

Halogen Atoms as Reactive Centers for the Introduction of Functional Side Chains into (Arene)ruthenium(0) Complexes^[‡]

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Dedicated to Professor Horst Kisch on the occasion of his 60th birthday

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Substitution of the naphthalene ligand of [(COD)(η^6 -naphthalene)Ru] (**2**) (COD = 1,5-cyclooctadiene) by suitable haloarenes (halogen = F, Cl, Br, I) affords several new mono- and dihaloarene(cyclooctadiene)ruthenium complexes. Depending on the number and position of the halogen and organyl substituents, the haloarenes form achiral or planar-chiral π -ligands; [(η^6 -bromoarene)(COD)Ru] complexes are prone to rapid bromine/lithium exchange with *n*BuLi at low temperatures, while the chloro and fluoro derivatives undergo *ortho*-metalation under the same conditions. The lithiated species react readily with chiral or achiral electrophiles such as chlorodiorganophosphanes, carbonyl chlorides, aldehydes, lactones, ketones, and epoxides to yield sub-

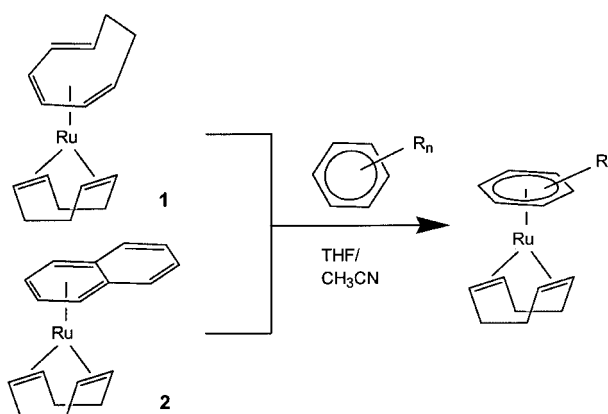
stituted [(η^6 -arene)(COD)Ru] complexes with donor functions in their side chains, inaccessible by other routes. Enantiopure complexes are obtained when achiral lithioarene complexes are combined with chiral electrophiles, but pairs of diastereomers are formed if the lithioarene ligand is a planar-chiral species. Dinuclear ruthenium complexes [1,1-bis{[(COD)(η^6 -phenyl)Ru]-1,4-butanediol} (**28**) and [1,1-bis{[(COD)(η^6 -4-fluorophenyl)Ru]-1,4-butanediol} (**30**) with two (η^6 -aryl)-(COD)Ru units linked by a common 1,4-butanediol side chain are formed through the reactions between the appropriate lithioarene complexes and γ -butyrolactone.

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Introduction

(Arene)ruthenium(0) complexes are useful catalysts for hydrogenation,^[2,3] isomerization,^[4] and dimerization^[5,6] reactions of alkenes. Their (arene)ruthenium(II) counterparts catalyze enantioselective hydrogen transfer to ketones^[7,8] and imines^[9] in the presence of enantiomerically pure chiral β -amino alcohols^[7] or 1,2-diamines,^[8,9] affording high yields and high *ees* at the same time. Thanks to the particular stability of the arene–metal bond,^[10] (arene)ruthenium complexes may be converted from Ru⁰ into Ru^{II} without the loss of the arene ligand, simply by addition of hydrochloric acid.^[2] Only the co-ligands that complete the coordination sphere are exchanged in parallel with the redox process. Of course, it would be very promising to perform the catalytic reactions of (arene)ruthenium complexes in both redox states with enantiopure species whose chirality was connected with the arene ligand. The preparation of [(η^6 -arene)-(COD)Ru] complexes is well known since the work of Bennett, Vitulli, and Pertici,^[3,11,12] who introduced [(COD)(η^6 -

1,3,5-cyclooctatriene)Ru] (**1**) and [(COD)(η^6 -naphthalene)Ru] (**2**) as suitable starting materials (Scheme 1).



