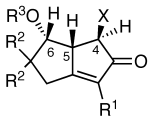
[10] Very similar yields and diastereoselectivities were obtained in the thermal PK reaction (CH_3CN, 80 °C) of the dicobalt complexes of the enynes **1** and **3**.

[11] The combination TMANO/molecular sieves has been recently reported as an efficient promoter in PK reactions: L. Pérez-Serrano, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *Org. Lett.* **1999**, *1*, 1187.

[12] Except for the free alcohols **1a** and **3a**, which proved to be rather unreactive in PK reactions. For instance, the alkyne dicobalt hexacarbonyl complex of **1a** did not react at all under thermal (CH_3CN, 80 °C) or TMANO-promoted conditions (CH_2Cl_2, RT). A very low yield of PK products **9a** (25% yield, *endo*/*exo* = 85/15) was obtained when the reaction was performed in the presence of TMANO and molecular sieves. In this case, instead of the PK cyclopentenone, the main product was the corresponding exocyclic 1,3-diene (see ref. [4]).

[13] As is usual in other 6-substituted bicyclo[3.3.0]octen-3-ones (for example, ref. [2c]), the coupling constant between H_5 and H_6 is a very simple and excellent criterion for stereochemical diagnosis. Thus, $J_{5,6}$ is much smaller in the *endo* isomers ($J_{5,6} = 3.6-4.8$ Hz, H_5/H_6 in *cis* relationship) than in the *exo* isomers ($J_{5,6} = 7.5-10.5$ Hz, H_5/H_6 in *trans* arrangement). Also, a characteristic trend was observed for the chemical shift of H_6 in the C-4 sulfonylated adducts: H_6 is significantly more deshielded in the *endo* isomer than in the *exo* isomer (see below), in accordance with the strong deshielding effect of the phenylsulfonyl group on the hydrogen atom in the 1,3-parallel arrangement. Additionally, these stereochemical assignments have been confirmed by NOESY experiments on the pairs of isomers *endo*/*exo* **9b** and *endo*/*exo* **13c**.

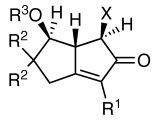
endo



X = SO_2Ph, $J_{5,6}$ = 3.6-4.1 Hz, $J_{4,5}$ = 4.1-4.6 Hz

X = H, $J_{5,6}$ = 3.5-4.8 Hz

exo



X = SO_2Ph, $J_{5,6}$ = 7.5-7.9 Hz, $J_{4,5}$ = 2.8-3.5 Hz

X = H, $J_{5,6}$ = 8.6-10.5 Hz,

X = SO_2Ph, $\Delta\delta_6 = \delta_{6,\ endo} - \delta_{6,\ exo}$ = 0.33-0.65 ppm (in $CDCl_3$)

[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141942. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] Recent examples: S. Fonquerna, R. Rios, A. Moyano, M. A. Pericàs, A. Riera, *Eur. J. Org. Chem.* **1999**, 3459, and references therein.

[16] For instance, see a) P. M. Breczinski, A. Stumpf, H. Hope, M. E. Krafft, J. A. Casalnuovo, N. E. Schore, *Tetrahedron* **1999**, *55*, 6797; b) J. Castro, A. Moyano, M. A. Pericàs, A. Riera, *Tetrahedron* **1995**, *51*, 6541.

[17] a) J. C. Carretero, R. Gómez Arrayás, *J. Org. Chem.* **1998**, *63*, 2993; b) J. Adrio, J. C. Carretero, R. Gómez Arrayás, *Synlett* **1996**, 640. Similar conformational preferences have been reported for γ-oxygenated α,β-unsaturated esters, see: c) B. W. Gung, M. B. Francis, *Tetrahedron Lett.* **1995**, *36*, 2579; d) B. W. Gung, M. B. Francis, *J. Org. Chem.* **1993**, *58*, 6177.

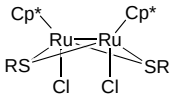
[18] In all the studied cases, only the *R* enantiomer of the (±)-(*E*)-γ-hydroxy-α,β-unsaturated sulfone was acetylated (J. C. Carretero, E. Domínguez, *J. Org. Chem.* **1992**, *57*, 3867).

[19] Specific rotations: (*S*)-**1a**: $[\alpha]_D^{20} = +28.0$ ($c = 1$, $CHCl_3$); (*R*)-**1d**: $[\alpha]_D^{20} = +5.1$ ($c = 1$, $CHCl_3$); (*S*)-**1c**: $[\alpha]_D^{20} = -25.1$ ($c = 1.8$, $CHCl_3$); (4*R*,5*R*,6*S*)-**9c**: $[\alpha]_D^{20} = +241$ ($c = 0.4$, $CHCl_3$); (5*R*,6*S*)-**10c**: $[\alpha]_D^{20} = +90.2$ ($c = 0.2$, $CHCl_3$).

