Notes

Flash Vacuum Thermolysis of η^5-Oxocyclohexadienyl Complexes of Ruthenium To Give η^5-Cyclopentadienyl Ligands

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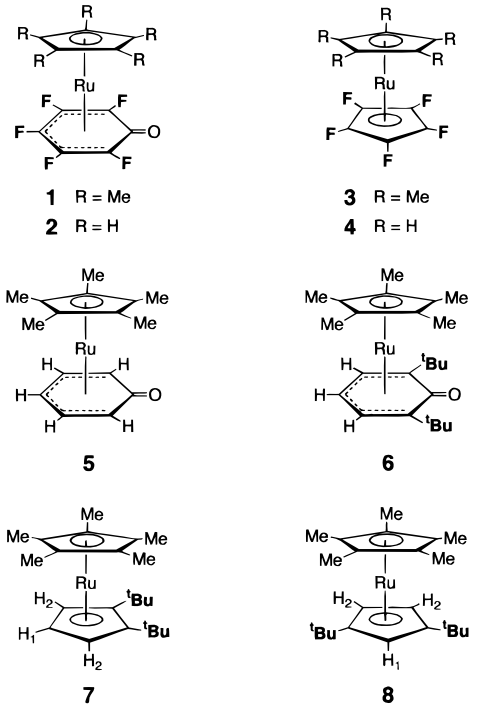
*Summary: The previously reported η^5-oxocyclohexadienyl complexes [Ru(C_5Me_5)(2−6-η-C_5H_5CO)] (**5**) and [Ru(C_5Me_5)(2−6-η-2,6-$C_5{}^tBu_2H_3CO$)] (**6**) have been prepared in better yields by treatment of [Ru(C_5Me_5)Cl]$_4$ with the thallium salts of the corresponding phenols. Subjection of **5** to flash vacuum thermolysis (FVT) results in extrusion of CO and formation of the known cyclopentadienyl complex [Ru(C_5Me_5)(C_5H_5); analogous FVT of **6** also results in extrusion of CO, but in addition to the expected product [Ru(C_5Me_5)(1,2-$C_5{}^tBu_2H_3$)] (**7**), the corresponding isomeric complex [Ru(C_5Me_5)(1,3-$C_5{}^tBu_2H_3$)] (**8**) is formed. Complexes **7** and **8** have been synthesized independently by solution phase chemistry in order to provide authentic samples for comparison; control experiments show that **7** and **8** do not interconvert under the thermolysis conditions and that no rearrangement of recovered starting material is observed.*

Introduction

In the technique of flash vacuum thermolysis (FVT), the compound to be thermolyzed is sublimed or evaporated under high vacuum. The gas-phase reactant passes through a hot zone, and products are condensed in the exit tube or a cold trap if the product is volatile or unstable. This can be a useful synthetic technique for making unstable molecules or for generating otherwise stable molecules via thermal pathways having a high activation barrier; at pressures ≤ 10^{-3} Torr, the amount of time (τ) that the reactant spends in contact with the hot zone is short (between 10^{-3} and 1 s) and depends only on the diameter of the tube, the length of hot zone, and the molecular velocity.[1−3] This technique has been used to extrude small, stable molecules like carbon dioxide, nitrogen, and sulfur dioxide from organic compounds[1] but has been particularly useful in generating five-membered rings from six-membered rings by extrusion of CO. For example, the conversion of anthrone to fluorene is effected at 900 °C in 29% yield;[4] in other applications *o*-benzoquinones are converted to cyclopentadienones,[5−7] 2-pyrone is transformed to furan,[8] and hexafluorocyclohexadienones afford hexafluorocyclopentadiene.[9]

Chart 1



We have previously demonstrated that FVT can be used extrude carbon monoxide from the η^5-pentafluorooxocyclohexadienyl (η^5-pentafluorophenoxide) ligands of complexes **1** and **2** (see Chart 1) to give the ruthenocenes **3** and **4** containing the pentafluorocyclopen-

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tadienyl ligand,[10,11] and we have extended this technique to the selective syntheses of partially fluorinated cyclopentadienyl ligands from the corresponding fluorinated phenols.[12] The latter reactions were selective in that the locations of fluorine substituents on the final cyclopentadienyl ring were invariably those expected from their relative locations on the fluorinated phenoxide precursor; no products arising from skeletal or substituent rearrangements during the FVT experiment were observed.

