Synthesis of Naphthoquinone-Fused Cyclobutadiene Ruthenium Complexes

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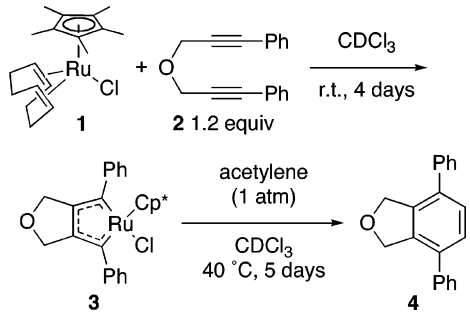
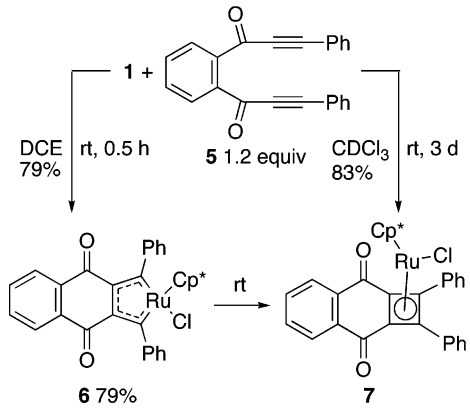
A coordinatively unsaturated ruthenacycle, which was formed from Cp*RuCl(cod) and 1,2-bis(phenylpropiolyl)benzene, was isomerized to a new sandwich complex consisting of a Cp* and a naphthoquinone-fused cyclobutadiene ligand at ambient temperature. On the other hand, the treatment of the same ruthenacycle with excess $AgBF_4$ at room temperature produced a tetramethylfulvene cyclobutadiene complex. In contrast, a cationic cyclobutadiene complex was formed from the isolated Cp*RuCl(cyclobutadiene) with excess $AgBF_4$.

Transition-metal-catalyzed cyclotrimerizations of alkynes have received continuous attention as a facile method to obtain aromatic molecules,[1] since the first report of Reppe and co-workers.[2] Especially, their intramolecular versions are synthetically useful, because they give polycyclic products chemoselectively.[3] In this context, we have recently developed the ruthenium(II)-catalyzed cycloaddition of 1,6-diynes with monoalkynes, affording bicyclic benzenes chemo- and regioselectively under mild conditions.[4] We have also reported that the Ru(II)-catalyzed cycloaddition of 1,2-bis(propiolyl)benzenes furnished anthraquinone derivatives in moderate to high yields.[5] During these studies, it was found that a ruthenium(II) precatalyst, Cp*RuCl(cod) **1** (Cp* = η^5-C_5Me_5), was treated with diyne **2** or **5** bearing a terminal phenyl substituent to give rise to ruthenacycle complex **3** or **6**, respectively (Schemes 1 and 2).[4b,5] The Ru(II)-catalyzed cycloaddition of the 1,6-diynes is considered to proceed via a ruthenacycle intermediate very similar to **3**.[4b,6] In fact, **3** reacted with acetylene at 40 °C to afford the expected terphenyl product **4** (Scheme 1).[4b] In contrast, the naphthoquinone-fused analogue **6** behaved in a totally different manner under the same reaction conditions to result in the formation of a new complex. Herein, we report the formation of naphthoquinone-fused cyclobutadiene complexes from **6**.

Scheme 1



Scheme 2



As previously reported,[5] the treatment of **1** with 1.2 equiv of **5** in 1,2-dichloromethane (DCE) at room temperature for 0.5 h gave **6** in 79% yield as dark red crystals after recrystallization (Scheme 2). The X-ray crystallographic analysis disclosed that **6** has a naphthoquinone-fused ruthenacycle framework. The Ru−C1 and Ru−C4 bond lengths are 1.990(2) and 2.009(2) Å, which are intermediate between those of the known ruthenacyclopentatriene-type complexes **I** and **II** (1.942(6) and 1.969(4) Å, respectively) and the ruthenacyclopentadiene phosphine complex **III** (2.059(5) and 2.092(4) Å) (Figure 1).[7−9] In striking contrast to the known ruthenacyclopentatrienes, the C1−C2 and C3−C4 bonds

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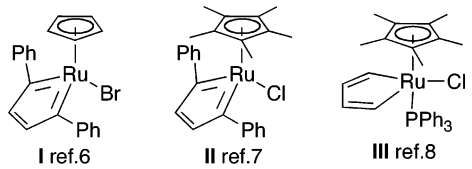

Figure 1. Precedent ruthenacycle complexes bearing a Cp-type ligand.

