Head-to-head Z Dimerization of Terminal Alkynes Catalyzed by Thiolate-bridged Diruthenium Complexes

Jing-Ping Qü, Dai Masui, Youichi Ishii, and Masanobu Hidai*
Department of Chemistry and Biotechnology, Graduate School of Engineering, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656

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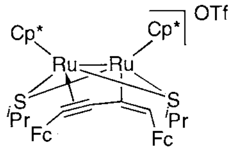
The thiolate-bridged diruthenium complexes [Cp*RuCl(μ-SR)$_2$RuCp*Cl] (R = Me, Et, ^{n}Pr) were found to be effective and highly selective catalysts for the head-to-head Z dimerization of various terminal alkynes including straight-chain aliphatic alkynes and those with functional groups.

Multinuclear complexes as a new tool in catalytic organic synthesis are the subject of current research activity, because they are expected to effect new or highly efficient catalytic processes through unique activation and transformation of substrate molecules at their multimetallic centers.[1] In the course of our continued study on the syntheses and reactivities of multinuclear noble metal complexes with bridging chalcogen ligands,[2] we have recently reported that the cationic diruthenium complex [Cp*RuCl(μ-S^{i}Pr)$_2$Ru(OH$_2$)Cp*][OTf] (**1**; Cp* = η^5-C$_5$Me$_5$) reacts readily with ferrocenylacetylene to give the dinuclear butenynyl complex [Cp*Ru{μ-C(=CHFc)C ≡ CFc}(μ-S^{i}Pr)$_2$RuCp*][OTf] (**2**, Fc = ferrocenyl), which further catalyzes stereoselective di- and trimerization of this alkyne.[3] However, complex **1** was not effective for the catalytic dimerization of other alkynes. Now we have found that the diruthenium complexes with MeS-, EtS- or ^{n}PrS-bridges [Cp*RuCl(μ-SR)$_2$RuCp*Cl] (**3**, R = Me; **4**, R = Et; **5**, R = ^{n}Pr) catalyze the stereoselective dimerization of various terminal alkynes including straight-chain aliphatic alkynes and those with functional groups to afford the head-to-head Z dimers.

In recent years, considerable efforts have been devoted to development of selective dimerization of terminal alkynes,[4] and several transition metal complexes have been reported to catalyze the head-to-head Z selective dimerization of aryl- and/or silylalkynes.[5] However, only a few catalysts such as mononuclear ruthenium and iridium complexes have been known to be effective for the selective dimerization of straight-chain aliphatic alkynes.[6]

Complex **3** was synthesized by the reaction of [Cp*RuCl$_2$]$_2$ with 2.5 equiv of MeSSiMe$_3$ in THF at room temperature in 77% yield and was fully characterized spectroscopically[7] as well as crystallographically.[8] When a solution of 1-octyne (1 mmol), complex **3** (0.065 mmol) and NH$_4$BF$_4$ (0.13 mmol) in dry MeOH (5 ml) was kept at 60 °C for 18 h, the alkyne was completely consumed and (*Z*)-hexadec-7-en-9-yne (**6**) was formed in 94% GLC yield (eq 1). No other regio- or stereoisomeric dimer of **6** was detected by GLC. Purification by silica-gel column chromatography followed by bulb-to-bulb distillation afforded pure **6** in 82% isolated yield.[9] A similar reaction in the absence of NH$_4$BF$_4$ also gave **6** stereoselectively but in slightly lower yield (90% conv., 81% GLC yield).