Scheme 1. Synthesis of [(η^6 -arene)(COD)Ru] complexes by ligand exchange

However, bulky, polar, or highly substituted arenes cannot be introduced in this way. An alternative route to such complexes utilizes bromine/lithium exchange between [(η^6 -bromoarene)(COD)Ru] complexes and *n*-butyllithium at

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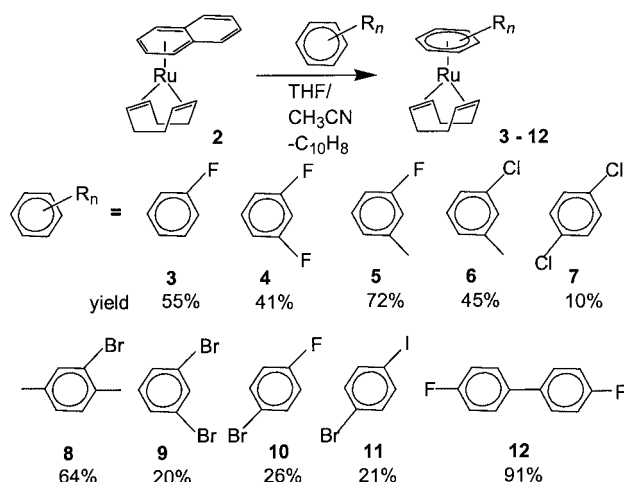
low temperatures.^[13] The lithiated species can be treated with alkyl chloroformates to form ester-substituted $[(\eta^6\text{-arene})(\text{COD})\text{Ru}]$ compounds. Through the introduction of chiral alkyl chloroformates [alkyl = (–)-menthyl], this directly affords enantiopure asymmetric complexes. To develop the high potential of this approach, we investigated the preparation and reactivity of (mono- and dihaloarene)ruthenium(o) complexes systematically. These allow the introduction of many electrophiles of choice. Examples are provided for chlorodiorganophosphanes, carbonyl chlorides, aldehydes, lactones, ketones, and epoxides. Novel (arene)ruthenium(o) complexes with donor functions such as PR_2 and OH in the side chain are of interest, as these functions should offer the potential to control the reactivity of the different types of (arene)ruthenium catalysts.

Results and Discussion

Preparation of $[(\text{COD})(\eta^6\text{-haloarene})\text{Ru}]$ Complexes

Mono- or dihaloarenes (fluorobenzene, 1,3-difluorobenzene, 3-fluorotoluene, 3-chlorotoluene, 1,4-dichlorobenzene, 2-bromo-1,4-xylene, 1,3-dibromobenzene, 1-bromo-4-fluorobenzene, 1-bromo-4-iodobenzene, and 4,4'-difluoro-1,1'-biphenyl) replace the naphthalene ligand of $[(\text{COD})(\eta^6\text{-naphthalene})\text{Ru}]$ (**2**) in the presence of acetonitrile at room temperature in moderate to excellent yield (Scheme 2). The reaction fails with the triply substituted arenes 3,5-dibromotoluene, 1,2,3- and 1,3,5-tribromobenzene, and 1,2,3-trichlorobenzene.

Two different tendencies are exemplified by the experimental results. If one halogen atom of an incoming arene ligand is accompanied by one or two organyl substituents, the yield increases, but it is reduced with a second halogen atom. So far, no trihalobenzenes have been coordinated successfully. The only dihalobenzene that gives yields of more than 50% is 1,4-dibromobenzene;^[13] in all other cases it is between 10 and 21%. As the minimum yield is obtained with 1,4-dichlorobenzene, there must be more than one reason for the diminishing effect, but electronegativity is most probably one of them. The electron-donating effects of the alkyl substituents favor π -complexation directly. As a consequence, even multiply alkyl-substituted arenes can be introduced. Not only 1,2,4-trimethylbenzene, but also 1,2,3,4-tetramethylbenzene, are prone to this type of reaction.^[3] Two of the (dihalobenzene)ruthenium complexes have been characterized by X-ray diffraction: $[(\eta^6\text{-1-bromo-4-fluorobenzene})(\text{COD})\text{Ru}]$ (**10**) and $[(\eta^6\text{-1-bromo-4-iodobenzene})(\text{COD})\text{Ru}]$ (**11**) (Figure 1). Thanks to the pronounced chemical differences between their halogen atoms, **10** and **11** are both suitable for stepwise substitution reactions.



