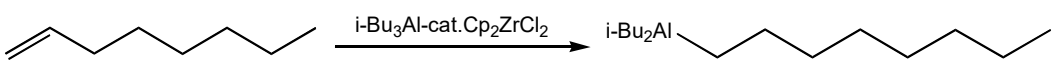


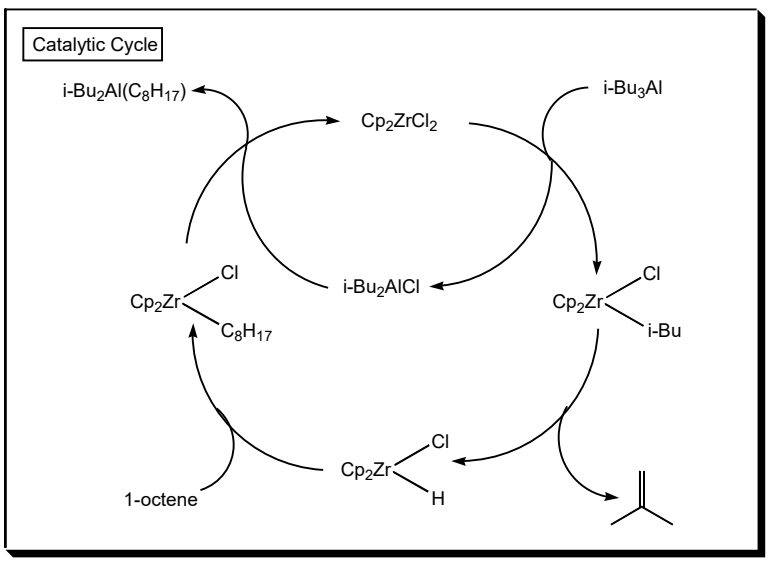
J.Am.Chem.Soc., 108, 6639 (1985)
Aldrichim. Acta, 18, 31 (1985)
Synthesis, 1 (1988)



J.Chem.Soc., Perakin Trans., I, 1589 (1985)

D. Cp_2ZrCl_2-Catalyzed Hydrometalation

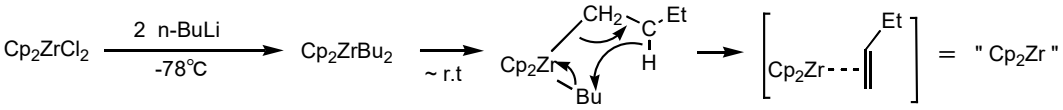




Tetrahedron. Lett., 21, 1501 (1985)
Pure. Appl. Chem., 53, 2333 (1981)

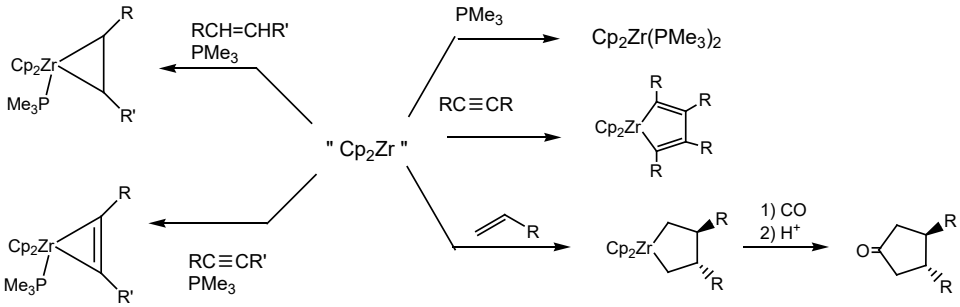
Organic Synthesis Using Zirconocene(II) Complexes

E. Negishi Reagent



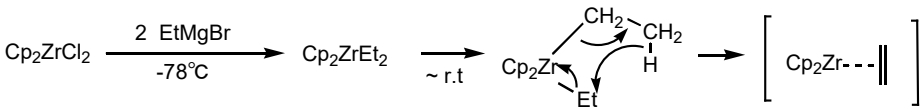
Tetrahedron Lett., 27, 2829 (1986)

