Fluxional Behavior of a Perpendicularly Coordinated μ_3-Alkyne Ligand on a Triruthenium Cluster. Synthesis and Structure of a μ_3-η^2:η^2(⊥)-Cycloalkyne Complex

Toshiro Takao, Satoshi Kakuta, Ryu-ichi Tenjimbayashi, Toshifumi Takemori, Eisuke Murotani, and Hiroharu Suzuki*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received October 3, 2004

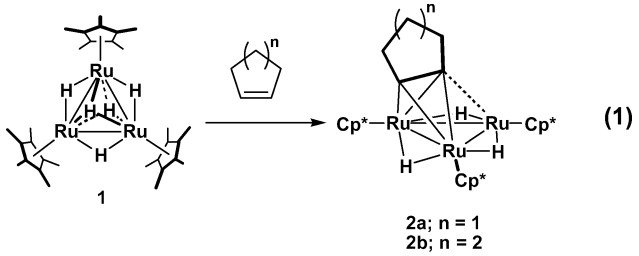
*Summary: Treatment of the triruthenium pentahydrido complex {Cp*Ru(μ-H)}$_3$(μ$_3$-H)$_2$ (**1**; Cp* = η$^{5-C_5}$Me$_5$) with cycloalkene resulted in exclusive formation of the μ$_3$-cycloalkyne complex {Cp*Ru(μ-H)}$_3$(μ$_3$-η^2:η^2(⊥)-C$_n$H$_{2n-4}$) (**2a**; n = 5, **2b**; n = 6) as a result of vinylic C−H bond cleavage. VT NMR studies revealed fluxional behavior of the perpendicularly coordinated cycloalkyne ligand. Reaction of **2b** with carbon monoxide afforded the 48-electron complex (Cp*Ru)$_3$(μ-CO)(μ$_3$-CO)(μ-H)(μ$_3$-η^2(∥)-C$_6$H$_8$) (**3b**) with a parallel-coordinated alkyne ligand.*

There have been several examples of a trimetallic μ_3-cycloalkyne complex formed by way of vinylic C−H bond cleavage of cyclic alkenes.[1] Such C−H bond cleavage clearly showed the cooperative interaction of adjacent metal centers of the cluster with cyclic alkenes and also implied promising usefulness of transition-metal clusters for organic synthesis. These μ_3-cycloalkyne complexes can be also regarded as a stabilized form of the highly strained cyclic alkyne by complexation. Adams et al. have elucidated that even a cyclobutyne can be stabilized on a triosmium cluster.[2]

Two distinct classes of the μ_3-alkyne complex are known so far;[3] one is that in which an alkyne ligand coordinates to one of the M−M bonds in a parallel fashion, which is common for 48-electron complexes, and the other is that in which an alkyne ligand coordinates to an M−M bond in a perpendicular fashion, which is characteristic of the coordinatively unsaturated 46-electron complexes. To the best of our knowledge, all of the μ_3-cycloalkyne complexes reported thus far adopted a parallel coordination geometry and there have been no isolated examples of a perpendicularly coordinated cycloalkyne complex. Such type of complex was only proposed for an intermediate in flipping of a μ-η^2(∥)-benzyne and μ-η^2(∥)-indyne ligand on a triosmium cluster.[1b−d]

In an earlier communication,[4] we reported the synthesis of perpendicularly coordinated μ_3-alkyne complexes by the reaction of the triruthenium pentahydrido complex {Cp*Ru(μ-H)}$_3$(μ_3-H)$_2$ (**1**; Cp* = η^5-C$_5$Me$_5$) with substituted alkynes. We report herein reactions of **1** with cyclic alkenes to yield perpendicularly coordinated cycloalkyne complexes and their fluxional behavior.

