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Pair-Selective Coupling of Alkynes with Alkenes on Zirconocene Complex

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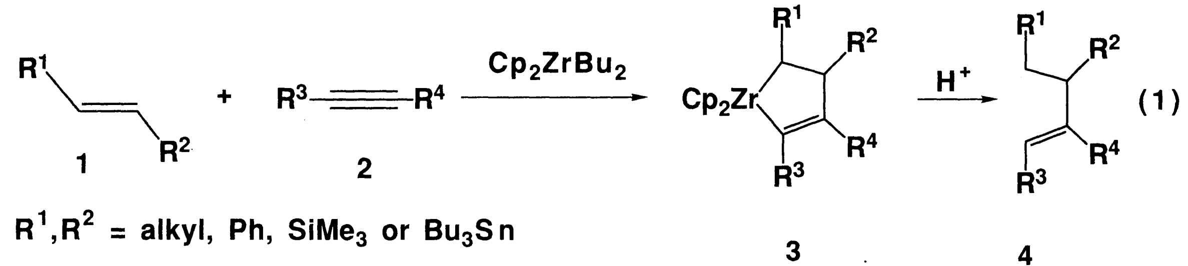
When ethylene and alkynes such as 4-octyne and diphenylacetylene were treated with Cp_2ZrBu_2, highly pair selective coupling products were formed in high yields. Similarly, styrene or trimethylvinylsilane also afforded cross coupling products with alkynes on zirconocene complex.

Although several useful procedures have been reported so far for cross coupling of alkynes with alkenes using zirconium complexes, they involved stabilization of alkene- or alkyne-complexes with phosphines,1) intramolecular coupling,2) or coupling of alkynes with ethylene produced in situ from Cp_2ZrEt_2.3) To the best of our knowledge no precedents have been reported for intermolecular pair-selective cross coupling reactions between alkynes and alkenes added to the zirconium complex without phosphine. This type of selective cross coupling reactions between alkynes and alkenes requires highly controlled conditions. We would like to describe here zirconium mediated pair selective cross coupling reactions of alkynes with alkenes with high regioselectivities.



R^1,R^2 = alkyl, Ph, $SiMe_3$ or Bu_3Sn

R^3,R^4 = alkyl, Ph or Me_3Si

(1)

Typical procedure for reactions with ethylene is as follows. Ethylene gas was introduced with bubbling into a solution of Cp_2ZrBu_2 ('zirconocene equivalent': Negishi reagent4)) prepared from 1.2 mmol of Cp_2ZrCl_2 (0.351 g) and 2.4 mmol of n-BuLi (1.6 M, 1.5 ml) in THF (5 ml) at -78 °C. The solution was gradually warmed to room temperature and then 1 mmol of 4-octyne (0.110 g) was added to it. After stirring the mixture for 1h at room temperature under ethylene atmosphere, cross coupling product 2,3-dipropylzirconacyclopentene was formed in >98% yield (based on 4-octyne by NMR). Hydrolysis of this mixture gave (Z)-4-ethyl-4-octene in 91% yield. Homo coupling product of 4-octyne was not detected. In the case of other alkenes such as styrene and trimethylvinylsilane, alkenes and alkynes were simultaneously added to a solution of Cp_2ZrBu_2 at -78 °C. And then the mixture was warmed to room temperature and stirred at room temperature for 1h. Cross coupling products were analyzed after hydrolysis.

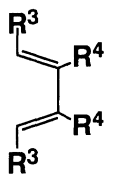
Table. Pair Selective Coupling of Alkynes with Alkenes a)

