

Synthesis and Catalytic Activity of η^1 -Allyl and η^3 -Allyl, Ethyl, and Hydrido Complexes of Ruthenium–Pentamethyl[60]fullerene

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η^1 -Allyl and η^3 -allyl, ethyl, and hydrido ruthenium complexes of pentamethyl[60]fullerene, $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{R}(\text{CO})_2$ ($\text{R} = \eta^1\text{-allyl, Et, H}$) and $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^3\text{-allyl})(\text{CO})$ were synthesized by the reaction of a chlorido complex $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{CO})_2$ with an allyl and an ethyl Grignard reagent or lithium aluminum hydride. Conversion of the η^1 -allyl com-

plex to the corresponding η^3 -allyl complex and the catalytic performance of the hydrido and the chlorido complexes in the isomerization reaction of 1-decene to internal decenes are described.

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Introduction

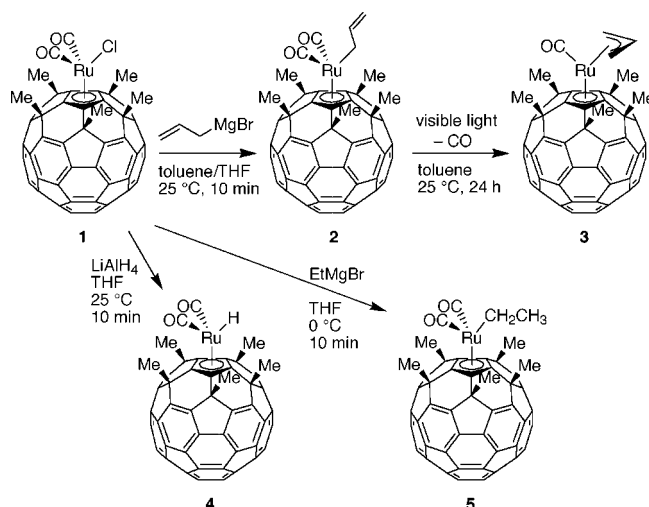
Cooperative effects of fullerene conjugated systems and transition metal atoms have attracted the interest of inorganic and organometallic chemists^[1] because of the possible $d\pi$ -conjugative synergy that may create new properties unavailable from individual systems.^[2] We have employed pentaorgano[60]fullerenes^[3] as η^5 -fullerene ligands and synthesized various metal–fullerene complexes involving Re ,^[4] Fe ,^[5] Ru ,^[6] Rh ,^[7] Ir ,^[8] Ni ,^[9] Pd ,^[9] and Pt ^[9] atoms. Among them, many ruthenium(II) complexes are particularly interesting because of stable facial coordination of the pentaor-

gano[60]fullerene ligands to the d^6 metal center with the octahedral geometry.^[6a] Indeed, ruthenium complex $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{CO})_2$ was obtained in high yield on a large scale and was used as a useful starting material for the study of the organometallic chemistry of the metal–fullerene complexes.^[6a] As an extension of our work in this area, we have investigated further derivatization of the ruthenium complex and obtained various ruthenium–pentamethyl[60]fullerene complexes. Herein we report the synthesis and catalytic activity of η^1 - and η^3 -allyl, ethyl, and hydrido ruthenium complexes of pentamethyl[60]fullerene (Scheme 1).

Results and Discussion

Synthesis of η^1 - and η^3 -Allyl Ruthenium Complexes of Pentamethyl[60]fullerene

Treatment of a solution of $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{CO})_2$ (**1**)^[6a] in toluene with a solution of allylmagnesium bromide in thf at 25 °C led to a ligand exchange reaction to afford η^1 -allyl complex **2**, $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^1\text{-allyl})(\text{CO})_2$, in quantitative yield (Scheme 1). Product **2** was purified by neutral alumina chromatography to remove magnesium salts. Decomposition of **2** through loss of the ruthenium metal was observed upon silica gel column chromatography, which resulted in the formation of an oxidized compound of pentamethyl[60]fullerene, $\text{C}_{60}\text{Me}_5\text{O}_2\text{OH}$.^[10] This product was identified by MS (APCI-) ($m/z = 844$ [M][–]). Compound **2** was isolated as an orange powder and was stable in air as a solid for over one month. Characterization of **2** was performed by ^1H and ^{13}C NMR, IR, and UV/Vis spectroscopic measurements, and combustion analysis. In the ^1H NMR spectrum, a set of three signals due to the olefinic protons was observed in lower field at $\delta = 4.86, 5.14,$ and 6.51 ppm, which indicates that the complex is a σ -allyl complex. The IR spectrum exhibited asymmetric and symmetric stretch-



Scheme 1. Syntheses of allyl, ethyl, and hydrido complexes.