Treatment of complex **1** with a large excess of cyclohexene in toluene at 140 °C resulted in exclusive formation of the μ_3-η^2:η^2(⊥)-cyclohexyne complex {Cp*Ru(μ-H)}$_3$(μ-η^2:η^2(⊥)-C$_6$H$_8$) (**2b**) (eq 1).[5] During this reaction, an equimolar amount of cyclohexane with **2b** was formed. This implied that 2 molar equiv of cyclohexene



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(5) A 50 mL glass autoclave was charged with toluene (10 mL) and {Cp*Ru(μ-H)}$_3$ (**1**; 94.7 mg, 0.133 mmol). Cyclopentene (0.45 mL, 5.11 mmol) was added with vigorous stirring. The solution was allowed to react for 48 h at 130 °C, and the color of the solution turned from dark purple to dark green. The solvent, remaining cyclopentene, and produced cyclopentane were then removed under reduced pressure, and 103 mg of **2a** was obtained as a dark green solid (99% yield). Complex **2b** was also prepared in a similar manner using cyclohexene. NMR data for **2a**: ^{1}H NMR (400 MHz, toluene-d_8, −50.0 °C, TMS) δ 3.80 (t, J_{H-H} = 6.8 Hz, 2H, μ_3-CCH_2−), 2.48 (quintet, J_{H-H} = 6.8 Hz, 2H, −CH$_2$CH_2CH$_2$−), 2.01 (s, 15H, C$_5$*Me$_5$*), 1.80 (s, 30H, C$_5$*Me$_5$*), 1.45 (t, J_{H-H} = 6.6 Hz, 2H, μ_3-CCH_2−), −10.30 (d, J_{H-H} = 4.1 Hz, 2H, Ru−*H*), −24.61 (t, J_{H-H} = 4.1 Hz, 1H, Ru−*H*); ^{13}C NMR (100 MHz, toluene-d_8, −45.0 °C, TMS) δ 216.8 (s, μ_2-*C*^{out}CH$_2$−), 92.0 (s, μ_3-*C*^{in}CH$_2$−), 90.0 (s, *C*$_5$Me$_5$), 85.8 (s, *C*$_5$Me$_5$), 39.4 (t, J_{C-H} = 127.5 Hz, −CH$_2$*C*H$_2$CH$_2$−), 37.0 (t, J_{C-H} = 128.8 Hz, −*C*H$_2$CH$_2$CH$_2$−), 34.5 (t, J_{C-H} = 125.9 Hz, −*C*H$_2$CH$_2$CH$_2$−), 13.1 (q, J_{C-H} = 127.7 Hz, C$_5$*Me$_5$*), 12.0 (q, J_{C-H} = 127.7 Hz, C$_5$*Me$_5$*). NMR data for **2b**: ^{1}H NMR (400 MHz, toluene-d_8, −55.0 °C, TMS) δ 4.27 (m, μ_3-CCH_2−), 1.96 (s, 15H, C$_5$*Me$_5$*), 1.84 (s, 30H, C$_5$*Me$_5$*), 1.52 (m, 2H, −CH_2−), 1.22 (m, 2H, −CH_2−), 1.14 (m, 2H, −CH_2−), 0.93 (m, 2H, μ_3-CCH_2−), −7.51 (d, J_{H-H} = 3.3 Hz, 2H, Ru−*H*), −24.68 (t, J_{H-H} = 3.3 Hz, 1H, Ru−*H*); ^{13}C NMR (100 MHz, toluene-d_8, −50.0 °C, TMS) δ 180.9 (s, μ_2-*C*^{out}CH$_2$−), 89.3 (s, *C*$_5$Me$_5$), 85.1 (s, *C*$_5$Me$_5$), 67.4 (s, μ_3-*C*^{in}CH$_2$−), 41.7 (t, J_{C-H} = 124.8 Hz, −*C*H$_2$−), 38.1 (t, J_{C-H} = 127.7 Hz, −*C*H$_2$−), 26.4 (t, J_{C-H} = 125.2 Hz, −*C*H$_2$−), 26.1 (t, J_{C-H} = 125.2 Hz, −*C*H$_2$−), 12.7 (q, J_{C-H} = 127.2 Hz, C$_5$*Me$_5$*), 12.1 (q, J_{C-H} = 127.2 Hz, C$_5$*Me$_5$*).