Scheme 2. Preparation of $[(\text{COD})(\eta^6\text{-haloarene})\text{Ru}]$ complexes

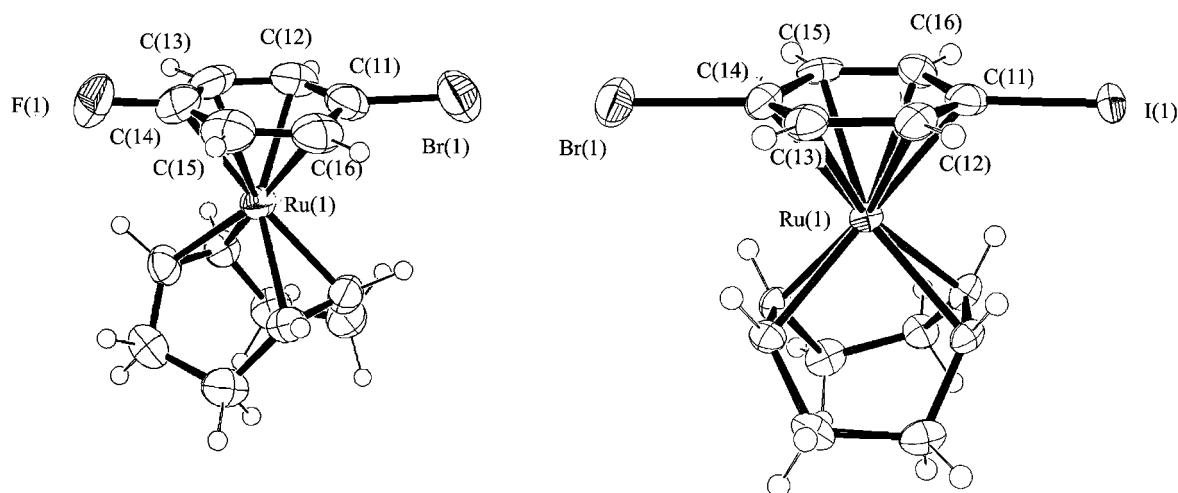
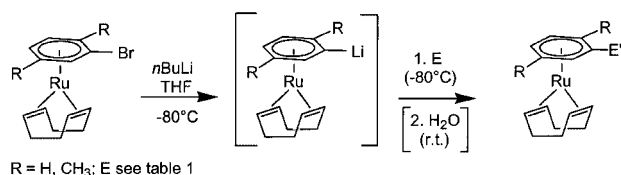


Figure 1. Molecular structures of **10** (left) and **11** (right) in the solid state; selected bond lengths [pm] for **10**: Ru(1)–C(11) 225.4(6), Ru(1)–C(12) 219.6(7), Ru(1)–C(13) 226.4(7), Ru(1)–C(14) 224.2(7), Ru(1)–C(15) 220.4(7), Ru(1)–C(16) 224.6(7); selected bond lengths [pm] for **11**: Ru(1)–C(11) 217.1(9), Ru(1)–C(12) 226.8(9), Ru(1)–C(13) 226.5(9), Ru(1)–C(14) 219.4(9), Ru(1)–C(15) 227.8(9), Ru(1)–C(16) 226.4(9)

The coordinated arene ring is boat-like and distorted in both cases, as two *para*-positioned ring carbon atoms are situated significantly closer to the central metal atom than the other four. In the case of **10** the average value is 220 pm for Ru(1)–C(12) and Ru(1)–C(15), but 225 pm for the other Ru–C_{ring} distances. The corresponding values for **11** are 218 pm for Ru(1)–C(11)/(14) versus 226 pm. This deviation from planarity is a known effect in [(η^6 -arene)(CO)₂Du] complexes.^[13,14] Its observation, undisturbed in the case of [(COD)(η^6 -1,4-dihalobenzene)Ru] complexes, provides evidence for the interligand influence of COD and arene ligands even in the case of electronegative 1,4-disubstitution of the arene.

Electrophilic Substitution of [(η^6 -bromoarene)(COD)Ru] Complexes

Metalation and subsequent reactions of organometallic compounds are standard derivatization methods.^[15] The electrophilic substitution of [(η^6 -bromoarene)(COD)Ru] complexes is initiated by a rapid bromine/lithium exchange at low temperatures. Examples are given for [(η^6 -2-bromo-