- C-C Bond Formation Reactions Using "Cp_2Zr"

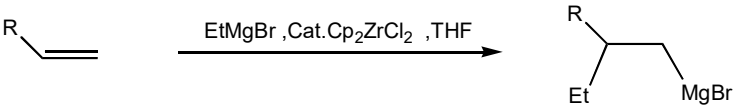


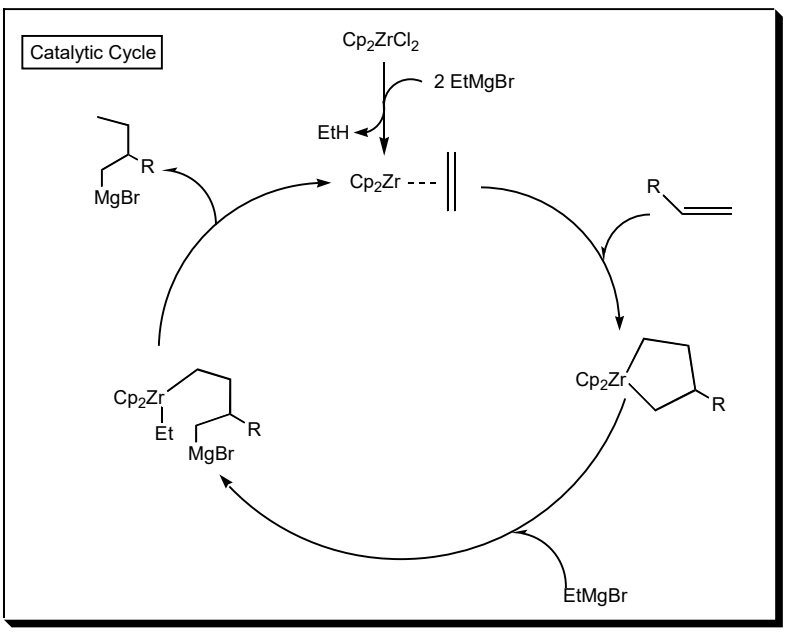
Journal of Synthetic Organic Chemistry Japan, 47, 2 (1989)
Synthesis., 1 (1988)
Aldrichim. Acta, 18, 31 (1985)
Chem.Rev.,88, 1047 (1989)

F. Zirconocene-Ethylene Complex



- C-C Bond Formation Reactions Using Zirconocene-Ethylene Complex

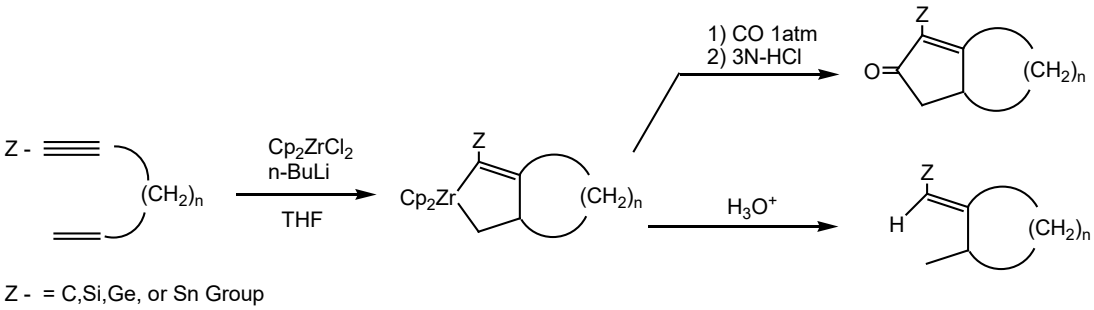




J. Am. Chem. Soc. 113, 6266 (1991)

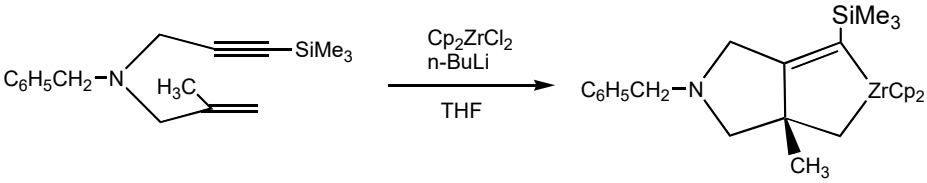
Organic Synthesis Using Zirconocene(II) Complexes

