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Tetrahedron Symposium-in-Print Number 102

Recent advances in the chemistry of zirconocenes

Guest editors: Keisuke Suzukia and Peter Wipfb

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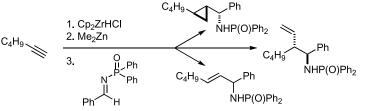
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REPORT

Selective carbon–carbon bond formations with alkenylzirconocenes Peter Wipf* and Ruth L. Nunes



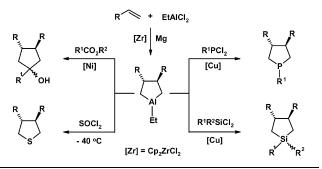
Recent progress in the preparation of alkenylzirconocenes, the transmetalation of zirconium to zinc, palladium, and rhodium, and lithium carbenoid insertions via the 1,2-metalate rearrangement are reviewed. In addition, the regioselective alkylzirconation of alkynes and Zr-promoted cyclizations of diynes are discussed.

ARTICLES

Zirconium-catalyzed preparation of aluminacyclopentanes and synthesis of fivemembered carbo- and heterocycles

Usein M. Dzhemilev,* Askhat G. Ibragimov, Ruslan R. Gilyazev and Leila O. Khafizova

Aluminacyclopentanes, generated in situ by cycloalumination of α -olefins using trialkyl- or alkylhalogenalanes in the presence of Cp₂ZrCl₂ were found to react selectively with carboxylic esters, thionyl chloride, dichlorophosphines and dichlorosilanes to give 5-membered carbo- and heterocycles in high yields.



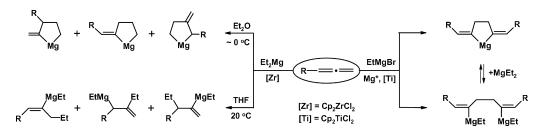
pp 1269-1279

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pp 1281–1286

Cyclo- and carbomagnesiation of 1,2-dienes catalyzed by Zr complexes Usein M. Dzhemilev,* Vladimir A. D'yakonov, Leila O. Khafizova and Askhat G. Ibragimov

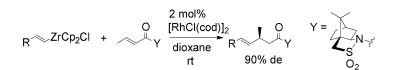
pp 1287-1291



The reaction of EtMgR' (R'=Et, Br) with 1,2-dienes in ethereal solutions catalyzed by Zr and Ti complexes was found to afford the products of cyclo- and (or) carbomagnesiation.

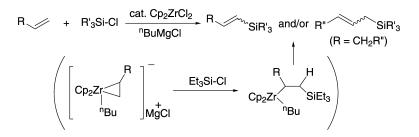
Rhodium-catalyzed 1,4-addition of alkenylzirconocene chlorides to electron deficient alkenes

Akito Kakuuchi, Takeo Taguchi and Yuji Hanzawa*



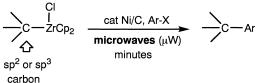
Reaction pathways of zirconocene-catalyzed silylation of alkenes with chlorosilanes Jun Terao, Yingshi Jin, Kazushi Torii and Nobuaki Kambe* pp 1301-1308

pp 1293-1299



Microwave accelerated, Ni/C-catalyzed cross-couplings of in situ-derived zirconocenes Bruce H. Lipshutz* and Bryan Frieman pp 1309-1316

Negishi couplings heterogeneous catalysis



 $[(C_5H_4R)_2Zr(\eta^2-C_6H_4)]$

 R^1 = aryl or alkyl

 $(C_5H_4R)_2$

(X= PR', SiR'2)

Intramolecular coupling of acetylenic groups of bis(alkynyl)phosphanes and silanes mediated by benzynezirconocene: a route to new mono- and tricyclic heterocycles

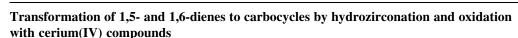
Nadine Pirio, Stéphane Bredeau, Laurence Dupuis, Peter Schütz, Bruno Donnadieu, Alain Igau, Jean-Pierre Majoral,* Jean-Claude Guillemin and Philippe Meunier*

X(C≡CPh)₂

 $\xrightarrow[THF, r.t.]{Bu_2ZrCp_2}{1a} \xrightarrow[R^2]{R^3} \xrightarrow[ZrCp_2XR]{R^3}$

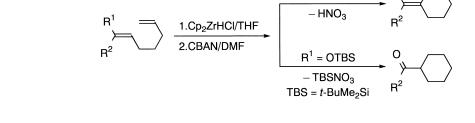
A general and convenient procedure for the regioselective synthesis of a variety of new mono- or tricyclic heterocycles incorporating either one or two heteroatoms is reported. It involves the thermolysis of Cp_2ZrPh_2 in the presence of bis(alkynyl)phosphanes or silanes followed by exchange reactions with halogenated phosphorus, germanium, tin, antimony and arsenic derivatives.