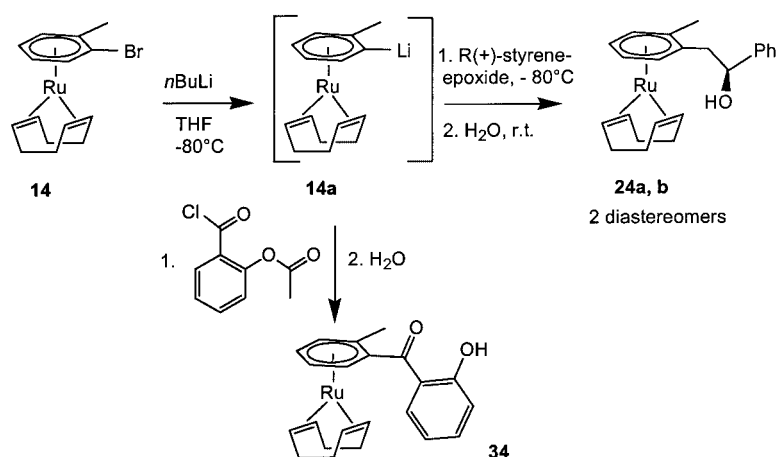
Scheme 3. Electrophilic substitution reaction of [(η^6 -bromoarene)-(COD)Ru] complexes

1,4-xylene)(COD)Ru] (**8**), [(η^6 -1-bromo-4-fluorobenzene)-(COD)Ru] (**10**), [(η^6 -bromobenzene)(COD)Ru] (**13**), [(η^6 -2-bromotoluene)(COD)Ru] (**14**),^[13] and *n*-butyllithium as the metalation agent. In all cases, the bromine/lithium exchange is accomplished within a few minutes in THF as the solvent at –80 °C, and the electrophiles are added at the same temperature immediately after its completion. In the case of OH-group formation, the reaction sequence finishes with a hydrolysis. We tested this type of reaction with chlorodiorganophosphanes, carbonyl chlorides, ketones, epoxides, aldehydes, and lactones as electrophiles. (Scheme 3, Table 1)

The reaction sequence proceeds very well, and so the introduction of side chains with phosphanyl, ester, oxo, and hydroxy groups, including phenolic hydroxy functions, is a favorable preparative route. The mononuclear and dinuclear complexes **15**–**34** are accessible in this way. We had previously attempted the direct preparation of some related complexes by ligand exchange as an alternative and straightforward approach and had failed in several interesting cases. Acidic hydrogen atoms, phosphanyl groups, and bulky substituents on incoming arene ligands block the arene ligand exchange reaction of ruthenium(o).^[1] Neither the NMR spectra, nor other experimental observations point to direct interactions between the donor centers of the side chains and the ruthenium atoms in **15**–**34**. As [(η^6 -arene)(COD)-Ru] complexes are closed-shell 18-valence electron species, there is no driving force for such an effect. The potential interaction will come into play when an electron-deficient situation is created for the ruthenium atom by oxidation or COD ligand displacement, through a catalytic application of the complexes.^[16]

Table 1. Products of electrophilic substitution of [(η^6 -bromoarene)(COD)Ru] complexes

Starting material	Electrophile E	Product	Yield (%)
13	CIP(<i>i</i> Pr) ₂	[(COD)(diisopropyl- η^6 -phenylphosphane)Ru] (15)	83
14	CIP(<i>i</i> Pr) ₂	[(COD)(diisopropyl- η^6 -2-tolylphosphane)Ru] (16)	86
13	CIP(<i>t</i> Bu) ₂	[(COD)(di- <i>tert</i> -butyl- η^6 -phenylphosphane)Ru] (17)	78
14	CIPPh ₂	[(COD)(diphenyl- η^6 -2-tolylphosphane)Ru] (18)	73
14	acetyl chloride	[(COD)(η^6 -2-methylacetophenone)Ru] (19)	90
13	pivalyl chloride	[(COD)(<i>tert</i> -butyl η^6 -phenyl ketone)Ru] (20)	94
14	pivalyl chloride	[(COD)(<i>tert</i> -butyl η^6 -2-tolyl ketone)Ru] (21)	91
13	ClCOPh <i>t</i> Bu	[(COD)(4- <i>tert</i> -butylphenyl η^6 -phenyl ketone)Ru] (22)	67
13	(1 <i>S</i>)-(–)-camphanic chloride	(–)-[(COD)(camphanoyl η^6 -phenyl ketone)Ru] (23)	43
14	(<i>R</i>)-(+)-styrene epoxide	[(COD){1-phenyl-2-(η^6 -2-tolyl)ethanol}Ru] (24a , 24b)	31
13	acetone	[(COD){dimethyl(η^6 -phenyl)methanol}Ru] (25)	65
13	cyclohexanone	[(COD)(η^6 -phenylcyclohexanol)Ru] (26)	69
13	γ -butyrolactone	[(COD)(3-hydroxypropyl η^6 -phenyl ketone)Ru] (27)	21
		[1,1-bis-[(COD)(η^6 -phenyl)Ru]-1,4-butanediol] (28)	45
10	γ -butyrolactone	[(COD)(η^6 -4-fluorophenyl 3-hydroxypropyl ketone)Ru] (29)	40
		[1,1-bis-[(COD)(η^6 -4-fluorophenyl)Ru]-1,4-butanediol] (30)	16
14	γ -butyrolactone	[(COD)(3-hydroxypropyl η^6 -2-tolyl ketone)Ru] (31)	44
13	1,2- <i>O</i> isopropylidene-3- <i>O</i> -methyl- α -D-xylopentodialdofuranose-(1,4)	[(COD){(6-methoxy-2,2-dimethyltetrahydrofuro[2,3- <i>d</i>]-[1,3]dioxol-5-yl)(η^6 -phenyl)methanol}Ru] (32a , 32b)	48
8	(–)-menthyl chloroformate	[(COD)(menthyl η^6 -1,4-xylene-2-carboxylate)Ru] (33a , 33b)	42
14	<i>o</i> -acetylsalicyl chloride	[(COD)(<i>o</i> -hydroxyphenyl η^6 -2-tolyl ketone)Ru] (34)	60

