Communications

Ruthenium-Promoted *Z*-Selective Head-to-Head Dimerization of Terminal Alkynes in Organic and Aqueous Media

Xingguo Chen,[†] Peng Xue,[†] Herman H. Y. Sung,[†] Ian D. Williams,[†]
Maurizio Peruzzini,[*,‡] Claudio Bianchini,[*,‡] and Guochen Jia[*,†]

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, and Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Via Madonna del Piano, snc, 50019 Sesto Fiorentino (Firenze), Italy

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Summary: [RuH(CH_3CN)(NP_3)]OTf effectively catalyzes the dimerization of both aliphatic and aromatic alkynes to give (Z)-enynes in high regio- and stereoselectivity. The catalytic system can tolerate a number of functional groups, which allows for its use in organic and aqueous medium.

Transition-metal-catalyzed dimerization reactions of terminal alkynes are attractive, atom-economic C−C bond forming reactions that can give products containing key structural units in natural products and materials.[1] Alkyne dimerization reactions are also potentially useful for making conjugated polymers or oligomers from diynes.[2c] Dimerization reactions of RC≡CH can produce several isomeric products, and the most common ones include (*Z*)-RCH═CHC≡CR, (*E*)-RCH═CHC≡CR, CH_2═C(R)C≡CR, *cis*-RHC═C═C═CHR, and *trans*-RHC═C═C═CHR. For practical applications in organic synthesis, ideally, one needs a catalytic system that gives only one desired isomer for a wide range of substrates. However, many of the reported catalytic systems actually give a mixture of some of the isomeric products, and the selectivities of the isomeric products often vary with the substituents of alkynes. Recently, there have been considerable efforts devoted to the understanding of the origins of the selectivity and the development of selective dimerization of terminal alkynes.[1−6] Where *Z*-selective head-to-head dimerization of terminal alkynes is concerned, several catalysts that can mediate selective dimerization of aromatic alkynes[2] or aliphatic alkynes[3] (with *Z* selectivity >90% or 100%) have been disclosed; however, systems that are effective for *Z*-selective head-to-head dimerization of both aromatic and aliphatic alkynes are very rare.

We have previously shown that tripodal phosphine complexes such as [RuH(X_2)(PP_3)]BPh_4, [OsH(N_2)(PP_3)]BPh_4, and RuH_2(PP_3) (X = N_2, H_2; PP_3 = P($CH_2CH_2PPh_2$)$_3$)[4] are excellent catalytic precursors for the selective dimerization of PhC≡CH and Me_3SiC≡CH to give (*Z*)-enynes. In a related study, Dahlenburg et al. have shown that the ruthenium complex RuH(Ph)(NP_3) (NP_3 = N($CH_2CH_2PPh_2$)$_3$)[5] catalyzes the dimerization of *n*-BuC≡CH to give (*Z*)-(*n*-Bu)CH═CHC≡C(*n*-Bu) with a selectivity >95%. Encouraged by these findings, we have synthesized the new complex [RuH(CH_3CN)(NP_3)]OTf (**3**; OTf = trifluoromethanesulfonate) and studied its catalytic property for alkyne dimerization, to see whether the *Z* selectivity can be achieved for a wider range of substrates. Indeed, the new complex was found to promote the selective dimerization of both aliphatic and aromatic alkynes to give (*Z*)-enynes. In addition, the system can tolerate a number of functional groups, including NH_2 and CO_2H, and the catalytic reactions can be carried out in organic and aqueous media.

The catalytic precursor [RuH(CH_3CN)(NP_3)]OTf (**3**) was synthesized by the route shown in Scheme 1. Treatment of $RuCl_2$(NP_3) (**1**)[5] with $NaBH_4$ in THF/ethanol produced the monohydride complex RuHCl(NP_3)

[†] The Hong Kong University of Science and Technology.

[‡] Istituto di Chimica dei Composti Organometallici (ICCOM-CNR).

