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Chiral arene ruthenium complexes Part 3.☆ [Ruthenium(η^6-arene)(η^4-1,5-cyclooctadiene)] complexes with N or O donor functions in the arene side chain

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Abstract

Arene ruthenium(0) complexes with carbonyl side chain functionalities like [Ru(η^6-C_6H_5COR)(η^4-COD)] or [Ru(η^6-*o*-$C_6H_4\{R^1\}COR$)(η^4-COD)] (COD = 1,5-cyclooctadiene; R = H, CH_3; R^1 = H, CH_3, OCH_3) are easily accessible by replacing the naphthalene ligand of [Ru(η^6-naphthalene)(η^4-COD)] (**1**) through an arene exchange reaction. These carbonyl species are susceptible to standard organic reactions of the carbonyl function, thus allowing the introduction of dangling side chains bearing highly polar functions like hydroxyl or amino groups. Aldol reaction of [Ru(*o*-$C_6H_4\{CH_3\}COCH_3$)(COD)] (**3**) with (−)-menthylchloroformate in the presence of LDA (LDA = lithium diisopropylamide) leads to a diastereomeric mixture of [Ru(menthyl-{3-oxo-3-η^6-*o*-tolyl}propionate)(COD)] (**10**). However, treatment of **3** with LDA and *o*-tolylaldehyde or benzaldehyde affords the unexpected products [Ru(1-η^6-*o*-tolyl-3-*o*-tolylpropan-1-one)(COD)] (**11**) and [Ru(1-η^6-*o*-tolyl-1-phenylpropan-1-one)(COD)] (**12**). A diastereoselective addition (88% de) of deprotonated menthylacetate to [Ru(*o*-tolylaldehyde)(COD)] (**4**) results in the formation of [Ru(menthyl 3-η^6-*o*-tolyl-3-hydroxypropionate)(COD)] (**13**). Racemic planar-chiral aldehyde complexes **2** and **4** react with amines giving the imination products in good yield. In case of reaction between **2** and (*R*)-*N*-amino-2-(methoxymethyl)-pyrrolidine (RAMP), diastereomeric [Ru(*N*-[[η^6-(2-methylphenyl]methylene]-(*R*)-2-(methoxymethyl)-1-pyrrolidinamine)(COD)] (**17**) is formed. The diastereomers (*R*,*R*)-**17** and (*S*,*R*)-**17** have been separated by fractional crystallisation. Asymmetric arene ruthenium complexes with a defined planar-chiral configuration are thus accessible. Reduction of [Ru(3-η^6-phenyl-(*R*)-methylbutyrate)(COD)] (**7**) with $LiAlH_4$ yields the chiral γ-alcohol [Ru(3-η^6-phenyl-(*R*)-1-butanol)(COD)] (**18**). A Wittig olefination converts the aldehyde complex **4** into a mixture of *E*- and *Z*-isomeric [Ru(1-η^6-*o*-tolyl-2-phenylethylene)(COD)] **21a** and **21b**, which were separated again by fractional crystallisation.

Keywords: Aldol reaction; Arene complexes; Chirality; Lithiation; Ruthenium; Wittig olefination

1. Introduction

Chiral Ru(η^6-arene) complexes are accessible by different routes. This includes the redox states 0 [2] and +2 [3–5] of the metal. An effective application of Ru^{II}(arene) complexes with chiral co-ligands has been found recently. They are excellent enantioselective hydrogen-transfer catalysts for organic carbonyl and imin groups, which are transferred into chiral alcohols or amines [6]. Enantiomerically pure 1,2-diamines or β-amino-alcohols are the co-ligands of choice.

To the best of our knowledge, activity and selectivity of the arene ruthenium catalysts are mainly studied as a function of the co-ligands, rather than the Ru(η^6-arene) fragment itself. This led us to the approach to study new synthetic strategies for the preparation of complexes in which the chirality depends on the arene ligand. We are mainly interested in three aspects: introduction of a functionalised arene ligand; further modifications of the side chain to introduce N or O donor groups and chiral information; and finally the isolation of optically pure complexes.

☆ Part 2: see Ref. [1].

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An easy access to $Ru^0(\eta^6$-arene) compounds is the naphthalene displacement reaction in [Ru^0(naphthalene)(COD)] by treatment with the arene of choice [7]. This pathway is limited to volatile arenes with only moderately reactive functional groups such as carbonyls, esters or halogen atoms. Several attempts by our group to introduce arenes with proton active groups like –OH or –NRH in this way failed until now.

In this paper we report about the preparation of [Ru^0(arene)(COD)] complexes with carbonyl side chain functions by arene displacement reaction and the conversion of the carbonyl groups by standard organic reactions into alcohols, imines, or alkenes. This includes the targeted introduction of a defined stereogenic centre by using arenes with chiral side chains and reactions between achiral or racemic [Ru(η^6-carbonylarene)(COD)] species with chiral agents.

2. Results and discussion

2.1. Naphthalene–arene exchange reaction

Following our earlier work [1,8], we reacted [Ru(naphthalene)(COD)] (**1**) with eight different mono- or disubstituted arenes, which bear aldehyde, ketone, ester, or amide functions as part of the side chain. The reactions proceed well and result in the formation of the desired [Ru(η^6-carbonylarene)(COD)] complexes **2**–**9** under mild reaction conditions in moderate to good yields (Scheme 1).

The smaller yields are observed for the aromatic amides and 3-bromoacetophenone. We believe that losses are caused in these cases by the more difficult removal of the obligatory excess of the incoming arenes due to their high boiling points as free ligands. In the case of *o*- or *m*-unsymmetrically disubstituted arenes, the planar-chiral complexes **2**–**5** are formed as racemates. Compounds **7** and **9** are examples for the targeted introduction of a defined stereogenic centre within the complexes. As assumed, the stereogenic centre of optically active [Ru(η^6-(*R*)-3-phenyl-methylbutyrate)(COD)] (**7**) remains unaffected by the coordination reaction. Its molecular structure, including the absolute configuration of the benzyl carbon atom was evaluated by an X-ray crystal structure determination (Fig. 1).

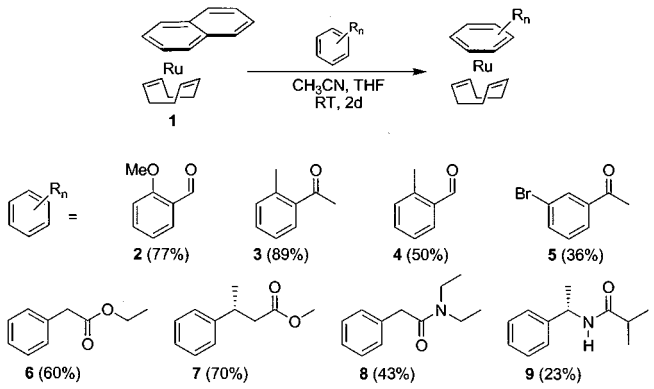
Owing to the acidity of the α-hydrogen atoms, complex **7** is a useful starting material for derivatization reactions at the neighbouring position to the stereogenic centre of the arene side chain (vide infra).

2.2. Aldol reaction of [Ru(η^6-carbonylarene)(η^4-COD)] complexes

Enolate chemistry plays an important role in the C–C bond forming processes for the preparation of complex organic molecules. As for the arene chromium tricarbonyl complexes [9], [Ru(η^6-carbonylarene)(COD)] systems are thus prone to the aldol type reaction. This includes electrophilic as well as nucleophilic reactivities when an enolizable moiety is present in the side chain of the arene ligand. In both cases, there is the possibility to get access to various functionalised arene ruthenium complexes. Examples for both reaction types will be given.

As for the free carbonylarene, it is possible to deprotonate the methyl group of [Ru(η^6-*o*-methylacetophenone)(η^4-COD)] (**3**) with LDA at low temperatures, and trap the generated enolate ion with (−)-(*R*)-menthylchloroformate as an electrophile. A diastereoisomeric mixture of [Ru(menthyl-{3-oxo-3-η^6-*o*-tolyl}-propionate)(COD)] (**10**) is obtained in 80% yield (Scheme 2).

If compound **3** is reacted with LDA and *o*-tolylaldehyde or benzaldehyde, respectively, then the isolated products did not consist of the expected β-hydroxyke-



Scheme 1.

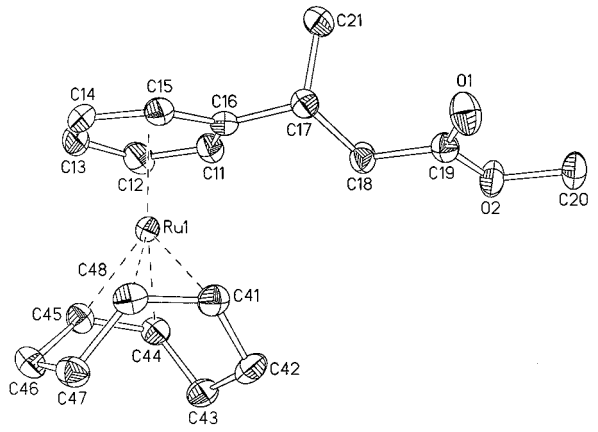
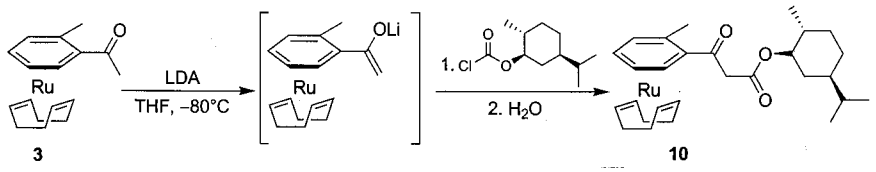


Fig. 1. Absolute molecular structure of **7** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: Ru1–C11 226.4(3), Ru1–C12 220.4(3), Ru1–C13 226.6(3), Ru1–C14 224.8(4), Ru1–C15 220.8(3), Ru1–C16 229.7(2); Ru1–C41 214.5(3), Ru1–C44 215.7(3), Ru1–C45 213.4(3), Ru1–C48 214.9(3).