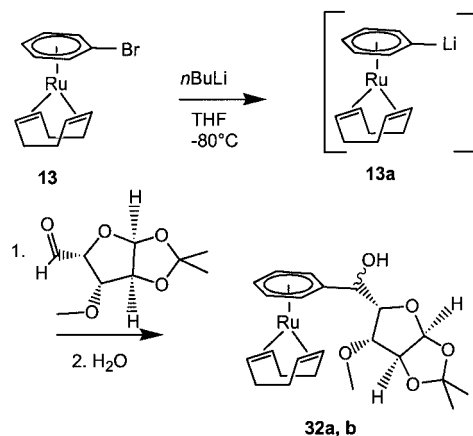
Scheme 4. Electrophilic substitution reactions of $[(\eta^6\text{-2-bromotoluene})(\text{COD})\text{Ru}]$ (**14**)

$[(\eta^6\text{-bromobenzene})(\text{COD})\text{Ru}]$ (**13**) is an achiral starting material and the same is true for its lithium exchange product $[(\eta^6\text{-lithiobenzene})(\text{COD})\text{Ru}]$ (**13a**). Treatment with optically pure $(1S)$ -(-)-camphanoyl chloride therefore directly affords enantiopure $(-)$ - $[(\text{COD})(\text{camphanoyl } \eta^6\text{-phenyl ketone})\text{Ru}]$ (**23**). The electrophilic substitution reaction does not affect the stereogenic centers of the incoming electrophile. Because of the planar chirality of their arene ligands, **8** and **14** consist of racemic mixtures of asymmetric compounds, and so a subsequent reaction with enantiopure electrophiles produces pairs of diastereomers. An example is the combination of **14** with (R) -(+)-styrene epoxide. The two C_1 -symmetric diastereomers **24a** and **24b** are formed in this way (Scheme 4).

Diastereomers **32a** and **32b** are also obtained by treatment of achiral **13** with 2-*O* isopropylidene-3-*O*-methyl- α -D-xylopentodialdofuranose-(1,4), as the transformation of its aldehyde function into a secondary benzyl alcohol by addition to the (arene)ruthenium fragment is not diastereoselective (Scheme 5).