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Publication on Web 11/23/2004

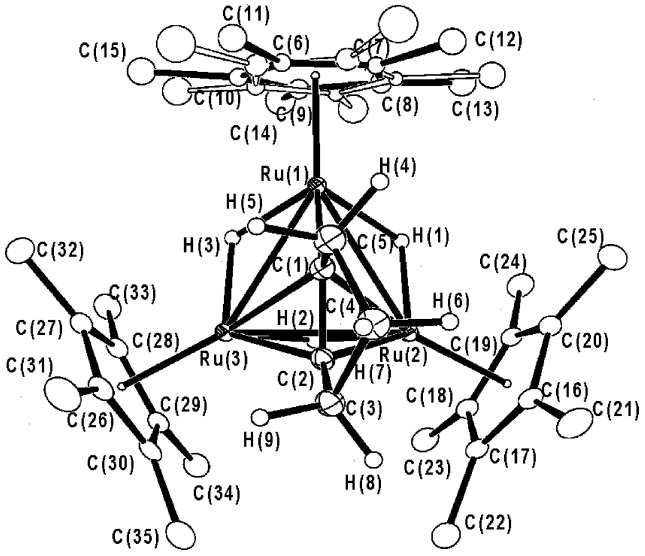

Figure 1. Molecular structure of **2a** with thermal ellipsoids at 30% probability level. Selected bond distances (Å) and angles (deg): Ru(1)−Ru(2), 2.8058(3); Ru(1)−Ru(3), 2.7968(3); Ru(2)−Ru(3), 2.8393(3); Ru(1)−C(1), 2.074(3); Ru(2)−C(1), 2.284(3); Ru(2)−C(2), 2.037(3); Ru(3)−C(1), 2.270(3); Ru(3)−C(2), 2.040(3); C(1)−C(2), 1.415(4); Ru(2)−Ru(1)−Ru(3), 60.90(1); Ru(1)−Ru(2)−Ru(3), 59.395(7); Ru(1)−Ru(3)−Ru(2), 59.707(7); Ru(1)−C(1)−Ru(2), 80.00(11); Ru(1)−C(1)−Ru(3), 80.01(11); Ru(2)−C(1)−Ru(3), 77.15(10); C(2)−C(1)−C(5), 106.7(3); C(1)−C(2)−C(3), 112.2(3); C(2)−C(3)−C(4), 102.0(3); C(3)−C(4)−C(5), 103.4(3); C(1)−C(5)−C(4), 104.6(3).

was required to complete the reaction. The first cyclohexene was hydrogenated with elimination of two hydrido ligands from **1**, and the second one underwent C−H bond cleavage followed by the elimination of dihydrogen. Cyclopentene reacted with **1** more readily than the cyclohexene did, and the μ_3-η^2:η^2(⊥)-cyclopentyne complex **2a** was formed at 80 °C.[5] This is most likely due to the smaller ring size of cyclopentene, and such shape selectivity seems to arise from the sterically restricted reaction field of **1** surrounded by the three bulky Cp* ligands.

X-ray diffraction studies of **2a** were carried out using a single crystal obtained from cold toluene solution, and the molecular structure of **2a** is shown in Figure 1.[6] It clearly demonstrates the perpendicular coordination of the cyclopentyne ligand to the Ru(2)−Ru(3) edge. The C(1)−C(2) length (1.415(4) Å) corresponds to the C−C bond distance of a coordinated olefin and is considerably longer than that of (Cp*Ru)$_3$(μ-H)$_2$(μ_3-CH)(μ_3-η^2(||)-C_5H_6) (1.33(1) Å), in which the cyclopentyne ligand is coordinated parallel to one of the three Ru−Ru bonds.[7] Such elongation between the acetylenic carbons strongly implies that the cycloalkyne moiety is effectively activated by the perpendicular coordination to the Ru_3 core.

Although the structural features of **2a** are almost the same as those of {Cp*Ru(μ-H)}$_3$(μ_3-η^2:η^2(⊥)-PhCCH), the bond angle around the inner acetylenic carbon is notably different; the C(2)−C(1)−C(5) angle of 106.7(3)° is significantly small for an sp^2 carbon. The corresponding angle in the μ_3(⊥)-phenylacetylene complex was found to be 118.6(5)°.[4]

In the ^{13}C NMR spectrum of **2a** measured at −50 °C, two singlets assignable to the acetylenic carbons were observed. The signal which appeared at δ 216.8 was assigned to the outer acetylenic carbon atom, C(2), and the other which appeared at δ 92.0 was assigned to the inner one, C(1). Since a significant upfield shift of the inner acetylenic carbon atom for the triply coordinating carbon atom has been shown in the study of the terminal alkyne complexes,[4] their assignment was based on the chemical shifts. While these chemical shifts are significantly downfield compared to those of the μ_3(⊥)-phenylacetylene complex {Cp*Ru(μ-H)}$_3$(μ_3-η^2:η^2-(⊥)-PhCCH) (C^{out}, δ 178.7; C^{in}, δ 66.3),[4] those of **2b**, which has a cyclohexyne ligand, appeared at regions similar to those of the phenylacetylene complex (C^{out}, δ 180.9; C^{in}, δ 67.4).