Cyclization of Terminal Diynes Catalyzed by Thiolate-Bridged Diruthenium Complexes: A Simple Synthetic Route to *endo*-Macrocyclic (*Z*)-1-En-3-ynes**

Yoshiaki Nishibayashi, Masashi Yamanashi, Issei Wakiji, and Masanobu Hidai*

Homogeneous catalysis by polynuclear transition metal complexes has been receiving much attention because the multimetallic sites are expected to provide unique reaction sites for activation and transformation of substrate molecules. These sites are anticipated to differ significantly from those of conventional monometallic centers coordinated by ancillary ligands.[1] Toward this end, our studies have long been focused on the synthesis and reactivity of polynuclear noble-metal complexes with bridging sulfur ligands.[2] Recently, we found that the thiolate-bridged diruthenium complexes $[Cp^*RuCl(\mu_2\text{-}SR)_2RuCp^*Cl]$ (**1**–**3**)($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me, Et, *n*Pr) catalyze the head-to-head *Z* dimerization of terminal alkynes containing straight-chain aliphatic and functional groups.[3] Although mononuclear ruthenium complexes such as $[Cp^*Ru(L)H_3]$ (L = phosphane) also catalyze the dimerization of terminal alkynes, such a highly regio- and stereoselective dimerization of a wide range of terminal alkynes has never been realized.[4] We have now extended our study of the catalytic activity of the diruthenium complexes to include the cyclization of terminal diynes. Preliminary results are described here.



1; R = Me
2; R = Et
3; R = *n*Pr
4; R = *i*Pr

Trost and co-workers have reported the palladium-catalyzed cyclization of α,ω-diynes to give the corresponding *exo*-macrocyclic 1-en-3-ynes in moderate yields and high regio- and stereoselectivities.[5] In sharp contrast, synthetic routes to *endo*-macrocyclic 1-en-3-ynes are extremely limited.[6] Actually, six steps are necessary to prepare (*Z*)-1-cyclododecen-3-yne from cyclododecanone and the total yield is less than 5%.[6] To the best of our knowledge, there is no report of a synthetic method for *endo*-macrocyclic (*Z*)-1-en-3-ynes from α,ω-diynes.[7]

Treatment of 1,15-hexadecadiyne[8] (**6a**) in methanol in the presence of $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*Cl]$ (**1**) (10 mol%) at

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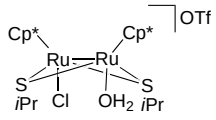
60 °C for 18 h afforded (*Z*)-1-cyclohexadecen-3-yne (**7a**) in 72 % yield as determined by gas-liquid chromatography (GLC). A dilute solution of **6a** (0.002 mol L^{-1}) was required to obtain **7a** in high yield. This new compound (**7a**) was fully characterized by NMR and IR spectroscopy, GC-MS, and elemental analysis (see Experimental Section). No regio- or stereoisomers of **7a** were detected by ^{1}H NMR spectroscopy or by GLC. However, dimers of **6a** were obtained in approximately 25 % yield by GLC. Interestingly, addition of NH_4BF_4 significantly improved both the catalytic activity and the selectivity (94 % yield: Table 1; entry 1).[9] As observed in the previous dimerization of terminal alkynes[3] the bridging thiolato ligands in the diruthenium complex were found to strongly influence the catalytic activity. The complex with the sterically demanding S*i*Pr group [Cp*RuCl(μ_2-S*i*Pr)$_2$RuCp*Cl] (**4**) exhibited only low catalytic activity, whereas the complexes with SEt and S*n*Pr groups (**2** and **3**, respectively) showed almost the same catalytic activity as **1**. Other diruthenium complexes such as [Cp*RuCl(μ_2-S*i*Pr)$_2$RuCp*(OH$_2$)]-OTf (**5**), [Cp*RuCl(μ_2-SH)$_2$-RuCp*Cl], and [Cp*RuCl(μ_2-Cl)$_2$-RuCp*Cl] were ineffective.