G. Intramolecular Bicyclization Reactions of Enynes Using "Cp_2Zr"

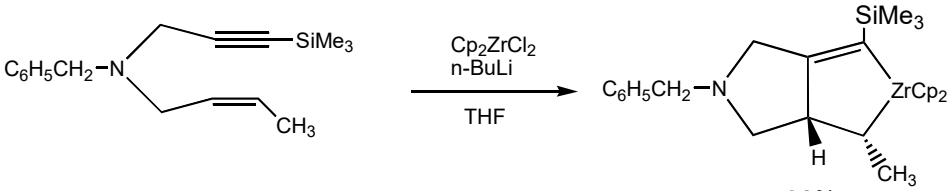


Z - = C,Si,Ge, or Sn Group

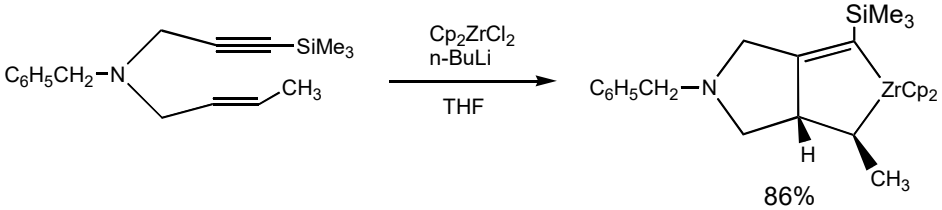
Tetrahedron Lett., 27, 2829 (1986)
J.Am.Chem.Soc., 107, 2568 (1985)
Journal of Synthetic Organic Chemistry Japan, 47, 2 (1989)



95%



92%

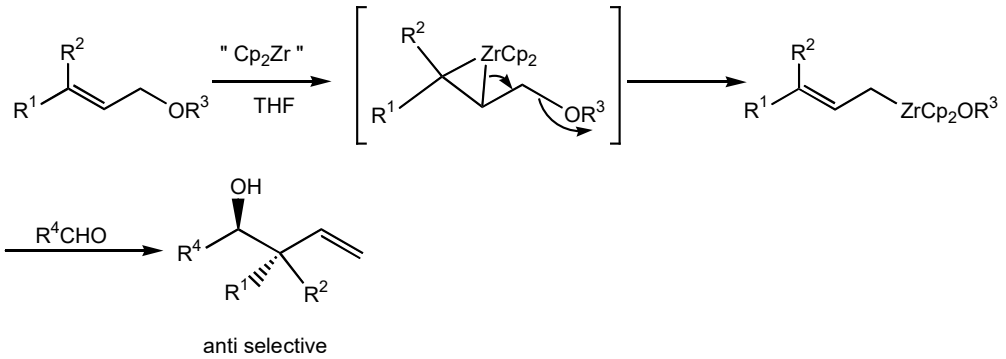


86%

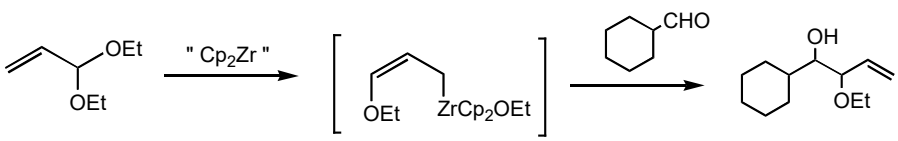
Tetrahedron Lett., 27, 2829 (1986)
Journal of Synthetic Organic Chemistry Japan, 47, 2 (1989)