(1) Reviews: (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (b) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (c) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703. (d) Yi, C. S.; Liu, N. *Synlett* **1999**, 281.

(2) *Z*-Selective head-to-head dimerization of aromatic alkynes: (a) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184. (b) Tazelaar, C. G. J.; Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936. (c) Katayama, H.; Nakayama, M.; Nakano, T.; Wada, C.; Akamastsu, K.; Ozawa, F. *Macromolecules* **2004**, *37*, 13. (d) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968. (e) Echevarren, A. M.; Lopez, J.; Santos, A.; Montoya, J. *J. Organomet. Chem.* **1991**, *414*, 393.

(3) *Z*-Selective head-to-head dimerization of aliphatic alkynes: (a) Qu, J. P.; Masui, D.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, 1003. (b) Jun, C.-H.; Lu, Z.; Crabtree, R. H. *Tetrahedron Lett.* **1992**, *33*, 7119. (c) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275. (d) Pavlik, S.; Gemel, C.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kichner, K. *J. Organomet. Chem.* **2001**, *617*, 301.

(4) (a) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (b) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616. (c) Barbaro, C.; Bianchini, C.; Peruzzini, M.; Polo, A.; Zanobini, F.; Frediani, P. *Inorg. Chim. Acta* **1994**, *220*, 5. (d) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837.

(5) Dahlenburg, L.; Frosin, K.-M.; Kerstan, S.; Werner, D. *J. Organomet. Chem.* **1991**, *407*, 115.

(6) Additional examples of recent work: (a) Schafer, M.; Wolf, J.; Werner, H. *Organometallics* **2004**, *23*, 5173. (b) Horacek, M.; Stepnicka, P.; Kubista, J.; Gyepes, R.; Mach, K. *Organometallics* **2004**, *23*, 3388. (c) Yang, C.; Nolan, S. P. *J. Org. Chem.* **2002**, *67*, 591. (d) Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 11107. (e) Lee, C. C.; Lin, Y. C.; Liu, Y. H.; Wang, Y. *Organometallics* **2005**, *24*, 136.

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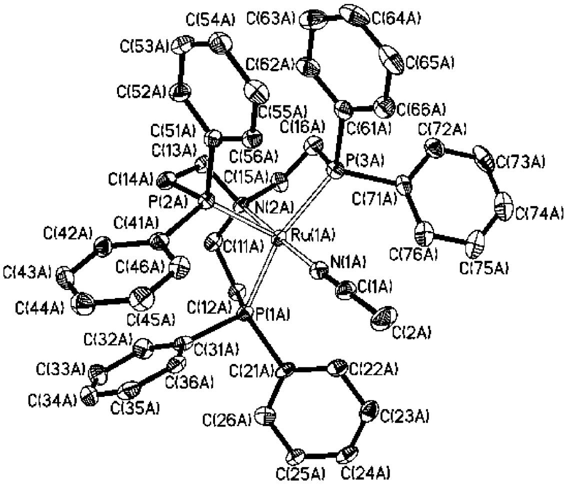
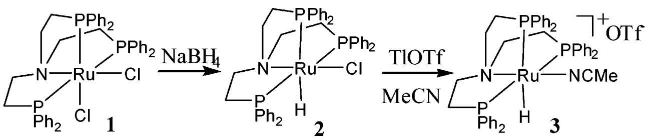


Figure 1. Molecular structure of the complex cation [RuH-(CH$_3$CN)(NP$_3$)]$^+$. Selected bond distances (Å) and angles (deg): Ru(1A)−N(1A), 2.024(4); Ru(1A)−N(2A), 2.169(4); Ru(1A)−P(1A), 2.2835(14); Ru(1A)−P(3A), 2.2983(15); Ru-(1A)−P(2A), 2.3386(14); N(1A)−Ru(1A)−N(2A), 178.16(16); N(1A)−Ru(1A)−P(1A), 96.36(12); N(2A)−Ru(1A)−P(1A), 84.42(11); N(1A)−Ru(1A)−P(3A), 94.66(12); N(2A)−Ru-(1A)−P(3A), 83.86(11); P(1A)−Ru(1A)−P(3A), 149.34(5); N(1A)−Ru(1A)−P(2A), 97.36(12); N(2A)−Ru(1A)−P(2A), 84.04(11); P(1A)−Ru(1A)−P(2A), 102.70(5); P(3A)−Ru-(1A)−P(2A), 104.13(5).