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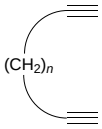
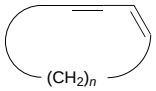
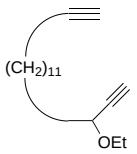
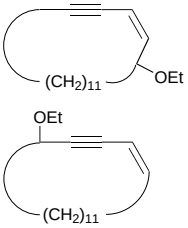
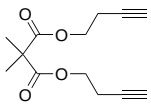
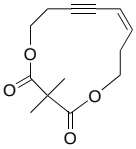
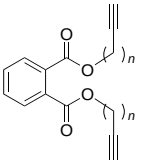
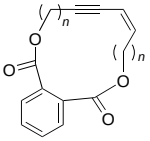
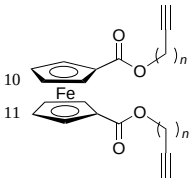
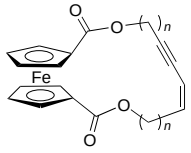
Reactions of other α,ω-diynes (**6**) in the presence of **1** and NH_4BF_4 have been investigated. The cyclization reactions of 1,13-tetradecadiyne (**6b**) and 1,11-dodecadiyne (**6c**) proceeded rapidly to afford the corresponding (*Z*)-1-en-3-ynes (**7b** and **7c**) in 69 and 48 % yields, respectively (Table 1; entries 2 and 3). In contrast, the reaction of 1,9-decadiyne (**6d**) under identical conditions did not occur smoothly. A longer reaction time was required to produce (*Z*)-1-cyclodecen-3-yne (**7d**) in 41 % yield (Table 1; entry 4). Noteworthy is that the 16-, 14-, and 10-membered ring products (**7a**, **7b** and **7d**) are new compounds. On the other hand, no cyclization of 1,7-octadiyne (**6e**) occurred, although after 24 h **6e** was almost completely consumed (Table 1; entry 5). The cyclization of the unsymmetrical diyne **8** under the same reaction conditions led to the formation of a mixture of two regioisomers (*Z*)-1-en-3-ynes **9** in 31 % yield (isomer ratio 2:1; Table 1; entry 6), whereas a 13-membered ring product **11** was obtained from a symmetrical diyne **10** in 72 % yield (Table 1; entry 7). Furthermore, cyclization of terminal diynes with a phenyl or ferrocenyl moiety (**12** and **14**, respectively) proceeded smoothly to give the corresponding *endo*-macrocyclic (*Z*)-1-en-3-ynes (**13** and **15**) in moderate to high yields (Table 1; entries 8–11). All the cyclized products were fully charac-

Table 1. Ruthenium-catalyzed cyclization of α,ω-diynes.[a]

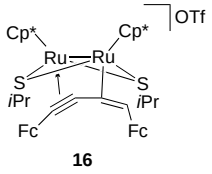
Entry	α,ω-Diynes			Time [h]	Conv. [%][b]	Product			Yield [%][c]
1		**6a**	$n=12$	1	>99		**7a**	$n=12$	78 (94)
2		**6b**	$n=10$	1	>99		**7b**	$n=10$	69 (81)
3		**6c**	$n=8$	1	>99		**7c**	$n=8$	48 (60)
4		**6d**	$n=6$	18	87		**7d**	$n=6$	41 (50)
5		**6e**	$n=4$	24	90		**7e**	$n=4$	0 (0)
6		**8**		48	75		**9**		31 (48)[d]
7		**10**		24	>99		**11**		72
8		**12a**	$n=2$	24	>99		**13a**	$n=2$	73
9		**12b**	$n=3$	72	–		**13b**	$n=3$	35
10		**14a**	$n=2$	24	–		**15a**	$n=2$	52
11		**14b**	$n=3$	72	–		**15b**	$n=3$	24

[a] All the reactions were carried out with α,ω-diyne (0.25 mmol), **1** (0.025 mmol), and NH_4BF_4 (0.05 mmol) in methanol (125 mL) at 60 °C. [b] Determined by GLC. [c] Yield of isolated product. The value in parenthesis is the yield determined by GLC. [d] Isomer ratio 2:1.

  1433-7851/00/3916-2910 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2000**, *39*, No. 16

terized by spectroscopic methods, MS, and elemental analysis. Their configuration was determined from the vinyl coupling constants in the ^{1}H NMR spectra, which are diagnostic of *cis* couplings. The molecular structure of one of the typical *endo*-macrocyclic (*Z*)-1-en-3-ynes, **15a**, was unambiguously determined by X-ray analysis, and an ORTEP drawing is shown in the Supporting Information.[10]

