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Rhodium-Catalyzed Cross Coupling of Unactivated Allenes and 1-Alkynes

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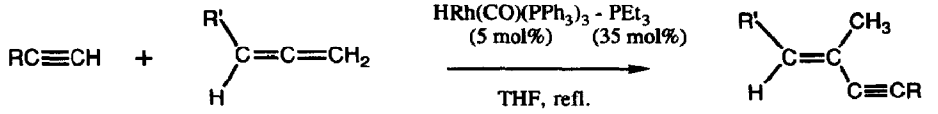
Abstracts: Mixture of $HRh(CO)(PPh_3)_3$ and Et_3P catalyzes cross coupling reaction of unactivated allenes and 1-alkynes. C-C bond formation takes place regioselectively at 2-position of allenes giving *endo*-(*E*)-enynes in high yields and selectivities. Added PEt_3 promotes the reaction and enhances the regio- and stereoselectivity.

Catalytic organometal addition to allenes is a versatile method to prepare olefinic compounds provided that the reaction to the three potentially reactive sites is regio- and stereoselectively controlled.[1] Addition of 1-alkynes to allenes catalyzed by palladium complexes was reported by Trost *et al.*[2] However, most of their reactions were conducted with highly activated allenyl esters, and modest yields of enynes were obtained with unactivated allenes. We now wish to report a rhodium catalyzed cross coupling reaction of unactivated allenes[3] and 1-alkynes, which gives conjugated *endo*-(*E*)-enynes in high yields and selectivities (Scheme 1).



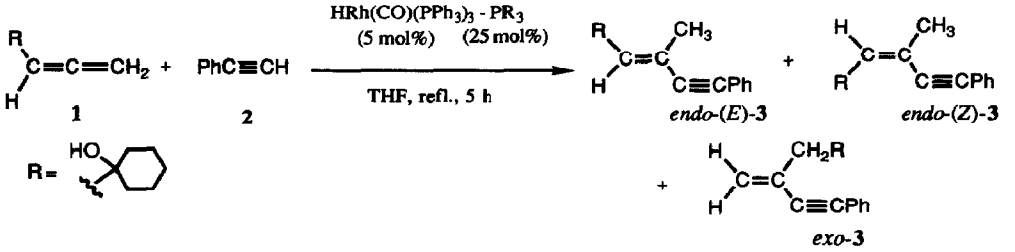
Scheme 1.

When allene **1** (0.5 mmol) and phenylacetylene (**2**) (0.75 mmol) are treated in refluxing THF (5 mL) for 5 h in the presence of $HRh(CO)(PPh_3)_3$ (0.025 mmol) and Et_3P (0.175 mmol),[4] coupling reaction takes place regioselectively at 2-position of **1** giving *endo*-(*E*)-**3** in 81% yield. (*E*)-Configuration was determined by NOE studies; ^{1}H-NMR ($CDCl_3$) δ 6.04 for *endo*-(*E*)-**3** and δ 5.90 for *endo*-(*Z*)-**3**. Dimerization of the alkyne[5] and polymerization of the allene are minimal under the reaction conditions. The yield and the selectivity considerably vary by added phosphines (Table 1). Trialkylphosphines with small alkyl groups promotes the reaction and enhances the regio- and stereoselectivities (entries 2 and 3). Liberation of PPh_3 on addition of PEt_3 to $HRh(CO)(PPh_3)_3$ was detected by ^{1}H-NMR. Triaryl phosphines also promote the reaction but in low selectivities (entries 5 and 6). Bidentate ligands, dppb, dppp, and dppf show preferences for *exo*-**3** (entries 10, 11, and 12). The high selectivity of the $HRh(CO)(PPh_3)_3$-PEt_3 catalyst is kinetically controlled, since no isomerization took place when pure *endo*-(*Z*)-**3** or a 4 : 1 mixture of *endo*-(*E*)-**3** and *exo*-**3** was subjected to the coupling reaction conditions.