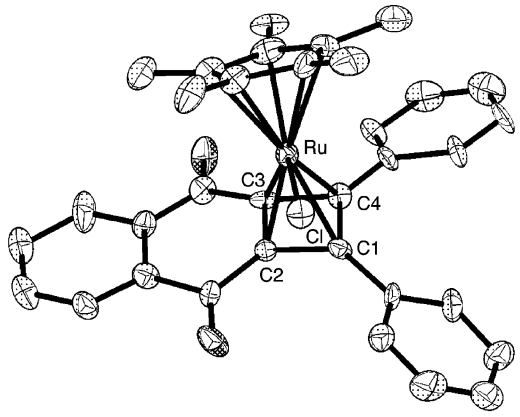

Figure 2. ORTEP diagram for **7**, showing one of two crystallographically unique molecules in the unit cell. Ellipsoids are shown at the 50% probability level. All hydrogen atoms were omitted for clarity.

(1.395(3) and 1.400(3) Å, respectively) are shorter than the C2−C3 bond (1.430(3) Å). Although **6** can be considered to be a coordinatively unsaturated metallacyclopentadiene in terms of these features, the ^{13}C NMR spectroscopy showed the characteristic carbene resonance of the C1 and C4 carbons at δ 263.89, as commonly observed for the previously reported ruthenacyclopentatrienes.[7,8]

The treatment of **6** with acetylene (1 atm) in DCE at ambient temperature gave no cycloadduct, but instead a small amount of a new product **7** was formed. In the absence of acetylene, the reaction of **1** with **5** in $CDCl_3$ was monitored by ^1H NMR spectroscopy. The initially formed ruthenacycle complex **6** decreased gradually and completely converted to **7** after stirring for 3 days. This behavior is in striking contrast to the rhodium analogue of **6**, which reacted with monoalkynes to give anthraquinones in refluxing xylene.[10] After recrystallization, **7** was isolated in 83% yield as black crystals. In its ^1H NMR spectrum, the Cp* ligand was observed as a singlet peak at δ 1.30. The absence of carbene carbons was confirmed by ^{13}C NMR spectroscopy. Finally, X-ray crystallography unambiguously disclosed that **7** is a ruthenium(II) sandwich complex consisting of the Cp* and naphthoquinone-fused cyclobutadiene ligands as shown in Figure 2. The unit cell contains the two crystallographically unique molecules **7**(A) and **7**(B). As summarized in Table 2, no remarkable difference was found in the C−C bond lengths (1.403(11)−1.485(9) Å) of the cyclobutadiene ligand, and the Ru−C2 and Ru−C3 distances are slightly shorter than those of Ru−C1 and Ru−C4. As a result, the [Cp*RuCl] fragment is tilted toward the naphthoquinone ring. The cyclobutadiene carbons resonated at δ 94.49 and 71.52 in the ^{13}C NMR spectrum.

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Table 1. Selected Bond Distances (Å) and Angles (deg) of 6 and 8

	6	**8**
Ru−Cl	2.3279(6)	2.365
Ru−C1	1.990(2)	1.990
Ru−C4	2.009(2)	1.990
C1−C2	1.395(3)	1.402
C2−C3	1.430(3)	1.423
C3−C4	1.400(3)	1.403
C1−Ru−C4	78.43(8)	79.960
Ru−C1−C2	118.08(15)	115.861
C1−C2−C3	113.11(19)	113.955

Table 2. Selected Bond Distances (Å) for Cyclobutadiene Complexes 7, 9, and 13

	7(A)	**7**(B)	**9**	**13**(A)	**13**(B)
Ru−C1	2.289(8)	2.283(7)	2.492	2.208(7)	2.206(7)
Ru−C2	2.107(7)	2.125(8)	2.143	2.145(8)	2.114(9)
Ru−C3	2.128(7)	2.104(6)	2.095	2.141(7)	2.162(8)
Ru−C4	2.271(7)	2.230(7)	2.340	2.285(7)	2.230(7)
Ru−X (Cl or N)	2.3840(19)	2.3839(19)	2.445	2.075(8)	2.040(8)
C1−C2	1.485(9)	1.479(10)	1.495	1.542(10)	1.448(10)
C2−C3	1.454(9)	1.422(11)	1.456	1.371(11)	1.487(10)
C3−C4	1.469(10)	1.474(8)	1.484	1.524(10)	1.433(10)
C4−C1	1.472(10)	1.403(11)	1.437	1.495(11)	1.400(10)