Scheme 2.

tones or α-β-unsaturated compounds. The ketones [Ru(1-η^6-*o*-tolyl-3-*o*-tolyl-propane-1-one)(η^4-COD)] (**11**) and [Ru(η^6-1-*o*-tolyl-3-phenylpropane-1-one)(η^4-COD)] (**12**) are formed instead. The yields, however, are quite good: 53% for **11** and 71% for **12** (Scheme 3).

The molecular structure of **11** was determined by a single-crystal X-ray structure analysis (Fig. 2).

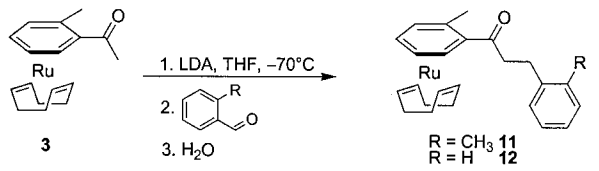
This crystal structure determination proves that all carbon atoms of both reaction components of the ruthenium complex **3** and the *o*-tolylaldehyde are present in product **11**, but the expected hydroxyl group of C103 is missing. The bonding distance between the carbon atoms C102 and C103 is typically in the range of a carbon–carbon single bond. As all hydrogen atoms of **11** have been located, this rules out a C–C double bond. The NMR spectra of **11** and **12** are consistent with the findings of the crystal structure determination of **11**.

The formation of complexes **11** and **12** can be related to an interaction of the ruthenium atom with one of the intermediate products of the reaction sequence, but the mechanism is unclear. In contrast to the rather unreactive carbonyl group of [Ru(η^6-*o*-methylacetophenone)(η^4-COD)] (**3**) that one of [Ru(η^6-*o*-tolylaldehyde)(η^4-COD)] (**4**) is well suited as an acceptor function towards all sort of nucleophiles, especially enolate ions, and the resulting β-hydroxycarbonyl compounds are stable enough for isolation. When **4** is reacted with the optically active enolate ion of (*R*)-menthylacetate, a diastereoisomeric mixture of [Ru(3-η^6-*o*-tolyl-3-hydroxy menthylpropionate)(η^4-COD)] (**13**) is isolated as a yellow oil in 80% yield (Scheme 4).

In this combination of an enantiopurepure enolate ion with a racemic aldehyde, a diastereoselective outcome of the aldol reaction was verified. According to the NMR spectra, the diastereoselectivity is 88% de. This fits the result obtained by the addition of phenyllithium to **4** [1], thus the same conformational preferences of the carbonyl group of starting material **4** apply to this type of reaction. With a cyclic transition state of the aldol reaction and a co-group, which is oriented opposite to the methyl group, the attack of the enolate is in favour to proceed from the distal side.

The optically pure complex **7** was tested as the starting material for an asymmetric aldol reaction. The deprotonation of the diastereotopic methylene protons was obtained again with LDA at low temperatures and benzylbromide was added as the electrophile. After the standard workup procedure, [Ru(η^6-((*R*)-(3-phenyl))-2-benzylbutyric acid methylester)(η^4-COD)] (**14**) was isolated in 75% yield as a mixture of diastereomers. The stereogenic centre in the vicinity of the reaction site ensures a diastereoselectivity of 80% de (Scheme 5).

On the basis of the reactivity of Ru(arenealdehyde) complexes, a diastereoselective additon of nucleophiles to the carbonyl group seems to be possible and this



Scheme 3.

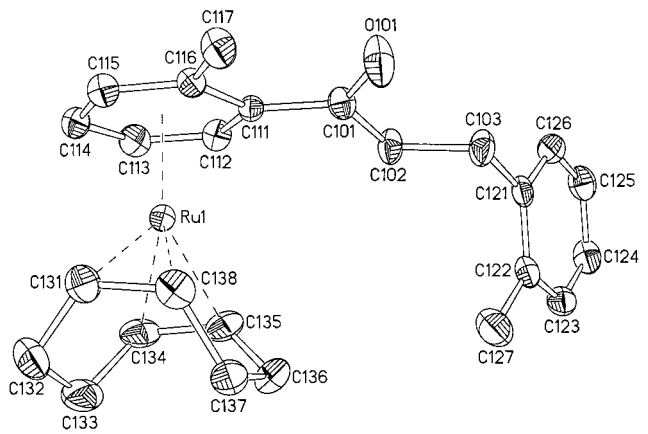
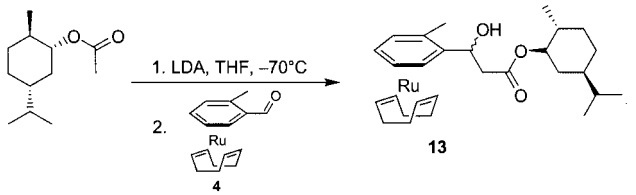
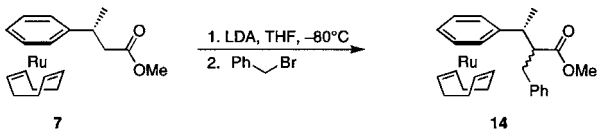


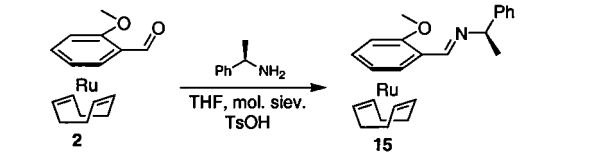
Fig. 2. Molecular structure of **11** in the solid state (one of the two independent molecules, one enantiomer). Hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: Ru1–C111 226.2(4), Ru1–C112 223.3(6), Ru1–C113 225.9(6), Ru1–C114 221.6(5), Ru1–C115 222.9(5), Ru1–C116 227.1(5); Ru1–C131 214.1(6), Ru1–C138 214.6(6), Ru1–C134 215.8(5), Ru1–C135 214.4(5) C102–C103 147.2(6).

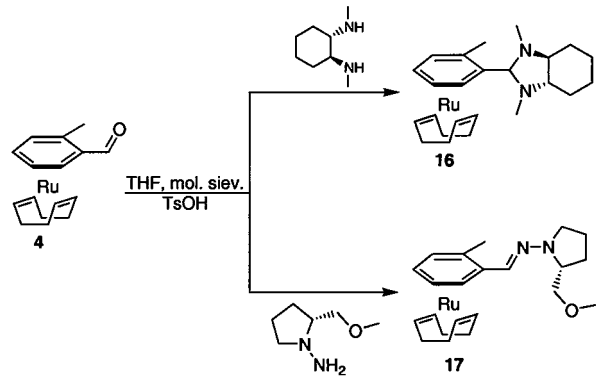


Scheme 4.



Scheme 5.





Scheme 6.

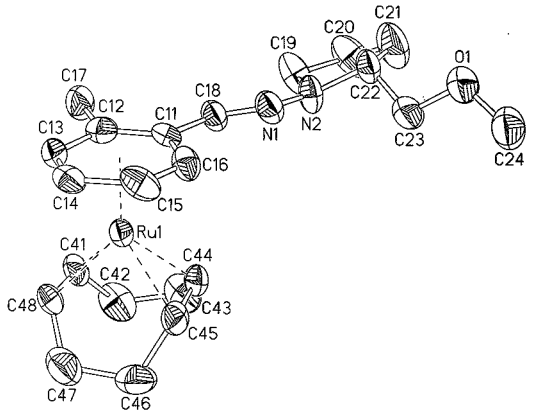


Fig. 3. Absolute molecular structure of **17a** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: Ru1–C11 227.5(6), Ru1–C12 226.5(6), Ru1–C13 219.1(7), Ru1–C14 224.8(7), Ru1–C15 230.1(7), Ru1–C16 222.8(5); Ru1–C41 210.3(7), Ru1–C44 212.9(6), Ru1–C45 212.1(9), Ru1–C48 213.4(6), C11–C18 146.7(8), N1–C18 127.1(7), N1–N2 135.9(6).

could lead to pathways towards planar-chiral systems in enantiomerically pure form. A simple approach to such planar-chiral compounds utilises the separation of a suited mixture of diastereomers. If [Ru(η^6-*o*-methoxybenzaldehyde)(η^4-COD)] (**2**) and [Ru(η^6-*o*-tolylaldehyde)(η^4-COD)] (**4**) are reacted with chiral amines such as (*S*)-phenylethylamine, (*R*,*R*)-*N*,*N*-dimethyl-1,2-diaminocyclohexane or (*R*)-*N*-amino-2-(methoxymethyl)-pyrrolidine (RAMP) the diastereomeric complexes [Ru(η^6-2-(*o*-methoxyphenyl)-(*S*)-ethylphenylimine)-(η^4-COD)] (**15**), [Ru(η^6-2-(2-methylphenyl)1,3-(*N*,*N*-dimethyl)diazaoctatetrahydroindane)(η^4-COD)] (**16**), and [Ru(*N*-[[η^6-(2-methylphenyl]methylene]-(*R*)-2-(methoxymethyl)-1-pyrrolidinamine)(COD)] (**17**) are formed straightforward. Owing to the racemic character of **2** and **4**, no diastereomeric excess was found in the reaction products. Attempts to separate the diastereomers have been successful for the hydrazone system **17** (Scheme 6).

The separation of the diastereomers **17a**/**17b** can be achieved by fractional crystallisation from *n*-hexane. The success of the separation progress can be monitored by NMR. As **17a** formed crystals of good quality, the crystal structure has been solved including the absolute configuration of the stereogenic centres. As the *R*-configuration of the heterocycle was reproduced correctly, it was possible to assign the *R*-configuration to the Ru atom of **17a**. Consequently, the ruthenium atom in **17b** has got a *S*-configuration (Fig. 3).

