CHEMISTRY LETTERS, pp. 499-502, 1983.

SELECTIVE [π6s + π2s] CYCLOADDITION OF A COORDINATED CYCLIC TRIENE WITH ALKYNES. FORMATION OF BICYCLO[4.2.2]DECATRIENE SKELETON ON A Ru(0) TEMPLATE

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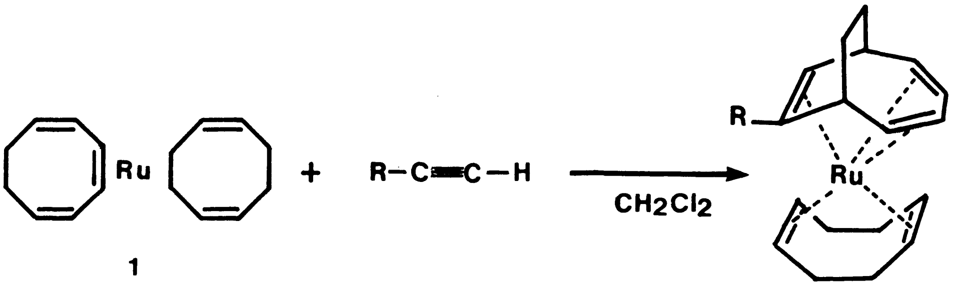
The 1,3,5-cyclooctatriene ligand of Ru(1-6-η-cyclooctatriene)-(1-2:5-6-η-cyclooctadiene) reacted with ethyne to yield Ru(η^4,η^2-bicyclo[4.2.2]deca-2,4,7-triene)(1-2:5-6-η-cyclooctadiene) by way of formal [π6s+π2s] cycloaddition with high selectivity. Propyne or 1-butyne gave analogous bicylodecatriene complexes.

Several olefin complexes of Ru(0) have been prepared in recent years, however, little has been studied on the reactivity of coordinated organic ligands excepting simple ligand exchange reactions.1)

In this paper, we report a highly periselective [π6s+π2s] cycloaddition between terminal acetylenes and coordinated 1,3,5-cyclooctatriene of Ru(1-6-η-C_8H_{10})(1-2:5-6-η-C_8H_{12}), **1**, to generate selectively coordinated bicyclo-[4.2.2]deca-2,4,7-trienes. When ethyne was bubbled to a dichloromethane(9 ml) solution of **1**(292 mg) for 1 h at 0°, color of the solution turned from yellow to deep orange. After removal of the solvent and chromatographic separation(alumina, n-hexane), orange crystals of Ru(η-$C_{10}H_{12}$)(η-C_8H_{12}), **2a**, were obtained in 95% yield.2) Based on NMR spectroscopic data and chemical evidence discussed later, **2a** is concluded to involve η^4,η^2-bicyclo[4.2.2]deca-2,4,7-triene which is formed by the thermally forbidden [π6s+π2s] cycloaddition between ethyne and coordinated 1,3,5-cyclooctatriene.3)

Similar cycloaddition of **1** took place with propyne and 1-butyne as trienophiles at 25° in 85 and 81% yields, respectively.2) Internal acetylenes,



2a R=H
2b R=CH_3
2c R=C_2H_5

such as 2-butyne, 3-hexyne, or dimethyl acetylenedicarboxylate, reacted with 1, however, other reactions occurred by the cleavage of allylic or propargylic C-H bonds of coordinated 1,5-cyclooctadiene or acetylenes to give complex products.

The ^{1}H NMR spectrum of the ethyne adduct, 2a, is shown in Fig. 1 together with several decoupling experiments(Fig. 1; b-d). The original spectrum suggests the presence of coordinated 1,5-cyclooctadiene which remained unchanged(Fig. 1; a, δ3.23, brs, 4H, CH= and 2.25, m, 8H, CH$_2$). The appearance of five sets of multiplets due to the η-C$_{10}$H$_{12}$Ru moiety indicates that the C$_{10}$H$_{12}$ ligand in 2a should have symmetrical structure. The selective irradiation of δ2.75 (Fig. 1; b) and 1.63 multiplets(Fig. 1; c) changed two olefinic signals at δ4.04 and 4.95, respectively. The former irradiation also modified multiplets at δ1.63 and 0.7-1.2. These decoupling experiments are fully consistent with the structure of the C$_{10}$H$_{12}$ ligand in 2a being bicyclo[4.2.2]deca-2,4,7-triene. At first glance, extremely high field shift of the terminal protons of the η^4-diene part(positions 2 and 5) seems unusual, however, similar high field shifts were found in several η^4-diene complexes.[4,5] The ^{13}C NMR spectrum of 2a was also in accord with the structure of η^4,η^2-bicyclo[4.2.2]decatriene{^{13}C NMR of 2a in C$_6$D$_6$(ppm); 68.0 and 33.9 due to 1-2:5-6-η-C$_8$H$_{12}$; 93.5, 60.8, and 29.4 for olefinic carbons, as

