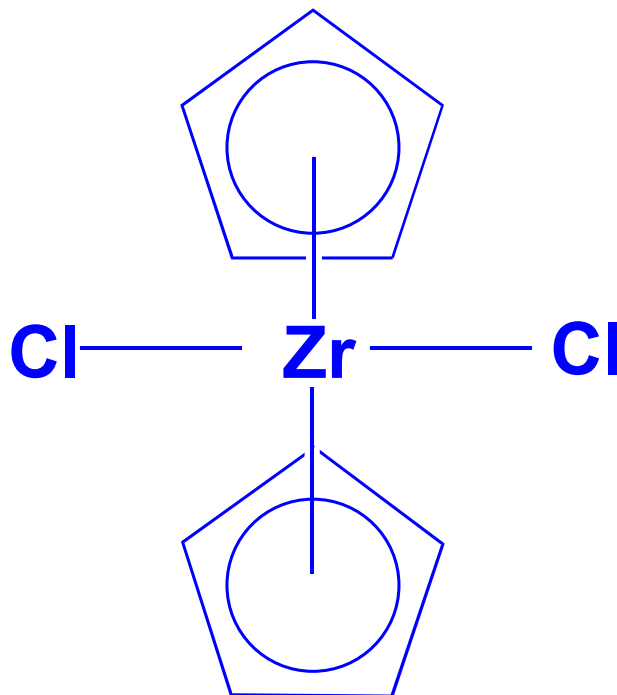


Zirconocene Dichloride

Technical Data



NICHIA CORPORATION

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 - ◆ Synthesis of Benzene Derivatives Using Zirconacyclopentadienes
8. Storage and Safety Handling etc.

1. General Features

- (1) Technologies involved were developed by Nichia's original ideas.
- (2) Consistently high/uniform quality was realized by the strict manufacturing process/quality control.
ex ; Schwartz Reagent, Negishi Reagent

We have strong customer-service engineering team in our V-plant listed on the last page. Please feel free to contact us at the nearest Nichia sales office if you are interested in Cp_2ZrCl_2 or other Zirconocene derivatives.

2. Product Guide

2-1. Physical and Chemical Properties

Chemical Name : Bis-Cyclopentadienyl Zirconium Dichloride
Zirconocene 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 Protic Solvents.
Slightly soluble in Aliphatic Hydrocarbon.

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

2-2. Assay and Impurities

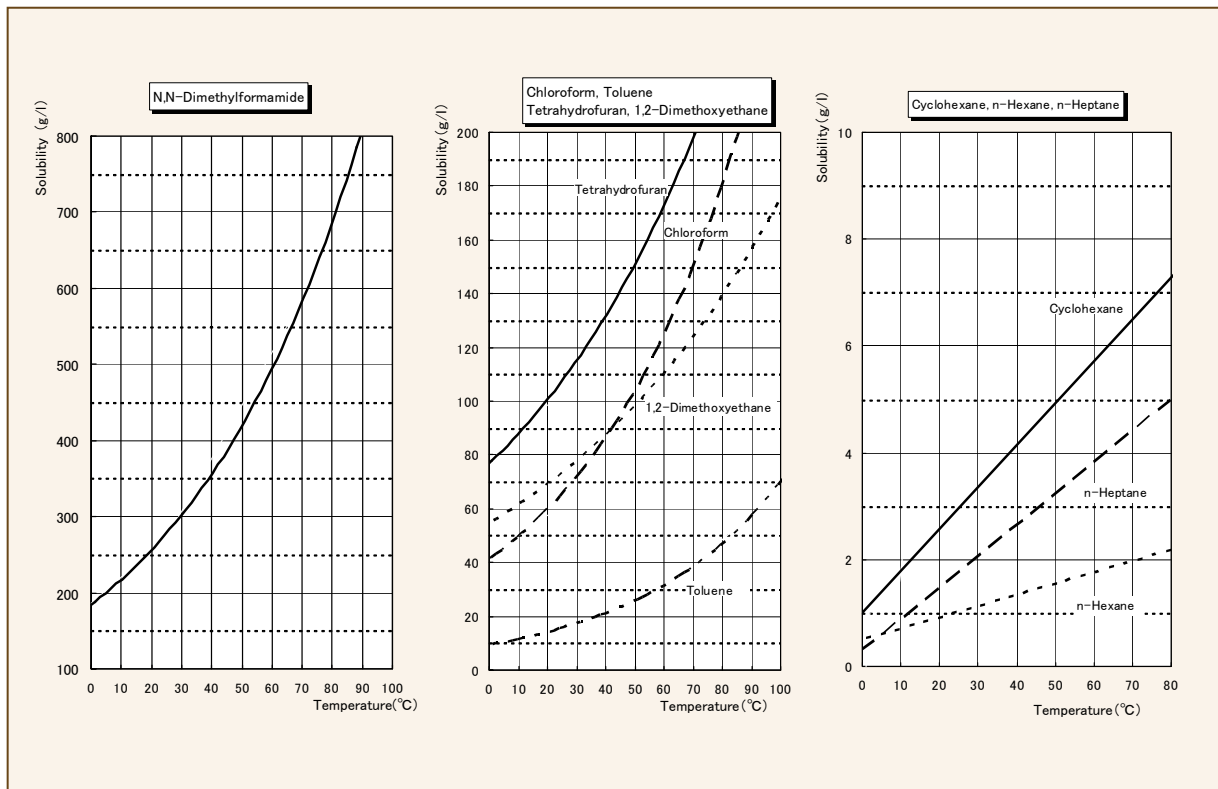
	Specifications	Typical Data	Theoretical Value
Purity	: $\geq 99.00\%$	99.83%	
Zirconium (Zr)	: $\geq 30.90\%$	31.16%	31.21%
Chlorine (Cl)	: $\geq 24.00\%$	24.20%	24.26%
Iron (Fe)	: $\leq 0.05\%$	0.002%	