From vinyl sulfides, sulfoxides and sulfones to vinyl zirconocene derivatives Shahera Farhat, Irena Zouev and Ilan Marek*



XR = SPr, SPh, S(O)Ph, SO₂Me, SO₂Ph

Takushi Azemi, Mitsuru Kitamura and Koichi Narasaka*



Zr-promoted 'pair'-selective and regioselective synthesis of penta-substituted benzene derivatives

Yves R. Dumond and Ei-ichi Negishi*

^{IIBu} Cp₂Zr H 2 ⁿHexC≡CLi Me THF, 23 °C, 14 h SiMe₃ 9 (9/10 = 94/6) 65% overall yield ^{IIBu} H HexC≡CLi NHex SiMe₃ 11 (53%, ≥93% isomeric purity)



pp 1329-1337

(E = GeEt₂, SnMe₂, PPh, AsPh, SbPh)



pp 1345–1352

pp 1317-1327

Synthesis of an enantiomerically pure 2,2,4-trisubstituted cyclobutanone building block by zirconocene-promoted deoxygenative ring contraction of structurally modified 4-vinvlfuranosides

Leo A. Paquette* and Ho-Jung Kang

OTBDPS TBDPSO-OTBDPS THF, 55 °C PMBO ΌН PMBO (1.9:1)

P(O)(OEt)₂

A study of the 1,2-addition of group IV metallacycles derived from 1-alkynylphosphonates to conjugated enones

Ofir Baum, Abed Al Aziz Quntar, Valery M. Dembitsky and Morris Srebnik*

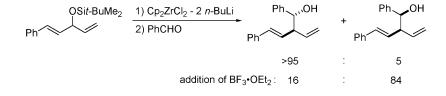
P(O)(OEt)₂ n-Bu P(O)(OEt)₂ Ъ 3 0 ML₂ = Ti(O-*i*Pr)₂ $ML_2 = ZrCp_2$ ЮΗ OH 4 50% yield 3 (50-55% yield) Cationic zirconocene- or hafnocene-based Lewis acids in organic synthesis:

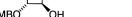
glycoside-flavonoid analogy Ken Ohmori, Keisuke Hatakeyama, Hiroki Ohrui and Keisuke Suzuki*

> OR RO OR $Cp_{Cp^{-}Zr^{++}}^{Cp_{-}Zr^{++}}_{(ClO_{4}^{-})_{2}}$ Cp_{Hf}⁺⁺ Cp[′] (ClO₄⁻)₂ RÒ х

Pentadienyl transfer reagents based on zirconium: preparation and reactions with carbonyl compounds

Philippe Bertus, Ludovic Drouin, Christophe Laroche and Jan Szymoniak*





LA = Lewis acid

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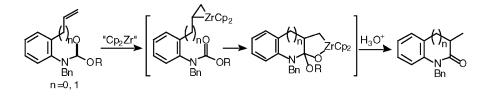
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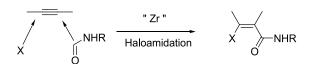
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Construction of nitrogen-heterocyclic compounds through zirconium mediated intramolecular alkene-carbonyl coupling reaction of *N*-(*o*-alkenylaryl)carbamate derivatives

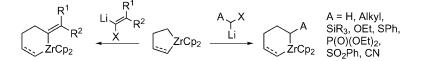
Yasushi Takigawa, Hisanaka Ito, Katsunori Omodera, Maiko Ito and Takeo Taguchi*



Haloamidation of alkynes and related reactions using zirconacycles and isocyanatespp 1393–1400Yanzhong Li, Hiroshi Matsumura, Masamichi Yamanaka and Tamotsu Takahashi*pp 1393–1400

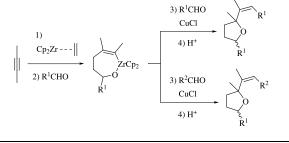


Ring expansion of 5- to 6-member zirconacycles by carbenoid insertion Sally Dixon, Shaun M. Fillery, Aleksandra Kasatkin, David Norton, Emma Thomas and Richard J. Whitby*



Reaction of oxazirconacycloheptenes with aldehydes mediated by CuCl: one-pot synthesis of tetrahydrofuran derivatives from four different components involving two molecules of the same or different aldehydes, an ethylene and an alkyne

Changjia Zhao, Jiang Lu, Zhiping Li and Zhenfeng Xi*



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Corresponding author () Supplementary data available via ScienceDirect

COVER

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