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ing vibrations of the carbonyl groups at 2016 and 1960 cm^{-1} , which suggests two carbonyl ligands remain on the ruthenium center.

We next investigated conversion of η^1 -allyl complex **2** into an η^3 -allyl complex through decarbonylation. Compound **2** did not react at all in C_6D_6 at 25 $^\circ\text{C}$ for 24 h. However, when the C_6D_6 solution of **2** was irradiated by visible light with 60 W incandescent light at 25 $^\circ\text{C}$ for 14 h, η^3 -allyl compound **3**, $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^3\text{-allyl})(\text{CO})$, formed. According to the ligand field theory, such as light-induced decarbonylation process involves electron transition to antibonding orbital of the metal–carbonyl bond. The effect of the strongly light-absorbing fullerene part is therefore apparent. The progress of the reaction was monitored by analysis of the ^1H NMR spectra (Figure 1). After three hours of irradiation, the η^1 - and η^3 -allyl complexes were observed in a 1:1 ratio. Irradiation for 14 h completed this conversion. On heating the reaction mixture to 110 $^\circ\text{C}$ in C_6D_6 for 24 h in a sealed tube, instead of the light irradiation, η^3 -allyl compound **3** slowly formed (only with ca. 10% conversion). It is known that an η^5 -cyclopentadienyl- η^3 -allyl metal complex exists in two isomeric forms: *exo* and *endo* isomers (Figure 2).^[11] In contrast, the present reaction produced only an *exo* isomer (see below). If a pathway of *endo*–*exo* interconversion exists (which may involve pseudorotation of the η^3 -allyl group about the allyl–metal bond axis or an equilibrium that goes through an η^1 -allyl intermediate), the experimental observation would suggest that the *exo* isomer is thermodynamically much more stable than the *endo* isomer. It must then be the steric bulk of the pentamethyl[60]fullerene ligand that is responsible for the *exo* preference. Such a tendency, though less pronounced, in the stability of the *exo* isomer has also been observed in usual η^5 -cyclopentadienyl- η^3 -allyl ruthenium systems.^[12]

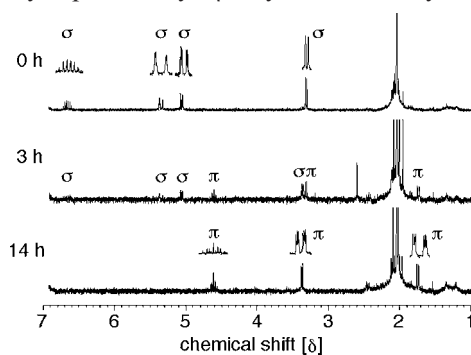


Figure 1. Conversion of **2** to **3** as monitored with ^1H NMR spectroscopic measurements.

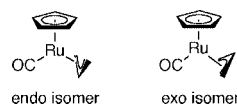


Figure 2. The *endo* and *exo* isomers of $\eta^5\text{-Cp-}\eta^3$ -allyl ruthenium carbonyl complex.

η^3 -Allyl complex **3** was isolated in 49% yield by preparative HPLC. Side products were the oxidized pentamethyl[60]fullerene and unidentified insoluble products.

Identification of the *exo* form of **3** was achieved by ^1H and ^{13}C NMR, IR, and UV/Vis spectroscopic measurements, and combustion analysis as well as an X-ray crystallographic study (Figure 3). The ^1H NMR spectrum displayed a signal pattern typical for an η^3 -allyl group. Signals due to the *syn* and *anti* protons on the terminal carbon atoms and one proton on the center carbon atom were observed at $\delta = 3.38$, 1.75, and 4.61, respectively. The IR spectrum showed one strong CO absorption at 1943 cm^{-1} . The X-ray analysis clearly showed the *exo* form of the η^3 -allyl ligand. As shown in the top view, the carbonyl ligand are located in the space among two methyl groups of the pentamethyl[60]fullerene ligand and the η^3 -allyl ligand. The side view indicates roughly parallel coordination of the η^3 -allyl ligand to the η^5 -cyclopentadienyl part of the pentamethyl[60]-fullerene moiety. The angle between a least-squares plane consisting of the three carbon atoms of the η^3 -allyl and that of the five carbon atoms of the η^5 -cyclopentadienyl part is 11.24(2) $^\circ$. Although some ruthenium η^3 -allyl complexes have been used in catalysis,^[13] complex **3** was too stable to show catalytic activity.