Analytical Data of Zirconocene Dichloride

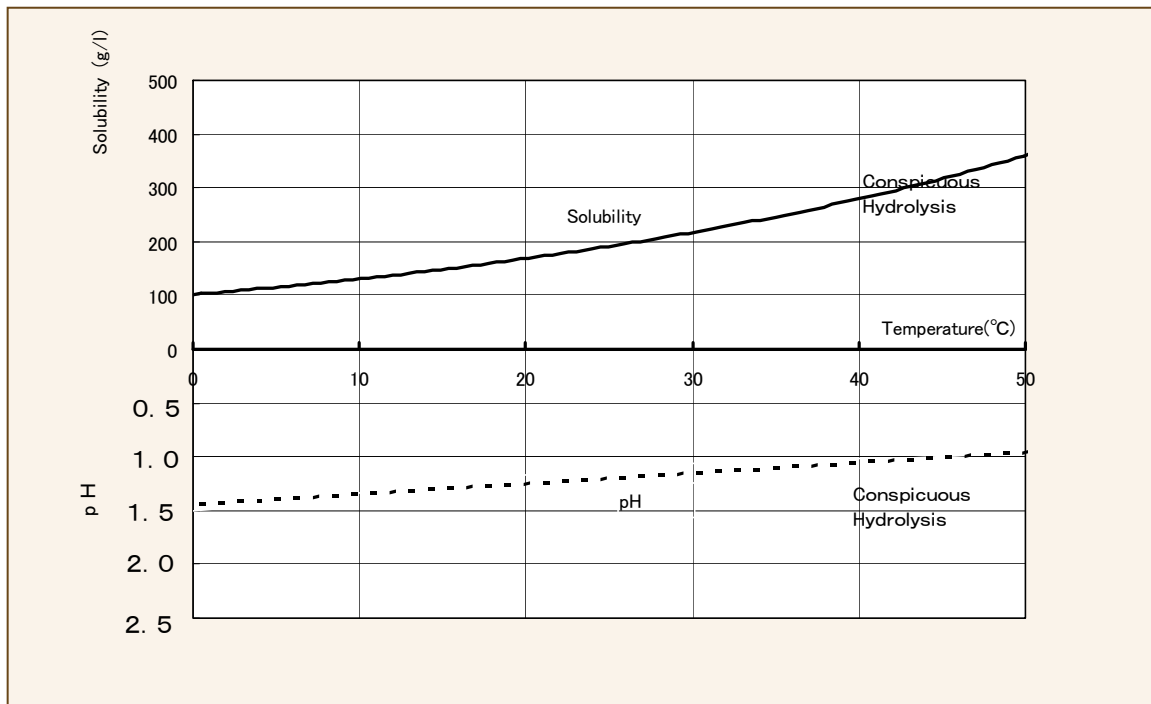
Suppliers	Zr(%)	Cl(%)	Cl/Zr (Molar Ratio)	Notes
Nichia	31.16	24.20	2.00	White Needle Crystal
Reagent A	31.19	24.22	2.00	Colored Crystal
Reagent B	31.09	24.24	2.01	
Reagent C	31.18	24.20	2.00	
Reagent D	31.20	24.21	2.00	
Theoretical Value	31.21	24.26	2.00	

Zr and Cl contents were determined in Nichia.