Run	Alkene	n equiv.	Alkyne	Temp	Time	Yield of cross coupling product	Alkyne dimer
	$R^1CH=CHR^2$		$R^3C\equiv CR^4$	℃	h	**4** /%	**5** /% b)
1	$CH_2=CH_2$	excess c)	$EtC\equiv CEt$	r.t.	1	91	0
2	$CH_2=CH_2$	excess c)	$PrC\equiv CPr$	r.t.	1	91	0
3	$CH_2=CH_2$	excess c)	$BuC\equiv CBu$	r.t.	1	96	0
4	$CH_2=CH_2$	excess c)	$PhC\equiv CPh$	r.t.	1	86	0
5	$CH_2=CH_2$	excess c)	$Me_3SiC\equiv CSiMe_3$	r.t.	1	0 d)	0
6	$CH_2=CH_2$	excess c)	$Me_3SiC\equiv CMe$	r.t.	1	94	6
7	$CH_2=CH_2$	excess c)	$PhC\equiv CMe$	r.t.	1	94	0
8	$CH_2=CH_2$	excess c)	$HexC\equiv CH$	r.t.	1	75 e)	0
9	$CH_2=CH_2$	excess c)	$PhC\equiv CH$	r.t.	1	61 f)	0
10	$HexCH=CH_2$	3	$PrC\equiv CPr$	r.t.	1	0 g)	43
11	$PhCH=CH_2$	1	$PrC\equiv CPr$	r.t.	1	64	11
12	$PhCH=CHMe$	1	$PrC\equiv CPr$	r.t.	1	0 h)	33
13	$Me_3SiCH=CH_2$	5	$PrC\equiv CPr$	r.t.	1	87	<4
14	$Me_3SiCH=CH_2$	3	$PrC\equiv CPr$	r.t.	1	75	5
15	$Me_3SiCH=CH_2$	1.5	$PrC\equiv CPr$	r.t.	1	71	12
16	$Me_3SiCH=CH_2$	1	$PrC\equiv CPr$	r.t.	1	66	16
17	$Me_3SiCH=CH_2$	5	$PhC\equiv CPh$	r.t.	1	>95	<3
18	$Me_3SiCH=CH_2$	5	$PhC\equiv CMe$	r.t.	1	85	<3
19	$Me_3SiCH=CH_2$	5	$PrC\equiv CMe$	r.t.	1	71 i)	<3
20	$Me_3SiCH=CHHex$	1	$PrC\equiv CPr$	r.t.	1	0 h)	>49
21	$Me_3Si(Me)C=CH_2$	1	$PrC\equiv CPr$	r.t.	1	0 h)	49
22	$Bu_3SnCH=CH_2$	5	$PrC\equiv CPr$	r.t.	1	62	13

a) Yields were determined by GC after hydrolysis of the reaction mixture. b) Maximum yield of alkyne dimer is 50%. c) Under ethylene atmosphere. d) Alkyne was recovered in 91%. e) Two regioisomers, (E)-3-decene and 2-ethyl-1-octene, were obtained in a ratio of 1.1:1. f) Two regioisomers, (E)-1-phenyl-1-butene and 2-phenyl-1-butene were obtained in a ratio of 1.4:1. g) 1-Octene dimer was obtained in 23% yield along with the formation of 16% of 1-octene/1-butene coupling product. h) Most of alkene remained unreacted. i) Two regioisomers, (E)-1-trimethylsilyl-3-methyl-3-heptene and (E)-3-propyl-5-trimethylsilyl-2-pentene were obtained in a ratio of 1.3:1.

Results are shown in Table. Alkynes easily dimerize to give **5** when treated with Cp_2ZrBu_2 even in the presence of an excess of 1-octene without forming cross coupling product (Run 10). However, when the reactions were carried out under ethylene atmosphere, only cross coupling products **3** of alkynes with ethylene were formed in high yields with high pair selectivities (Runs 1-9). It is noteworthy that no formation of alkyne dimer was detected under conditions used here for most cases (Runs 1-5,7-9). Preparation of **3** ($R^1 = R^2 = H$) by the reaction of alkynes with Cp_2ZrEt_2 and their reactions have been already documented.3)

Reactions of trimethylvinylsilane with 4-octyne on zirconocene afforded zirconacyclopentenes **3** ($R^1 = Me_3Si$, $R^2 = H$, $R^3 = R^4 = Pr$)5) in 93% yield. After hydrolysis the pair-selective cross coupling product **6**6) was obtained in 87% yield (isolated yield 74%) and less than 4% of homo coupling product of 4-octyne was formed (Run 13). This reaction proceeded with >98% of high regioselectivity for vinylsilane. The formation of regioisomer **7** was not detected. Deuterolysis instead of hydrolysis gave dideuterated product **8** in 70% isolated yield with >99% of deuterium incorporation. In the case of diphenylacetylene similar result was obtained. Pair selective cross coupling product zirconacyclopentene **3** ($R^1 = Me_3Si$, $R^2 = H$, $R^3 = R^4 = Ph$) was formed in >95% yield with >99% regioselectivity for $SiMe_3$ group (Run 17).