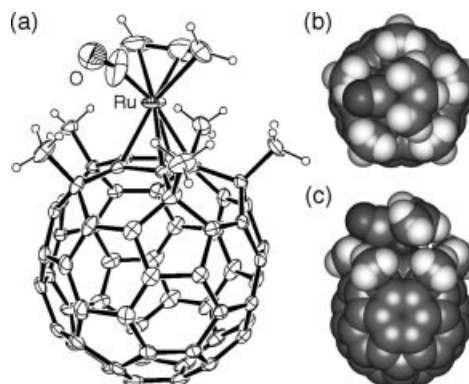


Figure 3. X-ray crystal structure of **3-CS**₂. Solvent molecules are omitted for clarity. (a) ORTEP drawing with 30% probability level ellipsoids. (b) CPK model, top view. (c) CPK model, side view.

Synthesis of Hydrido Ruthenium Complexes of Pentamethyl[60]fullerene

Synthesis of hydrido complex **4**, $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{H}(\text{CO})_2$, was performed next. We used three hydrogenation reagents: lithium aluminum hydride (LAH), diisobutylaluminum hydride (DIBAL), and sodium borohydride (NaBH_4). Target compound **4** was obtained in 76% isolated yield by the reaction of chlorido complex **1** with LAH in thf at 25 $^\circ\text{C}$ (Scheme 1). Treatment of **1** with DIBAL in thf afforded **4** in 42% yield. The reaction of **1** with NaBH_4 did not yield the desired hydrido complex but gave several unidentified complexes. This may be due to hydroboration taking place on the fullerene moiety of **1**. Characterization of **4** was performed by ^1H , ^{13}C NMR, IR, and UV/Vis spectroscopic measurements and combustion analysis. In the ^1H NMR spectrum, a proton signal characteristic of the hydride group was observed at $\delta = -10.07$ ppm. The IR spectrum exhibited asymmetric and symmetric vibration absorptions

Table 1. Isomerization of 1-decene to internal alkenes catalyzed by ruthenium–pentamethyl[60]fullerene complexes.

Entry	Catalyst	1-Decene [equiv.]	Temp. [°C]	Time [h]	Conversion [%]	Yield [%] 2-Decene (<i>E/Z</i>)	Other internal alkenes
1	4	10000	140	6	95	49 (2.0)	46
2	4	2600	100	16	24	14 (1.8)	10
3	4	2600	60	16	0	–	–
4	3	2600	100	16	0	–	–
5	1	2600	140	18	96	56 (1.8)	40
6	1	2600	100	16	12	ND	ND

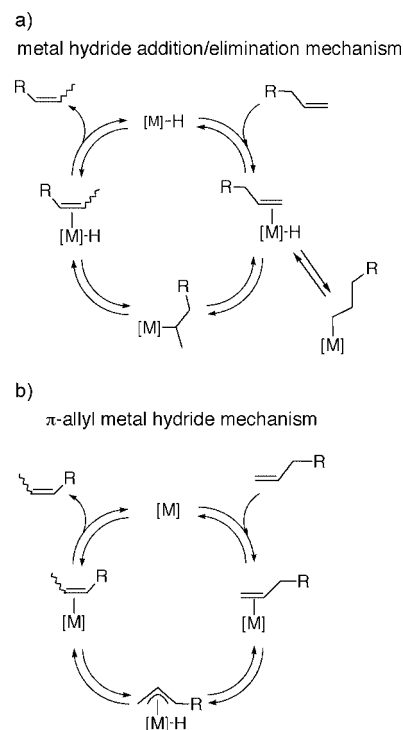
at 2062 and 2024 cm^{-1} that are due to the two carbonyl ligands.

We then examined the catalytic activity of the pentamethyl[60]fullerene ruthenium complexes in alkene isomerization reactions from terminal alkenes to internal alkenes. Many active catalysts using transition metal complexes, such as Fe, Pd, Rh, Pt, Ni, Ir, Ru, Cr, Ti, and Zr complexes, have been used in isomerization reactions of alkenes.^[14] In general, two reaction pathways have been considered. One is a metal hydride addition/elimination mechanism (Scheme 2a), and the other is a π -allyl metal hydride mechanism (Scheme 2b). Motivated by the former reaction mechanism, we used hydrido complex **4** in the isomerization reaction of 1-octene. Complex **4** was found to be catalytically active at high temperature. The reaction with the use of 0.01 mol-% of **4** for 6 h at 140 °C took place with 95% conversion to give 49% of 2-decene in an *E/Z* ratio of 2.0 and 46% of other internal alkenes (Table 1, Entry 1). When the reaction was heated to 100 °C with 0.083 mol-% of **4** for 18 h, only 24% conversion with a similar product distribution (Table 1, Entry 2) was observed, whereas the reaction heated at 25 or 60 °C did not afford any isomerization products at all (Table 1, Entry 3).