The ^{1}H and ^{13}C NMR spectra of both **2a** and **2b** were temperature dependent due to a dynamic process of the alkyne ligand. In the ^{1}H NMR spectra of **2a** recorded at −50 °C, two sharp signals for the Cp* groups with intensities of 15H and 30H were observed at δ 2.01 and 1.80, respectively. The hydrido ligands resonated at δ −10.28 (d, J_{H-H} = 4.1 Hz) and −24.61 (t, J_{H-H} = 4.1 Hz) with an intensity ratio of 2:1 at −50 °C, respectively. A fast puckering motion of the methylene groups at C(4) afforded time-averaged spectra and brought about a pseudo mirror plane with the acetylenic carbon atoms even at −70 °C.

All of the ^{1}H signals except for the methylene proton at the C(4) broadened at higher temperature, and two Cp* signals coalesced into one broad signal at −10 °C. Activation parameters were obtained from the line-shape analysis of the Cp* signals recorded at various temperatures (Figure 2); $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were estimated at 13.1 ± 0.1 kcal mol^{-1} and 0.7 ± 0.7 cal mol^{-1} K^{-1}, respectively. These values largely agreed with those obtained from the methylene signals of the C_5 ring within experimental errors ($\Delta H^{\ddagger}$ = 13.2 ± 0.1 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 1.0 ± 0.4 cal mol^{-1} K^{-1}). This fact shows that these spectral changes arise from an identical dynamic process of the cyclopentyne ligand.

Coalescence of the methylene protons at C(3) and C(5) implied the dynamic process shown in Scheme 1. The inner acetylenic carbon atom migrates to the outside of the Ru_3 core from **A-1** to **A-2** via **B-1**, in which the cyclopentyne coordinates in a parallel fashion to one of the Ru−Ru edges (Scheme 1A). We use the term "*switchback motion*" to refer to such a process. This corresponds to a reversed scheme for the flipping motion of the parallel coordinated alkyne ligand proposed by Deeming et al.[1b−d]

In our earlier communication, we noted the fluxional behavior of the μ_3-η^2:η^2(⊥)-phenylacetylene complex.[4] While two signals for the Cp* group appeared at low temperature, they coalesced into one signal at higher temperature, as observed in **2a**. In this case, site exchange between the inner and the outer carbons seemingly did not take place; only one isomer, which has a phenyl group on the inner carbon, has been found at each temperature.

(6) Crystal data: empirical formula $C_{35}H_{54}Ru_3$, T = 173 K, λ = 0.710 69 Å, space group $P\bar{1}$ (No. 2), a = 8.6307(2) Å, b = 11.0178(3) Å, c = 17.6259(4) Å, α = 89.201(2)°, β = 88.5530(14)°, γ = 78.6440(15)°, V = 1642.66(7) Å^3, Z = 2, D_c = 1.573 g/cm^3. The final structure for **2a** was refined to R1 = 0.0328 and wR2 = 0.0758 for 7427 observed reflections ($I > 2\sigma$) and 381 parameters.