Organic Synthesis Using Zirconocene(II) Complexes

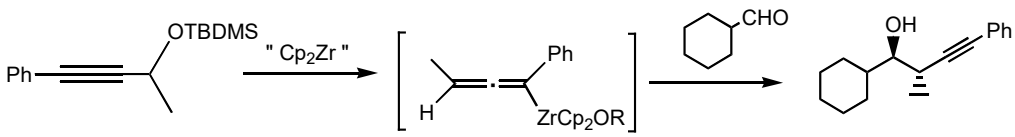
H. Preparation and Reactions of Allylic Zirconium Species



Entry	R^1	R^2	R^3	R^4	Yield (%)	anti : syn
1	Ph	H	Me	Ph	79	10 : 1
2	Ph	H	Bn	Ph	89	15 : 1
3	Ph	H	TBDMS	Ph	96	23 : 1
4	Ph	H	TBDMS	iPr	96	49 : 1
5	Me	H	TBDMS	Ph	41	——



without $BF_3 \cdot OEt_2$, 59%, anti/syn=14/86
with $BF_3 \cdot OEt_2$, 85%, anti/syn=77/23

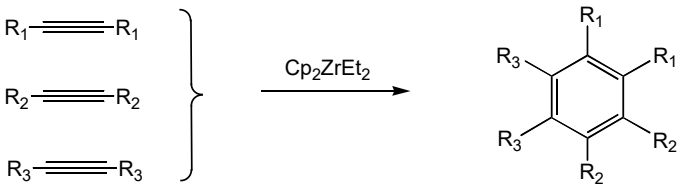


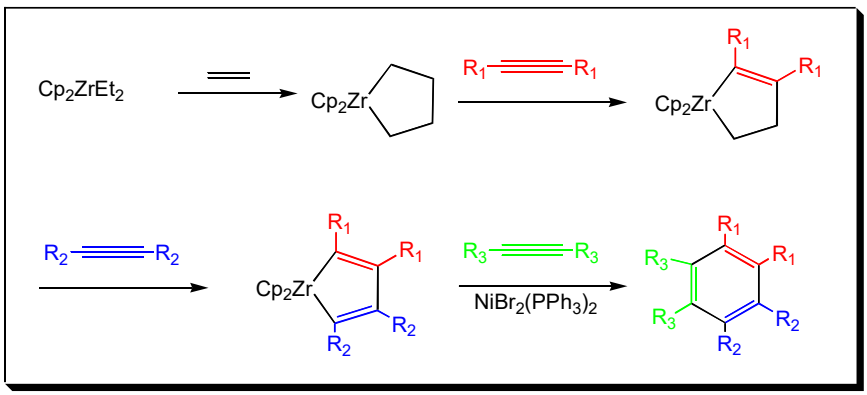
73%, anti/syn=22/1

Yakugaku Zasshi, 123, 933 (2003)

Organic Synthesis Using Zirconocene(II) Complexes

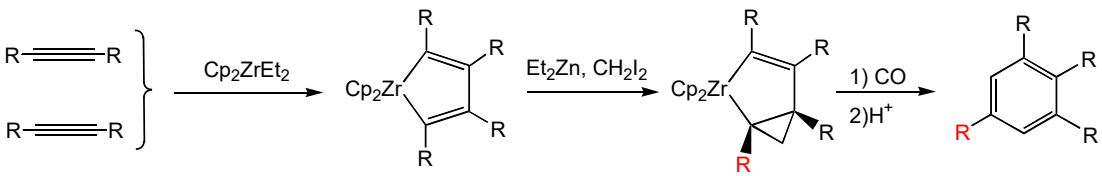
I. Synthesis of Benzene Derivatives Using Zirconacyclopentadienes





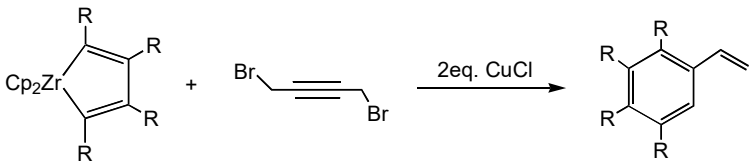
J.Am.Chem.Soc., 121, 11093 (1999)