In this reaction, high temperature was essential, which could be due to the high activation energy for decarbonylation of catalyst precursor **4** to the catalytically active monocarbonyl complex. We therefore attempted this alkene isomerization reaction at 25 °C with visible light irradiation which was effective for the conversion of **2** into **3**, but the isomerized products were not obtained. This may then be due to decomposition of the intermediates by further loss of the carbonyl ligand.

Allyl complex **3** did not show any catalytic activity in the alkene isomerization reaction even at 100 °C, whereas chlorido complex **1** gave the isomerized products in 96% conversion at 140 °C, and in 12% conversion at 100 °C. The latter result can be attributed to the formation of **4** from **1** in the presence of alkenes or to a catalytic cycle involving the π -allyl metal hydride (Scheme 2b).

Although ruthenium alkyl complexes having no β -hydrogen such as $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Me}(\text{CO})_2$ and $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{CH}_2\text{SiMe}_3)(\text{CO})_2$ ^[6a] have been synthesized, syntheses of ruthenium alkyl complexes having β -hydrogen atoms are still scarce.^[15] In the present fullerene complex series, we could synthesize a stable ruthenium ethyl complex $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Et}(\text{CO})_2$ (**5**) by the reaction of **1** with ethylmagnesium bromide in thf at 0 °C in 48% yield. This complex was perfectly stable and did not show any tendency of β -hydride



Scheme 2. Two possible mechanisms for transition-metal-catalyzed alkene isomerization.

elimination under light irradiation and under heating. We considered that the elimination reaction was inhibited because of either conformational or electronic effects of the $\eta^5\text{-C}_{60}\text{Me}_5$ moiety. One may recall the strong stabilization effect of this fullerene ligand in η^3 -allylnickel chemistry.^[9a]

Conclusion

We have synthesized η^1 -allyl and η^3 -allyl, ethyl, and hydrido ruthenium complexes of pentamethyl[60]fullerene and showed that the hydrido complex catalyzes the 1-decene isomerization reaction. The present set of experiments suggests new opportunities for the exploration of reactivities of the ruthenium–carbon and –hydrogen bonds, especially under excitation of the fullerene ligand by light irradiation.

Experimental Section

General Procedure: All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of argon by using standard Schlenk techniques. Toluene and thf were

distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{CO})_2$ was prepared according to the literature.^[6a] Solutions of *t*BuOK in thf and allylmagnesium bromide in thf were purchased from Sigma–Aldrich Co. and used as received. Other commercial reagents were used without purification. HPLC analyses were performed with a Shimadzu LC-10A system equipped with a SPD-M10A diode array detector and a Cosmosil-Buckyprep column (4.6 × 250 mm, Nacalai Tesque Co.). Preparative HPLC separations were performed by the use of a preparative scale Buckyprep column (20 mm × 250 mm). The ^1H and ^{13}C NMR spectra were recorded with a JEOL EX 400 spectrometer. The ^1H NMR spectra are reported in parts per million from internal tetramethylsilane and in the ^{13}C NMR spectra from 77.0 ppm (CDCl_3) or from 128.0 ppm (C_6D_6). Other spectra were recorded with the use of the following instruments: IR, ReactIR 1000; UV/Vis, JASCO V-570; mass spectra, Waters ZQ2000. Elemental analyses were performed at organic elemental analysis laboratory in the Department of Chemistry, University of Tokyo.