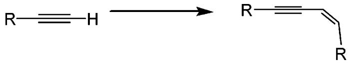
Scheme 1

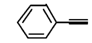
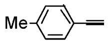
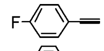
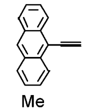
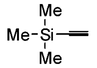
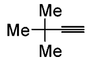
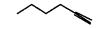
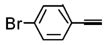
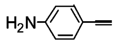
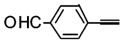
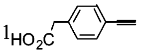
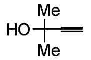
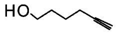
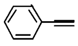
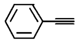
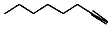
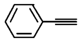
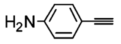
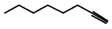
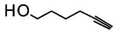


(**2**). Treatment of **2** in acetonitrile with TlOTf produced the cationic complex [RuH(CH$_3$CN)(NP$_3$)]OTf (**3**). The new complexes **2** and **3** have been characterized by NMR spectroscopy and elemental analysis.[7] The structure of **3** has also been confirmed by an X-ray diffraction study. A view of the complex cation is shown in Figure 1. In the solid state, complex **3** is reasonably air stable and can be exposed to air for at least 2 days without appreciable decomposition.

We initially tested the catalytic behavior of complexes **1**−**3** for the dimerization of PhC≡CH in toluene. When a toluene solution of PhC≡CH containing 0.5 mol % of **3** was heated for 11 h, the phenylacetylene was completely consumed. After purification by chromatography, the isolated product was identified to be (*Z*)-PhCH=CHC≡CPh. The stereochemistry was assigned on the basis of the observation of a ^3J(HH) value of 12.0 Hz for the olefinic protons. The other regio- and stereoisomeric dimers were apparently not produced or only produced in trace amounts, as they were not detected by NMR. Under similar conditions, complexes **1** and **2** were inactive for the catalytic dimerization of PhC≡CH, however.

Table 1. Dimerization of Terminal Alkynes Catalyzed by 3



entry	substrate	C/S ratio	solvent	T (°C)/time (h)	isolated yield
1		5/1000	toluene	110/11	92%
2		1/100	toluene	110/10	85%
3		1/100	toluene	110/12	81%
4		1/100	toluene	110/10	78%
5		1/100	benzene	80/24	88%
6		1/100	benzene	80/20	95%[a]
7		5/1000	toluene	110/17	32%[b]
8		5/1000	toluene	110/9	90%
9		1/100	toluene	110/15	87%
10		5/1000	toluene	110/12	86%[c]
11		2/100	isopropanol	100/24	73%
12		1/100	toluene	110/12	91%
13		2/100	toluene	110/33	77%[b]
14		5/1000	none	100/2	95%
15		3/10000	none	100/28	89%
16		2.5/1000	none	120/39	86%[d]
17		5/1000	water	100/16	86%
18		5/1000	water	100/12	85%
19		5/1000	water	100/36	84%[d]
20		1/100	water	100/33	64%[a,b]

[a] Not isolated; percent conversion determined in situ by NMR. [b] Contain 4% head-to-tail dimer. [c] Contains 3% trans dimer. [d] Contains 5% head-to-tail dimer.