We previously reported the reaction of complex **5** with ferrocenylacetylene at ambient temperature to form the butenynyl complex [Cp*Ru{μ_2-C(=CHFc)C≡CFc}(μ_2-S*i*Pr)$_2$-RuCp*]OTf (**16**; Fc = ferrocenyl), which catalyzes the stereoselective di- and trimerization of ferrocenylacetylene at 60 °C.[11] The ^{1}H NMR analysis of the reaction mixture of **1** and **6a** at room temperature or 60 °C did not show the formation of such intermediate complexes. However, the present cyclization of α,ω-diynes is also considered to involve a butenynyl intermediate **17** similar to **16**. Noteworthy is that **7a** was not obtained from the cyclization of **6a** by using [Ir(biph)(PMe$_3$)$_3$Cl] (biph = biphenyl-2,2′-diyl), which is known to be effective for the selective head-to-head *Z* dimerization of aliphatic terminal alkynes.[12]



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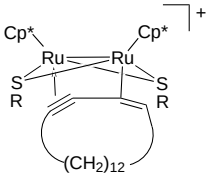

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In summary, we have a novel cyclization of α,ω-diynes, which is catalyzed by the thiolate-bridged diruthenium complexes **1**, **2**, and **3** to produce the corresponding *endo*-cyclic (*Z*)-1-en-3-ynes in moderate to high yields with complete stereoselectivities.

Experimental Section

Typical procedure for the cyclization: NH_4BF_4 (5.5 mg, 0.05 mmol), and **6a** (55 mg, 0.25 mmol) were added to a solution of complex **1** (16 mg, 0.025 mmol) in dry MeOH (125 mL). The reaction mixture was stirred at 60 °C for 1 h. The GLC analysis using naphthalene (10 mg) as an internal standard showed the formation of **7a** in 94 % yield. For the isolation of **7a**, the solvent was removed under reduced pressure and the residue was purified by HPLC ($CHCl_3$ eluent) to give pure **7a** (43 mg, 0.20 mmol, 78 %); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.34-1.50$ (br m, 20H, -CH_2-), 2.29–2.40 (m, 4H, CH_2C≡C, -CH=CHCH_2-), 5.44 (d, 1H, $J = 10.7$ Hz, -C*H*=CHCH$_2$-), 5.80 (dt, 1H, $J = 10.7$, 7.7 Hz, -CH=C*H*-CH$_2$-); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.2$ (t), 25.8 (t), 25.8 (t), 26.5 (t), 26.5 (t), 26.6 (t), 26.9 (t), 27.1 (t), 27.2 (t), 27.6 (t), 28.1 (t), 29.8 (t), 77.8 (s), 94.1 (s), 109.5 (d), 142.5 (d); GC-MS: *m*/*z* (%) 218 (17) [M^+], 189 (1), 161 (5), 147 (9), 133 (17), 105 (26), 91 (67), 79 (100), 67 (61), 41 (91); IR (neat): $\tilde{\nu}$ (cm^{-1}) = 1617 (C=C), 2211 (C≡C); elemental analysis calcd for $C_{16}H_{26}$: C 88.00, H 12.00; found: C 87.63, H 11.89.

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[7] F. Sondheimer, *Acc. Chem. Res.* **1972**, *5*, 81.
[8] W. S. Smith, O. F. Beumel, Jr., *Synthesis* **1974**, 441.
[9] The reaction of **1** with NH_4BF_4 is considered to afford a cationic, thiolate-bridged diruthenium complex with a vacant site.
[10] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137921. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[11] H. Matsuzaka, Y. Takagi, Y. Ishii, M. Nishio, H. Hidai, *Organometallics* **1995**, *14*, 2153.
[12] C.-H. Jun, Z. Lu, R. H. Crabtree, *Tetrahedron Lett.* **1992**, *33*, 7119.

A Semiconducting Lamella Polymer [{Ag(C_5H_4NS)}$_n$] with a Graphite-Like Array of Silver(I) Ions and Its Analogue with a Layered Structure**

Weiping Su, Maochun Hong,* Jiabao Weng, Rong Cao,* and Shaofang Lu

A great deal of work has recently been devoted to inorganic–organic hybrid-framework assemblies such as multilayer perovskites,[1] metal phosphonates[2] and metal–ligand networks[3] because of their potential as functional solid materials. The diversity of organic components used has resulted in numerous inorganic–organic hybrid frameworks with fascinating structural topologies.[1–4] By carefully selecting the organic components one hopes to tune the physical properties of this type of compound by tailoring their structures and thus realize various applications, including electrical conductivity,[4a,b] magnetism,[4c] catalysis,[4d,e] shape specificity,[4f] and ion exchange.[4g,h] Structural isomers of coordination polymers can be prepared by controlling the synthetic conditions such as temperature and medium.[5] By using different thiolate ligands containing N-donor groups we

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