$\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^1\text{-allyl})(\text{CO})_2$ (2): A solution of allylmagnesium bromide (0.090 mmol) in thf (0.090 mL) was added to a solution of **1** (30 mg, 0.030 mmol) in toluene (6 mL) under an atmosphere of argon at room temperature. After stirring for 10 min, a small amount of ethanol was added to the resulting brown solution. The solution was passed through a pad of neutral alumina, and the red-colored filtrate was dried under vacuum to obtain **2** (30 mg, 99% yield) as an orange powder. M.p. 215–220 °C (dec.). ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 6.51 (ddt, $^3J_{\text{H-H}} = 16.6$ (trans), 9.8 (cis), 8.4 Hz, 1 H, Ru-CH₂-CH), 5.14 (dd, $^3J_{\text{H-H}} = 16.6$ Hz (trans), $^2J_{\text{H-H}} = 1.9$ Hz (gem), 1 H, Ru-CH₂-CH=CH₂), 4.86 (dd, $^3J_{\text{H-H}} = 9.8$ Hz (cis), $^2J_{\text{H-H}} = 1.9$ Hz (gem), 1 H, Ru-CH₂-CH=CH₂), 3.32 (d, $^3J_{\text{H-H}} = 8.4$, 2 H, Ru-CH₂), 2.41 (s, 15 H, C_{60}Me_5) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 29.79 (1 C, Ru-CH₂CH=CH₂), 30.43 (5 C, C_{60}Me_5), 51.11 [5 C, $\text{C}_{60}(\text{sp}^3)$], 108.48 (1 C, Ru-CH₂CH=CH₂), 111.82 [5 C, $\text{C}_{60}(\text{Cp})$], 143.56 (10 C, C_{60}), 143.85 (10 C, C_{60}), 146.78 (1 C, Ru-CH₂CH=CH₂), 147.64 (5 C, C_{60}), 148.02 (10 C, C_{60}), 148.40 (5 C, C_{60}), 152.56 (10 C, C_{60}), 201.50 (2 C, CO) ppm. UV/Vis (toluene/2-propanol, 7:3): λ = 287, 355 (sh), 395 nm. IR (diamond probe): $\tilde{\nu}$ 1960 (s) (CO), 2016 (s). MS (APCI–): m/z = 993 [M^+], 952 [$\text{M} - \text{allyl}$]. HPLC (toluene/2-propanol, 7:3; flow rate: 1 mL min^{−1}): t_R = 8.2 min. $\text{C}_{70}\text{H}_{20}\text{O}_2\text{Ru}$ (994.00): calcd. C 84.58, H 2.03; found C 84.38, H 2.00.

$\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^3\text{-allyl})(\text{CO})$ (3): Compound **2** (30 mg, 0.030 mmol) was dissolved in toluene (12 mL) under an atmosphere of argon. This solution was stirred vigorously and irradiated with 60 W incandescent light at room temperature. After 24 h, the resulting red-colored solution was purified by preparative HPLC (toluene/2-propanol, 7:3; flow rate: 20 mL min^{−1}). The fractions containing **3** were collected, and the solvents were evaporated to dryness to obtain **3** (14 mg, 49% yield) as orange microcrystals. M.p. 240–245 °C (dec.). ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ = 4.61 (m, 1 H, H_{center}), 3.38 (dt, $^3J_{\text{H}(\text{center})-\text{H}(\text{syn})} = 6.8$ Hz, 2 H, H_{syn}), 2.05 (s, 15 H, C_{60}Me_5), 1.75 (dt, $^3J_{\text{H}(\text{center})-\text{H}(\text{anti})} = 11.2$ Hz, 2 H, H_{anti}) ppm. ^{13}C NMR (100 MHz; $\text{CDCl}_3/\text{CS}_2$, 1:1; 25 °C): δ = 30.45 (5 C, C_{60}Me_5), 33.69 (2 C, C_3H_5), 50.73 [5 C, $\text{C}_{60}(\text{sp}^3)$], 69.61 (1 C, C_3H_5), 106.77 [5 C, $\text{C}_{60}(\text{Cp})$], 143.28 (10 C, C_{60}), 143.77 (10 C, C_{60}), 146.65 (5 C, C_{60}), 147.73 (10 C, C_{60}), 148.14 (5 C, C_{60}), 153.05 (10 C, C_{60}), 192.50 (1 C, CO) ppm. UV/Vis (toluene/2-propanol, 7:3): λ = 291, 348 (sh), 394 nm. IR (diamond probe): $\tilde{\nu}$ 1943 (s) (CO). MS (APCI–): m/z = 965 [M^+]. HPLC (toluene/2-propanol, 7:3; flow rate: 1 mL min^{−1}): t_R = 7.39 min. $\text{C}_{69}\text{H}_{20}\text{ORu}$ (965.99): calcd. C 85.79, H 2.09; found C 84.68, H 2.01.

Synthesis of $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{H}(\text{CO})_2$ (4): To a solution of **1** (10 mg, 0.050 mmol) in thf (1.7 mL) was added powdered LiAlH_4 (0.38 mg,