2.3. Reduction of ruthenium-coordinated arylesters and amides with $LiAlH_4$

Until now we have not been able to coordinate arenes containing free hydroxy or primary amino functions in the arene side chain directly to the ruthenium atom. As such groups are of interest as dangling bonds with respect to the ruthenium atom, we tried the reduction of the ester group of enantiopure **7** with $LiAlH_4$.

As expected, the reduction is chemospecific and does not touch the stereogenic centre of the side chain. It thus transforms the enantiomerically pure arylester complex **7** into the optically active arylalcohol complex [Ru(η^6-(*R*)-3-phenylbutan-1-ol)(η^4-COD)] (**18**). This reaction seems to be a general one, which allows generating chiral [Ru(arene)(COD)] complexes which carry hydroxy functions at the side chain of the arene, thus the analogous reduction of **13** with $LiAlH_4$ affords a corresponding diastereomeric mixture of complexes **19** with a 1,3-dihydroxyl substitution pattern in the side chain of the ruthenium-coordinated arene ligand (Scheme 7).

In contrast to esters, amides are less reactive towards reduction with $LiAlH_4$. Nevertheless, the reduction of ruthenium-coordinated arylamides is possible with $LiAlH_4$. This is shown in the reduction of [Run(η^6-*N*,*N*,-diethyl-2-phenylacetamide)(η^4-COD)] (**8**) which forms [Ru(η^6-diethyl-2-phenylethylamine)(η^4-COD)] (**20**) in 60% yield.

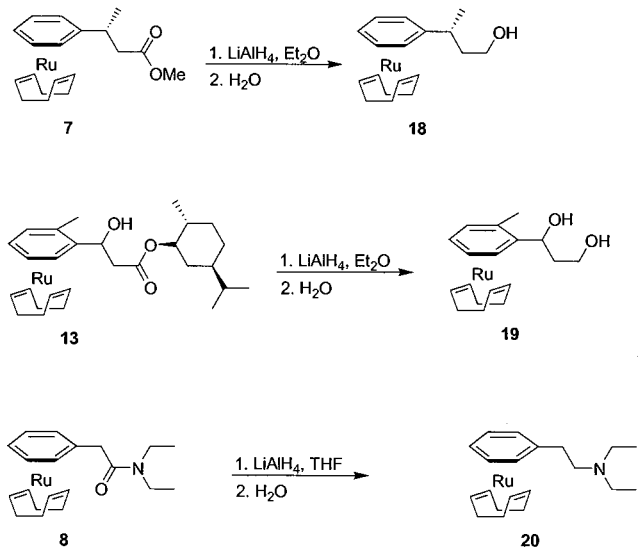
2.4. The Wittig olefination of carbonylarene ruthenium complexes

The Wittig reaction of alkylidenephosphoranes with aldehydes and ketones is a valuable and general method for regiospecific alkene formation. This includes car-

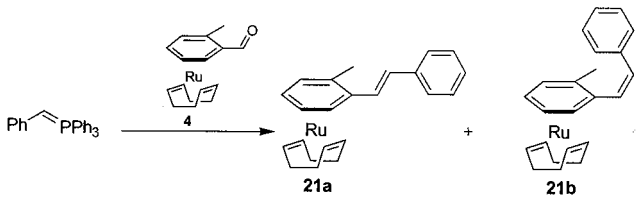
bonylarene chromium tricarbonyl complexes [10]. To complete our screening on the reactivity of π-coordinated carbonylarenes, we decided to apply this coupling reaction to one of our complexes. Thus, the aldehyde complex **4** was treated with in situ prepared benzylidenphosphorane (benzyltriphenylphosphoniumbromide–*n*-butyllithium) and the coupling results in a 55:45 mixture (^{1}H-NMR) of the *E*- and *Z*-isomeric π-coordinated stilbenes **21a** and **21b**. The mixture was obtained in 48% yield as an orange solid. In lithium salt-free reaction conditions [11,12] (sodium bis(trimethylsilyl)amide as base) the *E*:*Z* ratio (33:66; **21a**:**21b**) is affected in as expected. The separation of the isomers **21a** and **21b** was accomplished by fractional crystallisation from *n*-hexane (Scheme 8).

3. Conclusions

Standard organic synthetic procedures can be applied easily and in great diversity to the synthesis of new side chain functionalised arene ruthenium cyclooctadiene compounds. Especially the utilisation of carbonyl groups as functionalities for the further derivatization of arene ligands already complexed to the ruthenium atom provides a wide variety of possible reaction pathways. With aldol type reactions arene ruthenium compounds with even complex substitution patterns are accessible in a few steps. Especially, the successful separation of diastereomers, which contain a planar-chiral arene ligand open the gate to planar-chiral arene–ruthenim complexes in enantiomerically pure form.



Scheme 7.



Scheme 8.

4. Experimental

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 temperature (r.t.) in JEOL FT-NMR-EX 270, FT-JNM-GX 270, FT-JNM-LA-400 spectrometers, using dimethylpolysiloxane and solvent signals as internal standards. Mass spectra were recorded in a varian MAT 212 spectrometer. Microanalyses were performed at the analytical department of the institute, using Carlo Erba Elemental Analyser Mod. 1106. Column chromatography (15×1 cm) was accomplished with neutral degassed alumina (Merck, activity III). The complexes [Ru(naphthalene)(COD)] (**1**) [7] and [Ru(*o*-tolylaldehyde)(COD)] [1] (**4**) were prepared as reported in the literature.

*4.1. Synthesis of [Ru(arene)(COD)] **2**, **3**, **5**–**9**. General procedure*

Starting complex **1**, the desired arene ligand and MeCN are dissolved in THF and the mixture is stirred at r.t. for 2 days. Solvent, the excess of the arene and naphthalene are removed in vacuo. The resulting dark solid is dissolved and filtered through Al_2O_3 (activity III) with light petroleum ether or light petroleum ether–toluene (2:1). Removal of the solvent under reduced pressure yields the product complexes, which can be recrystallised from light petroleum ether, or a mixture of light petroleum ether–toluene.

*4.1.1. [Ru(η^6-o-methoxybenzaldehyde)(η^4-COD)] (**2**)*

[Ru(naphthalene)(COD)] (**1**) (1.73 g, 5.15 mmol), 2 ml MeCN, 11 g *o*-methoxybenzaldehyd and 100 ml THF; yield 1.378 g (3.98 mmol, 77%) [Ru(*o*-methoxybenzaldehyd)(COD)] (**2**) as a red solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 10.54 (s, 1H, aldehyd); 5.37 [dd, 1H, arene, $^3J_{H-H} = 5.4$ Hz, $^4J_{H-H} = 1.35$ Hz]; 4.94 [dt, 1H, arene, $^3J_{H-H} = 5.4$ Hz, $^4J_{H-H} = 1.35$ Hz]; 4.79 [t, 1H, arene, $^3J_{H-H} = 5.4$ Hz]; 4.06 [d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 3.43–3.30 (m, 4H, COD_{olef}); 2.79 (s, 3H, OCH_3); 2.25–2.19 (m, 8H, COD_{aliph}). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 186.8 (carbonyl); 92.7 (arene); 83.3 (arene); 79.8 (arene); 79.8 (arene); 79.1 (arene); 70.0 (arene); 65.4 (COD_{olef}); 64.7 (COD_{olef}); 55.3 (OCH_3); 34.5 (COD_{aliph}); 33.7 (COD_{aliph}). FDMS (2

kV); m/z: 345 [M^+] (100%). Anal. Found: C, 55.45; H, 6.04. Calc. for $C_{16}H_{20}O_2Ru$: C, 55.61; H, 5.86%.

4.1.2. [Ru(η⁶-o-methylacetophenone)(η⁴-COD)] (3)

[Ru(naphthalene)(COD)] (**1**) (1.09 g, 3.23 mmol), 1.0 ml MeCN, 10 ml *o*-methylacetophenone and 80 ml THF; yield 986 mg (89%) [Ru(*o*-methylacetophenone)(COD)] (**3**) as an orange solid.

^{1}H-NMR (C_6D_6, 269.9 MHz): δ 4.95 (1, 1H, arene); 4.77 (d, 1H, arene); 4.51 (t, 1H, arene); 4.40 (d, 1H, arene); (all $^3J_{H-H}$ arene = 6 Hz); 3.45–3.35 (m, 2H, COD_{olef}); 3.30–3.20 (m, 2H, COD_{olef}); 2.40–2.10 (m, 8H, COD_{aliph}); 2.25 (s, 3H, C**H**$_3$); 2.12 (s, 3H, C**H**$_3$). ^{13}C-NMR (100.4 MHz, C_6D_6): δ 189.9 (carbonyl); 101.6 (arene); 93.0 (arene); 91.4 (arene); 88.7 (arene); 87.8 (arene); 82.4 (arene); 65.6 (COD_{olef}); 63.9 (COD_{olef}); 34.5 (COD_{aliph}); 33.4 (COD_{aliph}); 28.5 (**C**H$_3$); 19.6 (**C**H$_3$). EIMS (70 eV); m/z: 343 [M^+] (100%), $C_{17}H_{22}ORu$.