The ruthenium cyclobutadiene complexes bearing a Cp or a Cp* ligand have been obtained directly from appropriate ruthenium complexes and monoalkynes.[11] While the intermediacy of metallacyclopentadienes in the formation of cyclobutadiene complexes from alkynes has been well documented,[12] the isomerization of the isolated ruthenacyclopentatrienes to the corresponding cyclobutadiene complexes has not been observed previously.[4b,7,8] In contrast, the relevant naphthoquinone-fused analogue **6** was slowly converted to **7** at ambient temperature. This unprecedented behavior might be attributed to its metallacycle moiety being close to a coordinatively unsaturated metallacyclopentadiene rather than a metallacyclopentatriene (see **I** and **II** in Figure 1).

On the basis of the exclusive conversion of **6** to **7**, the latter was expected to be more stable than the former. To know the thermodynamic properties of these compounds, we carried out density functional studies of model complexes **8** and **9**. First, their geometries were optimized at the B3LYP/LACVP* level (Figure 3). The obtained geometries were in good agreement with those of **6** and **7**, respectively (Tables 1 and 2). Then, their energies were evaluated by single-point energy calculations for the obtained geometries at the B3LYP level using larger basis sets (see Experimental Section). Contrary to our expectation, it was found that the cyclobutadiene complex **9** is thermodynamically less stable than the ruthenacycle **8** by 1.63 kcal/mol. The detail of the present isomerization is not clear at this stage, but the simple reductive elimination mechanism seems unlikely. The direct transformation of a related

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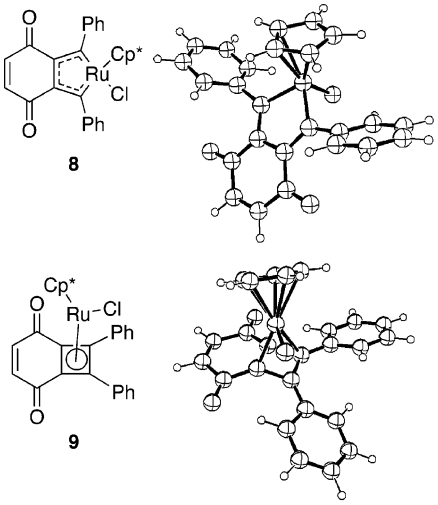
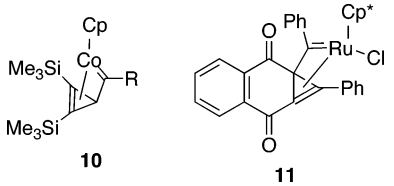


	E (au)	ZPE (kcal/mol)	ΔE (kcal/mol)
8	-1668.75975696	216.241	0
9	-1668.75881665	217.282	1.63

Figure 3. DFT-optimized structures of model complexes **8** and **9**.

cobaltacyclopentadiene, $CpCo(C_4H_4)$, into the corresponding cyclobutadiene complex was reported to be a symmetrically forbidden process due to the HOMO−LUMO crossing.[13] Vollhardt and co-workers, therefore, proposed the cyclopropenylcarbene complex **10** as an intermediate for the interconversion between the cyclobutadiene complexes and the cobaltacyclopentadienes.[14,15] The mechanism involving such an elusive intermediate could reasonably explain the formation of cyclobutadiene complexes from monoalkynes. However, a highly strained bicyclic species such as **11** is not conceivable for the cases involving diynes.[16]



The lack of the reactivity of **6** toward the cycloaddition with acetylene might be attributed to the steric crowding around the ruthenium center. To open the coordination site, we attempted chlorine ligand abstraction with a silver salt (Scheme 3). In the presence of excess 1-hexyne, **6** was treated with 4 equiv of $AgBF_4$ in THF at room temperature to give rise to a new product. In its ^1H NMR spectrum, the singlet signal of the Cp* ligand of **6** disappeared, but instead, three singlet signals were observed at δ 3.65, 1.08, and 1.00 with the integral ratio of 1:2:2. These observations suggest that the Cp* ligand was converted to a tetramethylfulvene ligand. Its methyl and methylene carbons are assigned to signals at δ 71.8, and 7.87 and 6.79, respectively, by the ^{13}C DEPT study. In addition, the sp^2 carbons of the cyclobutadiene and the fulvene ligands appeared at δ 105.35, 104.56, 95.90, 86.47, and 73.35 in the ^{13}C NMR spectrum. Whereas a single crystal suitable for X-ray study was not obtained, these spectral data allowed us to assign **12** to a tetramethylfulvene cyclobutadiene complex. The elemental and the FAB mass analyses also supported this structural assignment.