0.050 mmol) at 25 °C. After stirring for 10 min, the color of the solution changed from red to brown. After the reaction was quenched with a small amount of ethanol, the solution was evaporated to dryness. The residue was dissolved in toluene (10 mL), and the supernatant was separated from the insoluble salts by filtration. The filtrate was evaporated to dryness and dried under vacuum for 5 h to obtain the title compound (7.2 mg, 0.38 mmol, 76% yield). M.p. 180–190 °C (dec.). ^1H NMR (400 MHz; $\text{CDCl}_3/\text{CS}_2$, 1:1; 25 °C): δ = −10.07 (s, 1 H, Ru-H), 2.30 (s, 15 H, C_{60}Me_5) ppm. ^{13}C NMR (100 MHz; $\text{CDCl}_3/\text{CS}_2$, 1:1; 25 °C): δ = 32.16 (5 C, C_{60}Me_5), 49.88 [5 C, $\text{C}_{60}(\text{sp}^3)$], 110.70 [5 C, $\text{C}_{60}(\text{Cp})$], 143.41 (10 C, C_{60}), 143.82 (10 C, C_{60}), 146.55 (5 C, C_{60}), 147.63 (10 C, C_{60}), 148.19 (5 C, C_{60}), 152.34 (10 C, C_{60}), 199.73 (2 C, CO) ppm. UV/Vis (toluene/2-propanol, 7:3): λ = 287, 349 (sh), 396 nm. IR (diamond probe): $\tilde{\nu}$ 1962 (s) (CO), 2024 (s). MS (APCI–): m/z = 954 [M^+]. HPLC (toluene/2-propanol, 7:3; flow rate: 1 mL min^{−1}): t_R = 8.02 min. $\text{C}_{67}\text{H}_{16}\text{O}_2\text{Ru}$ (953.93): calcd. C 84.36, H 1.69; found C 84.01, H 1.41.

$\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Et}(\text{CO})_2$ (5): A solution of EtMgBr (0.075 mmol) in thf (0.083 mL) was added to a solution of **1** (50 mg, 0.050 mmol) in toluene (16 mL) under an atmosphere of argon at 0 °C. After stirring for 10 min, the resulting brown suspension was quenched with a small amount of ethanol and passed through a pad of silica gel. This eluent was purified by HPLC (toluene/2-propanol, 7:3; flow rate: 20 mL min^{−1}). The fractions containing the title compound were collected, and the solvents were evaporated to dryness. The solid was then dissolved again in a small amount of CS_2 , and this solution was dried under vacuum to obtain the title compound (23 mg, 0.025 mmol, 48% yield). M.p. 210–215 °C (dec.). ^1H NMR (400 MHz; $\text{CDCl}_3/\text{CS}_2$, 1:1; 25 °C): δ = 2.63 (q, $^3J_{\text{H-H}} = 7.6$ Hz, 2 H, Ru-CH₂CH₃), 2.40 (s, 15 H, C_{60}Me_5), 1.75 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 3 H, Ru-CH₂CH₃) ppm. ^{13}C NMR (100 MHz; $\text{CDCl}_3/\text{CS}_2$, 1:1; 25 °C): δ = −8.31 (1 C, Ru-CH₂CH₃), 23.19 (1 C, Ru-CH₂CH₃), 30.07 (5 C, C_{60}Me_5), 50.79 [5 C, $\text{C}_{60}(\text{sp}^3)$], 111.68 [5 C, $\text{C}_{60}(\text{Cp})$], 143.36 (10 C, C_{60}), 143.62 (10 C, C_{60}), 146.46 (5 C, C_{60}), 147.63 (10 C, C_{60}), 148.12 (5 C, C_{60}), 152.34 (10 C, C_{60}), 201.88 (2 C, CO) ppm. UV/Vis (toluene/2-propanol, 7:3): λ = 285, 355 (sh), 395 nm. IR (diamond probe): $\tilde{\nu}$ 2008 (s) (CO), 1950 (s). MS (APCI–): m/z = 981 [M^+]. HPLC (toluene/2-propanol, 7:3; flow rate: 1 mL min^{−1}): t_R = 7.67 min. $\text{C}_{69}\text{H}_{20}\text{O}_2\text{Ru}$ (981.99): calcd. C 84.40, H 2.05; found C 84.11, H 1.80.

NMR-Monitoring of Conversion from **2 to **3**:** Compound **2** was placed in an NMR tube connected to a vacuum system and C_6D_6 (0.6 mL) was transferred into it by trap-to-trap distillation. The NMR tube was sealed by flame and subjected to the reaction conditions: light irradiation with 60 W incandescent light or heating at 110 °C. Conversion of **3** into **2** was monitored by ^1H NMR spectroscopy.

Isomerization of 1-Decene: Compound **4** and 10000 equiv. of 1-decene were placed in a Schlenk tube and heated at 140 °C. After stirring at this temperature for 6 h, the solution was passed through a cotton plug and subjected to the ^1H NMR and GC measurements to estimate the product distributions. In the ^1H NMR spectrum, terminal and internal olefin protons were observed at δ = 4.9 ppm and δ = 5.4 ppm, respectively.