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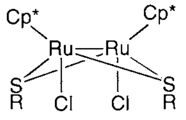
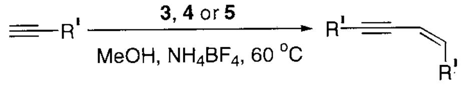


3 : R = Me
4 : R = Et
5 : R = ^{n}Pr



(1)

Table 1. Catalytic dimerization of 1-octyne by dinuclear complexes[a]

Catalyst	GC yield /%
[Cp*RuCl(μ$_2$-SMe)$_2$RuCp*Cl] (**3**)	94
[Cp*RuCl(μ$_2$-SEt)$_2$RuCp*Cl] (**4**)	92
[Cp*RuCl(μ$_2$-S^{n}Pr)$_2$RuCp*Cl] (**5**)	94
[Cp*RuCl(μ$_2$-S^{i}Pr)$_2$RuCp*Cl]	9
[Cp*RuCl(μ$_2$-SH)$_2$RuCp*Cl]	0
[Cp*RhCl(μ$_2$-SMe)$_2$RhCp*Cl]	0
[Cp*IrCl(μ$_2$-SMe)$_2$IrCp*Cl]	0
[Cp*RuCl(μ$_2$-Cl)$_2$RuCp*Cl]	10

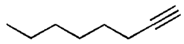
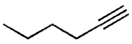
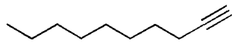
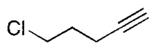
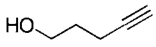
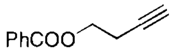
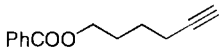
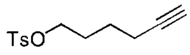
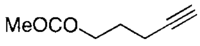
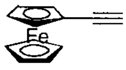
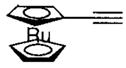
[a] 1-Octyne, 1 mmol; catalyst, 0.065 mmol; NH$_4$BF$_4$, 0.13 mmol; MeOH, 5 ml; 60 °C.

The bridging thiolato ligands in the diruthenium complex were found to strongly influence the catalytic activity (Table 1). The complex with sterically demanding ^{i}PrS ligands [Cp*RuCl(μ-S^{i}Pr)$_2$RuCp*Cl][10] was of only marginal activity, while the complexes with primary alkanethiolato bridges **4**[11] and **5**[12] showed catalytic activity comparable to that of **3**. The hydrosulfido complex [Cp*RuCl(μ-SH)$_2$RuCp*Cl][11] as well as the dirhodium and diiridium complexes analogous to **3** was totally ineffective.

Complex **3** was successfully used as the catalyst for the dimerization of a wide variety of terminal alkynes to give the head-to-head Z dimers[9] (Table 2). From a synthetic point of view, it would be interesting to point out that aliphatic alkynes including those with functional groups such as chloro, hydroxy, and ester groups can be converted into the corresponding head-to-head Z dimers in nearly complete regio- and stereoselectivity, although some of the functionalized substrates required a longer reaction time than 1-octyne. Ferrocenylacetylene yielded the head-to-head Z dimer as the sole product, while a similar reaction with complex **2** afforded a mixture of the dimer and the linear Z, Z trimer.[3] The reaction of methyl propiolate failed to give the corresponding dimer; a mixture of the cyclotrimerization products, trimethyl 1,2,4- and 1,3,5-benzenetricarboxylates (ca. 40:60), was formed in quantitative yield.

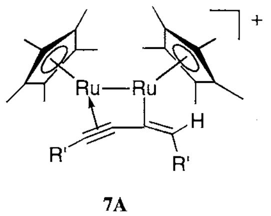
Although we have not succeeded in isolating a catalytic

Table 2. Catalytic dimerization of 1-alkynes by **3**[a]

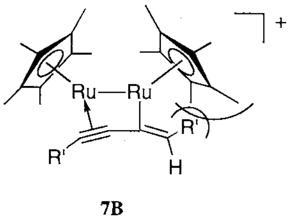
Alkyne	Time /h	Isolated yield /%
	18	82
	18	77
	18	61
	45	93
	240	66[b]
	18	81
	18	99
	80	90
	110	93
	18	100
	18	60[c]

[a] Alkyne, 1 mmol; **3**, 0.065 mmol; NH_4BF_4, 0.13 mmol; MeOH, 5 ml; 60 °C. [b] Recovery, 7% (^{1}H NMR). [c] Acetylruthenocene, 15% (^{1}H NMR).