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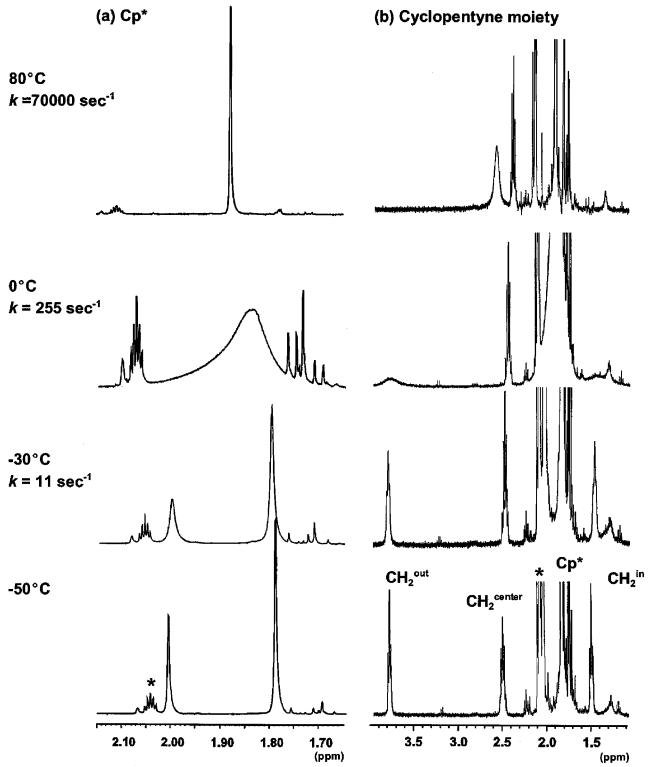
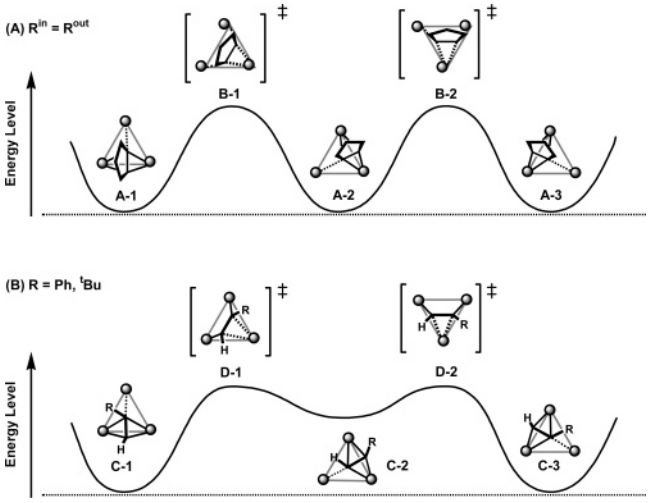


Figure 2. Variable-temperature ^{1}H NMR spectra of {Cp*Ru(μ-H)}$_3$(μ-η^2:η^2(⊥)-C_5H_6) (**2a**) in toluene-d_8 showing (a) the Cp* signals and (b) the methylene protons of the cyclopentyne ligand. Asterisks denote a residual proton in toluene-d_8 used for solvent.

Scheme 1

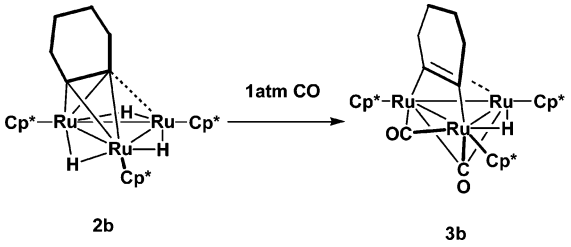


Morokuma and co-workers have calculated energy differences between two positional isomers of the μ_3-η^2:η^2(⊥)-phenylacetylene complex with regard to the substituents on the acetylenic carbons.[8] They estimated that the outer isomer was less stable than the inner one by 16.7 kcal mol^{-1}, due to the steric repulsion between the phenyl group and the Cp* groups. Therefore, equilibrium between the two isomers should largely shift toward the stable inner isomer. Thus, the outer isomer would not be observed in the NMR spectra. Although rotation of the alkyne ligand around the center of the Ru_3 triangle like a propeller does not exchange the acetylenic carbons, it would lead to the same spectral change. This mechanism, however, has been revealed to be energetically unfavorable by the ab initio studies.[8]

The energy profile of the switchback motion is shown in Scheme 1. When the alkyne ligand has the same substituents on each acetylenic carbon atom, the energy levels of **A-2** and **A-3** are the same as that of **A-1** (Scheme 1A). In contrast, when an alkyne ligand contains a large substituent on one acetylenic carbon atom (Scheme 1B), the outer isomer **C-2** is considerably unstabilized. Therefore, the population of **C-2** should be small, and as a result, the spectral change would be close to that of the direct path from **C-1** to **C-3**. These motions result in coalescence of the Cp* signals without any change in the signals stemming from the alkyne moiety.