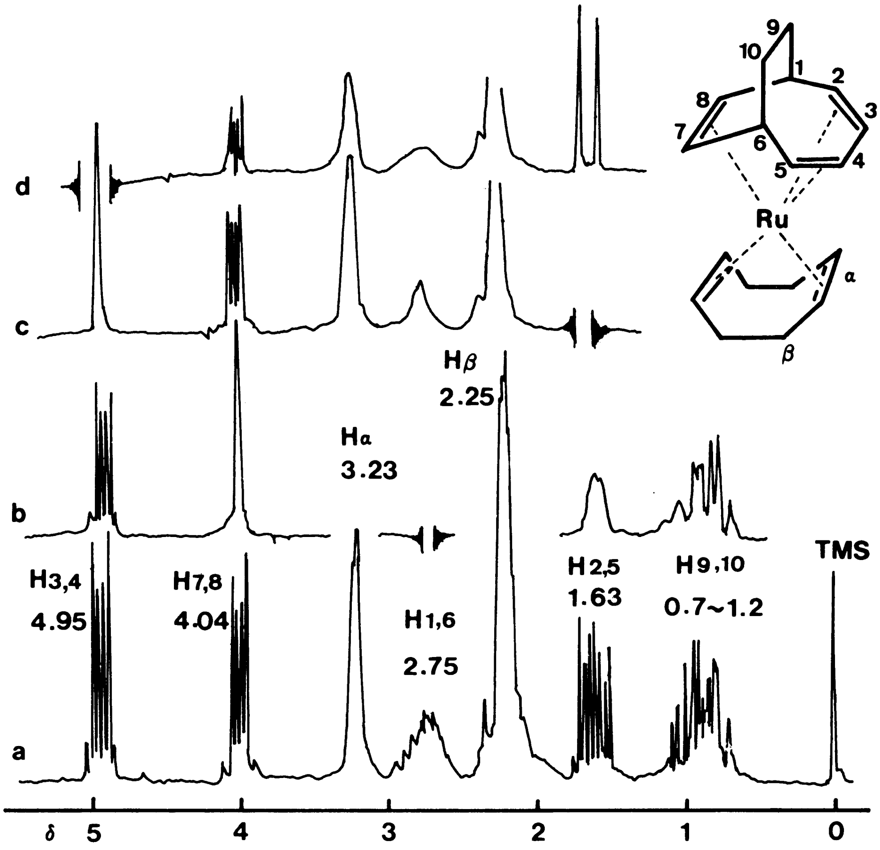


Fig. 1. ^{1}H NMR spectra of Ru(η^4,η^2-C$_{10}$H$_{12}$)(1-2:5-6-η-C$_8$H$_{12}$), 2a, at 25° in C$_6$D$_6$.

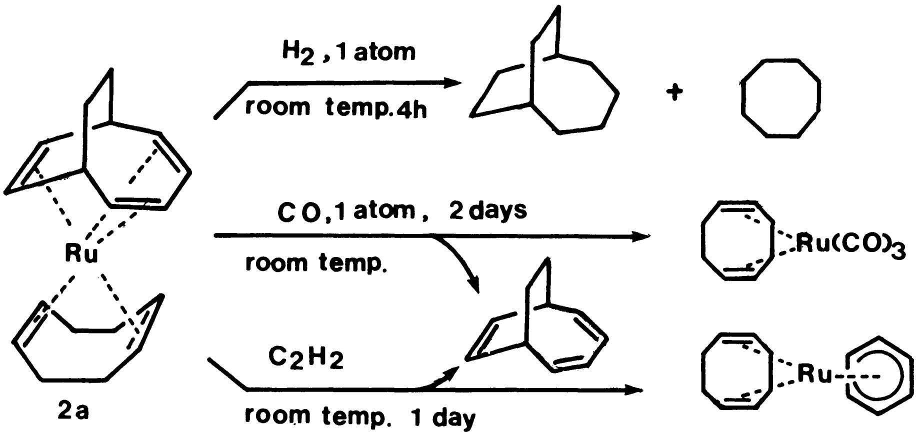
well as 35.1 and 25.2 for bridgehead and bridge carbons}. Consequently, the $C_{10}H_{12}$ ligand of 2a is concluded to be η^4,η^2-bicyclo[4.2.2]deca-2,4,7-triene which behaves as a six-electron ligand to fulfill coordinative saturation.