4.1.3. [Ru(η⁶-m-bromoacetophenone)(η⁴-COD)] (5)

[Ru(naphthalene)(COD)] (**1**) (502 mg, 1.48 mmol), 1.3 ml MeCN, 11.0 ml *m*-bromoacetophenone and 40 ml THF; yield 214 mg (0.52 mmol, 36%) [Ru(3-bromoacetophenone)(1,5-COD)] (**5**) as a red solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 5.83 (s, 1H, arene); 5.74 (d, 1H, arene, $^3J_{H-H}$ = 5.8 Hz); 5.06 (d, 1H, arene, $^3J_{H-H}$ = 6.0 Hz); 4.51 (t, 1H, arene, $^3J_{H-H}$ = 6.0 Hz); 3.61–3.50 (m, 2H, COD_{olef}); 3.37–3.27 (m, 2H, COD_{olef}); 2.18 (s, 8H, COD_{aliph}); 2.05 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 194.8 (carbonyl); 92.3 (arene); 91.7 (arene); 90.6 (arene); 88.5 (arene); 86.9 (arene); 83.7 (arene); 70.8 (COD_{olef}); 67.5 (COD_{olef}); 33.9 (COD_{aliph}); 33.5 (COD_{aliph}); 25.5 (**C**H$_3$). FDMS (2 kV); m/z: 407 [M^+] (100%), $C_{16}H_{19}OBrRu$.

4.1.4. [Ru(2-η⁶-phenylethylacetate)(η⁴-COD)] (6)

[Ru(naphthalene)(COD)] (**1**) (313 mg, 0.93 mmol), 5.0 ml 2-phenylethylacetate, 1.0 ml MeCN, 50 ml THF; yield 210 mg (0.56 mmol, 60%) [Ru(2-η⁶-phenylethylacetate)(η⁴-COD)] (**6**) as a brown solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 4.93–4.80 (d + t, 3H, arene); 4.71 (t, 2H, arene); (all $^3J_{H-H}$ arene = 6 Hz); 3.88 (q, 2H, OC**H**$_2$); 3.33 (s, 4H, COD_{olef}); 2.93 (s, 2H, PhC**H**$_2$); 2.33 (s, 8H, COD_{aliph}); 0.94 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 67.6 MHz): δ 170.1 (carbonyl); 96.6 (arene); 87.4 (arene); 87.0 (arene); 85.6 (arene); 61.7 (COD_{olef}); 60.6 (O**C**H$_2$); 39.2 (Ph**C**H$_2$); 34.1 (COD_{aliph}); 14.1(CH_3). FDMS (2 kV); m/z: 374 [M^+] (100%), $C_{18}H_{24}O_2Ru$.

4.1.5. [Ru(η⁶-(R)-3-phenylmethylbutyrate)(η⁴-COD)] (7)

[Ru(naphthalene)(COD)] (**1**) (556 mg, 1.65 mmol), 5.0 ml (*R*)-3-phenylmethylbutyrate, 1.0 ml MeCN and 50 ml THF; yield 434 mg (70%) [Ru((*R*)-3-phenylmethylbutyrate)(COD)] (**7**) as a brown solid.

^{1}H-NMR (C_6D_6, 269.9 MHz): δ 5.45 (t, 1H, arene); 4.65 (d, 2H, arene); 4.48 (t, 2H, arene H); (all $^3J_{H-H}$ arene = 6 Hz); 3.45 (s, 4H, COD_{olef}); 3.42 (s, 3H, OCH_3); 2.95–2.78 (m, 2H, CH_2); 2.50–2.25 (m, 9H, COD_{aliph}; CH_{benzyl}); 1.37 (d, 3H, CH_3). ^{13}C-NMR (C_6D_6, 67.9 MHz): δ 112.5 (arene); 89.0 (arene); 84.9 (arene); 84.6 (arene); 84.1 (arene); 83.7 (arene); 61.4 (COD_{olef}); 61.3 (COD_{olef}); 51.1 (O**C**H$_3$); 43.0 (**C**H$_2$); 34.4 (**C**H); 34.3 (COD_{aliph}); 34.1 (COD_{aliph}); 21.2 (**C**H$_3$). FDMS (2 kV); m/z: 387 [M^+] (100%). Anal. Found: C, 59.47; H, 7.14. Calc. for $C_{19}H_{26}O_2Ru$: C, 58.90; H, 6.81%. Optical rotation: $[\alpha]_D^{25} = -26.7°$.

4.1.6. [Ru(η⁶-N,N,-diethyl-2-phenyl acetamide)(η⁴-COD)] (8)

[Ru(naphthalene)(COD)] (**1**) (394 mg, 1.16 mmol), 5.0 ml *N*,*N*,-diethyl-2-phenyl acetamide, 1.5 ml MeCN, 50 ml THF; yield 200 mg (0.50 mmol, 43%) [Ru(η⁶-*N*,*N*,-diethyl-2-phenyl acetamide)(η⁴-COD)] (**8**) as a pale-brown solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 5.05 (d, 2H, arene-H$_o$, $^3J_{H-H}$ = 5.4 Hz); 4.98 (t, 1H, arene-H$_p$, $^3J_{H-H}$ = 5.4 Hz); 4.77 (t, 2H, arene-H$_m$, $^3J_{H-H}$ = 5.4 Hz); 3.39 (s, 4H, COD_{olef}); 3.14 (q, 2H, NC**H**$_2$, $^3J_{H-H}$ = 7.2 Hz); 3.05 (s, 2H, PhC**H**$_2$); 2.72 (q, 2H, NCH_2 $^3J_{H-H}$ = 7.2 Hz); 2.42–2.20 (m, 8H, COD_{aliph}); 0.92 (t, 3H, CH_3, $^3J_{H-H}$ = 7.2 Hz); 0.66 (t, 3H, CH_3, $^3J_{H-H}$ = 7.2 Hz). ^{13}C-NMR (C_6D_6, 67.7 MHz): δ 168.8 (CO); 99.9 (arene); 88.1 (arene); 87.9 (arene); 85.9 (arene); 62.0 (COD_{olef}); 42.5 (CH_2); 40.8 (CH_2); 38.3 (CH_2); 34.7 (COD_{aliph}); 14.9 (CH_3); 13.7 (CH_3). FDMS (2 kV); m/z: 400 [M^+] (100%). Anal. Found: C, 60.17; H, 7.16; N, 3.39. Calc. for $C_{20}H_{29}NORu$: C, 60.00; H, 7.29; N, 3.49%.

4.1.7. [Ru(η⁶-N-((S)-2-phenylethyl)isobutyric acid amide)(η⁴-COD)] (9)

[Ru(naphthalene)(COD)] (**1**) (395 mg, 1.17 mmol), 2.6 g *N*-((*S*)-2-phenylethyl)isobutyric acid amide, 1.5 ml MeCN, 100 ml THF; yield 110 mg (0.27 mmol, 23%) [Ru(η⁶-*N*-((*S*)-2-phenylethyl)isobutyric acid amide)(η⁴-COD)] (**9**) as a yellow solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 5.90 (d (br), 1H, NH, $^3J_{H-H}$ = 7.5 Hz); 5.35 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 4.96 (qi; 1H, PhC**H**, $^3J_{H-H}$ = 7.2 Hz); 4.79 (d, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 4.64 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 4.54 (d, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 4.24 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 3.40 (s, 4H, COD_{olef}); 2.25–2.20 (m, 8H, COD_{aliph}); 2.15 (ht, 1H, $(CH_3)_2$C**H**, $^3J_{H-H}$ = 6.9 Hz); 1.33 (d, 3H, C**H**$_3$CH, $^3J_{H-H}$ = 6.6 Hz); 1.14 (d, 6H, $CH_{3\text{-}iso\text{propyl}}$, $^3J_{H-H}$ = 6.9 Hz). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 175.1 (CO); 108.7 (arene); 87.5 (arene); 86.7 (arene); 86.3 (arene); 84.1 (arene); 83.6 (arene); 60.9 (COD_{olef}); 60.7 (COD_{olef}); 46.1 (Ph**C**H); 35.9 ($(CH_3)_2$**C**H); 34.4 (COD_{aliph}); 34.0 (COD_{aliph}); 20.3 (CH_3); 19.9 (CH_3); 19.8 (CH_3). FDMS (2 kV); m/z: 401 [M^+] (100%). Anal. Found: C, 59.68; H, 6.84; N, 4.29. Calc. for $C_{20}H_{29}NORu$: C, 60.00; H, 7.29; N, 3.49%.

4.2. Synthesis of [Ru(arene)(COD)] complexes **10–14** by aldol reaction. General procedure

A THF solution of [Ru(η^6-*o*-methylacetophenone)(η^4-COD)] (**3**) is cooled to −80 °C and added to a freshly prepared solution of lithiumdiisopropylamid in THF at −80 °C. After 30 min of stirring, the cold THF solution of the carbonyl compound is added dropwise. The mixture is allowed to reach r.t. within 3 h and 2 ml of degassed water is added. The solution is again stirred for 30 min and the solvent is removed in vacuo. The residue is redissolved in light petroleum ether–toluene (2:1) and filtered through Al_2O_3 (activity III). Elution with toluene and removal of the solvent under reduced pressure yields the desired complexes.

4.2.1. [Ru(menthyl-{3-oxo-3-η^6-*o*-tolyl}propionate)-(COD)] (**10**)

[Ru(η^6-*o*-methylacetophenone)(COD)] (**3**) (226 mg, 0.66 mmol), 0.19 ml (1.32 mmol) diisopropylamine, 0.53 ml (1.32 mmol) *n*-butyllithium (2.5 M in hexane), 0.29 ml (1.32 mmol) (−)-(*R*)-menthyl-chloroformate, 40 ml THF; yield 263 mg (0.50 mmol, 75%) [Ru(3-oxo-3-η^6-*o*-tolylmenthylpropionate)(η^4-COD)] (**10**) as a yellow oil.