3. Solubility in Various Solvents

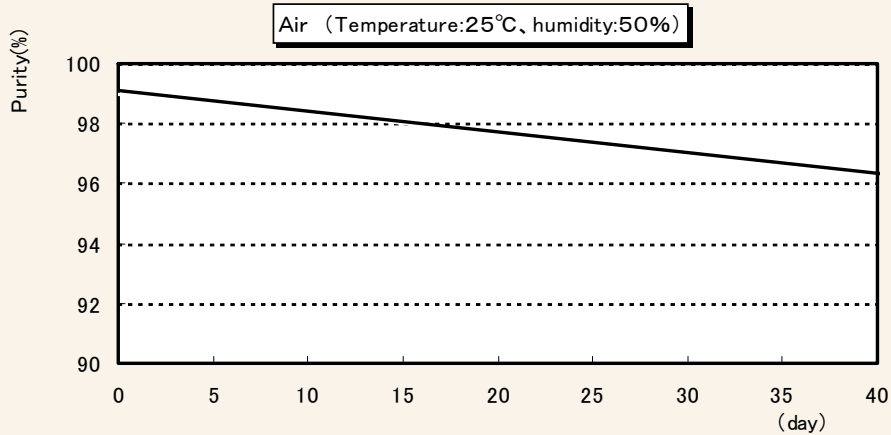


4. Solubility in Water and pH

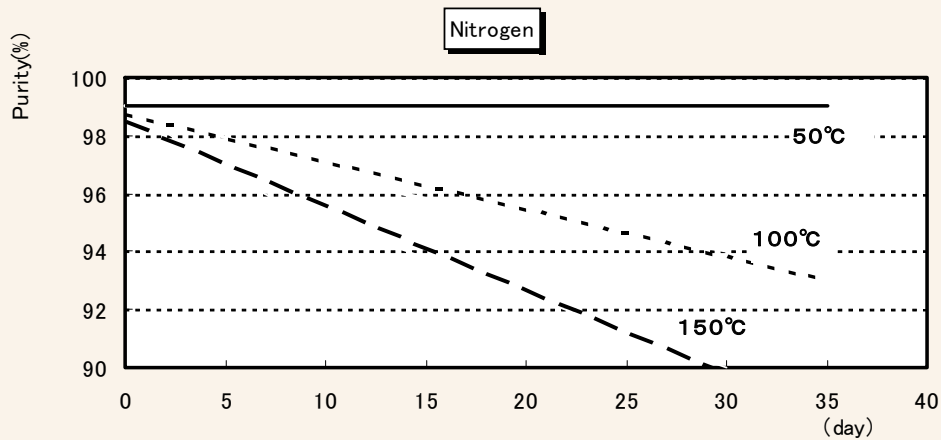


5. Stability

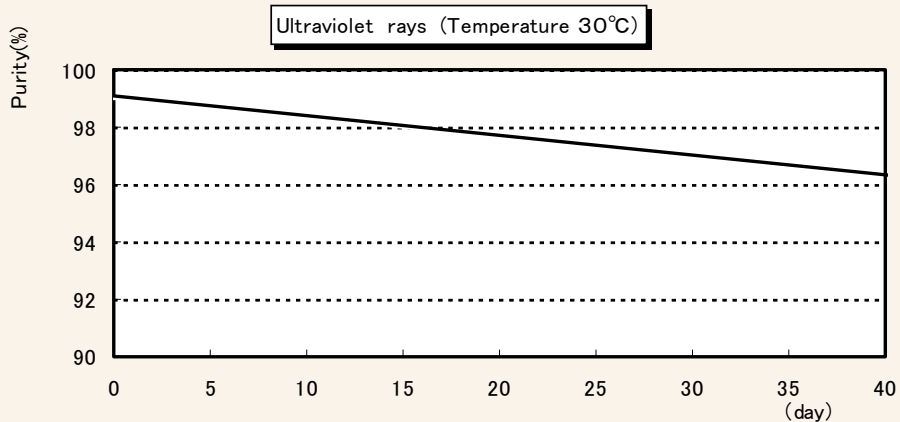
- (1) Zirconocene Dichloride is stable in nitrogen atmosphere under 50°C and its purity will not deteriorate.



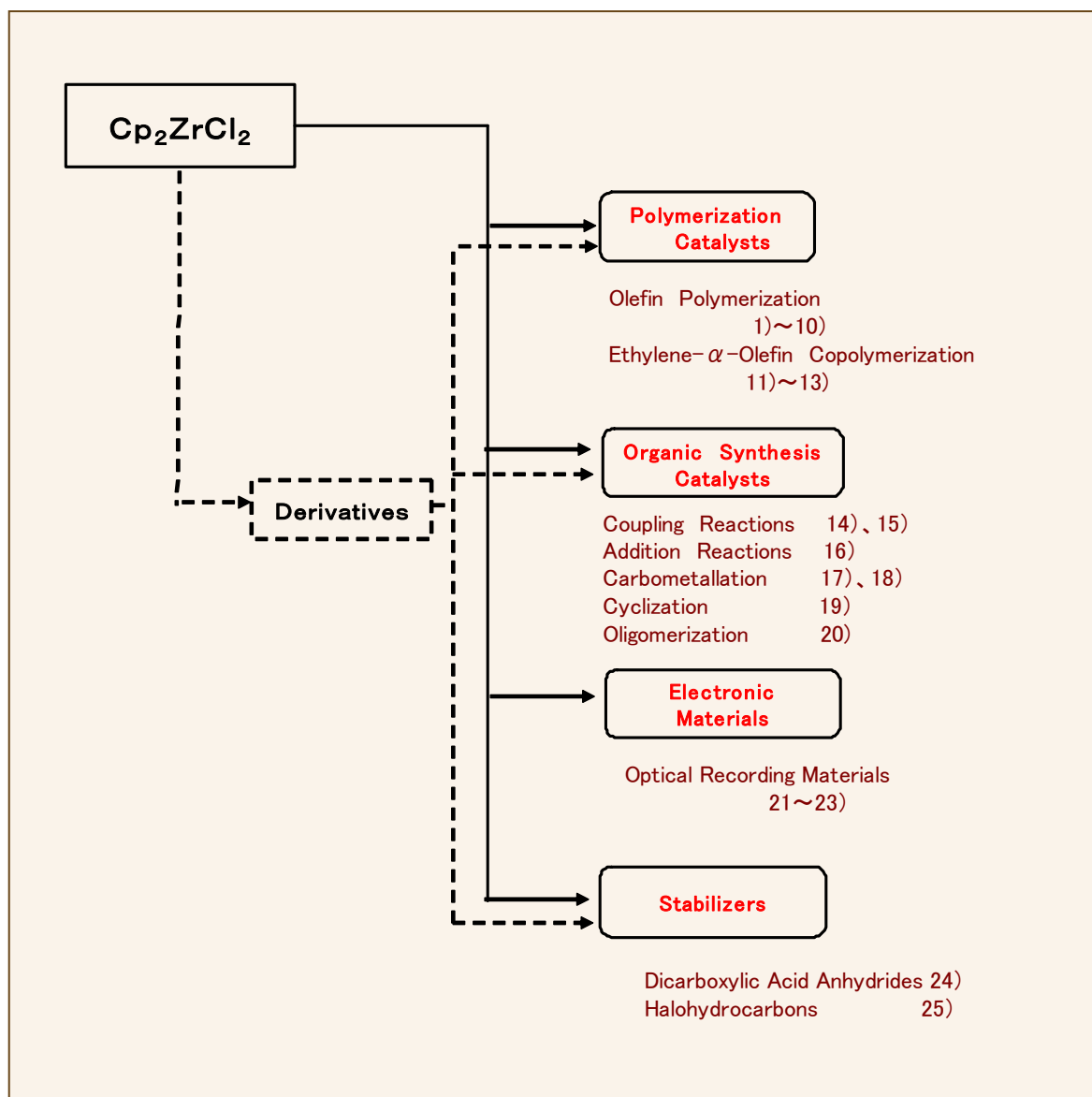
- (2) In open air its quality will deteriorate due to hydrolysis and influence of oxygen.