Reactions of a range of allenes and 1-alkynes are summarized in Table 2. *Endo*-(*E*)-enynes are obtained generally in high yields. The stereochemistry was determination by NOE. Olefinic protons of (*E*)-isomers appear at lower field in ^{1}H-NMR compared with (*Z*)-isomers. Aryl alkynes and silyl alkynes are more reactive

than aliphatic alkynes (*e. g.*, entries 1, 2, and 4). The stereoselectivity lowers for the latter with relatively hindered allene (entry 19). Behaviors of 2-hydroxy-2-methyl-3-butyne are intermediate between these two (*e. g.*, entry 3). Electronic effect is small in aryl alkynes (entries 10, 11, 12, and 13). Bulkiness of the substituent also does not affect the reaction (entries 15 and 16) except for (*o*-trimethylsilylphenyl)acetylene (entry 14), which reacts slower than **2** giving an isomeric mixture of enynes. Steric hindrances around the carbon-carbon triple bond retard the reaction, while those along the triple bond do not. Substituent effect in monosubstituted allenes is small (Table 2, entries 1, 5, 7, 10), if not extremely hindered (entry 21). An attempt of kinetic resolution in the coupling of **2** and 3-(*t*-butyldimethylsilyloxy)-1,2-octadiene using $HRh(CO)(PPh_3)_3$ and (+)-diop (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) gave *exo*-adduct as well as the recovery of the starting material, both of which were racemic. Reactions of disubstituted allenes, 5,6-undecadiene and 3-methyl-1,2-undecadiene, with phenylacetylene were either sluggish or complicated. The coupling reaction is substantially accelerated in acetonitrile solvent, although the regio- and stereoselectivity are lost (entries 9 and 20). Even a catalytic amount of acetonitrile changes the selectivities (Table 1, entries 1 and 13), and the nitrile probably is coordinating to rhodium metal modifying its catalyst properties.

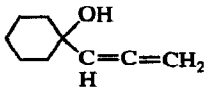
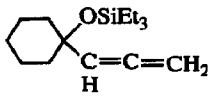
Table 1. Effect of Added Phosphines on the Coupling Reaction of **1** and **2**.



entry	PR_3	yield/%	*endo* : *exo*	*E* : *Z*
1	none	22	5.7 : 1	1.4 : 1
2	Et_3P [a]	81	> 20 : 1	> 20 : 1
3	Bu_3P	83	> 20 : 1	17 : 1
4	*i*-Pr_3P	9	1.5 : 1	1.7 : 1
5	Ph_3P	38	3.3 : 1	3.3 : 1
6	(*o*-Tol)$_3P$	56	1.5 : 1	1 : 1
7	$(MeO)_3P$	10	0.25 : 1	0.3 : 1
8	$(Me_2N)_3P$	7	4.3 : 1	3.3 : 1
9	dppe [b]	trace		
10	dppp [b]	29	0.8 : 1	> 20 : 1
11	dppb [b]	42	0.3 : 1	> 20 : 1
12	dppf [b]	25	0.4 : 1	0.45 : 1
13	CH_3CN	33	1.8 : 1	0.8 : 1

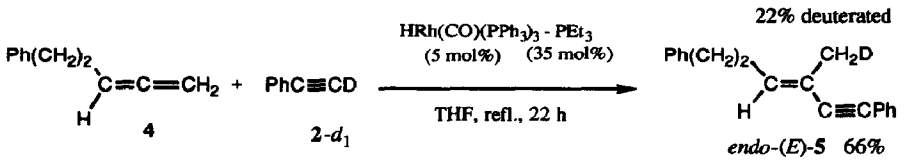
a) 35 mol% phosphine was used. b) dppe: $Ph_2P(CH_2)_2PPh_2$. dppp: $Ph_2P(CH_2)_3PPh_2$. dppb: $Ph_2P(CH_2)_4PPh_2$. dppf: 1,1'-bis(diphenylphosphino)ferrocene.

Table 2. Cross Coupling Reaction of Allenes and 1-Alkynes.[a)]

entry	allene	R	time/h	yield/%	*endo* : *exo*	*E* : *Z*
1	$PhCH_2CH_2CH=C=CH_2$	Ph	9	68	> 20 : 1	> 20 : 1
2		TMS	11	65	> 20 : 1	> 20 : 1
3		$Me_2C(OH)$	25	60	> 20 : 1	> 20 : 1
4		*n*-C_5H_{11}	48	76	> 20 : 1	17 : 1
5	*t*-$BuMe_2SiOCH_2CH=C=CH_2$	Ph	22	88	> 20 : 1	> 20 : 1
6		*n*-C_5H_{11}	20	46	> 20 : 1	> 20 : 1
7	*n*-$BuCH(OH)CH=C=CH_2$	Ph	9	68	> 20 : 1	> 20 : 1
8		TMS	13	70	> 20 : 1	10 : 1
9			2	53	13 : 1	2.9 : 1[b)]
10		Ph	5	81	> 20 : 1	> 20 : 1
11		*m*-ClC_6H_4	7.5	91	20 : 1	20 : 1
12		*o*-FC_6H_4	15	89	> 20 : 1	20 : 1
13		3,4,5-$(MeO)_3C_6H_2$	10	88	> 20 : 1	10 : 1
14		*o*-$TMSC_6H_4$	36	65	4 : 1	2 : 1
15		TMS	18	72	> 20 : 1	> 20 : 1
16		*t*-$BuPh_2Si$	24	89	> 20 : 1	> 20 : 1
17		$Me_2C(OH)$	14	84	> 20 : 1	7 : 1
18		*t*-Bu	30	65[c)]	> 20 : 1	1.6 :1
19		*n*-C_5H_{11}	48	49	3 : 1	1 : 1
20			5	43	2.7 : 1	1.7 : 1[b)]
21		Ph	48	66	20 : 1	> 20 : 1