We then explored the catalytic dimerization reactions of other terminal alkynes with **3**. The results are summarized in Table 1. Aromatic alkynes such as 4-MeC$_6$H$_4$C≡CH, 4-FC$_6$H$_4$C≡CH, and 9-anthrylacetylene were all selectively converted to the corresponding (*Z*)-enynes when heated in toluene in the presence of 1 mol % of **3**. Complex **3** is also catalytically active for the dimerization of silylalkynes and aliphatic alkynes, although the reactions were slower than those with aryl alkynes. In contrast, the selectivity was maintained: Me$_3$SiC≡CH and Me$_3$CC≡CH were transformed to (*Z*)-Me$_3$SiCH=CHC≡CSiMe$_3$ and (*Z*)-Me$_3$CCH=CHC≡CCMe$_3$, respectively, upon heating in benzene. When straight-chain aliphatic alkynes RC≡CH, for example 1-hexyne and 1-octyne, were used, the selectivity in the *Z* isomers decreased slightly and the reactions produced a mixture of (*Z*)-RCH=CHC≡CR and CH$_2$=C(R)C≡CR in ratios of ca. 100:4 and 100:5, respectively. The lower *Z* selectivity in the reactions of 1-hexyne and 1-octyne is not unexpected, as a similar trend in *Z* selectivity has been also reported for the dimerization of *n*-BuC≡CH and *t*-BuC≡CH mediated by TpRuCl(PPh$_3$)$_2$ (Tp = hydrotris(pyrazol-1-yl)borate)[3c] and [Ir(biph)(PMe$_3$)$_3$Cl]/2AgBF$_4$ (biph = biphenyl-2,2′-diyl).[3b] For example, in the reactions assisted by TpRuCl(PPh$_3$)$_2$, the *Z* selectivity is 100% for *t*-BuC≡CH and only 25% for *n*-BuC≡CH.

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[7] See the Supporting Information for experimental and spectroscopic details of the new compounds.

The present catalytic system can tolerate a number of functional groups. Under conditions similar to those used for the dimerization of phenylacetylene, $4\text{-BrC}_6\text{H}_4\text{C}{\equiv}\text{CH}$, $4\text{-NH}_2\text{C}_6\text{H}_4\text{C}{\equiv}\text{CH}$, and $\text{Me}_2\text{C(OH)C}{\equiv}\text{CH}$ were all selectively converted to the corresponding (*Z*)-enynes; the straight-chain aliphatic alkynol $\text{HO(CH}_2)_4\text{C}{\equiv}\text{CH}$ was converted to (*Z*)-$\text{HO(CH}_2)_4\text{CH}{=}\text{CHC}{\equiv}\text{C(CH}_2)_4\text{OH}$ and $\text{CH}_2{=}\text{C((CH}_2)_4\text{OH)C}{\equiv}\text{C(CH}_2)_4\text{OH}$ in a ratio of ca. 100:4. The selectivity of the latter reaction is similar to that with 1-hexyne. It is interesting to note that the propargyl alcohol $\text{Me}_2\text{C(OH)C}{\equiv}\text{CH}$ is dimerized to a dienone rather than to enynes under the influence of $[\text{CpRu(CH}_3\text{CN)}_3]\text{BF}_4$.[8]

Our catalytic system can also tolerate the aldehydic group. Thus, the aldehyde $4\text{-HCOC}_6\text{H}_4\text{C}{\equiv}\text{CH}$ was converted predominantly to (*Z*)-$\text{HOCC}_6\text{H}_4\text{CH}{=}\text{CHC}{\equiv}\text{CC}_6\text{H}_4\text{-CHO}$, although the reaction produced also a small amount (ca. 3%) of (*E*)-enyne. Even *p*-$\text{HO}_2\text{CCH}_2\text{C}_6\text{H}_4\text{C}{\equiv}\text{CH}$, which has a carboxylic acid group, can be transformed to the corresponding (*Z*)-enyne when heated in 2-propanol in the presence of **3**. In contrast, ruthenium complexes such as $\text{Ru(PR}_3)_2(\text{allyl})_2$ and Cp*Ru(COD) promote the addition of carboxylic acids to $\text{HC}{\equiv}\text{CR}$ to give exclusively alkenyl esters[9a] or dimerized dienyl esters.[9b] It is noteworthy that the regioselective formation of alkenyl esters is catalyzed by the Rh(I) NP_3 derivative $[\text{RhH(NP}_3)]$.[10]