- (3) It's quality will deteriorate under the influence of ultraviolet rays.



6. Applications (Examples)

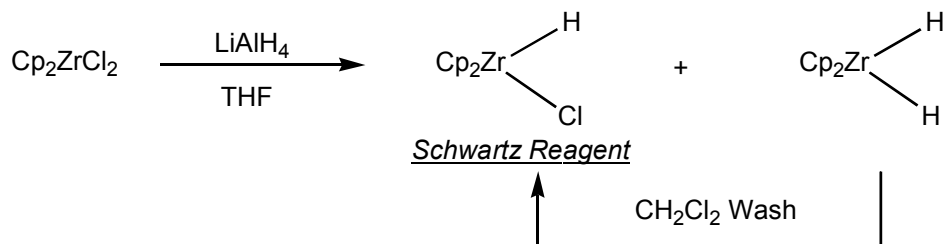


References of Applications

- 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 (1986)
- 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

Schwartz Reagent

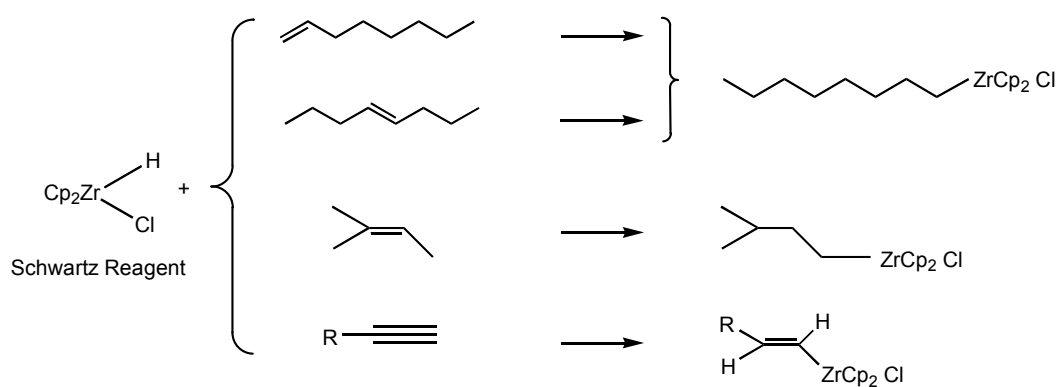


Tetrahedron Lett., **28**, 3895 (1987)

J.Org.Chem., **56**, 2590 (1991)

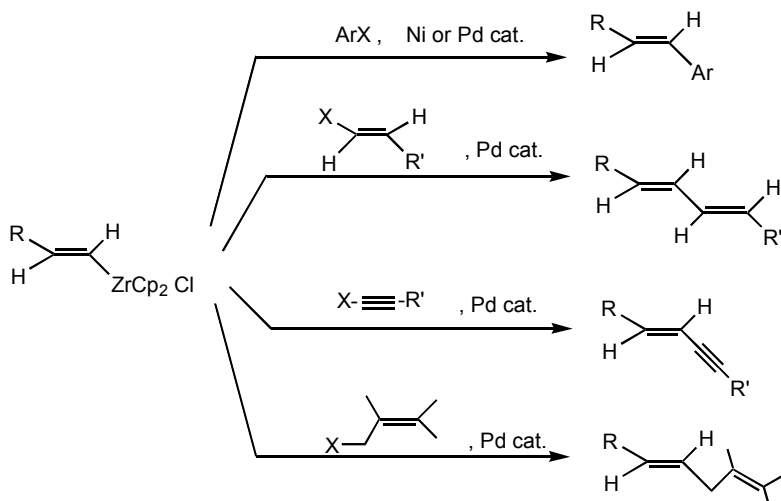
Tetrahedron Lett., **31**, 7257 (1990)

Hydrozirconation



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

Cross Coupling Reaction

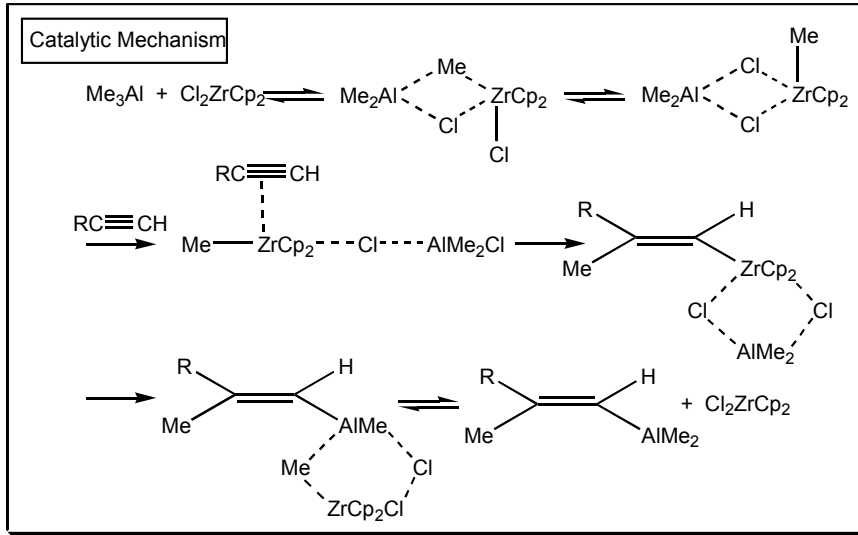
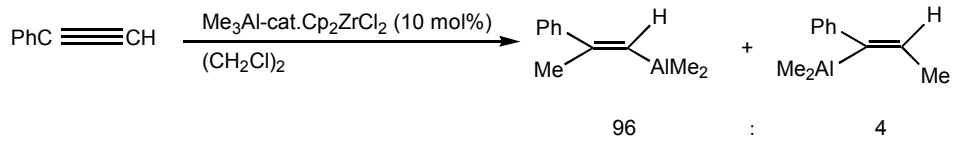