X-ray Crystallographic Analysis: Single crystals of **3** suitable for X-ray diffraction studies were grown and subjected to data collection. The data sets were collected with a MacScience DIP2030 Imaging Plate diffractometer by using Mo- K_α (graphite monochromated, λ = 0.71069 Å) radiation. The structure of **3** was solved by direct methods (SIR97).^[16] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-

matrix least-squares method by using SHELXL-97.^[17] Hydrogen atoms were placed at calculated positions and refined with riding mode on their corresponding carbon atoms. In the subsequent refinement, the function $\Sigma \omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \Sigma (|F_o| - |F_c|)/\Sigma |F_o|$ and $wR_2 = [\Sigma \omega(F_o^2 - F_c^2)^2/\Sigma (\omega F_o^4)]^{1/2}$. CCDC-632009 contains the supplementary crystallographic information for 3. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

- [1] a) A. H. H. Stephens, M. L. H. Green, *Adv. Inorg. Chem.* **1997**, *44*, 1–43; b) A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123–2165.
- [2] D. M. Guldi, N. Martin (Eds.), *Fullerenes: From Synthesis to Optoelectronic Properties*, Kluwer Academic Publishers, Dordrecht, **2002**.
- [3] a) M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 12850–12851; b) H. Iikura, S. Mori, M. Sawamura, E. Nakamura, *J. Org. Chem.* **1997**, *62*, 7912–7913; c) M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, E. Nakamura, *J. Organomet. Chem.* **2000**, *599*, 32–36; d) M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, E. Nakamura, *Chem. Lett.* **2000**, 270–271; e) E. Nakamura, H. Isobe, *Acc. Chem. Res.* **2003**, *36*, 807–815; f) R. Hamasaki, Y. Matsuo, E. Nakamura, *Chem. Lett.* **2004**, *33*, 328–329; g) Y.-W. Zhong, Y. Matsuo, E. Nakamura, *Org. Lett.* **2006**, *7*, 1463–1466; h) Y. Matsuo, A. Muramatsu, K. Tahara, M. Koide, E. Nakamura, *Org. Synth.* **2006**, *83*, 80–87.
- [4] M. Toganoh, Y. Matsuo, E. Nakamura, *Angew. Chem. Int. Ed.* **2003**, *42*, 3530–3532.
- [5] a) M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2002**, *124*, 9354–9355; b) E. Nakamura, *Pure Appl. Chem.* **2003**, *75*, 427–434; c) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 13974–13975; d) E. Nakamura, *J. Organomet. Chem.* **2004**, *689*, 4630–4635; e) R. H. Herber, I. Nowik, Y. Matsuo, M. Toganoh, Y. Kuninobu, E. Nakamura, *Inorg. Chem.* **2005**, *44*, 5629–5635; f) Y. Matsuo, H. Isobe, T. Tanaka, Y. Murata, M. Murata, K. Komatsu, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17148–17148; g) Y. Matsuo, K. Tahara, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 7154–7155; h) D. M. Guldi, G. M. A. Rahman, R. Marczak, Y. Matsuo, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 9420–9427; i) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 9586–9587.
- [6] a) Y. Matsuo, E. Nakamura, *Organometallics* **2003**, *22*, 2554–2563; b) Y. Matsuo, Y. Kuninobu, S. Ito, E. Nakamura, *Chem. Lett.* **2004**, *33*, 68–69; c) Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 8457–8466; d) Y. Matsuo, Y. Mitani, Y.-W. Zhong, E. Nakamura, *Organometallics* **2006**, *25*, 2826–2832.
- [7] a) M. Sawamura, Y. Kuninobu, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 12407–12408; b) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Organomet. Chem.* **2003**, *683*, 295–300; c) Y. Matsuo, E. Nakamura, *Inorg. Chim. Acta* **2006**, *359*, 1979–1982.
- [8] a) Y. Matsuo, A. Iwashita, E. Nakamura, *Organometallics* **2005**, *24*, 89–95; b) Y. Matsuo, A. Iwashita, E. Nakamura, *Chem. Lett.* **2006**, *35*, 858–859.
