A Specific Route to Enantiomerically Pure Asymmetric (η^6-Arene)(η^4-1,5-cyclooctadiene)Ru(0) Complexes☆

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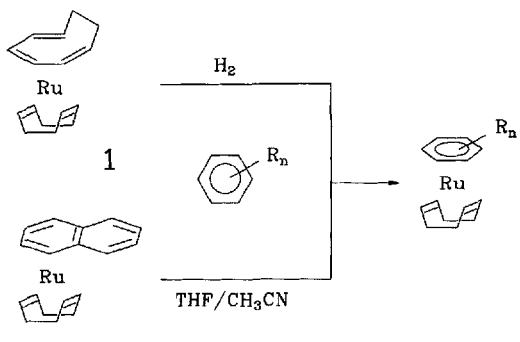
Chiral or achiral (arene)(COD)Ru complexes can be made by replacing the η^6-ligands of (η^4-1,5-COD)(η^6-1,3,5-cyclooctatriene)Ru (**1**) or (η^4-1,5-COD)(η^6-naphthalene)Ru (**2**) by a suitable arene. This well known reaction has been extended to mono- and dibromoarenes and we report a novel route to substituted (arene)(COD)Ru species, utilizing (bromoarene)-(COD)Ru as starting materials. These facilitate a rapid bromine-lithium exchange reaction with *n*BuLi at low temperatures and the lithiated species react readily with alkyl chloroformates as electrophiles. By using chiral electrophiles [alkyl = (−)-menthyl] enantiomerically pure or diastereomeric complexes containing CO_2R^* groups are formed, depending on the symmetry of the original complex. A diastereomeric 1:1 mixture was separated by recrystallization. All (arene)-(COD)Ru complexes tested so far are useful as catalysts for the hydrogenation of simple alkenes at room temperature.

Arene ruthenium(0) complexes are useful catalysts for hydrogenation[1,2], isomerization[3], and dimerization[4,5] reactions of alkenes, while arene ruthenium(II) complexes are excellent enantioselective hydrogen transfer catalysts for the hydrogenation of ketones[6,7] and imines[8] in the presence of enantiomerically pure chiral β-aminoalcohols[6] or 1,2-diamines[7,8] producing both high yields and high e.e.'s. Due to the particular stability of the arene−metal bond[9], arene ruthenium complexes may be converted in good yield from Ru^0 to Ru^{II} without loss of the arene ligand, simply by addition of hydrochloric acid[1]. Only the coligands which complete the coordination sphere are exchanged in parallel to the redox process.

Clearly, it would be very promising to carry out the catalytic reactions of arene ruthenium complexes in both redox states with enantimerically pure chiral species, whose chirality is due to the arene ligand. To the best of our knowledge reactions of this type have not been reported, despite the fact that some chiral arene ruthenium complexes are known[10,11]. Synthesis of such complexes requires the preparation of the desired chiral arene as a first step and then involves either a ligand exchange reaction of the precursor complex in the presence of hydrogen gas[10] or reduction of the arene to form the corresponding chiral cyclohexadiene derivative which is rearomatised upon complexation[11]. Both approaches have their limitations, as several functional groups are not stable towards hydrogen in the presence of the catalytically active ruthenium complexes (vide supra) and many potentially interesting chiral arene derivatives are not amenable to the cyclohexadiene route. We thus investigated a novel route to chiral arene ruthenium(0) complexes with 1,5-cyclooctadiene (COD) as coligand, which offers access to the corresponding arene ruthenium dichlorides, too, by reacting them with HCl as outlined above. Preparation of (arene)(COD)Ru complexes is well-known since the work of Bennett and Vitulli[2,10,12,13] who introduced (η^4-COD)(η^6-1,3,5-cyclooctatriene)Ru (**1**) and (η^4-COD)(η^6-naphthalene)Ru (**2**) as starting materials (Scheme 1).

Scheme 1



R = alkyl, alkenyl, aryl, OR, C(O)R, CN, Cl, $AsPh_2$, PPh_2

As bulky, polar, or highly substituted arenes are not very useful in these reactions, it would be profitable to introduce a substituent R into the complex with the help of substitution reactions at the periphery of arene ligands being already complexed to Ru^0. Reactions of this type have not yet been reported in the literature.

Here we present the first synthesis and lithiation of (bromoarene)(COD)Ru complexes. The lithiated species readily react with electrophiles, thereby forming novel substituted (arene)(COD)Ru complexes. By introducing chiral electrophiles, this leads directly to enantiomerically pure

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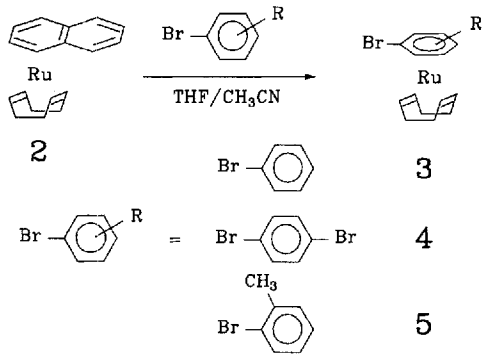
asymmetric complexes. For comparison, another example was also prepared by a ligand exchange reaction. Preliminary reactivity studies on some of the new (arene)(COD)Ru complexes reveal their potential as catalysts for hydrogenation reactions of alkenes.

Preparation of (Bromoarene)(COD)Ru Complexes

Bromoarenes (bromobenzene, 1,4-dibromobenzene, and 2-bromotoluene) replace the naphthalene ligand of (COD)(naphthalene)Ru (**2**) in the presence of acetonitrile in good yields (62 to 74%) at room temperature (Scheme 2). Analogous experiments, utilizing (COD)(1,3,5-cyclooctatriene)Ru (**1**) as the (COD)Ru-source were unsuccessful. (Bromobenzene)(COD)Ru (**3**) and (COD)(1,4-dibromobenzene)Ru (**4**) are achiral compounds, whereas (2-bromotoluene)(COD)Ru (**5**) forms a racemic mixture of planar chiral enantiomers as a consequence of the prochirality of the arene ligand. The bromoarene ruthenium complexes **3** to **5** are slightly air sensitive, although their purification and characterization was not particularly problematic and all spectroscopic properties were in accord with those of related π-arene complexes.