Yukigoseikagaku Kyokaishi, **47**, 2 (1989)

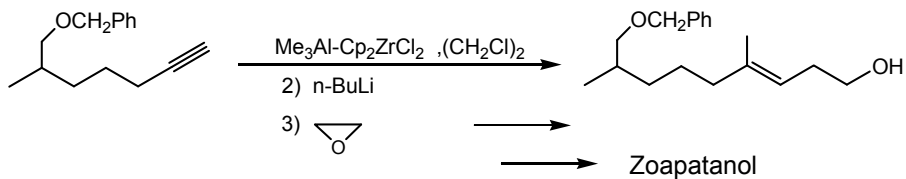
J.Am.Chem.Soc., **109**, 2393 (1987)

Tetrahedron Lett., **30**, 4299 (1989)

Cp₂ZrCl₂-Catalyzed Carbometalation

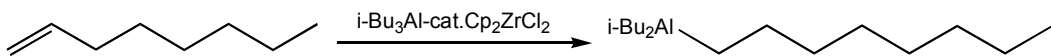


J. Am. Chem. Soc., **108**, 6639 (1985)
Aldrichim. Acta, **18**, 31 (1985)
Synthesis, 1 (1988)

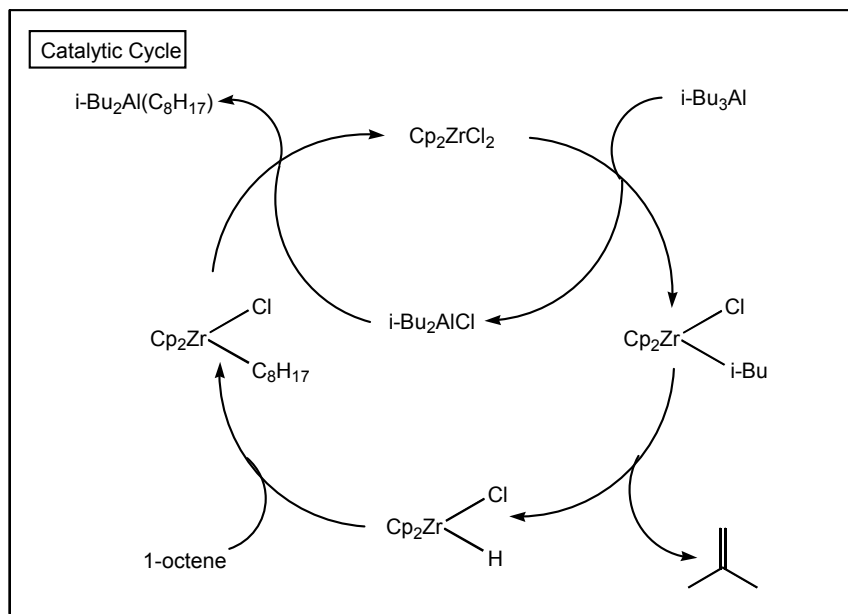


J. Chem. Soc., Perkin Trans., I, 1589 (1985)

Cp₂ZrCl₂-Catalyzed Hydrometalation

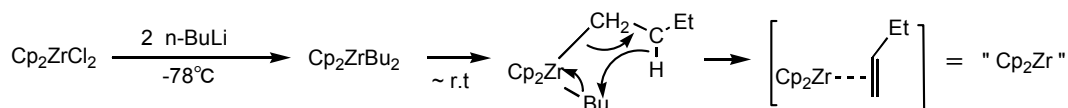


Tetrahedron. Lett., **21**, 1501 (1985)
Pure. Appl. Chem., **53**, 2333 (1981)



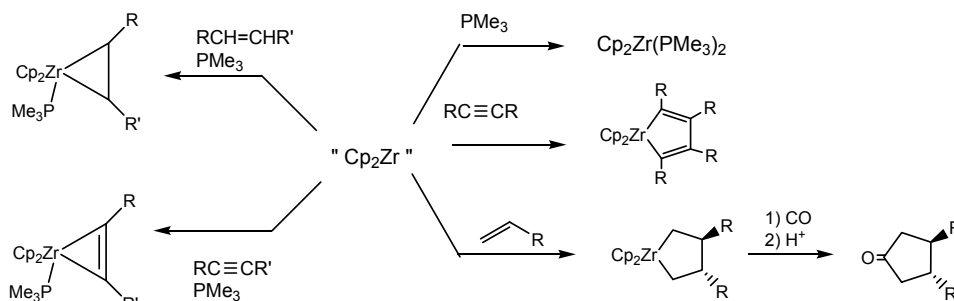
~ Organic Synthesis Using Zirconocene(II) Complexes ~

Negishi Reagent



C-C Bond Formation Reactions Using "Cp₂Zr"

Tetrahedron Lett., **27**, 2829 (1986)



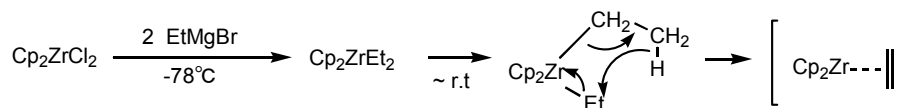
Yukigoseikagaku Kyokaiishi, **47**, 2 (1989)

Synthesis., 1 (1988)