Activation parameters for the switchback motion of the cyclohexyne ligand of **2b** were also estimated by the line-shape analyses of the Cp* signals ($\Delta H^{\ddagger} = 14.5 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 6.3 \pm 0.5$ cal mol^{-1} K^{-1}). While the central methylene signal of the five-membered ring of **2a** did not show any temperature dependence, all of the methylene signals of **2b** broadened at higher temperature.

Since the μ_3-η^2:η^2(⊥)-alkyne complexes were coordinatively unsaturated, it is anticipated that **2** would react with 2e donors. Treatment of **2b** with 1 atm of CO resulted in quantitative formation of the μ_3-η^2(∥)-cyclohexyne complex (Cp*Ru)$_3$(μ-η^2(∥)-C_6H_8)(μ_3-CO)(μ-CO)(μ-H) (**3b**) (eq 2).[9] The parallel coordination of the



(2)

cyclohexyne ligand was confirmed by the X-ray diffraction studies, and the structure of **3b** is shown in the Supporting Information (Figure S-5). Such a transformation from perpendicular to parallel coordination associated with formation of a 48e configuration has been reported.[10] Complex **3b** can be regarded as a frozen intermediate of the *switchback motion*.

We will continue research into the fluxional behavior of the alkyne ligand on the trimetallic cluster in relation

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(9) A 50 mL flask was charged with toluene (5 mL) and **2b** (46.8 mg, 0.059 mmol). The reaction solution was frozen by liquid nitrogen and degassed. After 1 atm of CO was introduced into the flask, the flask was gradually warmed to 60 °C and the solution was allowed to react for 30 min. The color of the solution turned from dark green to red. The solvent was then removed under reduced pressure, and 49 mg of **3b** was obtained as a red solid (98% yield). NMR data for **3b**: ^{1}H NMR (400 MHz, benzene-d_6, 23 °C, TMS) δ 2.90 (m, 1H, −CH*H*−), 2.50 (m, 1H, −CH*H*−), 2.33 (m, 1H, −CH*H*−), 1.76 (s, 15H, C$_5$*Me$_5$*), 1.75 (s, 15H, C$_5$*Me$_5$*), 1.72 (s, 15H, C$_5$*Me$_5$*), 1.44 (m, 2H, −C*H*$_2$−), 1.27 (m, 2H, −C*H*$_2$−), −14.35 (s, 1H, Ru−*H*); ^{13}C NMR (100 MHz, benzene-d_6, 23 °C, TMS) δ 261.5 (s, μ_3-*C*O), 238.4 (s, μ-*C*O), 173.9 (s, μ_2-*C*CH$_2$−), 143.5 (s, μ_2-C*C*H$_2$−), 99.1 (s, μ_3-*C*^{in}CH$_2$−), 97.3 (s, *C*$_5$Me$_5$), 96.1 (s, *C*$_5$Me$_5$), 38.2 (t, J_{C-H} = 127.8 Hz, −*C*H$_2$−), 37.7 (t, J_{C-H} = 126.2 Hz, −*C*H$_2$−), 24.4$_2$ (t, J_{C-H} = 124.5 Hz, −*C*H$_2$−), 24.3$_7$ (t, J_{C-H} = 124.5 Hz, −*C*H$_2$−), 10.6 (q, J_{C-H} = 126.8 Hz, C$_5$*Me$_5$*), 9.4 (q, J_{C-H} = 126.8 Hz, C$_5$*Me$_5$*), 9.3 (q, J_{C-H} = 126.8 Hz, C$_5$*Me$_5$*).

to the electronic effect of the substituents of the alkyne ligand and the metal centers.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (Grant Nos. 15205009 and No. 14078101, "Reaction Control of Dynamic Complexes") and the 21st Century COE program from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Professor B. E. Mann (University of Sheffield) for fruitful discussion about the fluxional behavior of the alkyne ligand. We also acknowledge Kanto Chemical Co., Inc., for generous gifts of pentamethylcyclopentadiene.

Supporting Information Available: Text, tables, and figures giving synthetic details and spectral data for compounds **2a**, **2b**, and **3b**, results of the dynamic NMR studies for **2a** and **2b**, and X-ray crystallographic files of **2a** and **3b**; X-ray data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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