Scheme 2

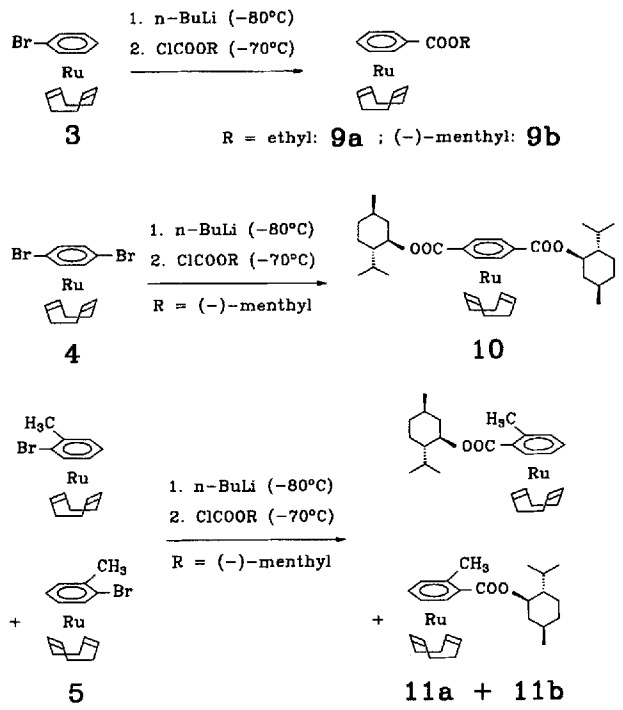


In addition, we synthesized (COD)(trimethylsilylbenzene)Ru (**6**), and (COD)(ethyl 3-phenylbutyrate)Ru (**7**) by the same method.

Lithiation and Electrophilic Substitution of (Bromoarene)(COD)Ru Complexes

Bromine-lithium exchange of the complexes **3** to **5** with *n*-butyllithium was accomplished at −80°C within few minutes. The electrophiles had to be added immediately after completion of the rapid lithiation reaction at −70°C. Substitution of the two bromine atoms of **4** could be carried out in a stepwise manner. Products of monosubstitution and the chemistry based on such compounds will be reported later. Here we want only to present the results of the 1,4-dilithiation of **4**. Alkyl chloroformates ClCOOR (**8**) have been identified as particularly suitable electrophiles to react with lithiated Ru complexes and they are commercially available in some variability, including enantiomerically pure chiral species. We started our investigations with ClCOOR, R = Et (**8a**) and R = (−)-menthyl (**8b**). Both selectively replace the lithium atoms of the metallated species by ester groups. In this way we obtained (alkyl benzoate)-(COD)Ru complexes (**9a**, **9b**) from **3** and **8**, terephthalic acid diester complex (**10**) from **4** and **8b**, and (−)-menthyl 2-methylbenzoate complexes (**11a**, **11b**) from racemic **5** and **8b**, respectively, in good yields throughout (Scheme 3).

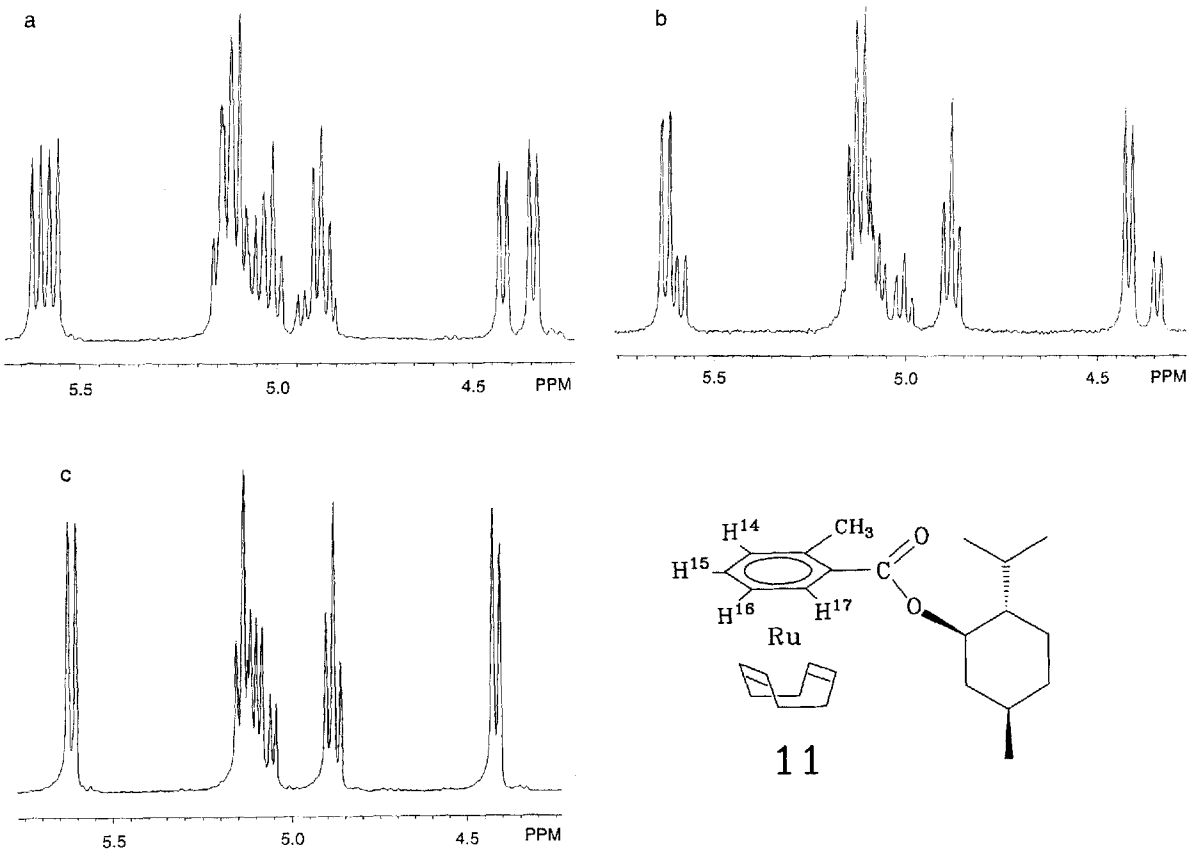
Scheme 3



9a is an achiral compound. **9b** and **10** are enantiomerically pure chiral complexes, exhibiting C_1 (**9b**) and C_2 (**10**) symmetry, respectively, as their asymmetric substructures remain unchanged throughout the reaction sequence. Combination of lithiated racemic **5** with chiral **8b** necessarily yields a 1:1 mixture of C_1-symmetric diastereomers **11a** and **11b**, by adding the planar chirality of an unsymmetrically substituted π-arene ligand to the asymmetry of the menthyl group. The mixture **11a/11b** has been prepared independently and by a different route by a member of the Bennett group[14]. All properties of the compounds **9a**, **9b**, **10**, **11a** and **11b** are in line with their proposed structure and symmetry. Handling of the novel bromoarene ruthenium complexes presented no special problems. All were found to be stable, especially so in the solid state, but slightly air sensitive in solution.