The formation of coordinated bicyclo[4.2.2]deca-2,4,7-triene was further supported by the following chemical evidence. When a dichloromethane solution of 2a was treated with H_2(1 atom) at room temperature, bicyclo[4.2.2]decane was isolated by glc.6) Carbon monoxide(1 atom) reacted slowly with 2a in dichloromethane at room temperature for 2 days to give bicyclo[4.2.2]deca-2,4,7-triene and known (1-2:5-6-C_8H_{12})Ru(CO)$_3$.7,8) The absence of any carbonylation product of the $C_{10}H_{12}$ hydrocarbon ligand is in favor of the η^4-coordination mode at the C2-C5 moiety rather than a ruthenacyclopent-3-ene structure.

The liberation of the bicyclodecatriene was also observed by the reaction of excess ethyne with 2a in dichloromethane at room temperature, and it accompanied formation of known Ru(η^6-C_6H_6)(1-2:5-6-η-C_8H_{12})1f)in 42% yield. Formation of the η^6-benzene complex is explained in terms of the cyclotrimerization of three ethyne molecules on the ruthenium center.

Spectroscopic results and chemical evidence, described above, strongly indicate that coordinated 1,3,5-cyclooctatriene of 1 reacted with terminal acetylenes to give bicyclo[4.2.2]deca-2,4,7-triene ligands with high [π6s+π2s] periselectivity on the Ru(0) template.

Acknowledgement. One of the authors(K. I.) is indebted to the Ministry of Education, Science, and Culture for a grant in aid and to Mitsubishi Chemical Industries Co Ltd. for generous support of this work. Authors thank to the Research Center of Chemometrics for measurement of FX-90Q NMR spectrometer.



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2) 2a, Mp. 78-79° dec. Anal. Calcd. for $C_{18}H_{24}Ru$; C, 63.31; H, 7.08. Found; C, 63.07; H, 7.36. Spectral data were shown in the text.
2b, Mp. 56-57°. Anal. Calcd. for $C_{19}H_{26}Ru$; C, 64.20; H, 7.37. Found; C, 63.32; H, 7.36. ^1H NMR(in C_6D_6), δ4.95(m, 2H, diene internal), 4.28(d, 1H, olefinic), 3.27(m, 4H) and 2.4-2.6(m, 8H) for C_8H_{12}, 2.8-3.1(m, 2H, bridgehead) 1.1-1.7(m, 2H, diene terminal), 1.95(s, 3H, CH_3), and 0.95(m, 4H, bridge).
2c, Mp. 66-67°, Anal. Calcd. for $C_{20}H_{28}Ru$; C, 65.01; H, 7.64. Found; C, 64.73; H, 7.69. ^1H NMR(in C_6D_6), δ4.74-5.09(m, 2H, diene terminal), 4.05 (d, 1H, olefinic), 3.39(m, 2H, C_8H_{12}), 2.4-3.0(m, 4H, C_8H_{12} and bridgehead), 1.98-2.41(m, 10H, C_8H_{12} and methylene), 0.91(t, 3H, CH_3), and 0.7-1.5(m, 6H, diene terminal and bridge).

3) The first example of transition metal mediated $[\pi 6s+\pi 2s]$ cycloaddition was reported in the case of a cycloheptatriene iro(0) complex under ultraviolet irradiation with particular acetylenes, however, yields of products were extremely low; R. E. Davies, T. A. Dodds, T. H Hseu, J. C. Wagnon, T. Davon, J. McKennis, and R. Pettit, J. Am. Chem. Soc., 96, 7562 (1974). A related study on different periselectivity was reported; M. Green, S. M. Heathcock, T. W. Turney, D. M. P. Mingos, J. Chem. Soc., Dalton Trans., 1977, 204. The present results are the first example in organoruthenium chemistry, with coordinated 1,3,5-cyclooctatriene, and with simple alkynes.

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5) H. Yasuda, Y. Kajiwara, K. Mashima, K. Nagasuna, K. Lee, and A. Nakamura, Organometallics, 1, 388 (1982) and references therein.

6) $C_{10}H_{18}$, M^+, Calcd., 138.141; Found, 138.140.

7) $C_{10}H_{12}$, M^+, Calcd., 132.094; Found, 132.099. Spectral data were compared with those by R. T. Seidner, N. Nakatsuka, and S. Masamune, Can. J. Chem., 48, 187 (1970).

8) Infrared and ^1H NMR spectra were identical with reported data; A. J. Deeming, S. S. Ullah, A. J. D. Domingos, B. F. G. Johnson, and J. Lewis, J. Chem. Soc., Dalton Trans., 1974, 2093.

(Received February 16, 1983)