^{1}H-NMR (C_6D_6, 270 MHz): δ 5.34 (m, 4H, $CH_{2\text{-}\beta\text{-ketoester}}$); 5.25 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 5.24 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.86 (d, 1H, arene, $^3J_{H-H} = 5.5$ Hz); 4.83 (d, 1H, arene, $^3J_{H-H} = 5.5$ Hz); 4.62–4.49 (m, 4H, arene + 1H $CH_{menthyl}$); 4.27 (d, 1H, arene; $^3J_{H-H} = 5.5$ Hz); 4.25 (d, 1H, arene, $^3J_{H-H} = 5.5$ Hz); 3.48–3.40 (m, 4H, COD_{olef}); 3.29–3.20 (m, 4H, COD_{olef}); 2.33–2.20 (m, 16H, COD_{aliph}); 2.02–1.93 (m, 2H, menthyl); 1.91 (s, 6H, *o*-CH_3); 1.37–1.25 (m, 6H, menthyl); 1.08–0.82 (m, 8H, menthyl); 0.77 (d, 3H, $CH_{3\text{-}iso\text{propyl}}$, $^3J_{H-H} = 7.1$ Hz); 0.75 (d, 3H, $CH_{3\text{-}iso\text{propyl}}$, $^3J_{H-H} = 6.7$ Hz); 0.72 (d, 3H, $CH_{3\text{-}iso\text{propyl}}$, $^3J_{H-H} = 6.7$ Hz); 0.71 (d, 3H, $CH_{3\text{-}iso\text{propyl}}$, $^3J_{H-H} = 7.1$ Hz); 0.64 (d, 3H, CH_3, $^3J_{H-H} = 6.3$ Hz); 0.63 (d, 3H, CH_3, $^3J_{H-H} = 6.2$ Hz); 0.60–0.42 (m, 2H, menthyl). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 153.0 (CO), 152.9 (CO); 152.6 (CO); 152.6 (CO); 106.9 ($CH_{2\text{-}\beta\text{-ketoester}}$); 100.1 (arene); 100.0 (arene); 99.5 (arene); 99.4 (arene); 86.6 (arene); 86.5 (arene); 86.3 (arene); 86.2 (arene); 86.0 (arene); 85.9 (arene); 85.8 (arene); 85.8 (arene); 79.0 (menthyl); 78.9 (menthyl); 64.7 (COD); 64.6 (COD); 63.1 COD); 63.1 (COD); 47.3 (menthyl); 40.8 (menthyl); 34.1 (COD); 34.1 (COD); 33.9 (COD); 31.3 (menthyl); 27.2 (menthyl); 26.5 (menthyl); 26.5 (menthyl); 23.6 (menthyl); 23.5 (menthyl); 21.9 (menthyl, 20.8 (menthyl), 20.7 (menthyl); 17.4 (menthyl); 16.5 (CH_3-arene). FDMS (2 kV); *m*/*z*: 526 [M^+] (100%). Anal. Found: C, 63.96; H, 8.79. Calc. for $C_{28}H_{31}O_3Ru$: C, 63.89; H, 7.65%.

4.2.2. [Ru(1-η^6-*o*-tolyl-3-*o*-tolylpropane-1-one)-(η^4-COD)] (**11**)

[Ru(η^6-*o*-methylacetophenone)(COD)] (**3**) (524 mg, 1.53 mmol), 0.15 ml (2.20 mmol) diisopropylamine, 0.88 ml (2.20 mmol) *n*-BuLi (2.5 M in hexane), 0.24 ml (2.00 mmol) *o*-tolylaldehyd, 50 ml THF; yield 362 mg (0.81 mmol, 53%) [Ru(3-η^6-*o*-tolyl-1-*o*-tolyl-propane-1-one)(η^4-COD)] (**11**) as a red solid. ^{1}H-NMR (C_6D_6, 400 MHz): δ 7.19–7.02 (m, 4H, tolyl); 5.41 (t, 1H, arene); 4.63 (d, 1H, arene); 4.43 (t, 1H, arene); 4.33 (d, 1H, arene); (all $^3J_{H-H}$ arene = 6 Hz); 3.38–3.34 (m, 2H, COD_{olef}); 3.24–3.21 (m, 2H, COD_{olef}); 3.15–2.95 (m, 3H, alkyl); 2.77–2.70 (m, 1H, alkyl), 2.19 (m, 11H, COD_{aliph}, + CH_3); 2.09 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 200.4 (CO); 140.2 (tolyl); 136.0 (tolyl); 130.5 (tolyl); 129.2 (tolyl); 126.5 (tolyl); 126.4 (tolyl); 101.7 (arene); 93.1 (arene); 91.4 (arene); 88.7 (arene); 87.2 (arene); 82.4 (arene); 65.7 (COD_{olef}); 64.0 (COD_{olef}); 41.0 (CH_2); 34.2 (COD_{aliph}); 33.8 (COD_{aliph}); 28.2 (CH_2); 19.6 (CH_3); 19.2 (CH_3). FDMS (2 kV); *m*/*z*: 448 [M^+] (100%). Anal. Found: C, 67.07; H, 7.08. Calc. for $C_{25}H_{30}ORu$: C, 67.10; H, 6.80%.

4.2.3. [Ru(η^6-1-*o*-tolyl-3-phenylpropane-1-one)-(η^4-COD)] (**12**)

[Ru(η^6-*o*-methylacetophenone)(COD)] (**3**) (254 mg, 0.74 mmol), 0.21 ml (1.48 mmol) diisopropylamine, 0.60 ml (1.48 mmol) *n*-BuLi (2.5 M in hexane), 0.16 ml (1.48 mmol) benzaldehyde, 40 ml THF; yield 227 mg (71%) [(η^4-COD)(η^6-1-*o*-tolyl-3-phenylpropane-1-one)-Ru] (**12**) as a red solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 7.20–6.95 (m, 5H, phenyl); 5.45 (t, 1H, arene); 4.75 (d, 1H, arene); 4.42 (t, 1H, arene); 4.29 (d, 1H, arene); 3.40–3.31 (m, 2H, COD_{olef}); 3.22–3.12 (m, 2H, COD_{olef}); 3.10–2.90 (m, 3H, alkyl); 2.83–2.69 (m, 1H, alkyl); 2.15 (s, 8H, COD_{aliph}); 2.05 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 200.1 (CO); 142.2 (phenyl); 130.8 (phenyl); 128.8 (phenyl); 128.6 (phenyl); 128.3 (phenyl); 126.5 (phenyl); 101.3 (arene); 93.4 (arene); 91.5 (arene); 88.5 (arene); 87.3 (arene); 82.4 (arene); 65.7 (COD_{olef}); 63.9 (COD_{olef}); 42.4 (CH_2); 34.3(COD_{aliph}); 33.7 (COD_{aliph}); 30.8 (CH_2); 19.6 (CH_3). FDMS (2 kV); *m*/*z*: 433 [$M]^+$, $C_{24}H_{28}ORu$.

4.2.4. [Ru(3-η^6-*o*-tolyl-3-hydroxy menthylpropionate)(η^4-COD)] (**13**)

A mixture of 0.21 ml diisopropylamine (1.46 mmol), 20 ml THF, 0.56 ml *n*-BuLi (2.5 M in hexane) (1.40 mmol) is stirred at −20 °C for 20 min. All reaction components are then cooled to −80 °C, 0.18 ml (−)-(*R*)-menthylacetate (0.85 mmol) in 5 ml THF are added, followed by a solution of 240 mg (0.73 mmol) [Ru(*o*-tolylaldehyd)(COD)] (**4**) in 10 ml THF 10 min later. The reaction mixture is stirred at −80 °C for another hour. It is allowed to reach r.t., hydrolysed

with degassed H_2O and the solvents are removed in vacuo. Chromatography on Al_2O_3 (activity III) with toluene as eluent resulted in 312 mg (0.59 mmol, 81%) [Ru(3-η⁶-*o*-tolyl-3-hydroxypropionic-acidmenthyl ester)(η⁴-COD)] (**13**) as a yellow oil.

^{1}H-NMR (major diastereomer, C_6D_6, 270 MHz): δ 5.53 (m, 2H, arene); 5.23–5.10 (m, 2H, hydroxyl), 5.05 (d, 2H, arene); 4.86 (dt, 2H, menthyl); 4.45–4.30 (m, 4H, arene); 3.43–3.35 (m, 4H, COD_{olef}); 3.20–3.10 (m, 4H, COD_{olef}); 2.92–2.75 (m, 4H, CH_2); 2.57 (ddd, 2H, CH_2); 2.35–2.15 (16 H, COD_{aliph}); 2.10–1.95 (m, 4H, menthyl); 1.62 (s, 6H, *o*-CH_3); 1.45–1.30 (m, 4H, menthyl); 1.20–1.15 (m, 2H, menthyl); 1.0–0.70 (6H, menthyl); 0.85 (t, 12H, $CH_{3\text{-}isopropyl}$); 0.75 (d, 3H, $CH_{3\text{-menthyl}}$); 0.62 (d, 3H, $CH_{3\text{-menthyl}}$). ^{13}C-NMR (major diastereomer, C_6D_6, 67.7 MHz): δ 170.5 (CO); 108.8 (arene); 108.8 (arene); 97.9 (arene); 97.8 (arene); 88.9 (arene); 88.6 (arene); 86.0 (arene); 85.8 (arene); 85.6 (arene); 83.9 (arene); 83.6 (arene); 74.3 (CHOH); 65.5 (menthyl-C1); 62.6 (COD); 60.6 (COD); 47.3 (alkyl); 47.3 (alkyl); 43.0 (alkyl); 42.9 (alkyl); 41.3 (alkyl); 34.5 (COD); 34.4 (alkyl); 34.2 (COD); 31.4 (alkyl); 27.2 (alkyl); 26.5 (alkyl); 23.7 (alkyl); 22.1 (CH_3); 20.9 (CH_3); 16.6 (CH_3); 16.1 (CH_3). FDMS (2 kV); *m*/*z*: 526 [M^+] (100%), $C_{28}H_{42}O_3Ru$.