In the absence of 1-hexyne, the yield of **12** was decreased to 19%. The role of the alkyne additive for this transformation is unclear. The formation of the fulvene ligand probably occurs prior to the formation of the cyclobutadiene, because the treatment of **7** with excess $AgBF_4$ gave rise to a cationic cyclobutadiene complex instead of **12** (Scheme 3). After recrystallization from CH_3CN-Et_2O, **13** bearing a coordinated acetonitrile was isolated in 37% yield. The remaining Cp* ligand was observed in its ^1H NMR spectrum as a singlet at δ 1.44. The structure of **13** was unambiguously confirmed by X-ray crystallography as shown in Figure 4.

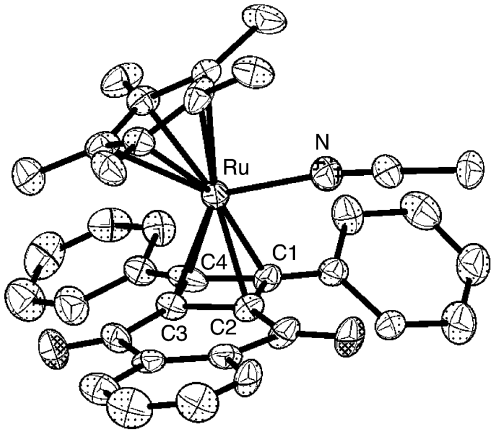
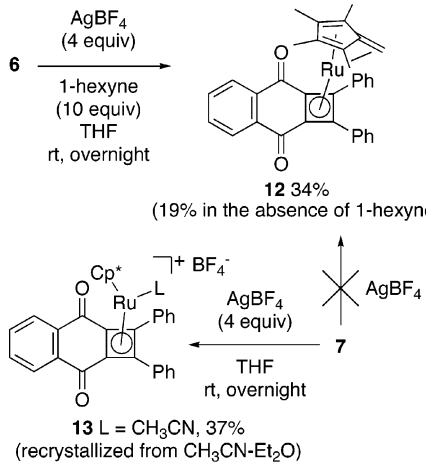


Figure 4. ORTEP diagram for **13**, showing one of two crystallographically unique molecules in the unit cell. Ellipsoids are shown at the 50% probability level. All hydrogen atoms and BF_4^- were omitted for clarity.

Scheme 3



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In conclusion, we found that the coordinatively unsaturated ruthenacycle **6**, which was formed from Cp*RuCl(cod) and the diketodiyne **5**, was isomerized to the naphthoquinone-fused cyclobutadiene complex **7** at ambient temperature. On the other hand, the treatment of **6** with excess $AgBF_4$ at room temperature produced the tetramethylfulvene cyclobutadiene complex **12**. In contrast, the cationic cyclobutadiene complex **13** was formed from **7** upon treatment with $AgBF_4$ at room temperature.

Experimental Section

General Considerations. ^1H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solution. Flash chromatography was performed with a silica gel column (Merck Silica gel 60) eluted with mixed solvents (hexane/AcOEt). Elemental analyses were performed by the Microanalytical Center of Kyoto University. Melting points were obtained in sealed capillary tubes and are uncorrected. 1,2-Dichloroethane was distilled from CaH_2 and degassed. $RuCl_3 \cdot xH_2O$ was purchased from N. E. Chemcat Corporation. Cp*RuCl(cod) was obtained according to the literature procedures.[16] 1,2-Bis(phenylpropiolyl)benzene **5** was reported in the literature.[17]