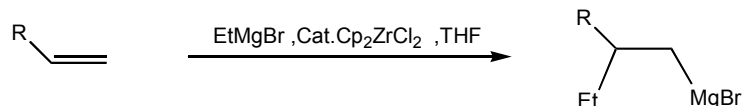
Aldrichim. Acta, **18**, 31 (1985)

Chem.Rev., **88**, 1047 (1989)

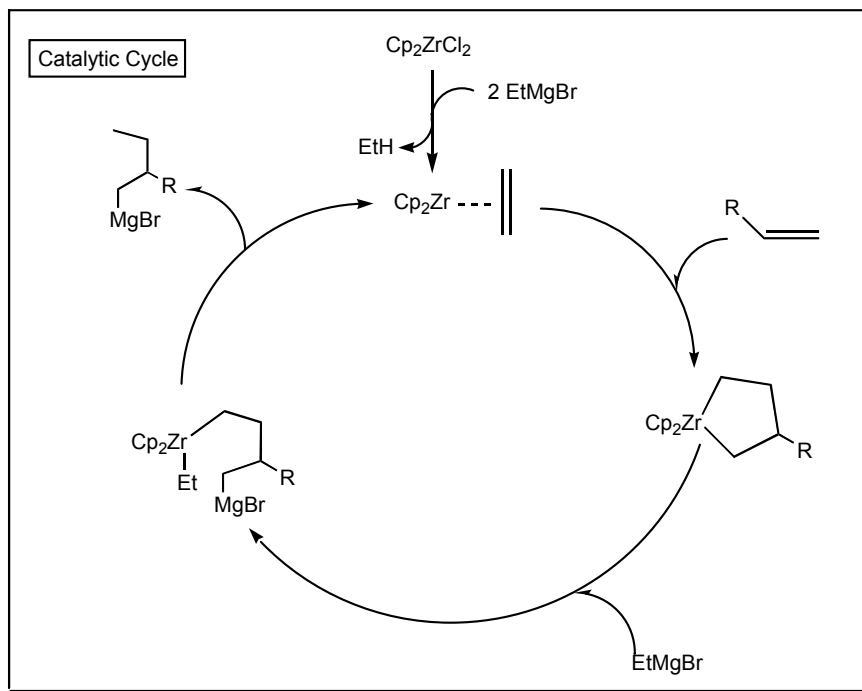
Zirconocene-Ethylene Complex



C-C Bond Formation Reactions Using Zirconocene-Ethylene Complex

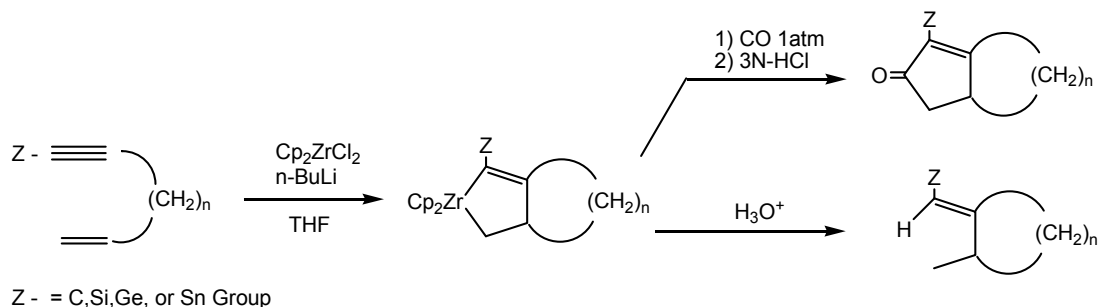


J. Am. Chem. Soc. **113**, 6266 (1991)

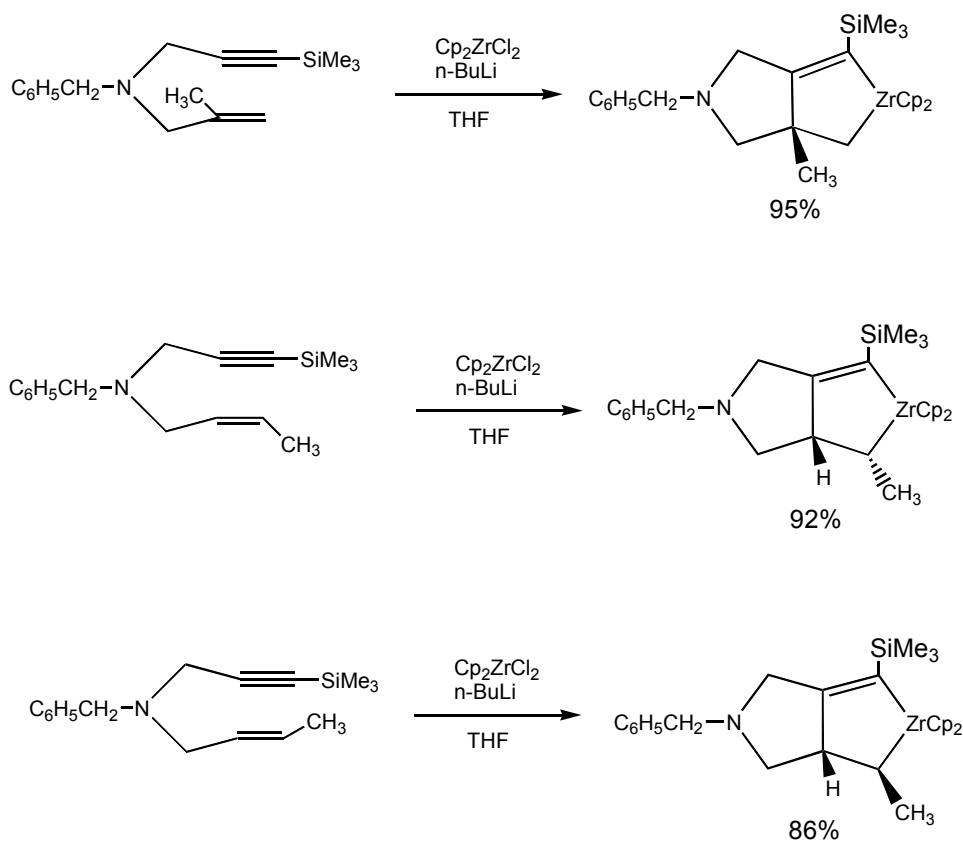


~ Organic Synthesis Using Zirconocene(II) Complexes ~

Intramolecular Bicyclization Reactions of Enynes Using "Cp₂Zr"