Isolation of one of the diastereomers **11a** and **11b** was accomplished by fractional crystallization from pentane. The progress of separation can be unambigously followed by NMR spectroscopy as illustrated in Figure 1. Starting with the 1:1 mixture (Figure 1a) we observe two pairs of doublets close to δ = 5.6 and 4.4, which are attributable to the π-arene protons H^{14} and H^{17} respectively, and their *o*-coupling to the adjacent protons H^{15} and H^{16}. The latter exhibit triplets around δ = 5. After the first crystallization a notable decrease in two of the doublets is observable (Figure 1b) and a second step (Figure 1c) effectively completes the process. The same principal observation can be made

Figure 1. Isolation of diastereomer **11a** under NMR control (^{1}H NMR of the π-arene proton part of the spectra, 269.6 MHz, C_6D_6, room temperature). a: 1:1 Mixture of **11a** + **11b**, as obtained from the reaction. b. Rediluted material after crystallization from pentane. c. Rediluted material after second crystallization from pentane, purity ca. 98%

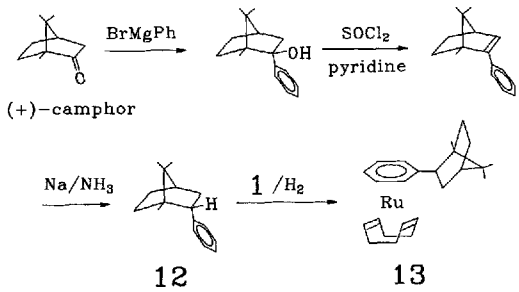


throughout all NMR spectra, as the remaining number of lines is always half of the starting value. To date, it has not been possible to prepare suitable single crystals of the isolated diastereomer for an X-ray structure determination, thus the absolute configuration of the complex has yet to be determined. Systematic NMR investigations on this matter are in progress.

Direct Synthesis of a Chiral (Arene)(COD)Ru Complex

As all reports on the catalytic properties of arene ruthenium(0) complexes utilize non-polar substituted arenes as ligands, synthesis of an enantiomerically pure chiral (arene)(COD)Ru complex without a functional group was attempted by a ligand exchange reaction as well. The desired chiral arene ligand (−)-*endo*-phenylbornane **12** was synthesized in three steps from (+)-camphor in 23% overall yield as described in the literature[15,16,17]. Reaction of **12** with **1** in the presence of hydrogen gas (compare Scheme 1) afforded the chiral complex (+)-(COD)(*endo*-phenylbornane)Ru **13** in 50% yield (Scheme 4).

Scheme 4



Structural Investigations

The molecular structures of complexes **10** and **13** give an insight into the influence of the chiral substituents on the complexes in the crystalline state. To the best of our knowledge, this is the first report on structural features of chiral (π-arene)Ru(0) complexes (Figure 2, 3; Table 1).

As there are no unusually short intermolecular distances in the crystals, packing effects of the neutral molecules should not contribute much to the details of the structures. Reasons for structural particularities are thus preferably interpreted in terms of intramolecular interactions. As expected, the stereochemistry of both chiral groups, bornyl and menthyl, of the arene ligand remain unchanged in the course of the complexation reaction. As in (benzene)-(COD)Ru[18], the carbon atoms of the arene rings of **10** and **13** are located close to, but not exactly on a plane. Consequently, the arene rings of the (arene)(COD)Ru complexes

Figure 2. Molecular structure of **10** in the solid state. Hydrogen atoms have been omitted for clarity

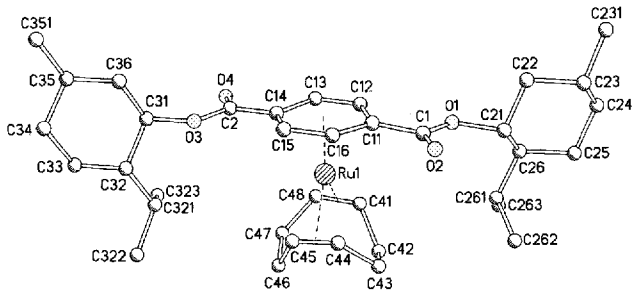


Figure 3. Molecular structure of one of the four independent molecules in the unit cell of **13**. The other three do not exhibit significant differences. Hydrogen atoms have been omitted for clarity

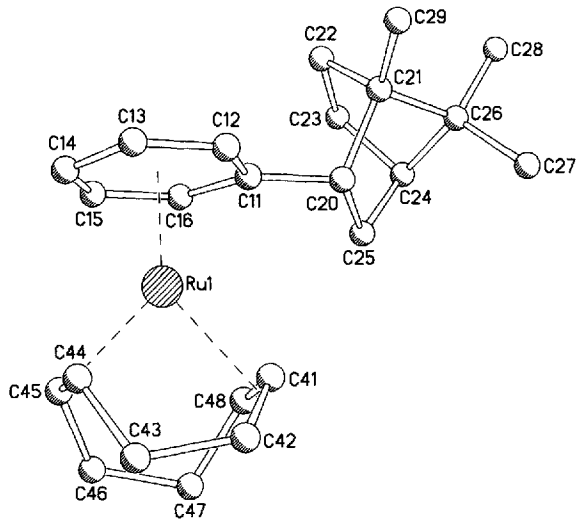


Table 1. Selected bond lengths of **10** and **13** in pm

	10	**13**		**10**	**13**
Ru-C11	224.2 (6)	225.3 (8)	Ru-C41	212.9 (6)	215.9 (7)
Ru-C12	223.5 (8)	224.6 (9)	Ru-C44	212.1 (7)	213.0 (10)
Ru-C13	224.7 (6)	225.0 (8)	Ru-C45	214.4 (7)	212.6 (9)
Ru-C14	222.1 (6)	220.4 (8)	Ru-C48	213.2 (6)	215.6 (8)
Ru-C15	227.4 (7)	224.8 (7)			
Ru-C16	225.5 (6)	226.5 (9)			

are distorted in a boat-like fashion. The angles between the best planes defined by the C_4-units C11,C12,C13,C14, and C14,C15,C16,C11, respectively, are 5.1° for **10**, 2.8° for **13**, and 5.2° for (benzene)(COD)Ru.