Synthesis of Ruthenacycle 6. To a solution of Cp*RuCl(cod) (130.2 mg, 0.343 mmol) in degassed 1,2-dichloroethane (1 mL) was added a solution of a diketodiyne **5** (140.2 mg, 0.419 mmol) in degassed 1,2-dichloroethane (3 mL) at 0 °C. The solution was further stirred at room temperature for 30 min. The solution was concentrated in vacuo, and the residue was recrystallized from $CHCl_3$/ether to afford **6**·$CHCl_3$ (196.3 mg, 78.9%) as dark red crystals: mp 178.5−178.9 °C; IR ($CHCl_3$) 1656 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 15 H), 7.01 (d, J = 7.2 Hz, 4 H), 7.20 (t, J = 7.2 Hz, 4 H), 7.46 (tt, J = 7.5, 1.5 Hz, 2 H), 7.64 (dd, J = 6.0, 3.3 Hz, 2 H), 8.05 (dd, J = 6.0, 3.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.20, 108.45, 125.63, 127.04, 127.07, 127.62, 133.19, 133.71, 148.59, 155.67, 178.28, 263.89; MS (FAB) m/z (%): 606 (39) [M^+], 571 (100) [M^+ − Cl]. Anal. Calcd (%) for $C_{35}H_{30}Cl_4O_2Ru$ (725.49): C, 57.94; H, 4.17. Found: C, 58.07; H, 4.15.

Synthesis of Cyclobutadiene Complex 7. To a solution of Cp*RuCl(cod) (376.9 mg, 0.993 mmol) in degassed $CDCl_3$ (1 mL) was added a solution of diketodiyne **5** (410.0 mg, 1.23 mmol) in degassed $CDCl_3$ (4 mL) at 0 °C. The solution was further stirred at room temperature for 3 days. The solution was concentrated in vacuo, and the residue was recrystallized from $CHCl_3$/ether to afford **7**·$CHCl_3$ (601.8 mg, 83.5%) as black crystals: mp 221.3−222.2 °C; IR ($CHCl_3$) 1654 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 15 H), 7.30−7.40 (m, 6 H), 7.61 (dd, J = 6.0, 3.6 Hz, 2 H), 7.81 (dd, J = 8.1, 1.8 Hz, 4 H), 8.04 (dd, J = 6.0, 3.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.91, 71.52, 94.49, 101.77, 126.15, 127.85, 128.83, 129.96, 130.45, 132.81, 134.87, 183.81; MS (FAB) m/z (%) 606 (84) [M^+], 571 (100) [M^+ − Cl]. Anal. Calcd (%) for $C_{35}H_{30}Cl_4O_2Ru$ (725.49): C, 57.94; H, 4.17. Found: C, 57.93; H, 4.18.

Synthesis of Tetramethylfulvene Complex 12. To a solution of $AgBF_4$ (67.5 mg, 0.347 mmol) and 1-hexyne (79.9 mg, 0.973 mmol) in degassed THF (5 mL) was added a solution of **6**·$CHCl_3$ (66.5 mg, 0.0917 mmol) in degassed THF (35 mL) at room temperature. The solution was further stirred at room temperature overnight. The solution was concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/AcOEt, 7:1) to give **12** (17.8 mg, 34.1%) as red solids: mp 190.8−191.3 °C; IR ($CHCl_3$) 1638 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 6 H), 1.08 (s, 6 H), 3.65 (s, 2 H), 7.17−7.22 (m, 2 H), 7.33 (t, J = 7.2 Hz, 4 H), 7.48 (dd, J = 5.7, 3.3 Hz, 2 H), 7.70 (d, J = 7.2 Hz, 4 H), 7.96 (dd, J = 5.7, 3.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.79 (CH_3), 7.87 (CH_3), 71.82 (CH_2), 73.35, 86.47, 95.90, 104.56, 105.35, 125.30, 126.66, 127.21, 128.10, 131.59, 134.20, 134.87, 180.60; MS (FAB) m/z (%) 570 (100) [MH^+]. Anal. Calcd (%) for $C_{34}H_{28}Cl_4O_2Ru$ (569.65): C, 71.69; H, 4.95. Found: C, 71.66; H, 4.98.

Synthesis of Cationic Cyclobutadiene Complex 13. To a solution of $AgBF_4$ (180.7 mg, 0.928 mmol) in degassed THF (5 mL) was added a solution of **7**·$CHCl_3$ (142.2 mg, 0.196 mmol) in degassed THF (35 mL) at room temperature. The solution was further stirred at room temperature overnight. The solution was concentrated in vacuo, and the residue was recrystallized from CH_3CN/ether to afford **13**·CH_3CN (53.9 mg, 37.2%) as black crystals: mp 201.9−202.5 °C; IR ($CHCl_3$) 2349, 2273, 1663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 15 H), 2.07 (s, 3 H), 2.16 (s, 3 H), 7.45−7.48 (m, 6 H), 7.70−7.76 (m, 6 H), 8.07 (dd, J = 5.7, 3.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.10, 4.25, 8.62, 73.39, 96.52, 104.15, 126.59, 127.76, 128.89, 129.94, 130.34, 132.17, 133.59, 134.08, 181.92; MS (FAB) m/z (%) 612 (19) [M^+], 571 (100) [M^+ − CH_3CN]. Anal. Calcd (%) for $C_{38}H_{35}BF_4N_2O_2Ru$ (739.57): C, 61.71; H, 4.77; N, 3.79. Found: C, 61.96; H, 4.89; N, 3.42.