For liquid substrates, the dimerization reactions can be carried out neat without additional organic solvents. Thus, $\text{PhC}{\equiv}\text{CH}$ and 1-octyne can be converted to the corresponding (*Z*)-enynes by heating in the presence of **3**. The catalytic efficiency of **3** for the dimerization of $\text{PhC}{\equiv}\text{CH}$ is remarkable. For example, almost complete conversion of phenylacetylene to the (*Z*)-enyne can be achieved in 2 h with a catalyst/substrate ratio of 5/1000 or in 28 h with a catalyst/substrate ratio of 3/10 000. Most previously reported dimerization reactions of alkynes were carried out with more than 1% catalyst.

Chemical reactions in aqueous medium are of growing importance because of many potential advantages, such as alleviation of environmental problems associated with the use of organic solvents.[11] Since the catalytic system can tolerate polar functional groups and complex **3** has some solubility in polar solvents, the dimerization reactions were attempted in water. Surprisingly, $\text{PhC}{\equiv}\text{CH}$, $4\text{-NH}_2\text{C}_6\text{H}_4\text{C}{\equiv}\text{CH}$, 1-octyne, and $\text{HO(CH}_2)_4\text{C}{\equiv}\text{CH}$ could all be dimerized in water with a selectivity for the *Z* isomers essentially identical with that observed in organic medium. To our knowledge, these are the first examples of selective catalytic dimerization of alkynes to give (*Z*)-enynes carried out in water.[12] It is known that ruthenium complexes (e.g. $\text{CpRuCl(PPh}_3)_2$ and $(\text{PNP})\text{RuCl}_2(\text{PPh}_3))$ can promote either the hydration[13] or the hydrolysis of alkynes.[14] In our case, no product resulting from either reaction was detected.

A detailed mechanism for the dimerization reactions mediated by the $[\text{Ru(NP}_3)]^+$ system is not yet clear, as the intermediates of the dimerization reactions have not been identified. On the other hand, it has been established that dimerization of $\text{RC}{\equiv}\text{CH}$ mediated by the very similar precursor $[\text{RuH(X}_2)(\text{PP}_3)]\text{BPh}_4$ ($\text{X}_2 = \text{H}_2, \text{N}_2$) proceeds through the coupling of vinylidene and acetylide ligands.[4] Thus, it is very likely that the present formation of (*Z*)-enynes may involve a similar mechanism. The small amounts of head-to-tail dimers in the reactions of 1-octyne and 1-hexyne are presumably formed by direct insertion of alkynes into metal–acetylide bonds.

In summary, we have found that the ruthenium complex $[\text{RuH(CH}_3\text{CN)(NP}_3)]\text{OTf}$ can efficiently mediate the dimerization of both aliphatic and aromatic alkynes in a highly regio- and stereoselective manner to give (*Z*)-enynes. The catalyst is reasonably air stable and can tolerate a number of functional groups, which allows for its use in organic and aqueous media.

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Supporting Information Available: Text and tables giving experimental procedures and characterization data and a CIF file giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2001**, *123*, 8862.

(9) (a) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247. (b) Le Paih, J.; Monnier, F.; Derien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* **2003**, *125*, 11964.

(10) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **1990**, *9*, 1155.

(11) Joo, F. *Aqueous Organometallic Catalysis*; Kluwer: Dordrecht, The Netherlands, 2001.

(12) Rh-catalyzed dimerization reactions of arylalkynes to give mixtures of enynes in toluene/pyridine/water are known: Baidossi, W.; Goren, N.; Blum, J.; Schumann, H.; Hemling, H. *J. Mol. Catal.* **1993**, *85*, 153.

(13) Tokunaga, M.; Suzuki, T.; Koga, N.; Fukushima, T.; Horiuchi, A.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 11917. (b) Grotjahn, D. B.; Lev, D. A. *J. Am. Chem. Soc*. **2004**, *126*, 12232.

(14) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585.