*4.2.5. [Ru(η⁶-((R)-(3-phenyl))-2-benzylbutyric acid methylester)(η⁴-COD)] (**14**)*

A mixture of 0.12 ml diisopropylamine (0.80 mmol), 30 ml THF, 0.40 ml *n*-BuLi (1.6 M in hexane, 0.63 mmol) is stirred for 20 min at −20 °C. All reaction components are then cooled to −80 °C, 207 mg [Ru((*R*)-3-η⁶-phenylmethylbutyrate)(COD)] (**7**) (0.53 mmol) in 5 ml THF are added, followed by a solution of 0.065 ml (0.53 mmol) benzylbromide 10 min later. The reaction mixture is stirred for another hour at −80 °C, is allowed to reach r.t. and is hydrolysed with degassed H_2O. The solvents are removed in vacuo. Chromatography on Al_2O_3 (activity III) with toluene as eluent resulted in 183 mg (0.38 mmol, 73%) [Ru(η⁶-((*R*)-(3-phenyl))-2-benzylbutyric acid methylester)(η⁴-COD)] (**14**) as a yellow oil.

^{1}H-NMR (major diastereomer, C_6D_6, 270 MHz): δ 7.07–6.95 (m, 5H, phenyl); 5.33 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 5.19 (d, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 5.13 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 3.99 (d, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 3.48 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 3.56–3.44 (m, 2H, COD_{olef}); 3.38–3.26 (m, 2H, COD_{olef}); 3.05 (s, 3H, OCH_3); 2.92–2.62 (m, 4H, alkyl); 2.42–2.16 (m, 8H, COD_{aliph}); 1.43 (d, 3H, CH_3, $^3J_{H-H}$ = 5.4 Hz). ^{13}C-NMR (major diastereomer, C_6D_6, 67.7 MHz): δ 173.8 (CO); 140.2 (phenyl); 129.4 (phenyl); 128.7 (phenyl); 126.7 (phenyl); 110.9 (arene); 89.4 (arene); 88.8 (arene); 87.6 (arene); 82.6 (arene); 79.7 (arene); 62.1 (COD_{olef}); 61.3 (COD_{olef}); 56.2 (alkyl); 50.9 (OCH_3); 40.4 (alkyl); 35.2 (alkyl); 34.8 (COD_{aliph}); 33.9 (COD_{aliph}); 16.9 (CH_3). FDMS (2 kV); *m*/*z*: 477 [M^+] (100%). Anal. Found: C, 66.01; H, 7.32. Calc. for $C_{26}H_{32}O_2Ru$: C, 65.38; H, 6.75%.

*4.3. [Ru(η⁶-2-(o-methoxyphenyl)-(S)-ethylphenylimine)-(η⁴-COD)] (**15**)*

A solution of 500 mg (1.44 mmol) [(η⁴-COD)(η⁶-*o*-methoxybenzaldehyde)Ru] (**2**), 291 mg (2.45 mmol) (*S*)-phenylethylamine and 10 mg *p*-toluenesulfonicacid in 100 ml THF is stirred over molecular sieves for 5 days at r.t. The solution is filtered and the solvents are removed under reduced pressure. The oily residue is dissolved in *n*-hexane and chromatography on Al_2O_3 (deactivated with 5% NEt_3) with cyclohexane–toluene (1:2) as eluent resulted in 259 mg (0.57 mmol, 40%) [Ru(η⁶-2-(*o*-methoxyphenyl)-(*S*)-ethylphenylimine)-(η⁴-COD)] (**15**) as a yellow oil.

^{1}H-NMR (C_6D_6, 270 MHz): δ 8.57 (s, 1H, imine); 8.47 (s, 1H, imine); 7.37 (d, 4H, phenyl, $^3J_{H-H}$ = 7.6 Hz); 7.20–7.00 (m, 6H, phenyl); 6.36 (d, 1H, arene, $^3J_{H-H}$ = 5.2 Hz); 6.22 (d, 1H, arene, $^3J_{H-H}$ = 6.0 Hz); 5.09 (t, 1H, arene, $^3J_{H-H}$ = 5.7 Hz); 5.01 (t, 1H, arene, $^3J_{H-H}$ = 5.4 Hz); 4.67 (d, 1H, arene, $^3J_{H-H}$ = 5.7 Hz); 4.55–4.48 (m, 2H, arene); 4.30–4.20 (3H, arene, Benzyl); 3.75–3.22 (m, 8H, COD_{olef}); 3.11 (s, 3H, OCH_3); 3.08 (s, 3H, OCH_3); 2.45–2.05 (m, 24H, COD_{aliph}); 1.46 (t, 6H, 2 CH_3). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 155.7 (imine); 155.4 (imine); 146.8 (phenyl); 146.5 (phenyl); 139.0 (phenyl); 138.9 (phenyl); 129.2 (phenyl); 128.9 (phenyl); 128.8 (phenyl); 128.5 (phenyl); 127.7 (phenyl); 127.6 (phenyl); 127.6 (phenyl); 127.5 (phenyl); 92.6 (arene); 92.6 (arene); 83.7 (arene); 82.9 (arene); 82.8 (arene); 81.9 (arene); 79.9 (arene); 79.4 (arene); 71.5 (arene); 71.4 (arene); 71.0 (arene); 70.7 (arene); 64.4 (COD_{olef}); 64.4 (COD_{olef}); 63.7 (COD_{olef}); 63.6 (COD_{olef}); 56.4 (OCH_3); 56.3 (OCH_3); 36.3 (Benzyl); 35.8 (COD_{aliph}); 33.9 (COD_{aliph}); 33.7 (Ph**C**H); 27.3 (CH_3); 25.5 (CH_3). FDMS (2 kV); *m*/*z*: 448 [M^+] (100%). Anal. Found: C, 62.83; H, 7.13; N, 2.74. Calc. for $C_{24}H_{29}NORu$: C, 64.29; H, 6.52; N, 3.12%.

*4.4. [Ru(η⁶-2-(2-methylphenyl)1,3-(N,N-dimethyl)-diazaoctadehydroindane)(η⁴-COD)] (**16**)*

A solution of 490 mg (1.48 mmol) [Ru(η⁶-*o*-methylbenzaldehyde)(η⁴-COD)] (**4**), 213 mg (1.50 mmol) (*R*,*R*)-*N*,*N*-dimethyl-1,2-diaminocyclohexane and 5 mg *p*-toluenesulfonicacid in 60 ml THF is stirred over molecular sieves for 5 days at r.t. The solution is filtered and the solvents are removed under reduced pressure. The oily residue is dissolved in *n*-hexane and chromatography through Al_2O_3 (deactivated with 5% NEt_3) with cyclohexan–toluene (1:2) as eluent resulted in 354 mg (0.78 mmol, 53%) [Ru(η⁶-2-(2-methyl-

phenyl)1,3 - (*N*,*N* - dimethyl)diazaoctadehydroindane)-(η^4-COD)] (**16**) as a yellow oil.

^{1}H-NMR (C_6D_6, 270 MHz): δ 5.62–5.55 (m, 2H, arene); 5.29 (t, 1H, arene, $^3J_{H-H} = 6.0$ Hz); 4.27–4.71 (m, 2H, arene); 4.64 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.41 (s, 1H, benzyl-H); 4.16 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.03 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 3.72 (s, 1H, CH_{benzyl}); 3.58–3.50 (m, 2H, COD_{olef}); 3.45–3.37 (m, 2H, COD_{olef}); 3.30–3.17 (m, 4H, COD_{olef}); 2.78–2.69 (m, 1H, $CH_{cyclohex}$); 2.67 (s, 3H, CH_3N); 2.40–2.10 (m, 16H, COD_{aliph}); 2.30 (s, 3H, CH_3N); 2.28 (s, 3H, CH_3N); 2.09–2.03 (m, 1H, $CH_{cyclohex}$); 1.93 (s, 3H, CH_3N); 1.92 (s, 3H, *o*-CH_3); 1.88–1.63 (m, 6H, $CH_{2\text{-}cyclohex}$); 1.57 (s; 3H, *o*-CH_3); 1.24–0.96 (m, 10H, $CH_{2\text{-}cyclohex}$). ^{13}C-NMR (C_6D_6, 100.4 MHz): δ 104.2 (arene); 103.8 (arene); 101.3 (arene); 94.6 (arene); 90.5 (arene); 90.4 (arene); 88.1 (arene); 87.4 (arene); 87.1 (arene); 86.1 (arene); 85.8 (arene); 85.6 (arene); 84.4 (benzyl); 82.3 (benzyl); 69.8 (cyclohexyl); 69.0 (cyclohexyl); 68.1 (cyclohexyl); 67.2 (cyclohexyl); 63.4 (COD); 62.3 (COD); 61.1 (COD); 60.9 (COD); 40.0 (N–CH_3); 37.7 (N–CH_3); 36.5 (N–CH_3); 36.1 (N–CH3); 35.2 (COD); 34.2 (COD); 34.0 (COD); 33.2 (COD); 29.9 (cyclohexyl); 29.6 (cyclohexyl); 29.3 (cyclohexyl); 27.8 (cyclohexyl); 25.3 (cyclohexyl); 24.9 (cyclohexyl); 24.7 (cyclohexyl); 24.5 (cyclohexyl); 17.5 (*o*-CH_3); 16.3 (*o*-CH_3). FDMS (2 kV); *m*/*z*: 453 [M^+] (100%), $C_{24}H_{36}N_2Ru$.