intermediate, the ^{1}H NMR analysis of the crude reaction mixture obtained from the catalytic dimerization of ferrocenylacetylene by **3** in the absence of NH_4BF_4 (conv. 100%) revealed that complex **3** was essentially the only ruthenium species existing after the catalysis. Moreover, complex **3** was recovered in 91% yield from this mixture after purification by column chromatography.[13] These observations strongly suggest that the dinuclear core of **3** is retained during the catalysis. On the basis of the previous findings about the reactivities of complexes **1** and **2**,[14] it is assumed that the present catalytic reaction involves the formation of a dinuclear vinylidene alkynyl complex followed by its conversion into a butenynyl complex **7A**.[15] This intermediate yields the head-to-head *Z* dimer on protonolysis. The stereoisomeric intermediate **7B** is considered to be disfavored due to the steric congestion between the Cp* ligand on the vinylruthenium center and the alkyl substituent (R') *cis* to the ruthenium atom. Further study on the reaction mechanism is in progress.



7A



7B

(The SR ligands are omitted for clarity.)

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7 ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 30H, Cp*), 2.51 (s, 6H, S*Me*). Anal. Found: C, 41.32; H, 5.69%. Calcd. for $C_{22}H_{36}Cl_2Ru_2S_2$: C, 41.44; H, 5.69%.

8 Crystallographic data for **3**: $C_{22}H_{36}Cl_2Ru_2S_2$, $M = 637.69$, monoclinic, space group *C2/c*, $a = 8.565(2)$ Å, $b = 16.105(2)$ Å, $c = 18.273(2)$ Å, $\beta = 101.62(1)^\circ$, $V = 2469.0(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.715$ gcm^{-3}, $F(000) = 1288.00$, μ(Mo Kα) = 16.16 cm^{-1}, $R = 0.032$, $R_w = 0.028$ for 2241 reflections with $I > 3\sigma(I)$. The molecular structure is closely related to that of **4**.[11]

9 *cis*-Hexadec-7-en-9-yne: ^{1}H NMR ($CDCl_3$) δ 0.887, 0.894, (t×2, 3H each, $J = 6.8$ Hz, Me), 1.29-1.57 (m, 16H, methylene), 2.24-2.36 (m, 4H, C=C-CH_2-, C≡C-CH_2-), 5.42 (m, 1H, $J = 10.6$ Hz C*H*=CH-^{n}Hex), 5.80 (dt, 1H, $J = 10.6$, 7.6 Hz, CH=C*H*-^{n}Hex). All the dimerization products were fully characterized by ^{1}H and ^{13}C NMR. Their stereochemistry was determined on the basis of the vinyl coupling constants (δ 5.29 – 6.44 ppm, $J = 9.5 – 11.4$ Hz), which are diagnostic of *cis* couplings.

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12 ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 6H, $J = 7.6$ Hz, SCH_2CH_2*Me*), 1.55 (s, 30H, Cp*), 1.72 (sextet, 4H, $J = 7.6$ Hz, SCH_2C*H*$_2$Me), 1.72 (m, 4H, SC*H*$_2$$CH_2$Me). Anal. Found: C, 45.12; H, 6.39%. Calcd. for $C_{26}H_{44}Cl_2Ru_2S_2$: C, 45.01; H, 6.39%.

13 In the catalytic dimerization of ferrocenylacetylene in the presence of NH_4BF_4, the ^{1}H NMR spectrum of the reaction mixture showed the presence of a dinuclear cationic complex (^{1}H NMR (acetone-*d*$_6$) δ 1.64 (s, Cp*, 15H), 1.75 (s, Cp*, 15H), 2.41 (s, SMe, 6H)) as a sole metal species, which is identical to that formed by the reaction of **3** with NH_4BF_4 in MeOH.

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