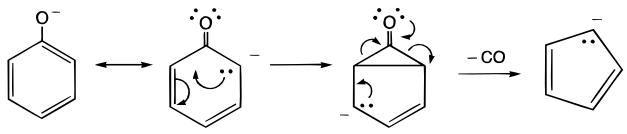
Other ruthenium compounds containing η^5-oxocyclohexadienyl ligands have been reported. A complex containing the parent phenoxide ligand was prepared in methanol from acid/base reaction of $[Ru(C_5Me_5)(OMe)]_2$ and excess phenol.[13] The presence of excess phenol results in 2 equiv of phenol hydrogen-bonded to the oxygen atom of the η^5-oxocyclohexadienyl ligand, but treatment with base removes the hydrogen-bonded phenol to afford **5**.[13] An analogous compound **6** was prepared from $[Ru(C_5Me_5)Cl]_4$ and the lithium salt of 2,6-di-*tert*-butyl phenol in 20% yield; apparently no attempt was made to optimize the yield of the crystallographically characterized product.[14] More recently the phenoxo complex **5** and an isomer of **6** derived from 1,4-di-*tert*-butylphenol have been prepared in better yields.[15]

We have been interested in transition metal complexes of the 1,2-di-*tert*-butylcyclopentadienyl ligand.[16−20] The successful conversion of fully and partially fluorinated oxocyclohexadienyl ligands to the corresponding cyclopentadienyl ligands by FVT suggested this methodology could be used for the preparation of a compound containing the 1,2-di-*tert*-butylcyclopentadienyl ligand from **6**. Here we describe the results of this and related experiments, illustrating the first example of a rearrangement process during the FVT reaction of η^5-oxocyclohexadienyl ligands.

Results and Discussion

Complex **5** can be prepared directly, without coordinated phenol, from the metathesis reaction of $[Ru(C_5Me_5)Cl]_4$ and the thallium salt of phenol in 63% yield. Similarly complex **6** was prepared in 80% yield from the ruthenium tetramer and the thallium(I) salt of 2,6-di-*tert*-butylphenol in refluxing THF. Not surprisingly, FVT of **5** at 720 °C affords 27% conversion to give the known pentamethylruthenocene $[Ru(C_5Me_5)(C_5H_5)]$[21,22] in 57% yield. No effort was made to optimize the conditions of this experiment. However, the corresponding FVT of **6** at 590 °C resulted in the formation of two products: **7**, containing the expected 1,2-di-tert-butylcyclopentadienyl ligand; its isomer **8**, containing the corresponding 1,3-di-tert-butyl-substituted cyclopentadienyl ring. Integration of the ^{1}H NMR spectrum of the crude material recovered after pyrolysis indicated a 7:9:1 mixture of **6:7:8**.

Scheme 1



The mixture of products was separated from the starting material by column chromatography, and the major thermolysis product was separated from the ruthenocene mixture by fractional crystallization or gradient sublimation. The resultant white solid is soluble in hydrocarbons and crystallizes from 95% ethanol. It was identified as isomer **7** by comparison with an authentic sample prepared in 75% yield by reaction of the ruthenium tetramer $[Ru(C_5Me_5)Cl]_4$ with (1,2-di-*tert*-butylcyclopentadienyl)lithium. The ^{1}H NMR spectrum of **7** includes a triplet (H_1) and a doublet (H_2) coupled by 3 Hz for the cyclopentadienyl ring protons; its $^{13}C\{^1H\}$ NMR spectrum exhibits the expected seven resonances. Similarly, an authentic sample of **8** was prepared in 85% yield by reaction of $[Ru(C_5Me_5)Cl]_4$ with (1,3-di-*tert*-butylcyclopentadienyl)lithium. White solid **8** is soluble in hydrocarbons and crystallizes from absolute ethanol. Not unexpectedly the NMR spectra of isomer **8** are similar to that of **7**, but a much small coupling of 1 Hz between the triplet (H_1) and doublet (H_2) resonances is observed in the ^{1}H NMR spectrum.

A pure sample of each isomer **7** and **8** was subjected to the FVT experiment under the conditions used for thermolysis of precursor **6**; each isomer passed through unchanged. Samples of recovered starting material were unchanged, indicating that isomerization of **6** prior to extrusion of CO is not a viable pathway for formation of **8**. Clearly, rearrangement occurs during the thermolysis of **6** and the mixture of isomeric cyclopentadienyl products is that of kinetic control.