- [9] a) Y. Kuninobu, Y. Matsuo, M. Toganoh, M. Sawamura, E. Nakamura, *Organometallics* **2004**, *23*, 3259–3266; b) Y. Matsuo, K. Tahara, M. Sawamura, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 8725–8734.
- [10] a) H. Al-Matar, P. B. Hitchcock, A. G. Avent, R. Taylor, *Chem. Commun.* **2000**, 1071–1072; b) H. Al-Matar, A. K. Abdul-Sada, A. G. Avent, P. W. Fowler, P. B. Hitchcock, K. M. Rogers, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **2002**, 53–58; c) R. Taylor, *C. R. Chimie* **2006**, *9*, 982–1000.
- [11] a) J. W. Faller, *Adv. Organomet. Chem.* **1977**, *16*, 211–239; b) D. H. Gibson, W. L. Hsu, A. L. Steinmetz, *J. Organomet. Chem.* **1981**, *208*, 89–102.
- [12] a) J. W. Faller, B. V. Johnson, T. P. Dryja, *J. Organomet. Chem.* **1974**, *65*, 395–400; b) E. W. Abel, S. Moorhouse, *J. Chem. Soc., Dalton Trans.* **1973**, 1706–1711.
- [13] a) J.-L. Renaud, B. Demerseman, M. D. Mbaye, C. Bruneau, *Curr. Org. Chem.* **2006**, *10*, 115–133; b) T. Kondo, T. Mitsudo, *Curr. Org. Chem.* **2002**, *6*, 1163–1179; c) V. Cadierno, P. Crochet, S. E. Garcia-Garrido, J. Gimeno, *Curr. Org. Chem.* **2006**, *10*, 165–183.
- [14] a) Fe: P. W. Jolly, F. G. A. Stone, K. Mackenzie, *J. Chem. Soc.* **1965**, 6416–6420; b) Pd: P. Golbern, F. Scheinmann, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2870–2875; c) Rh: E. J. Corey, J. W. Suggs, *J. Org. Chem.* **1973**, *38*, 3224; d) Ni: C. F. Lochow, R. G. Miller, *J. Org. Chem.* **1976**, *41*, 3020–3022; e) Ir: D. Baudry, M. Ephritikhine, H. Felkin, *J. Chem. Soc., Chem. Commun.* **1978**, 694–695; f) Ru: H. Suzuki, Y. Koyama, Y. Moro-oka, T. Ikawa, *Tetrahedron Lett.* **1979**, 1415–1418; g) Cr: M. Sodeoka, H. Yamada, M. Shibasaki, *J. Am. Chem. Soc.* **1990**, *112*, 4906–4911; h) Pt: H. C. Clark, H. Kurosawa, *Inorg. Chem.* **1973**, *12*, 357–362; i) Ti, Zr: A. Ohff, V. V. Burlakov, U. Rosenthal, *J. Mol. Cat. A: Chem.* **1996**, *105*, 103–110.
- [15] a) W.-K. Wong, K. W. Chiu, J. A. Statler, G. Wilkinson, M. Motevalli, M. B. Hursthouse, *Polyhedron* **1984**, *3*, 1255–1265; b) K. P. Finch, J. R. Moss, M. L. Niven, *Inorg. Chim. Acta* **1989**, *166*, 181–188; c) S. I. Black, A. C. Skapski, G. B. Young, *J. Chem. Soc., Chem. Commun.* **1989**, 911–913; d) S. J. Archer, K. P. Finch, H. B. Friedrich, J. R. Moss, A. M. Crouch, *Inorg. Chim. Acta* **1991**, *182*, 145–152; e) F. R. Lemke, D. J. Szalda, R. M. Bullock, *J. Am. Chem. Soc.* **1991**, *113*, 8466–8477; f) J. L. Hubbard, A. Morneau, R. M. Burns, O. W. Nadeau, *J. Am. Chem. Soc.* **1991**, *113*, 9180–9184; g) A. Takahashi, Y. Mizobe, H. Matsuzaka, S. Dev, M. Hidai, *J. Organomet. Chem.* **1993**, *456*, 243–253; h) A. Takahashi, Y. Mizobe, T. Tanase, M. Hidai, *J. Organomet. Chem.* **1995**, *496*, 109–115; i) M. J. Burn, M. G. Fickers, F. J. Hollander, R. G. Bergman, *Organometallics* **1995**, *14*, 137–150; j) M. A. Gafoor, A. T. Hutton, J. R. Moss, *J. Organomet. Chem.* **1996**, *510*, 233–241; k) S. Fabre, P. Kalck, G. Lavigne, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1092–1095; l) T. Funaioli, C. Cavazza, F. Marchetti, G. Fachinetti, *Inorg. Chem.* **1999**, *38*, 3361–3368; m) H. B. Friedrich, R. A. Howie, M. O. Onari, *Acta Crystallogr., Sect. E* **2003**, *59*, m145–m147; n) M. Lail, C. M. Bell, D. Conner, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *Organometallics* **2004**, *23*, 5007–5020.
- [16] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
- [17] G. M. Sheldrick, *Programs for Crystal Structure Analysis (Release 97–2)*, Göttingen, Germany, **1998**.

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