*4.4.1. [Ru(N-[[η^6-(2-methylphenyl]methylene]-(R)-2-(methoxymethyl)-1-pyrrolidinamine)-(COD)] (**17**)*

A solution of 800 mg (2.43 mmol) [Ru(η^6-*o*-methylbenzaldehyde)(η^4-COD)] (**4**), 0.32 m (2.43 mmol) (*R*)-*N*-amino-2-(methoxymethyl)-pyrrolidine and 10 mg *p*-toluenesulfonicacid in 80 ml THF is stirred over molecular sieves for 5 days at r.t. The solution is filtered and the solvents are removed under reduced pressure. The oily residue is dissolved in *n*-hexane and chromatography on Al_2O_3 (activity III) with toluene as eluent resulted in 1 g (2.26 mmol, 93%) of **17** as a orange solid.

^{1}H-NMR (C_6D_6, 270 MHz): δ 6.91 (s, 2H, $CH_{hydrazon}$); 5.69 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 5.64 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 5.30 (t, 1H, arene, $^3J_{H-H} = 5.7$ Hz); 5.27 (t, 1H, arene, $^3J_{H-H} = 5.7$ Hz); 4.95 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.89 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.42 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.37 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 3.63–3.48 (m, 4H, pyrrolidinyl); 3.41–3.22 (m, 8H, COD_{olef}, +2H, pyrrolidinyl); 3.10 (s, 3H, OCH_3); 3.05 (s, 3H, OCH_3); 3.00–2.82 (m, 2H, pyrrolidinyl); 2.59–2.48 (m, 2H, pyrrolidinyl); 2.40–2.21 (m, 16H, COD_{aliph}); 2.01 (s, 3H, CH_3); 1.96 (s, 3H, CH_3); 1.68–1.52 (m, 6H, pyrrolidinyl); 1.45–1.31 (m, 2H, pyrrolidinyl). ^{13}C-NMR (C_6D_6, 67.7 MHz): δ 129.0 (N=C–H); 102.3 (aren); 102.2 (aren); 100.4 (aren); 99.9 (aren); 92.1 (aren); 92.1 (aren); 87.8 (aren); 87.5 (aren); 87.4 (aren); 87.3 (aren); 81.8 (aren); 81.5 (aren); 77.0 (NCH_2R); 76.7 (NCH_2R); 66.2 (COD); 65.9 (COD); 65.5 ($NCHR_2$); 65.2 ($NCHR_2$); 65.2 (COD); 60.8 (OCH_3); 60.7 (OCH_3); 51.0 (OCH_2R); 50.5 (OCH_2R); 36.7 (COD); 36.5 (COD); 36.0 (COD); 35.8 (COD); 32.3 (NCHR); 29.0 (CH_2); 28.9 (CH_2); 24.2 (CH_2); 24.1 (CH_2); 19.4 (CH_3); 19.3 (CH_3). FDMS (2 kV); *m*/*z*: 441 [M^+] (100%). Anal. Found: C, 60.32; H, 7.82; N, 5.99. Calc. for $C_{22}H_{32}N_2ORu$: C, 59.84; H, 7.31; N, 6.34%.

*4.4.2. Separation of diastereomers (R,S)-**17a**, (S,R)-**17b***

The mixture of diastereomers **17** (200 mg) are dissolved in 3 ml *n*-hexane. After the threefold fractional crystallisation at −20 °C 60 mg of **17a** (*R*,*R*) are obtained as orange blocks and 40 mg of **17b** (*S*,*R*) as yellow needles. According to ^{1}H-NMR, both are spectroscopically pure (>99%) diastereomers.

*4.4.2.1. **17a** (R,R).* ^{1}H-NMR (C_6D_6, 270 MHz): δ 6.91 (s, 1H, $CH_{hydrazone}$); 5.64 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 5.30 (t, 1H, arene, $^3J_{H-H} = 5.7$ Hz); 4.95 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.37 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 3.63–3.48 (m, 2H, pyrrolidinyl); 3.41–3.22 (m, 4H, COD_{olefin}, +1H pyrrolidinyl); 3.10 (s, 3H, OCH_3); 3.00–2.82 (m, 1H, pyrrolidinyl); 2.59–2.48 (m, 1H, pyrrolidinyl); 2.40–2.21 (m, 8H, COD_{aliph}); 2.01 (s, 3H, CH_3); 1.68–1.52 (m, 3H, pyrrolidinyl); 1.45–1.31 (m, 1H, pyrrolidinyl). ^{13}C-NMR (C_6D_6, 67.7 MHz) δ 129.0 (N=C–H); 102.3 (arene); 102.2 (arene); 91.1 (arene); 86.4 (arene); 85.8 (arene); 81.5 (arene); 77.0 (NCH_2R); 66.2 (COD_{olef}); 65.9 ($NCHR_2$); 65.5 (COD_{olef}); 60.8 (OCH_3); 50.5 (OCH_2R); 36.5 (COD_{aliph}); 35.8 (COD_{aliph}); 29.0 (CH_2); 24.2 (CH_2); 19.4 (CH_3). Optical rotation angles (r.t., toluene): $[\alpha]_{589} = -342°$; $[\alpha]_{578} = -366°$; $[\alpha]_{633} = -257°$.

*4.4.2.2. **17b** (S,R).* ^{1}H-NMR (C_6D_6, 270 MHz): δ 6.92 (s, 1H, $CH_{hydrazone}$); 5.69 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 5.27 (t, 1H, arene, $^3J_{H-H} = 5.7$ Hz); 4.89 (t, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 4.42 (d, 1H, arene, $^3J_{H-H} = 5.4$ Hz); 3.63–3.48 (m, 2H, pyrrolidinyl); 3.41–3.22 (m, 4H, COD_{olef}, +1H, pyrrolidinyl); 3.05 (s, 3H, OCH_3); 3.00–2.82 (m, 1H, pyrrolidinyl); 2.59–2.48 (m, 1H, pyrrolidinyl); 2.40–2.21 (m, 8H, COD_{aliph}); 1.96 (s, 3H, CH_3); 1.68–1.52 (m, 3H, pyrrolidinyl); 1.45–1.31 (m, 1H, pyrrolidinyl). ^{13}C-NMR (C_6D_6, 67.7 MHz): δ 127.9 (N=C–H); 100.4 (arene); 99.9 (arene); 90.1 (arene); 86.0 (arene); 85.4 (arene); 80.0 (arene); 75.1 (NCH_2R); 64.3 (COD); 63.5 ($NCHR_2$); 63.3 (COD); 58.8 (OCH_3); 49.1 (OCH_2R); 34.7 (COD); 33.9 (COD); 27.0 (CH_2); 22.3 (CH_2); 17.4 (CH_3). Optical rotation angles (r.t., toluene): $[\alpha]_{589} = +310°$; $[\alpha]_{578} = +342°$; $[\alpha]_{633} = +236°$.

*4.5. [Ru(η^6-(R)-3-phenylbutan-1-ol)(η^4-COD)] (**18**)*

To a suspension of 65 mg $LiAlH_4$ (1.70 mmol) in 50 ml Et_2O a solution of 1.1 g (2.84 mmol) of Ru(methyl-

(*R*)-3-phenylbutyrate)(COD) (**7**) in 10 ml of Et_2O is added dropwise. The yellow solution is stirred for 5 h and then hydrolysed with an excess of $Na_2SO_4 \cdot 12H_2O$. After filtration and removal of the solvents, 1.01 g (80%) [Ru((*R*)-3-η⁶-phenyl-1-butanol)(η⁴-COD)] (**18**) is isolated as a yellow oil.

^{1}H-NMR (C_6D_6, 270 MHz): δ 5.34 (t, 1H, arene); 4.80–4.72 (m, 2H, arene); 3.51–3.35 (m, 6 H, COD_{olef}, CH_2); 2.43–2.17 (m, 8H, COD_{aliph}, + 1H, OH, + 1H, H_{benzyl}); 1.70 (sept, 1H, CH_2); 1.50 (sept, 1H, CH_2); 1.22 (d, 3H, CH_3). ^{13}C-NMR (C_6D_6, 100.4 Mhz): δ 114.3 (arene); 89.4 (arene); 85.6 (arene); 84.7 (arene); 84.0 (arene); 82.8 (arene); 61.4 (COD_{olef}); 61.1 (COD_{olef}); 60.6 (CH_2O); 41.5 (CH_2); 34.6 (COD_{aliph}); 34.1 (COD_{aliph}); 33.9 (CH_{benzyl}); 21.3 (CH_3). FDMS (2 kV); *m*/*z*: 359 $[M]^+$, $C_{18}H_{26}Oru$. Optical rotation angles (r.t., toluene): $[\alpha]_{589} = -64°$; $[\alpha]_{578} = -16°$; $[\alpha]_{633} = -24°$.

4.6. [Ru(1-η⁶-*o*-tolyl-propane-1,3-diol)(η⁴-COD)] (**19**)

To a suspension of 13 mg (0.332 mmol) $LiAlH_4$ in 50 ml Et_2O a solution of 236 mg (0.44 mmol) [Ru(3-η⁶-*o*-tolyl-3-hydroxymenthylpropionate)(η⁴-COD)] (**13**) in 5 ml Et_2O is added. The yellow solution is stirred for 3 h. The mixture is hydrolyzed with degassed water and after stirring for 30 min the solvents are evaporated under reduced pressure. Redissolution with light petroleum ether–toluene (2:1) and chromatography on SiO_2 (deactivated with 5% H_2O) with THF–toluene (1:1) as eluent afforded 127 mg (76%) of pure yellow [Ru(1-η⁶-*o*-tolyl-propane-1,3-diol)(η⁴-COD)] (**19**). ^{1}H-NMR (C_6D_6, 270 MHz): δ 5.73 (t, 1H, arene); 5.18 (d, 1H, arene); 4.68 (dd, 1H, OH); 4.51 (d, 1H, arene); 4.29 (1H, arene); 3.88–3.75 (m, 1H, alkyl); 3.73–3.65 (m, 1H, alkyl); 3.44–3.20 (m, 2H, COD_{olef}); 3.17–3.09 (m, 2H, COD_{olef}); 2.81 (broad, 1H, OH); 2.35–2.12 (m, 8H, COD_{aliph}); 1.85–1.79 (m, 1H, alkyl); 1.75–1.60 (m, 1H, alkyl); 1.48 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 67.7 MHz): δ 109. 8 (arene); 96.5 (arene); 89.4 (arene); 86.5 (arene); 85.1 (arene); 84.0 (arene); 67.5 (C–OH); 62.2 (COD_{olef}); 60.8 (C–OH); 60.4 (COD_{aliph}); 39.8 (CH_2); 15.8 (CH_3). FDMS (2 kV); *m*/*z*: 375 $[M^+]$ (100%). Anal. Found: C, 57.72; H, 6.75. Calc. for $C_{18}H_{26}O_2Ru$: C, 57.60; H, 7.00%.