The extrusion of carbon monoxide and subsequent ring contraction from the oxocyclohexadienyl ligand can be related to the fragmentation of phenoxide ion. Using negative ion chemical ionization mass spectrometry, the fragmentation of phenoxide ion by collisionally activated dissociation has been observed in the gas phase;[23] one fragmentation pathway was loss of CO and formation of the cyclopentadienyl anion. The mechanism proposed to account for this fragmentation is shown in Scheme 1 and involves rearrangement of phenoxide ion to a bicyclic intermediate with subsequent chelotropic loss

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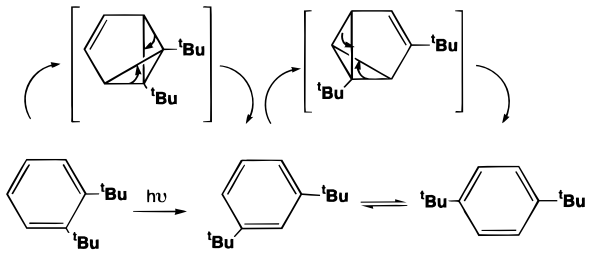
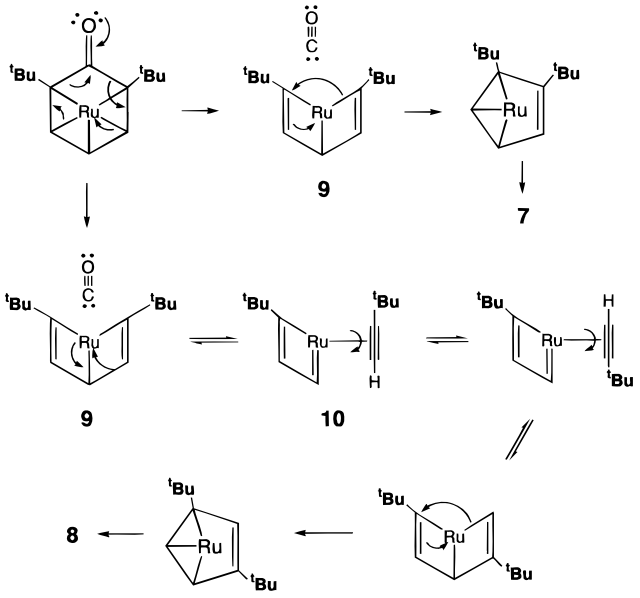
Scheme 2



of CO affording the cyclopentadienyl anion. While such a mechanism can account for formation of **7** from **6**, it cannot account for the observed product **8**. An interchange of ring substituents (H and ^{t}Bu) could be responsible for the observed product mixture, but this seems quite unlikely; a skeletal transformation during the thermolysis mechanism seems more a more probable, lower energy event. By way of analogy, 1,2-di-*tert*-butylbenzene isomerizes photochemically to its 1,3 and 1,4 isomers as shown in Scheme 2.[25] No cross-alkylations were detected, and consequently, isomerization by way of migrating free alkyl radicals was considered less likely than some type of annular isomerization. Isomerizations could proceed via one or more valence isomers of benzene; rearrangements via benzvalene intermediates are shown in Scheme 2. Examples of stable metallabenzenes are now well-known,[26−32] and metallabenzenes have been implicated as intermediates en route to η^5-cyclopentadienyl compounds.[33−35] A metallabenzene intermediate, formed after extrusion of carbon monoxide, could either ring close to give the 1,2-di-*tert*-butylcyclopentadienyl-substituted product **7** or rearrange via a valence isomer of metallabenzene and then ring close to give **8**. But formation of a planar metallabenzene from an η^5-oxocyclohexadienyl ligand requires enormous changes in the metal−carbon interactions, and we suggest a least motion pathway which involves less draconian disruption of the bonding.