a) All the products were characterized by ^{1}H-NMR, ^{13}C-NMR, IR, and MS. b) Reaction in CH_3CN. c) The reaction was carried out with 2 mol equiv. of 1-alkyne at 80 °C in a sealed tube.

Reaction of phenylacetylene-d_1 (**2**-d_1) with allene **4** in refluxing THF for 22 h gave the *endo*-(*E*)-**5** in 66% yield with 22% deuteration at the methyl group (Scheme 2). No deuteration at olefinic hydrogen indicates the absence of the product isomerization. Apparently, the reaction of **2**-d_1 is slower than **2** (*Cf.* Table 2, entry 1), which suggests the involvement of hydrogen migration process at the rate determining step. The low deuteration ratio may be attributable to scrambling most probably with phosphine protons. C-H activation of triphenylphosphine with a rhodium complex is known.[6] The solvent is not responsible here, since no product deuteration takes place in the reaction in THF-d_8.



Scheme 2.

Shown in Figure 1 are possible transition states which explain the isomer formation based on the following assumptions; 1) the coupling reaction takes place *via* hydrometalation and reductive elimination, 2) regio- and stereoselectivities are kinetically determined at the hydrometalaltion step, 3) phosphine ligands are located at the *trans*-position in the tetra-coordinated square planer intermediate. In the transition states **B** and **C**, which give *endo*-(*Z*)-adduct and *exo*-adduct, respectively, the steric repulsions between the rhodium ligands and allene substituent **R** are serious. Therefore, *endo*-(*E*)-adduct is form *via* the transition state **A**. Related discussions were made in hydrogenation reaction of 1-alkenes with the same rhodium complex, $HRh(CO)(PPh_3)_3$.[7] It may be interesting to note, however, that both 1-alkynes[8] and allenes[9] resisted to the hydrogenation forming stable alkynylrhodium and π-allylrhodium complexes, respectively. Apparently, further studies are required on the chemical properties of this useful rhodium hydride catalyst.

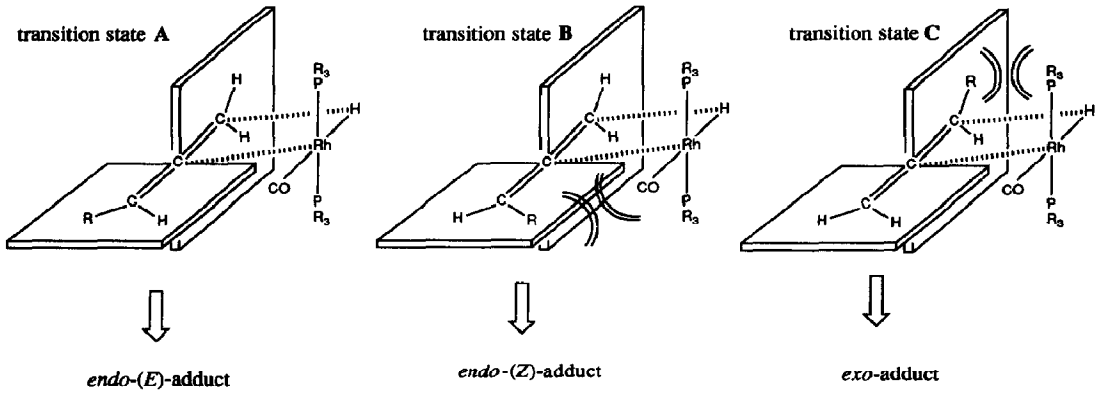


Figure 1.

References and Notes

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4. At first, the coupling reaction was examined with rhodium and ruthenium catalysts in the absence of phosphine. Penta-coordinated hydride complexes $HRh(CO)(PPh_3)_3$, $HRh(PPh_3)_4$, or $H_2Ru(PPh_3)_4$ exhibited some activity, while $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $[Rh(COD)Cl]_2$, *etc.*, were much less effective.
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