4.7. [Ru(η⁶-*N*,*N*-diethyl-2-phenylethylamine)(η⁴-COD)] (**20**)

To a suspension of 7 mg (0.15 mmol) $LiAlH_4$ in 35 ml THF a solution of 100 mg (0.24 mmol) [Ru(η⁶-*N*,*N*,-diethyl-2-phenyl acetamide)(η⁴-COD)] **8** in 5 ml THF is added. The yellow solution is refluxed for 2 h and then stirred over night. Hydrolysis and filtration through Al_2O_3 (activity III) with toluene–THF (1:1) as eluent resulted in 62 mg (67%) [Ru(η⁶-*N*,*N*-diethyl-2-phenylethylamine)(η⁴-COD)] (**20**) as a yellow oil.

^{1}H-NMR (C_6D_6, 270 MHz): δ 4.99 (t, 1H, arene, $^3J_{H-H} = 6.0$ Hz); 4.75–4.68 (m, 4H, arene); 3.44 (s, 4H, COD_{olef}); 2.69–2.22 (m, 8H, COD_{aliph} + 8H, CH_2); 0.91 (t, 6H, CH_3). ^{13}C-NMR (C_6D_6, 67.7 MHz): δ 106.6 (aren); 89.4 (aren); 88.0 (aren); 86.4 (aren); 62.7 (COD_{olef}); 56.3 ($CH_{2\text{-benzyl}}$); 48.6 (CH_2); 35.7 (COD_{aliph}); 33.3 (CH_2); 31.7 (CH_2); 13.9 (CH_3). FDMS (2 kV); *m*/*z*: 386 $[M^+]$ (100%), $C_{20}H_{31}NRu$.

4.8. [Ru(1-η⁶-*o*-methylphenyl-2-phenyl-ethene)-(η⁴-1,5-COD)] (**21a**, **21b**)

A solution of 0.32 ml (0.8 mmol) *n*-butyllithium (2.5 M in hexane) is added dropwise to a stirred suspension of 346 mg (0.8 mmol) benzyltriphenylphosphoniumbromide in THF at − 20 °C. After 5 min a THF solution of 165 mg (0.5 mmol) [Ru(η⁶-*o*-tolylaldehyde)(η⁴-1,5-COD)] (**4**) is added to the dark-red reaction mixture. The cooling bath is removed and the mixture is warmed to r.t. over a period of 2 h. The solution is evaporated to dryness, redissolved in 20 ml of toluene and 10 ml of water is added. After 20 min of stirring, the toluene phase is collected with a syringe, dried over $MgSO_4$ and filtered through Al_2O_3. The alumina is extracted by light petroleum ether–toluene 10:1. The combined organic phases afford 190 mg of a mixture of **21a** and **21b**. The mixture is dissolved in *n*-hexane and within a few days at − 30 °C orange crystals are obtained. Chromatography on Al_2O_3 (activity III, eluent light petroleum ether–toluene 10:1) gave 96 mg [Ru(*E*-1-η⁶-*o*-methylphenyl-2-phenyl-ethene)(η⁴-COD)] (**21**).

4.8.1.1. E-isomer ***21a***. ^{1}H-NMR (C_6D_6, 399.65 MHz): δ 7.32 (m, 2H, H_{phenyl}); 7.08 (m, 3H, H_{phenyl}); 7.00 (d, 1H, $H_{olef.}$, $^3J_{H-H} = 16$ Hz); 6.71 (d, 1H, $H_{olef.}$, $^3J_{H-H} = 16$ Hz); 5.14 (t, $1H_{arene}$, $^3J_{H-H} = 5.6$ Hz); 5.05 (t, $1H_{arene}$, $^3J_{H-H} = 5.6$ Hz); 4.86 (d, $1H_{arene}$, $^3J_{H-H} = 5.6$); 4.40 (d, $1H_{arene}$, $^3J_{H-H} = 5.6$ Hz); 3.35 (m, 4H, COD_{olef}); 2.32 (m, 8H, $COD_{aliph.}$); 1.90 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 100.40 MHz): δ 137.9 (phenyl); 130.1 (phenyl); 129.0 (phenyl); 126.7 (phenyl); 124.9 (phenyl); 101.4 (arene); 98.6 (arene); 89.8 (arene); 85.9 (arene); 85.7 (arene); 80.1 (arene); 64.6 (COD_{olef}); 64.0 (COD_{olef}); 34.6 (COD_{aliph}); 34.0 (COD_{aliph}); 17.4 (CH_3). EIMS (70 eV); *m*/*z*: 404 $[M]^+$ (100%).

4.8.1.2. Z-isomer ***21b***. ^{1}H-NMR (C_6D_6, 399.65 MHz): δ 7.00 (m, $5H_{phenyl}$); 6.46 (d, 1H, $H_{olef.}$, $^3J_{H-H} = 12$ Hz); 6.27 (d, 1H, $H_{olef.}$, $^3J_{H-H} = 12$ Hz); 4.92 (t, $1H_{arene}$ $^3J_{H-H} = 5.2$ Hz); 4.81 (t, $1H_{arene}$, $^3J_{H-H} = 5.2$ Hz); 4.68 (d, $1H_{arene}$, $^3J_{H-H} = 5.2$ Hz); 4.44 (d, $1H_{arene}$, $^3J_{H-H} = 5.2$ Hz); 3.35 (m, 4H, COD_{olef}); 2.32 (m, 8H, $COD_{aliph.}$); 1.82 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 100.40 MHz): δ 137.9 (phenyl); 130.1 (phenyl); 129.0 (phenyl); 126.7

Table 1
Crystal data and structure refinement parameters for **7**, **11**, **17a**

	7	**11**	**17a**
Empirical formula	$C_{19}H_{26}O_2Ru$	$C_{25}H_{30}ORu$	$C_{22}H_{32}N_2ORu$
Formula weight	387.47	447.56	441.57
Temperature (K)	200(2)	200(2)	298(2)
Colour, shape	Yellow, block	Red, plate	Orange, block
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions			
a (Å)	6.520(1)	28.651(2)	7.472(3)
b (Å)	12.513(2)	10.364(1)	8.345(2)
c (Å)	20.385(3)	14.039(2)	32.965(11)
α (°)	90.0	90.0	90.0
β (°)	90.0	103.34(1)	90.0
γ (°)	90.0	90.0	90.0
V (Å^3)	1663.1(4)	4056.2(8)	2056(1)
Z	4	8	4
ρ_{calc} (g cm^{-1})	1.547	1.466	1.427
Absorption coefficient, (mm^{-1})	0.948	0.785	0.775
Absorption correction	Empirical [15]	Empirical [15]	None
$F(000)$	800	1856	920
Crystal size (mm)	$0.80 \times 0.50 \times 0.36$	$0.50 \times 0.45 \times 0.20$	$0.38 \times 0.20 \times 0.10$
Reflections measured	5358	11600	
Independent reflections	4417	8844	3726
No. refined parameters	277	668	235
Absolute structure parameters	0.02(4)	–	−0.03(6)
R_1 [$F_o \geq 4\sigma(F)$]	0.0426	0.0404	0.0455
wR_2	0.0775	0.0931	0.0810
Goodness-of-fit at F^2	1.023	0.800	0.817
Largest difference peak and hole (e Å^{-3})	0.707; −0.595	1.402; −0.984	0.409; −0.620

(phenyl); 124.9 (phenyl); 101.1 (arene); 99.9 (arene); 88.1 (arene); 86.7 (arene); 85.5 (arene); 84.4 (arene); 63.7 (COD_{olef}); 34.4 ($COD_{aliph.}$); 34.2 ($C_{CODaliph.}$); 17.3 (s, CH_3). EIMS (70 eV); m/z: 404 $[M]^+$ (100%).

4.9. Crystal structures determination

Suitable crystals of **7**, **11** and **17a** were taken directly out of the mother liquor. Data were collected in a Siemens P4 diffractometer for **7**, **11** and in a Nicolet R3m/V for **17a**, using Mo–K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structures were solved by direct methods and refined on F^2 using full-matrix least-squares procedures (SHELXTL 5.03 [13] or SHELXTL NT 5.10 [14]). Non-hydrogen atoms were refined anisotropically. For **7** and **11** hydrogen atom positions were taken from a difference Fourier synthesis and refined with a fixed common isotropic displacement parameter. For **17a** hydrogen atoms were geometrically positioned with an isotropic displacement parameter tied to those of their carrier atoms by a factor of 1.2 or 1.5. Other experimental details are given in Table 1 [15].

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 163135, 163136 and 163137 for compounds **7**, **11**, **17a**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[15] Absorption correction with XABS2: S. Parkin, B. Moezzi, H. Hope, J. Appl. Crystallogr. 28 (1995) 53 ($T_{min} = 0.0575$, $T_{max} = 0.1527$, $T_{min} = 0.472$, $T_{max} = 0.995$).