A mechanism invoking a Dewar metallabenzene is shown in Scheme 3. CO extrusion as shown leads to a Dewar metallabenzene intermediate **9**, which can collapse to the major product **7** as shown. Isomerization can proceed via the metallacyclobutadiene intermediate **10**, in which rotation of the alkyne and re-formation of the Dewar metallabenzene are followed by collapse to afford **8**. This mechanism is in accord with the solution studies by Schrock of reactions of metallacyclobutadienes with alkynes which give cyclopentadienyl complexes with similar skeletal scrambling.[35] This rearrangement pathway is presumably driven by steric effects between *tert*-butyl groups in intermediate **9** and does not appear to be a significant pathway in corresponding thermolyses of complexes bearing less sterically demanding fluorine substituents.[12]

Scheme 3



Experimental Section

General Procedures. All reactions except FVT experiments were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over Aquasorb. All solvents were obtained from Fisher Scientific and distilled under nitrogen over one of the following drying agents: THF and diethyl ether over K/benzophenone; methylene chloride, petroleum ether, and acetonitrile over CaH_2. Aromatic and unsaturated components of 35−65 °C petroleum ether were removed before distillation by prolonged stirring over concentrated H_2SO_4 followed by washing with 10% aqueous solution of KOH. Infrared spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer or a Perkin-Elmer Model 1600 FT-IR spectrophotometer. The FVT experiments were performed on a Fisher Isotemp Model 186 tube furnace. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY). ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer or a Varian Unity Plus 300 System in the solvent indicated. All ^{1}H and ^{13}C{^{1}H} shifts are reported as ppm downfield of internal TMS and are referenced to the solvent peak. *J* values are given in hertz.

$RuCl_3 \cdot 3H_2O$ was obtained from Johnson-Matthey Aesar/Alfa, and $[RuCp^*Cl]_4$ was prepared following the literature procedure.[36] Thallium(I) ethoxide was purchased from Strem. Phenols and *n*-butyllithium (2.0 M in cyclohexane) were purchased from Aldrich. Thallium(I) ethoxide was purchased from Strem. The thallium salts of the phenols were prepared from the phenol and thallous ethoxide in petroleum ether.[12] (1,2-Di-*tert*-butylcyclopentadienyl)lithium was prepared as previously described.[16] 1,3-Di-*tert*-butylcyclopentadiene was purchased from Quantum Design, Inc. (Austin, TX).

Preparation of [Ru(C_5Me_5)(2−6-η-C_5H_5CO)] (5). The thallium salt of phenol (0.22 g, 0.74 mmol) was combined with $[Ru(C_5Me_5)Cl]_4$ (0.20 g, 0.18 mmol) in THF (25 mL). The slurry

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was allowed to stir at ambient temperature for a period of 21.5 h and concentrated *in vacuo*, and the resulting residue was extracted with diethyl ether (2 × 20 mL). The combined yellow extracts were filtered through Celite and concentrated under reduced pressure. The crude residue was sublimed under reduced pressure to afford a cream colored solid (0.15 g, 63%). ^{1}H NMR ($CDCl_3$): δ 1.88 [s, 15 H, $C_5(CH_3)_5$], 4.78 (apparent dd, 2H$_1$, $^3J_{1-2} = 7$, $^4J_{1-3} = 1$), 4.87 (tt, 1H$_3$, $^3J_{2-3} = 5$, $^4J_{1-3} = 1$), 5.06 (apparent dd, 2H$_2$, $^3J_{2-3} = 5$, $^3J_{1-2} = 7$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.88 [$C_5(CH_3)_5$], 78.54, 86.17, 91.55, 116.17, 150.34 (*C*O); IR (CH_2Cl_2): $\nu_{CO} = 1555$ cm^{-1}. These data are consistent with literature data reported for **5**.[13]

FVT of [Ru(C$_5$Me$_5$)(2−6-η-C$_5$H$_5$CO)] (5). Compound **5** (0.030 g, 0.091 mmol) was slowly heated under dynamic vacuum (10^{-4} Torr) and allowed to pass through a quartz tube (0.48 cm × 60 cm) at 720 °C. The solid product condensed at ambient temperature in the exit tube and was rinsed from the tube with methylene chloride. ^{1}H NMR of the crude product (0.027 g) indicated a mixture of the starting material and [Ru(C$_5$Me$_5$)(C$_5$H$_5$)] was present. The conditions for formation of the product were not optimized. The product was separated from the starting material by chromatography (silica gel). Elution with hexane afforded a white solid (0.004 g, 57% based on 27% conversion). ^{1}H NMR ($CDCl_3$): δ 1.94 [s, 15 H, $C_5(CH_3)_5$], 4.16 (s, 5H, C_5H_5). These data are consistent with literature data.[21] Elution with methanol afforded the recovered starting material **5** (0.022 g, 73%).