Table 3. Crystal Data and Structure Refinement for 7·$CHCl_3$ and 13·CH_3CN

	7·$CHCl_3$	**13**·CH_3CN
empirical formula	$C_{70}H_{60}Cl_8O_4Ru_2$	$C_{76}H_{70}B_2F_8N_4O_4Ru_2$
fw	1450.92	1479.12
cryst syst	triclinic	triclinic
space group	$P1$	$P1$
unit cell dimens		
a (Å)	9.63035(5)	9.8491(9)
b (Å)	10.0871(5)	12.1189(11)
c (Å)	17.2611(9)	14.7018(14)
α (deg)	104.3550(10)	99.005(2)
β (deg)	93.7220(10)	100.104(2)
γ (deg)	106.2240(10)	102.127(2)
volume (Å^3)	1539.12(14)	1654.6(3)
Z	1	1
density(calcd) (Mg/m^3)	25.046	22.266
absorp coeff (mm^{-1})	14.217	8.006
F(000)	11776	11340
cryst size (mm)	0.1 × 0.4 × 0.8	0.1 × 0.5 × 0.6
index ranges	$-6 \le h \le 13$, $-13 \le k \le 13$, $-23 \le l \le 23$	$-13 \le h \le 13$, $-16 \le k \le 13$, $-20 \le l \le 14$
no. of reflns collected	12 208	12 987
no. of indep reflns [R(int)]	9790 [0.0199]	10 443 [0.0244]
no. of data/restraints/params	9790/3/767	10 443/3/879
goodness-of-fit on F^2	1.094	1.070
final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0302$, $wR_2 = 0.0818$	$R_1 = 0.0367$, $wR_2 = 0.0979$
R indices (all data)[a]	$R_1 = 0.0323$, $wR_2 = 0.0879$	$R_1 = 0.0392$, $wR_2 = 0.1005$
largest diff peak and hole (e·Å^{-3})	0.809 and −0.996	1.361 and −0.637

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR = \Sigma[(w(F_o^2 - F_c^2)^2)]/\Sigma(wF_o^2)^{1/2}$.

Crystallographic Structural Determination of 7·$CHCl_3$ and 13·CH_3CN. Single crystals of **7**·$CHCl_3$ and **13**·CH_3CN suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$/ether and CH_3CN/ether, respectively. Single crystals were mounted on a quartz fiber, and diffraction data were collected in the θ range of 1.23−29.15° for **7**·$CHCl_3$ and 1.44−29.19° for **13**·CH_3CN at 173 K on a Brucker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and refined by full-matrix least squares on F^2 by using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All

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hydrogen atoms were placed in calculated positions. Final refinement details are compiled in Table 3.

Computational Methods. The Q-chem 2.0 program[19] in the Spartan '02 software package[20] was used for geometry optimizations, and the single-point energy calculations for the obtained geometries were performed with the Gaussian 98 program package.[21] All geometries of intermediates and transition states were fully optimized at the B3LYP[22]/LACVP* level of theory. The LACVP* basis set uses a double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LanL2 ECP)[23] for Ru and the 6-31G(d) basis sets[24] for other elements. The vibrational frequencies and zero-point energy (ZPE) were calculated at the same level of theory. The obtained structures were characterized by the number of imaginary frequencies (one or zero for transition or ground states, respectively). Visual inspection of imaginary vibrational modes was also performed with the Spartan '02 software package. The energy calculations were performed at the B3LYP level using the basis sets consisting of a [6s5p3d2f1g] contracted valence basis set with the Stuttgart−Dresden−Bonn energy-consistent pseudopotential[25] for Ru and the 6-311++G(d,p) basis sets[26] for other elements.

The supplementary crystallographic data for this paper [CCDC 235937 (**7**·$CHCl_3$) and CCDC 235938 (**13**·CH_3CN)] can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files for **7**·$CHCl_3$ and **13**·CH_3CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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