The molecules of **10** exhibit an approximate C_2 symmetry in the solid state, which is not caused by the symmetry of the space group of the crystal. The two ester groups for example are oriented in opposite directions, thus creating a C_2-symmetric electrical field in the vicinity of the metal atom. We believe the COD coligands of the complexes to be the best monitors for the symmetric features of the arene ruthenium fragments. The degree of deformation of the coordinated COD by the chiral arene for example, may be defined by the dihedral angle between the planes C41,C45,C48 and C41,C44,C45, respectively. This value is 9.6° for **10** and 7.3° for **13**. The higher value for **10** was hoped-for, as two chiral side chains contributing to the deformation of the COD from opposite sides should lead to a more pronounced effect, whereas the chiral part of **13** is located only at one side of the periphery of the molecule. The influence of the bulk of the substituent of **13** is the obvious reason for a non-parallel arrangement of the best plane through the arene ring carbon atoms on the one side and the best plane through the olefinic carbon atoms of the COD ligand on the other. These intersect at an angle of 3.4° for **13**, but are parallel for (benzene)(COD)Ru. We take this experimental proof of an induced asymmetry of coordinated COD ligands of ruthenium(0) as an indication of the potential usefulness of such chiral arene complexes in enantioselective catalytic reactions. The hydrogenation of alkenes, for example, is believed to take place in this particular part of the coordination sphere of the ruthenium atom, after substitution of the COD ligand (vide infra).

Preliminary Catalytic Investigations

The new (arene)(COD)Ru complexes **3**, **6**, **7**, **9a**, **9b**, **11**, and **13** have been tested as catalysts for the hydrogenation of alkenes. This type of catalytic reaction was reported by Vitulli et al. in 1984[1] for 1-pentene, 1-hexane, and 2-ethyl-1-hexene, utilizing (arene)(COD)Ru (arene = benzene, *p*-xylene, mesitylene) as catalysts. Such reactions were conducted at room temperature, with a hydrogen pressure of 20 bar. In this way, the alkenes were completely reduced, leading to the corresponding alkanes. On completion of such reactions, at least part of the catalyst could be recovered from the reaction mixture.

All the (arene)(COD)Ru complexes tested to date have shown similar catalytic activity. Under the conditions mentioned above, 1-hexene was reduced quantitatively in their presence (Scheme 5; Table 2) and the intact complexes were subsequently identified in the reaction mixtures.

Scheme 5

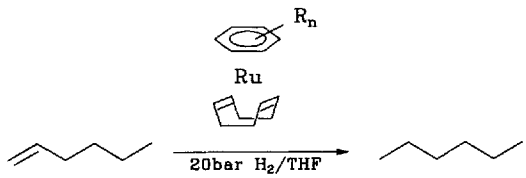


Table 2. Hydrogenation of 1-hexene in the presence of (arene)-(COD)Ru complexes[a]

Catalyst (mmol)	Reaction time (h) [b]
[($C_6H_5SiMe_3$)(COD)Ru] (0.11) **6**	15
[(phenylbornane)(COD)Ru] (0.16) **13**	88
[(C_6H_5COOEt)(COD)Ru] (0.14) **9a**	65
[(C_6H_5-$(CH_2)_3$-COOEt)(COD)Ru] (0.12) **7**	47
[(C_6H_5COOmenthyl)(COD)Ru] (0.14) **9b**	64
[(C_6H_4MeCOOmenthyl)(COD)Ru] (0.08) **11**	96
[(C_6H_5Br)(COD)Ru] (0.14) **3**	44

[a] 24 mmol 1-hexene, 5 ml THF, 20 bar H_2, room temperature. – [b] Maximum time required for quantitative hydrogenation of hexene.

In contrast to the findings of Vitulli, we observed a significant influence of the arene ligand on the turnover frequency of the reaction, which is represented by the time required for the quantitative hydrogenation of hexene. Bulky ligands required longer reaction times than smaller ones. Thus, with the exception of the $SiMe_3$-substituted complex **6**, our bulky substituted compounds were found to be slower catalysts. It required 10 h, for example, to produce a 99% yield of hexane by 0.20 mmol (benzene)(COD)Ru[1], but 88 h by 0.16 mmol phenylbornane complex **13** under comparable reaction conditions (Table 2). This may be taken as an indication of the significant role that the arene ruthenium fragment plays in the catalytic cycle, as proposed by Vitulli, however, although this has yet to be proven. Comparable experiments utilizing the new chiral arene ruthenium complexes in the redox states (0) and (II) with prochiral alkenes and ketones are in progress and we are engaged in extending the electrophilic substitution reaction of arene ruthenium complexes to other electrophiles. This is a principal route to arene ruthenium complexes bearing various functional groups at the periphery of the arene ligands. In particular, complexes with polar groups such as hydroxy or amino at some distance from the arene ring are very promising, in the light of the catalytic enantioselective transfer hydrogenation reactions of Noyori and coworkers (vide supra). Our aim is a better understanding of the catalytic reactions and, of course, the preparation of catalysts for practical use.

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Experimental Section

All reactions were carried out under a dry, oxygen-free, nitrogen atmosphere. Solvents were purified by conventional methods, distilled and stored under nitrogen. – NMR spectra were recorded close to room temp. on Jeol JNM-PMX 60, FT-JNM-EX 270, and FT-JNM-GX 270 spectrometers, using dimethylpolysiloxane and solvent signals as internal standards. – Mass spectra were recorded on a Varian MAT 212 spectrometer. – Microanalyses were performed at the analytical department of the institute, using Carlo Erba Elemental Analysers Mod. 1106 and Mod. 1108. – Capillary gas chromatograms were recorded on a Philips PYE UNICAM PU 4500 equipped with a 60 m Superkowa column. – Optical rotation angles were determined on a Schmidt und Haensch Digitalpolarimeter Polartronic E. – Column chromatography (15 × 1 cm) was accomplished with neutral degassed alumina (Merck), deactivated with 5% degassed water, or degassed silica (Merck).

The original complexes (COD)(1,3,5-cyclooctatriene)Ru (**1**) and (COD)(naphthalene)Ru (**2**) were prepared as reported in the literature[10,11,19].

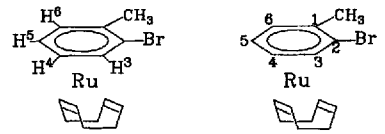
The ligand (–)-*endo*-phenylbornane **12** was synthesized according to the literature in three steps from (+)-camphor[15,16,17].

Synthesis of (Arene)(COD)Ru Complexes by Ligand Exchange Reaction of **2**. – *General Procedure:* Starting complex **2**, the desired arene ligand, and acetonitrile were dissolved in THF and the mixture was stirred at room temp. for 2 days. Solvent, excess arene and naphthalene were removed in vacuo, again at room temp. The resulting dark solid was dissolved in light petroleum ether and chromatographed on Al_2O_3/5% H_2O. Removal of the solvent under reduced pressure yielded the pure yellow complexes, which were recrystallized from light petroleum ether or pentane.