Preparation of [Ru(C$_5$Me$_5$)(2−6-η-2,6-C$_5$^{t}Bu$_2$H$_3$CO)] (6). The thallium salt of 2,6-di-*tert*-butylphenol (0.70 g, 1.70 mmol) was added to $[Ru(C_5Me_5)Cl]_4$ (0.44 g, 0.40 mmol) in THF (30 mL). The mixture was heated to reflux overnight, cooled to ambient temperature and filtered through a plug of silica gel, and the yellow filtrate was concentrated *in vacuo*. The crude product was crystallized from 2:1 hexane/diethyl ether at −78 °C to give yellow crystals (0.60 g, 84%). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 18H, ^{t}Bu), 1.83 [s, 15 H, $C_5(CH_3)_5$], 4.33 (t, 1H$_2$, $^3J_{1-2} = 6$), 5.12 (d, 2H$_2$, $^3J_{1-2} = 6$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.80 [$C_5(CH_3)_5$], 29.48 [C(*C*H$_3$)$_3$], 34.45 [*C*(CH$_3$)$_3$], 73.90, 84.5, 88.79 [*C*$_5$(CH$_3$)$_5$], 102.36, 156.64 (*C*O). IR (CH_2Cl_2): $\nu_{CO} = 1538$ cm^{-1}. These data are consistent with literature data reported for **6**.[14]

FVT of [Ru(C$_5$Me$_5$)(2−6-η-2,6-C$_5$^{t}Bu$_2$H$_3$CO)] (6). Compound **6** (0.116 g, 0.263 mmol) was slowly heated under dynamic vacuum (10^{-4} Torr) and allowed to pass through a quartz tube (0.8 cm × 60 cm) at 590 °C. A shiny black film was deposited on the length of the tube placed in the hot zone of the furnace. This film was insoluble in aqua regia and contained ruthenium and carbon.[12] The product mixture condensed as a yellow oil at ambient temperature in the exit tube and was rinsed from the tube with diethyl ether. ^{1}H NMR of the crude product (0.092 g) indicated a mixture of **6**−**8** was present in a ratio of 7:9:1, respectively. The starting material **6** was separated from the ruthenocenes by column chromatography on silica gel. Elution with pentane afforded the mixture of ruthenocenes **7** and **8** (0.034 g, 52%; 60% conversion), and subsequent elution with diethyl ether afforded unreacted starting material (0.046 g, 40%). ^{1}H NMR indicated the recovered starting material had not rearranged. Fractional crystallization of the ruthenocene mixture from 95% EtOH afforded **7** as white needles (0.24 g, 34%; 60% conversion); **7** could also be separated from the ruthenocene mixture by gradient sublimation (−30 to +170 °C, 10^{-4} Torr). For spectroscopic and other data on **7** and **8**, see below.

Independent Synthesis of [Ru(C$_5$Me$_5$)(η^5-1,2-C$_5$^{t}Bu$_2$H$_3$)] (7). $[Ru(C_5Me_5)Cl]_4$ (0.098 g, 0.09 mmol) and (1,2-di-*tert*-butylcyclopentadienyl)lithium (0.066 g, 0.36 mmol) were combined with THF (10 mL). The resulting mixture was allowed to stir at ambient temperature overnight (16 h). The solvent was removed under reduced pressure, and the residue was extracted with petroleum ether (3 × 5 mL). Solvent was removed from the combined extracts under reduced pressure. The crude product was passed down a silica gel column (2.5 cm × 4 cm). Elution with pentane (100 mL) and evaporation of the solvent afforded the ruthenocene **7**, as a white solid (0.111 g, 75%), mp 102.7−103.5 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 18 H, ^{t}Bu), 1.90 [s, 15 H, $C_5(CH_3)_5$], 3.79 (t, 1H$_1$, $^3J_{1-2} = 3$), 4.16 (d, 2H$_2$, $^3J_{1-2} = 3$). ^{13}C NMR ($CDCl_3$): δ 12.46 [q, $^1J_{CH} = 126$, $C_5(CH_3)_5$], 32.07 [decet, $^2J_{CH} = 4$, *C*(CH$_3$)$_3$], 33.88 [quartet of septets, $^1J_{CH} = 126$, $^3J_{CH} = 5$, C(*C*H$_3$)$_3$], 70.45 (d of multiplets, $^1J_{CH} = 173$, CH$_1$), 74.24 (dt,$^1J_{CH} = 171$, $^3J_{CH} = 7$, CH$_2$), 84.51 [m, *C*$_5$(CH$_3$)$_5$], 101.22 [m, *C*C(CH$_3$)$_3$]. Anal. Calcd for $C_{21}H_{36}Ru$: C, 66.79; H, 8.77. Found: C, 67.02; H, 8.84.