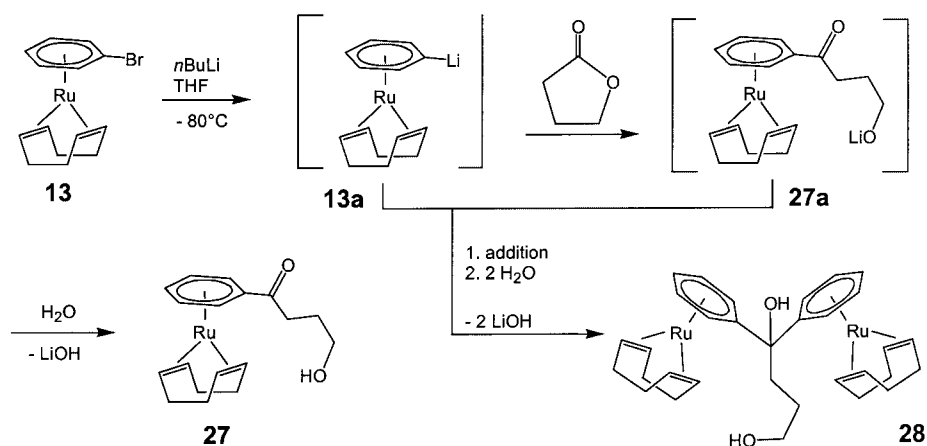
To our surprise, electrophilic substitution of **14** with *o*-acetylsalicyloyl chloride causes a spontaneous cleavage of the ester group, which was replaced by a phenolic OH group in the end product. Lithiated **14a** thus yields $[(3\text{-hydroxyphenyl } \eta^6\text{-2-tolyl ketone})(\text{COD})\text{Ru}]$ (**34**) as the only isolable product. (Scheme 4) Complex **34** was our target product from the beginning, as it contains an OH group at a suitable distance from the metal atom, but the experimental finding represents a nice shortcut in the right direction. As in the case of the (bromoarene)ruthenium complexes, the handling of the novel compounds **15** to **34** causes no problems. All are stable in the solid state, show no sign of hydrolysis, and are only slightly air-sensitive in solution.

Another surprising result occurred when the bromine/lithium exchange product **13a** of bromobenzene complex **13**

Scheme 5. Preparation of diastereomeric furanose-substituted complexes **32a** and **32b**

was treated with γ -butyrolactone. Not only was the designed ring-opening/addition product $[(\text{COD})(3\text{-hydroxypropyl } \eta^6\text{-phenyl ketone})\text{Ru}]$ (**27**) formed (in moderate yield), but dinuclear $[1,1\text{-bis}\{(\text{COD})(\eta^6\text{-phenyl})\text{Ru}\}\text{-1,4-butanediol}]$ (**28**) was isolated as the main product. The results obtained from the combination of the 1-bromo-4-fluorobenzene complex **10** and γ -butyrolactone are very similar, except that the yield of mononuclear product $[(\text{COD})(\eta^6\text{-4-fluorophenyl } 3\text{-hydroxypropyl ketone})\text{Ru}]$ (**29**) exceeds that of dinuclear $[1,1\text{-bis}\{(\text{COD})(\eta^6\text{-4-fluorophenyl})\text{Ru}\}\text{-1,4-butanediol}]$ (**30**).

The first addition intermediate **27a**, most probably due to a high ketone reactivity,^[1] couples with its lithiobenzene precursor complex **13a** to form a 1,4-butanediolate interme-

Scheme 6. Formation of dinuclear (arene)ruthenium complex **28**

diolate. Both branches of the reaction sequence are terminated by hydrolysis, the lithium ions being replaced by hydrogen atoms. (Scheme 6)

This route represents a new and effective pathway to benzyl carbon atom linked (bisarene)diruthenium complexes. A special property is the bifunctionalization of the common 1,4-butanediol side chain. Both dinuclear complexes **28** and **30** have been characterized by X-ray diffraction: their molecular structures are depicted in Figure 2.

The X-ray results are in full accordance with the analytical and spectroscopic findings on the complexes, which confirm their dinuclear nature, the introduction of only one

side chain per $\{(\eta^6\text{-aryl})(\text{COD})\text{Ru}\}_2$ unit, and the absence of ketone functions. The molecular structures of **28** and **30** in the solid state represent different rotamers. This applies to the relative orientation of the $(\eta^6\text{-aryl})(\text{COD})\text{Ru}$ complex units as well as for the 1,4-butanediol chains. In the case of **28** the two (COD)Ru fragments are located opposite to the C116–C117–C214 bond angle of the bridging benzyl carbon atom C117. Its reduction to 106.3° is a consequence of that arrangement. In contrast to that, the (COD)Ru(2) fragment of **30** interacts directly with the arene ligand of Ru(1) and the corresponding C116–C117–C216 benzyl carbon bond angle of **30** is increased significantly. The