- Synthesis of 1,2,3,5-Tetrasubstituted Benzene Derivatives



J.Am.Chem.Soc., 124, 388 (2002)

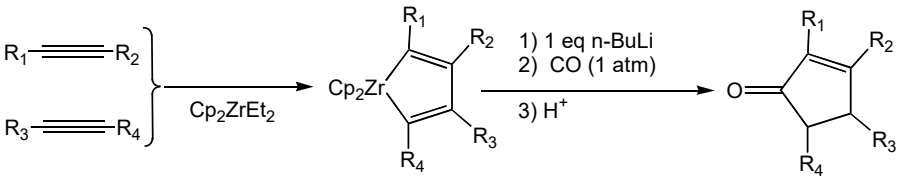
- Synthesis of Benzene Derivatives Mediated by Copper(I) Salts

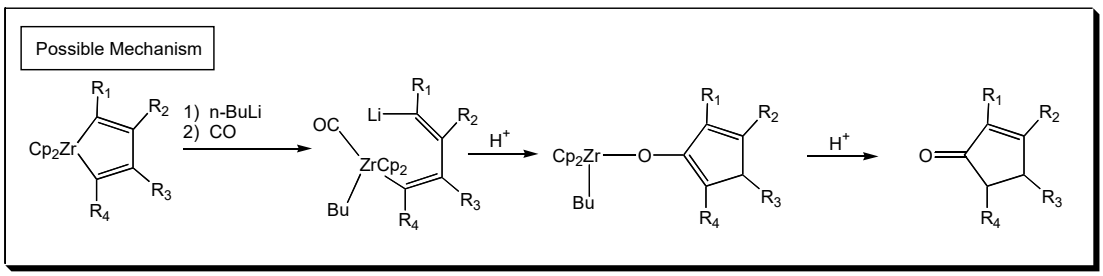


Tetrahedron 58, 1107 (2002)

Organic Synthesis Using Zirconocene(II) Complexes

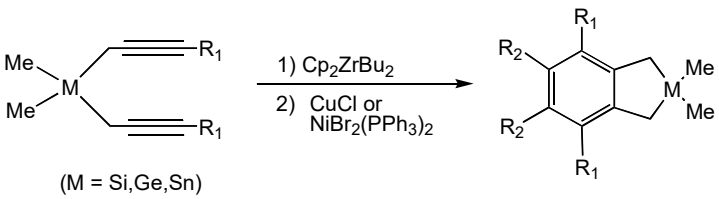
- Synthesis of Cyclopentenones Using Zirconacyclopentadienes





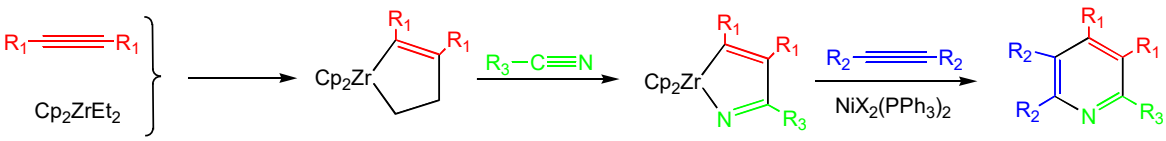
J.Am.Chem.Soc., 121, 1094 (1999)

- Synthesis of Benzoheterocyclic Compounds Using Zirconacyclopentadienes



Heterocycles., 54, 943 (2001)

- Synthesis of Pyridine Derivatives Using Zirconacyclopentadienes



J.Am.Chem.Soc., 124, 5059 (2002)

8. 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 Zirconocene 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:

  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 zirconium hydroxide by a neutralization treatment.
  Or mix the product with a combustible solvent, incinerate, and dispose of the zirconium 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} 30mg/kg

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

■ Contact:

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

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NICHIA CORPORATION TOKYO SALES OFFICE
13F Tamachi Center Building34-7, Shiba 5-Chome, Minato-Ku, TOKYO 108-0014, JAPAN
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