(Bromobenzene)(COD)Ru (**3**): Reaction mixture: **2** (1.29 g, 3.8 mmol), bromobenzene (20 ml), 40 ml of THF, and 1 ml of acetonitrile. Yield 0.97 g (2.6 mmol, 69%) of **3**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.85 (d, $^3J(H^oH^m)$ = 6 Hz, 2H; H^o), 4.78 (t, $^3J(H^mH^p) = {}^3J(H^mH^o)$ = 6 Hz, 2H; H^m), 4.18 (t, 1H; H^p), 3.55 (m, 4H; H-olef. COD), 2.35 (m, 8H; H-aliph COD). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 90.2 (C-*o*), 89.8 (C-*i*), 86.7 (C-*m*), 83.0 (C-*p*), 65.1 (C-olef. COD), 34.1 (C-aliph. COD). – MS (70 eV, EI): *m/z* (%): 368 (56) [M^+], 285 (60) [$M^+ - H_2Br$], 206 (100) [$C_8H_8Ru]^+$, 180 (82) [$C_6H_6Ru]^+$, 166 (36) [$C_5H_5Ru]^+$, 153 (33) [$C_4H_4Ru]^+$, 128 (22), 102 (30) [$Ru]^+$, 77 (72) [$C_6H_5]^+$. – $C_{14}H_{17}BrRu$ (366.3): calcd. C 45.91, H 4.68; found C 46.58, H 5.10.

(COD)(1,4-Dibromobenzene)Ru (**4**): Reaction mixture: **2** (0.50 g, 1.5 mmol), 1,4-dibromobenzene (3.6 g, 15.3 mmol), 50 ml of THF, and 1 ml of acetonitrile. Yield 0.41 g (0.9 mmol, 62%) of **4**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.15 (s, 4H; H-ar.), 3.45 (s, 4H; H-olef. COD), 2.30 (m, 8H, H-aliph. COD). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 90.3 (C-ar.), 86.5 (C-ar.), 69.1 (C-olef. COD), 33.9 (C-aliph. COD). – MS (70 eV, EI): *m/z* (%): 445 (85) [M^+], 364 (70) [M^+ – Br], 282 (40) [M^+ – 2 Br], 235 (100) [$C_6H_4Br_2]^+$, 206 (100) [$C_8H_8Ru]^+$. – $C_{14}H_{16}Br_2Ru$ (445.1): calcd. C 37.77, H 3.62; found C 37.86, H 3.44.

(2-Bromotoluene)(COD)Ru (**5**): Reaction mixture: **2** (2.5 g, 7.4 mmol), 2-bromotoluene (15 ml), 100 ml of THF, and 2 ml of acetonitrile. Yield 2.9 g (5.5 mmol, 74%) of **5**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.35 (d, ^3J = 5 Hz, 1H; H-ar.), 4.85 (t, ^3J = 5 Hz, 1H; H-ar.), 4.80 (d, ^3J = 5 Hz, 1H; H-ar.), 4.23 (t, ^3J = 5 Hz, 1H; H-ar.), 3.49 (m, 2H; H-olef. COD), 3.32 (m, 2H; H-olef. COD), 2.35 (m, 8H; H-aliph. COD), 1.99 (s, 3H; CH_3). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 102.4 (C-ar.), 93.2 (C-ar.), 89.0 (C-ar.), 88.9 (C-ar.), 86.6 (C-ar.), 82.9 (C-ar.), 66.4 (C-olef. COD), 65.5 (C-olef. COD), 34.5 (C-aliph. COD), 33.6 (C-aliph. COD), 19.5 (CH_3), 19.5 (CH_3). – MS (70 eV, EI): *m/z* (%): 381 (83) [M^+], 351 (30) [$M^+ - C_2H_6$], 289 (58) [$M^+ - H_2Br$], 206 (100) [$C_8H_8Ru]^+$, 167 (28) [$C_6H_6Ru]^+$, 91 (40) [$C_7H_7]^+$. – $C_{15}H_{19}BrRu$ (380.3): calcd. C 47.38, H 5.04; found C 47.32, H 5.11.



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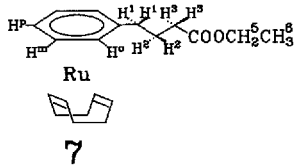
(COD)(Trimethylsilylbenzene)Ru (**6**): Reaction mixture: **2** (189 mg, 0.5 mmol), trimethylsilylbenzene (2 ml, 11.6 mmol), 20 ml of THF, and 1 ml of acetonitrile. Yield 163 mg (0.45 mmol, 90%) of **6**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.70 (m, 1H; H^p), 4.52 (m, 4H; $H^{m,o}$), 3.53 (m, 4H; H-olef. COD), 2.32 (m, 8H; H-aliph. COD), 0.3 (s, 9H; $SiMe_3$). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 92.9 (C-*i*), 90.6 (C-*m,o*), 88.1 (C-*m,o*), 85.6 (C-*p*), 61.0 (C-olef. COD), 34.7 (C-aliph. COD), 0.0 ($SiMe_3$). – MS (70 eV, EI): *m/z* (%): 360 (70) [M^+], 345 (9) [$M^+ - CH_3$], 330 (24) [$M^+ - 2\ CH_3$], 317 (12) [$M^+ - C_3H_7$], 287 (50) [$M^+ - C_3H_9Si$], 206 (21) [$C_8H_8Ru]^+$, 180 (13) [$C_6H_6Ru]^+$, 135 (27) [$C_6H_5SiC_3H_9$-$CH_3]^+$, 73 (33) [$C_3H_9Si]^+$. – $C_{17}H_{26}RuSi$ (359.6): calcd. C 56.79, H 7.29; found C 55.65, H 7.97.