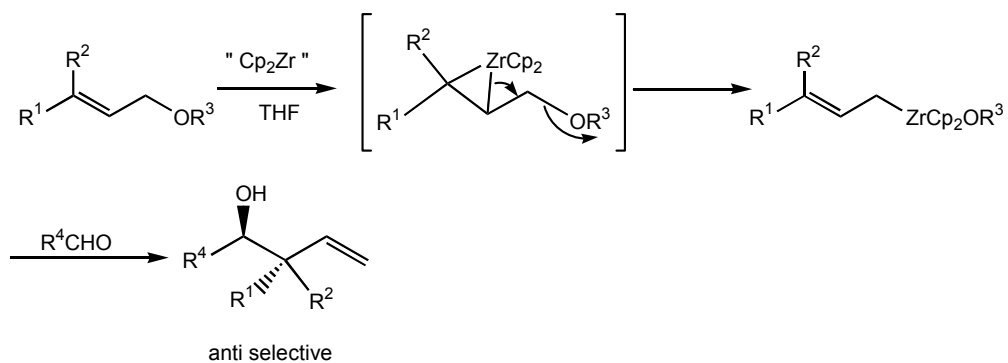


Tetrahedron Lett., 27, 2829 (1986)
J. Am. Chem. Soc., 107, 2568 (1985)
Yukigoseikagaku Kyokaiishi, 47, 2 (1989)

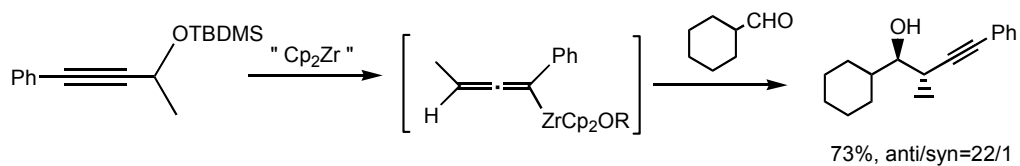
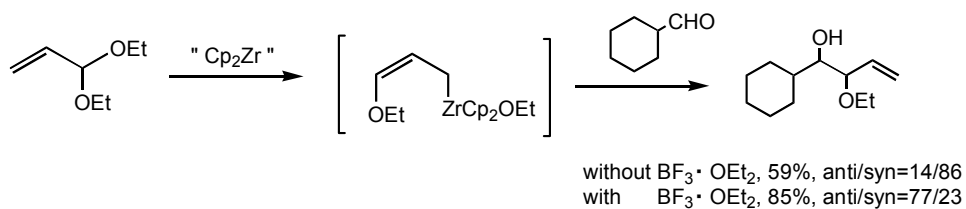


Tetrahedron Lett., 27, 2829 (1986)
Yukigoseikagaku Kyokaiishi, 47, 2 (1989)

Preparation and Reactions of Allylic Zirconium Species



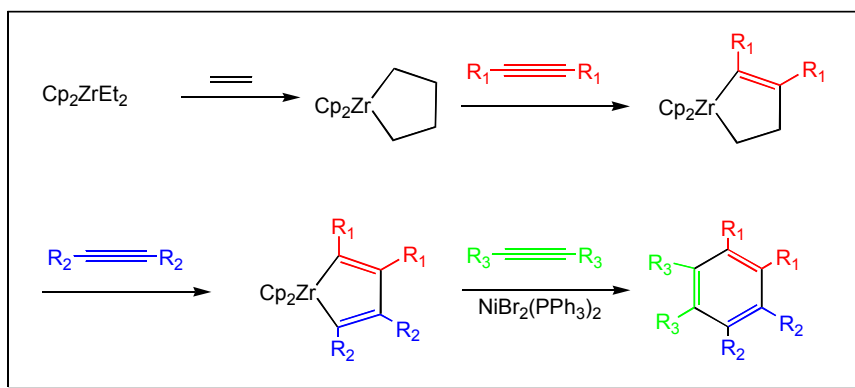
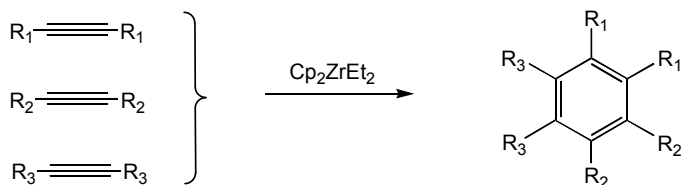
Entry	R ¹	R ²	R ³	R ⁴	Yield (%)	anti : syn
1	Ph	H	Me	Ph	79	10 : 1
2	Ph	H	Bn	Ph	89	15 : 1
3	Ph	H	TBDMS	Ph	96	23 : 1
4	Ph	H	TBDMS	iPr	96	49 : 1
5	Me	H	TBDMS	Ph	41	—



Yakugaku Zasshi., **123**, 933 (2003)