Independent Synthesis of [Ru(C$_5$Me$_5$)(η^5-1,3-C$_5$^{t}Bu$_2$H$_3$)] (8). A solution of 1,3-di-*tert*-butylcyclopentadiene (0.21 g, 1.18 mmol) in THF (10 mL) was cooled to 0 °C using an ice bath, and *n*-BuLi (1.90 M in cyclohexane, 0.62 mL) was added dropwise via syringe. The resulting solution was allowed to warm to ambient temperature over a period of 1.5 h. The solution was again cooled to 0 °C and then added via cannula to a 0 °C slurry of $[Ru(C_5Me_5)Cl]_4$ (0.31 g, 0.28 mmol) in THF (10 mL). The red-orange mixture was allowed to stir overnight at ambient temperature. The solvent was removed in vacuo, and the resulting residue was extracted with petroleum ether (3 × 10 mL). After removal of the solvent an amber oil (0.54 g) was obtained, which solidified on standing. Sublimation of the solid followed by crystallization from absolute ethanol afforded the white solid **8** (0.35 g, 74%), mp 86.4−87.3 °C ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 18 H, ^{t}Bu), 1.91 [s, 15 H, $C_5(CH_3)_5$], 3.90 (d, 2H$_2$, $^3J_{1-2} = 1$), 4.06 (t, 1H$_1$, $^3J_{1-2} = 1$). ^{13}C NMR ($CDCl_3$): δ 12.52 [q, $^1J_{CH} = 126$, $C_5(CH_3)_5$], 30.59 (decet, $^2J_{CH} = 4$, *C*(CH$_3$)$_3$), 31.00 [quartet of septets, $^1J_{CH} = 125$, $^3J_{CH} = 5$, C(*C*H$_3$)$_3$], 66.43 (dt, $^1J_{CH} = 169$, $^3J_{CH} = 6$, CH), 68.74 (dt,$^1J_{CH} = 171$, $^3J_{CH} = 77$, CH), 84.25 [m, *C*$_5$(CH$_3$)$_5$], 105.14 [m, *C*C(CH$_3$)$_3$]. ^{1}H NMR (C_6D_6): δ 1.20 (s, 18 H, ^{t}Bu), 1.89 [s, 15 H, $C_5(CH_3)_5$], 3.95 (d, 2H$_2$, $^3J_{1-2} = 1$), 4.16 (t, 1H$_1$, $^3J_{1-2} = 1$). ^{13}C NMR (C_6D_6): δ 12.77 [q, $^1J_{CH} = 126$, $C_5(CH_3)_5$], 30.85 [decet, $^2J_{CH} = 4$, *C*(CH$_3$)$_3$], 31.32 [quartet of septets, $^1J_{CH} = 125$, $^3J_{CH} = 5$, C (*C*H$_3$)$_3$], 66.51 (dt, $^1J_{CH} = 169$, $^3J_{CH} = 6$, CH$_1$), 69.29 (dt, $^1J_{CH} = 170$, $^3J_{CH} = 7$, CH$_2$), 84.49 [m, *C*$_5$(CH$_3$)$_5$], 105.32 [m, *C*C(CH$_3$)$_3$]. Anal. Calcd for $C_{21}H_{36}Ru$: C, 66.79; H, 8.77. Found: C, 66.98; H, 8.87.

Control Experiments: FVT of 7 and 8. Complex **7** (0.020 g, 0.048 mmol) was slowly heated under dynamic vacuum (10^{-4} Torr) and allowed to pass through a quartz tube (0.48 cm × 60 cm) at 590 °C. The product (0.019 g) condensed at ambient temperature in the exit tube and was rinsed from the tube with diethyl ether. A ^{1}H NMR spectrum ($CDCl_3$) confirmed that **7** had not rearranged to **8**. An analogous reaction with pure **8** also showed no rearrangement to **7**.

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