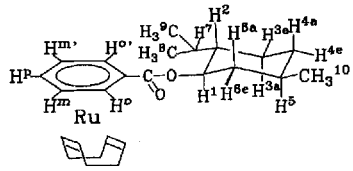
(COD)(Ethyl 3-Phenylbutyrate)Ru (**7**): Reaction mixture: **2** (270 mg, 0.8 mmol), ethyl 3-phenylbutyrate (2 g, 10 mmol), 50 ml of THF, and 1 ml of acetonitrile. Yield 217 mg (0.54 mmol, 68%) of **7**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.00 [t, $^3J(H^pH^m)$ = 4.9 Hz, 1H; H^p], 4.70 (m, 4H; H^o, H^m), 4.00 [q, $^3J(H^5H^6)$ = 7 Hz, 2H; H^5], 3.45 [s(br), 4H; H-olef. COD], 2.35 (m, 8H; H-aliph. COD), 2.15 [t, $^3J(H^1H^2)$ = 7.6 Hz, 2H; H^1], 2.05 [t, $^3J(H^3H^2)$ = 7.6 Hz, 2H; H^3], 1.70 (qn, 2H; H^2), 1.05 (t, 3H; H^6). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 173.0 (C-4), 105.4 (C-*i*), 88.1 (C-*p*), 86.2 (C-ar.), 84.9 (C-ar.), 61.5 (C-olef. COD), 60.1 (C-5), 34.3 (C-aliph. COD), 33.6 (C-1), 32.9 (C-3), 26.7 (C-2), 14.3 (C-6). – MS (70 eV, EI): *m/z* (%): 402 (100) [M^+], 371 (11) [M^+ – OMe], 357 (12) [M^+ – OEt], 325 (11) [M^+ – C_6H_5], 294 (9) [M^+ – COD], 250 (78) [(M^+ – COD) – CO_2], 220 (90) [(M^+ – COD) – CO_2 – C_2H_6], 206 (32) $[C_8H_8Ru]^+$, 180 (20) $[C_6H_6Ru]^+$, 147 (26) [L^+ – OEt], 119 (81) $[C_8H_7O]^+$, 91 (80) $[C_7H_8]^+$. – $C_{20}H_{28}O_2Ru$ (401.5): calcd. C 59.83, H 7.03; found C 60.31, H 7.68.



Bromine-Lithium Exchange and Electrophilic Substitution Reactions of (Bromoarene)(COD)Ru Complexes. – General Procedure: The original complexes were dissolved in THF, cooled to −80°C, and a solution of *n*-butyllithium in hexane was added via a syringe. The reaction mixture was stirred for 10 min and the requisite alkyl chloroformate was added at −70°C. The temperature was then increased to room temperature over a period of 2 h and the solvents were removed in vacuo. The resulting dark residue was extracted with light petroleum ether and toluene and the combined extracts were filtered over Al_2O_3/5% H_2O, yielding a yellow solution. Additional removal of the solvent in vacuo and redilution of the resulting yellow oil in petroleum ether allowed purification by column chromatography on Al_2O_3/5% H_2O. By-products were eluted first, with light petroleum ether, as a pale yellow solution. (Alkylbenzoate)(COD)Ru complexes were eluted next, with toluene/light petroleum ether (1:1), as a darker yellow solution. Evaporation of the solvent and recrystallization from pentane afforded the pure complexes.

(COD)(Ethyl Benzoate)Ru (**9a**): Reaction mixture: (bromobenzene)(COD)Ru **3** (150 mg, 0.4 mmol), 20 ml of THF, 2.5 M *n*-butyllithium in hexane (0.24 ml, 0.6 mmol), and ethyl chloroformate (**8a**) (0.06 ml, 0.6 mmol). Yield: 104 mg (0.29 mmol, 72%) of **9a**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 6.08 [d, $^3J(H^oH^m)$ = 5 Hz, 2H; H^o], 4.97 [t, $^3J(H^mH^o)$ = $^3J(H^mH^p)$ = 5 Hz, 2H; H^m], 4.58 (t, 1H; H^p), 4.10 [q, $^3J(H^{CH2}H^{CH3})$ = 7 Hz, 2H; CH_2-ethyl], 3.60 (m, 4H; H-olef. COD), 2.30 (m, 8H; H-aliph. COD), 1.05 (t, 3H; CH_3-ethyl). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 167.4 (C-carbonyl), 89.2 (C-ar.), 88.8 (C-ar.), 81.5 (C-ar.), 63.8 (C-olef. COD), 60.7 (CH_2-ethyl), 34.0 (C-aliph. COD), 14.4 (CH_3-ethyl). – MS (70 eV, EI): *m/z* (%): 360 (100) [M^+], 330 (60) [M^+ – C_2H_6], 285 (37), 258 (40), 206 (76) $[C_8H_8Ru]^+$, 180 (56) $[C_6H_6Ru]^+$, 105 (70) $[C_6H_5COOEt\text{-}C_2H_5O]^+$. – $C_{17}H_{22}O_2Ru$ (359.4): calcd. C 56.81, H 6.17; found C 57.22, H 6.53.

(–)-(COD)(Menthyl Benzoate)Ru (**9b**): Reaction mixture: **3** (200 mg, 0.54 mmol), 20 ml of THF, 2.5 M *n*-butyllithium in hexane (0.36 ml, 0.9 mmol), and (−)-menthyl chloroformate (**8b**) (0.19 ml, 0.9 mmol). Yield: 210 mg (0.45 mmol, 83%) of **9b**. – $[\alpha]_D^{25}$ = −37.7 (*c* = 0.96 in THF). – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 6.10 [d, $^3J(H^{o'}H^{m'})$ = 6 Hz, 1H, $H^{o'}$], 5.95 [d, $^3J(H^oH^m)$ = 6 Hz, 1H; H^o], 5.13 [dt, $^3J(H^1H^2)$ = $^3J(H^1H^{6a})$ = 11.6 Hz, $^3J(H^1H^{6e})$ = 4.5 Hz, 1H; H^1], 4.94 [t, $^3J(H^mH^o)$ = $^3J(H^mH^p)$ = 6 Hz, 1H; H^m], 4.85 [t, $^3J(H^pH^m)$ = $^3J(H^pH^{m'})$ = 6 Hz, 1H; H^p], 4.79 (t, 1H; $H^{m'}$), 3.65 (m, 4H; H-olef. COD), 2.35 (m, 8H; H-aliph. COD), 2.21 (m, 2H; H^7H^{6e}), 1.51 (m, 3H; H^2 $H^{3e}H^{4e}$), 1.25 (m, 1H; H^5), 1.09 [pq, $^3J(H^{6a}H^1)$ = $^3J(H^{6a}H^{6e})$ = $^3J(H^{6a}H^5)$ = 12 Hz, 1H; H^{6a}], 0.97 [d, $^3J(H^{8\text{ or }9}H^7)$ = 6 Hz, 3H; $H^{8\text{ or }9}$], 0.94 [d, $^3J(H^{8\text{ or }9}H^7)$ = 6 Hz, 3H; $H^{8,9}$], 0.9–0.6 (m, 2H; $H^{3a}H^{4a}$), 0.81 [d, $^3J(H^{10}H^5)$ = 6.3 Hz, 3H; H^{10}]. – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 167.2 (C-11), 89.1 (C-*m*), 88.8 (C-*o*), 88.4 (C-*m'*), 88.1 (C-*o'*), 83.9 (C-*i*), 82.5 (C-*p*), 74.7 (C-1), 64.0 (COD-olef.), 63.6 (COD-olef.), 47.6 (C-2), 41.5 (C-6), 34.5 (C-4), 34.3 (COD-aliph.), 33.8 (COD-aliph.), 31.5 (C-5), 26.7 (C-7), 23.3 (C-3), 22.1 (C-8 or C-9), 21.0 (C-8 or C-9), 16.6 (C-10). – MS (70 eV, EI): *m/z* (%): 470 (27) [M^+], 331 (31) [M^+ – $C_{10}H_{19}$], 302 (42) [M^+ – $C_{11}H_{20}O$], 206 (50) $[C_8H_8Ru]^+$, 180 (32) $[C_6H_6Ru]^+$, 105 (56) $[C_6H_5CO]^+$, 77 (66) $[C_6H_5]^+$. – $C_{25}H_{36}O_2Ru$ (469.6): calcd. C 63.94, H 7.73; found C 63.57, H 8.78.