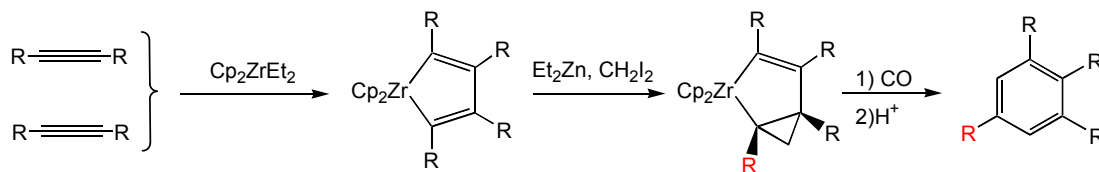
~ Organic Synthesis Using Zirconocene(II) Complexes ~

Synthesis of Benzene Derivatives Using Zirconacyclopentadienes



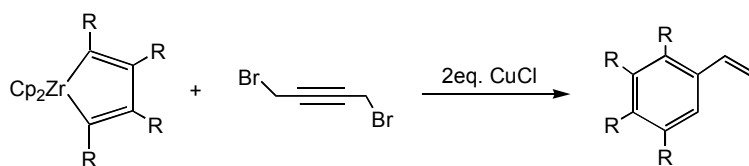
J. Am. Chem. Soc., **121**, 11093 (1999)

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



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

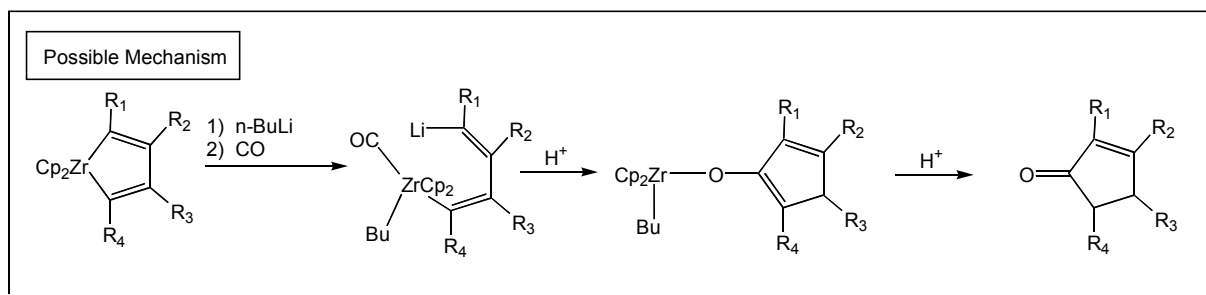
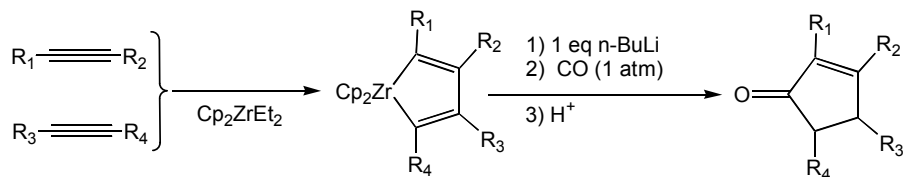
○ Synthesis of Benzene Derivatives Mediated by Copper(I) Salts



Tetrahedron **58**, 1107 (2002)

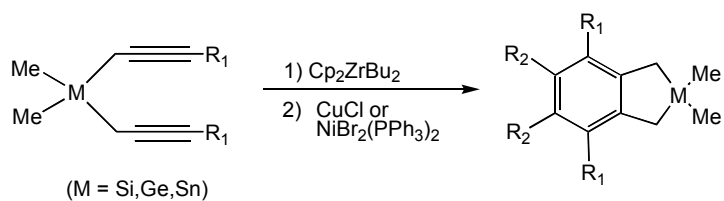
~ Organic Synthesis Using Zirconocene(II) Complexes ~

○ Synthesis of Cyclopentenones Using Zirconacyclopentadienes



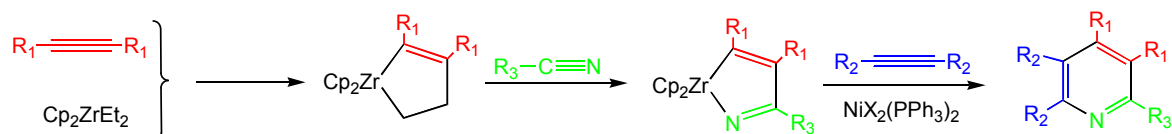
J. Am. Chem. Soc., 121, 1094 (1999)

○ 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

8-1. Storage

Store in a cool/dark place with reasonable ventilation.
Avoid direct radiation of sun beam to the container.

8-2. Handling

Unsealing (opening) of the container must be done under dry Nitrogen atmosphere. When resealing, the inner space of container must be filled with ample amount of dry Nitrogen gas. Zirconocene Dichloride must be sealed very tightly and stored in a place mentioned above. Things (utensils, pipes, equipment, etc) which come in contact with this product must be well-dried before use. When solvent must be used, well-dehydrated micro moisture solvents is recommended.

8-3. First-aid Treatment

If Zirconocene Dichloride adheres to a hand or face, it may cause allergic breakouts. It must be immediately washed off with ample amount of clean water. For protection, please use the protective devices as follows:
Rubber gloves • Protective glasses • Dust-protection masks, etc

8-4 Fire Fighting Procedure

If fire breaks out, move all the containers to a safe place where fire cannot reach. In case that this chemical catches a fire, use plenty of water or powder fire extinguisher to fight fire.

8-5. Waste Disposal

Waste disposal can be accomplished either by hydrolysis or by incineration. Hydrolyze in acid or alkaline aqueous solution to separate Zirconium Hydroxide by neutralization. Burn with flammable solvent to give Zirconium Oxide. Either waste must be disposed in accordance with industrial waste regulations.

■ The contents of this brochure are updated as of March, 2010.

■ Reference

(The manufacturer & engineering department)

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