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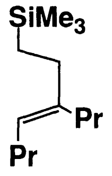

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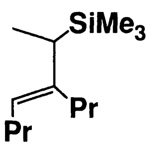

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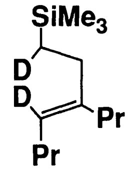

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To achieve the high pair-selectivity the addition of an excess (5 equiv) vinylsilane was required. When 3 equiv, 1.5 equiv and one equiv of vinylsilane were used for cross coupling with 4-octyne, yields of cross coupling products decreased (75%, 71%, and 66%, respectively) with decrease of vinylsilane and homo coupling of 4-octyne increased (5%, 12%, and 16%, respectively) (Runs 14-16). Similarly, in the case of diphenylacetylene the use of one equiv of vinylsilane afforded lower pair-selectivity. Homo coupling product was formed in 7-9% yield. Non-symmetrical alkyne such as 1-phenylpropyne was also investigated. Interestingly the cross coupling reaction of 1-phenylpropyne with 5 equiv of vinylsilane afforded high regioselectivity not only for silyl group but also for Me and Ph groups (Run 18).

Cross coupling products were not produced when alkene has an alkyl substituent except H which usually occupies β-position of zirconacycles7) (Run 10). In addition, the use of disubstituted alkenes was unsuitable for cross coupling reactions (Runs 12, 20, 21).

Cross coupling of alkynes with ethylene proceeded via zirconacyclopentane. In fact, an excess of ethylene gas reacted with Cp_2ZrBu_2 to give zirconacyclopentane quantitatively under conditions used here as expected. Replacement of Zr-CH_2CH_2- moiety of zirconacyclopentane by alkynes resulted easily in the formation of zirconacyclopentene compounds **3**.8) It is also known that zirconacyclopentene **3**, in turn, reacts with second alkynes to produce alkyne dimerization products **5** via β,β'-C-C bond cleavage.1a,2d,9) Under ethylene atmosphere, however, the alkyne dimerization was suppressed and zirconacyclopentene compounds **3** formed in situ were stabilized.

To make clear the mechanism for the case of trimethylvinylsilane, the reaction of 4-octyne with vinylsilane on zirconocene was examined by NMR in the presence of PMe_3. The build up of alkyne complex was observed and then product **3** (R^1 = Me_3Si, R^2 = H, R^3 = R^4 = Pr) was gradually produced. The cross coupling product was not so stable in the presence of alkyne. It slowly decomposed to give alkyne dimerized product.[3,7)] An excess of vinylsilane accelerates the desired cross coupling and protects the product **3** from dimerization reaction as observed in the case of reactions with ethylene.

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5) **3** (R^1 = Me_3Si, R^2 = H, R^3 = R^4 = Pr, R^1 = Me_3Si): ^{13}C NMR (C_6D_6/THF, Me_4Si): δ 0.76, 14.63, 15.38, 22.17, 24.64, 29.92, 37.74, 40.00, 56.62, 110.13, 111.71, 143.21, 183.07.

6) **5**: ^1H NMR ($CDCl_3$, Me_4Si): δ -0.01 (s, 9H), 0.55-0.65 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H), 1.25-1.50 (m, 4H), 1.9-2.1 (m, 6H), 5.15 (t, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ -1.70, 13.92, 14.25, 15.16, 21.63, 23.30, 29.86, 30.85, 32.02, 123.41, 141.78. High resolution MS; Found: 212.1980, Calcd for $C_{13}H_{28}Si$: 212.1960.

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