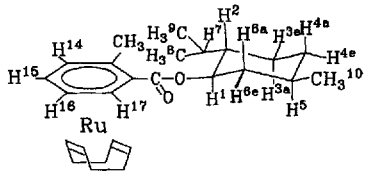


(–)-(COD)(1,4-Bismenthyl Terephthalate)Ru (**10**): Reaction mixture: (COD)(1,4-dibromobenzene)Ru **4** (110 mg, 0.25 mmol), 10 ml of THF, 1.6 M *n*-butyllithium in hexane (0.6 ml, 1 mmol), and (−)-menthyl chloroformate (**8b**) (0.3 ml, 1.3 mmol). Yield: 112 mg (0.17 mmol, 68%) of **10**.

Designation of nuclei analogous to **9b**. – $[\alpha]_D^{25}$ = −81.2 (*c* = 0.61 in THF). – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 6.1 (d, 2H; H-ar., ^3J = 6 Hz), 5.95 (d, 2H; H-ar., ^3J = 6 Hz), 5.15 [dt, $^3J(H^1H^2)$ = $^3J(H^1H^{6a})$ = 10.8 Hz, $^3J(H^1H^{6e})$ = 4.3 Hz, 1H, H^1], 3.78 (m, 4H; H-olef. COD), 2.35 (m, 4H; H^7H^{6e}), 2.2 (m, 8H; H-aliph. COD), 1.5 (m, 6H; $H^2H^{3e}H^{4e}$), 1.25 (m, 2H; H^5), 1.1 (m, 2H, H^{6a}), 0.98 (d, 6H, $H^{8\text{ or }9}$), 0.93 (d, 6H; $H^{8,9}$), 0.9–0.6 (m, 4H; $H^{3a}H^{4a}$), 0.82 (d, 6H; H^{10}). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 167.2 (C-11), 90.5 (C-ar.), 89.3 (C-ar.), 82.4 (C-*i*), 74.9 (C-1), 67.2 (C-olef.), 66.1 (C-olef.), 47.5 (C-2), 41.4 (C-6), 34.7 (C-aliph.), 34.4 (C-aliph.), 32.8 (C-4), 31.4 (C-5), 26.7 (C-7), 23.6 (C-3), 22.1 (C-8 of C-9), 20.9 (C-8 or C-9), 16.6 (C-10). – MS (70 eV, EI): *m/z* (%): 651 (85) [M^+], 512 (35) [M^+ – $C_{10}H_{19}$], 373 (60) [M^+ – $C_{20}H_{38}$], 206 (50) $[C_8H_8Ru]^+$. – $C_{36}H_{54}O_4Ru$ (651.8): calcd. C 66.33, H 8.35; found C 66.65, H 8.79.

(+)-(COD)(Menthyl 2-Methylbenzoate)Ru (**11a**): Reaction mixture: (2-bromotoluene)(COD)Ru (**5**) (250 mg, 0.66 mmol), 50 ml of THF, 2.5 M *n*-butyllithium in hexane (0.6 ml, 1.5 mmol), and (−)-menthyl chloroformate (**8b**) (0.32 ml, 1.5 mmol). Yield: 188 mg (0.39 mmol, 59%) of **11** as a diastereomeric oil. Isolation of diastereomer **11a** by fractional crystallization from pentane, yielding 50 mg of **11a**. – $[\alpha]_D^{25}$ = 560 (*c* = 0.09 in THF). – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.67 [d, $^3J(H^{17}H^{16'})$ = 5 Hz, 1H; H^{17}], 5.18 [t, $^3J(H^{15}H^{14})$ = $^3J(H^{15}H^{16})$ = 5 Hz, 1H; $H^{15'}$], 5.14 [dt, $^3J(H^1H^2)$ = $J(H^1H^{6a})$ = 11 Hz, $^3J(H^1H^{6e})$ = 4 Hz, 1H; H^1], 4.93 [t, $^3J(H^{16}H^{17})$ = $^3J(H^{16}H^{15})$ = 5 Hz, 1H; H^{16}], 4.47 (d, 1H; H^{14}), 3.61 (m, 2H; H-olef. COD), 3.46 (m, 2H; olef. COD), 2.40 (s, 3H; H^{18}), 2.37 (m, 8H; H-aliph. COD), 2.30 (m, 1H; H^7), 2.17 (m, 1H; H^{6e}),

1.50 (m, 3H; $H^2H^{3e}H^{4e}$), 1.25 (m, 1H; H^5), 1.05 [pq, $^3J(H^{6a}H^1)=^3J(H^{6a}H^{6e})=^3J(H^{6a}H^1)=12$ Hz, 1H; H^{6a}], 0.99 [d, $^3J(H^{8,9}H^7)=6$ Hz, 6H; H^8H^9], 0.82 [d, $^3J(H^{10}H^5)=6$ Hz, 3H, H^{10}], 0.95–0.65 (m, 2H; $H^{3a}H^{4a}$). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 167.9 (C-11), 105.5 (C-ar.), 90.6 (C-ar.), 89.4 (C-ar.), 86.2 (C-ar.), 85.4 (C-ar.), 82.8 (C-ar.), 74.30 (C-1), 65.7 (COD-olef.), 64.3 (COD-olef.), 47.7 (C-2), 41.4 (C-6), 34.5 (C-4), 34.3 (COD-aliph.), 33.9 (COD-aliph.), 31.5 (C-5), 26.4 (C-7), 23.2 (C-3), 22.2 (C-18), 21.2 (C-8 or C-9), 19.9 (C-8 or C-9), 16.3 (C-10). – MS (70 eV, EI): *m/z* (%): 484 (79) [M^+], 345 (94) [$M^+ - C_{10}H_{19}$], 316 (49) [$M^+ - C_{11}H_{20}O$], 301 (27) [$M^+ - C_{11}H_{21}O$], 272 (20), 206 (49) [$C_8H_8Ru]^+$, 180 (28) [$C_6H_6Ru]^+$, 138 (100) [$C_{10}H_{18}]^+$. – $C_{26}H_{38}O_2Ru$ (483.7): calcd. C 64.57, H 7.92; found C 64.00, H 8.51.

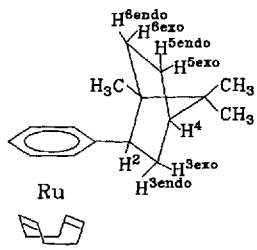


11

(+)-(COD)(endo-Phenylbornane)Ru (**13**): (–)-*endo*-Phenylbornane (**12**) (1.09 g, 5.1 mmol) was added to a solution of (1,5-COD)(1,3,5-cyclooctatriene)Ru (**1**) (1.14 g, 3.6 mmol) in 20 ml of light petroleum ether and stirred at room temp. for 20 h under a hydrogen atmosphere (1 bar). After removal of most of the solvent in vacuo, the concentrated solution was chromatographed on Al_2O_3/5% H_2O. Light petroleum ether allowed elution of a yellow solution. Solvent, excess free ligand **12** and other by-products were removed in vacuo at ambient to elevated temperatures (max. 80°C). The residue was dissolved with a small amount of light petroleum ether and chromatographed again on Al_2O_3/5% H_2O using light petroleum ether as eluent. On removal of the solvent, 770 mg (1.8 mmol, 50%) pure, yellow **13** was obtained, which could be recrystallized from light petroleum ether. – $[\alpha]_D^{25}=24.9$ ($c=2.13$ in THF). – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.41 (d, $^3J=6$ Hz, 1H; H-ar.), 5.22 (m, 2H; H-ar.), 4.25 (m, 1H; H-ar.), 4.16 (m, 1H; H-ar.), 3.61 (m, 2H; H-olef. COD), 3.45 (m, 2H; H-olef. COD), 2.52 [ddd, $^3J(H^2H^{3exo})=13$ Hz, $^3J(H^2H^{3endo})=5.4$ Hz, $^3J(H^2H^4)=3$ Hz, 1H; H^2], 2.40 (m, 8H; H-aliph. COD), 2.16 [tt, $^2J(H^{3exo}H^{3endo})=^3J(H^{3exo}H^2)=13$ Hz, $^3J(H^{3exo}H^4)=^4J(H^{3exo}H^{5exo})=4$ Hz, 1H; H^{3exo}], 1.80–1.50 (m, 3H; H^{5exo},H^{6exo},H^4), 1.44 (dd, 1H; H^{3endo}), 1.25–1.07 (m, 2H; H^{5endo},H^{6endo}), 0.90 (s, 3H; CH_3), 0.86 (s, 3H; CH_3), 0.68 (s, 3H; CH_3). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 107.2 (C-*i*), 89.2 (C-ar.), 87.7 (C-ar.), 87.2 (C-ar.), 85.3 (C-ar.), 81.3 (C-ar.), 61.7 (C-olef. COD), 60.5 (C-olef. COD), 50.2 (C-1 or C-7), 49.8 (C-1 or C-7), 49.3 (C-2), 45.5 (C-4), 34.4 (C-aliph. COD), 34.4 (C-aliph. COD), 34.0 (C-3), 29.1 (C-5 or C-6), 28.3 (C-5 or C-6), 20.1 (CH_3), 18.7 (CH_3), 14.5 (CH_3). – MS (70 eV, EI): *m/z* (%): 424 (100) [M^+], 409 (12) [$M^+ - CH_3$], 394 (18) [$M^+ - 2\ CH_3$], 379 (13) [$M^+ - 3\ CH_3$], 325 (13), 310 (20), 299 (24), 284 (20), 206 (23) [$C_8H_8Ru]^+$, 180 (15) [$C_6H_6Ru]^+$. – $C_{24}H_{34}Ru$ (423.6): calcd. C 68.05, H 8.09; found C 67.71, H 8.37.

Catalytic Hydrogenation Reactions: The hydrogenation experiments were performed in a stainless-steel autoclave (150 ml) at room temp. A glass vial, containing the (arene)(COD)Ru catalyst, solvent and substrate were introduced into the autoclave, which was subsequently charged with hydrogen (20 bar). The reaction mixture was stirred throughout the course of the experiment.

Hydrogenation of 1-Hexene: Reaction mixtures contained 0.1 to 0.2 mmol (arene)(COD)Ru, 5 ml of THF, and 3 ml of 1-hexene (24 mmol). Work-up procedure: After discharging the autoclave, the volatile compounds of the yellow but muddy reaction mixture were removed at room temp. under reduced pressure, collected in a trap at –196°C, and analysed by GLC. The solid residue was dissolved in C_6D_6 and filtered over Al_2O_3/5% H_2O directly into an NMR tube. All used (arene)(COD)Ru complexes could be identified by their NMR spectra this way. For further details see Table 2.



13

Table 3. Crystallographic details of **10** and **13**

	10	**13**
Empirical formula	$C_{36}H_{54}Ru$	$C_{24}H_{34}Ru$
Colour, form	orange plates	light-yellow prisms
Size (mm)	0.4 x 0.3 x 0.2	0.6 x 0.4 x 0.4
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
Unit cell dimensions (pm)	a = 1048.0 (2)	a = 1173.8 (4)
	b = 1618.9 (3)	b = 1390.0 (6)
	c = 1994.1 (4)	c = 1413.0 (5)
	α = 90°	α = 118.74 (4)°
	β = 90°	β = 90.03 (3)°
	γ = 90°	γ = 102.41 (3)°
Volume (10^6 pm^3)	3383.2 (12)	1959.6 (16)
Z	4	4
Molecular mass	651.86	423.6
Density (calcd.)	1.280 g/cm^3	1.436 g/cm^3
Absorption coefficient	0.499 mm^{-1}	0.804 mm^{-1}
Reflections measured	10385	10477
Independent reflections	6530	10383
Goodness-of-fit at F^2	0.554	1.144
R_1	0.038	0.041
wR_2	0.058	0.128
$F(000)$	1384	888

Crystal Structure Determinations: Suitable crystals of **10** and **13** were taken directly out of the mother liquor. Data were collected on a Siemens P4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. The crystal structures were solved by direct methods (SHELXS-86) and refined by SHELXL-93. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were taken from a Fourier difference calculation for **10**. In the case of **13**, hydrogen atoms are geometrically positioned. There are four independent molecules in the unit cell of **13**, all with the same absolute configuration. The absolute structures were determined; Flack-x-parameter is –0.08(4) for **10** and 0.02(4) for **13**. Other experimental details are given in Table 3. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405631 for **10** and CSD-405632 for **13**, the names of the authors, and the journal citation.

* Dedicated to Professor *Rolf Gleiter* on the occassion of his 60th birthday.
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