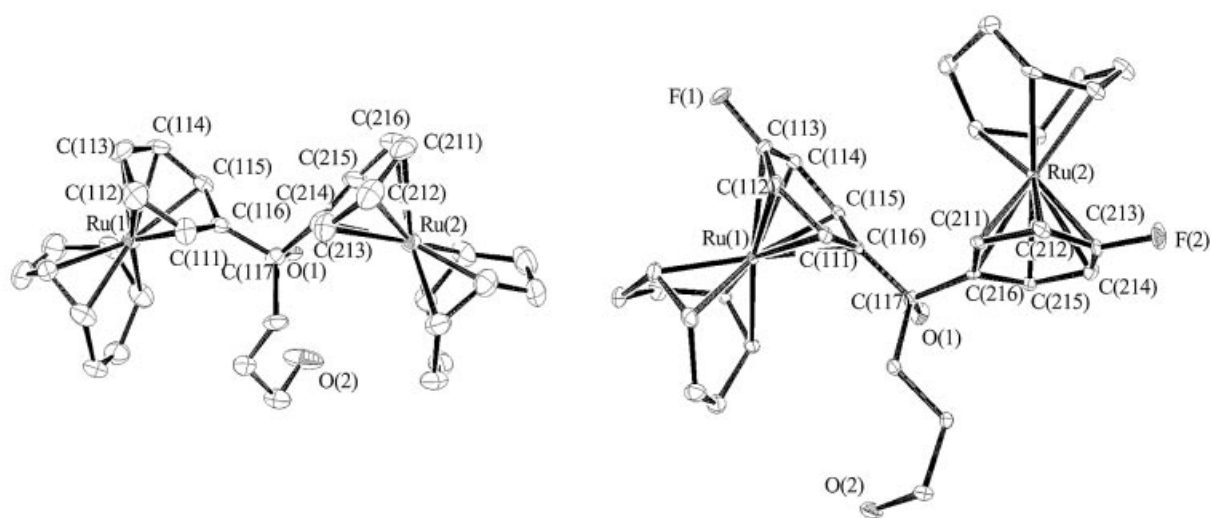


Figure 2. Molecular structures of [1,1-bis $\{(\text{COD})(\eta^6\text{-phenyl})\text{Ru}\}$ -1,4-butanediol] (**28**, left) and [1,1-bis $\{(\text{COD})(\eta^6\text{-4-fluorophenyl})\text{Ru}\}$ -1,4-butanediol] (**30**, right) in the solid state; hydrogen atoms have been omitted for clarity; selected bond lengths [ppm] of **28**: Ru(1)–C(111) 227.6(7), Ru(1)–C(112) 220.0(8), Ru(1)–C(113) 225.9(7), Ru(1)–C(114) 225.3(7), Ru(1)–C(115) 222.0(6), Ru(1)–C(116) 231.1(6); bond angle $^\circ$: C(116)–C(117)–C(214) = $106.3(5)$; selected bond lengths [ppm] of **30**: Ru(1)–C(111) 223.7(3), Ru(1)–C(112) 219.3(3), Ru(1)–C(113) 225.9(2), Ru(1)–C(114) 228.0(3), Ru(1)–C(115) 220.7(3), Ru(1)–C(116) 229.4(2); bond angle $^\circ$: C(116)–C(117)–C(216) = $112.19(19)$

Ru–C_{aryl} bond lengths of both species cover a range from 220 to 231 pm. As in the case of the dihaloarene complexes, the arene ligands are slightly boat-like distorted.

The molecular packing of the dinuclear complexes in the solid state is dominated by the formation of infinite zigzag chains of the 1,4-butanediol substituents by intermolecular O–H–O bridges. (Figure 3).

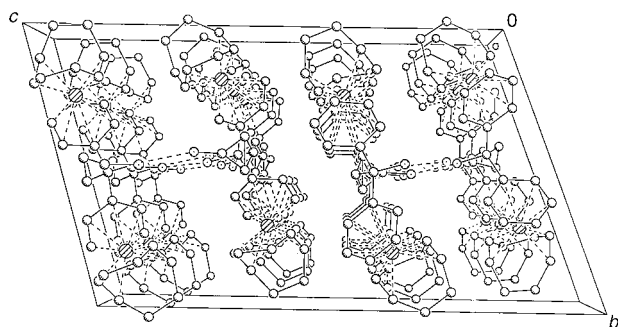


Figure 3. Molecular packing of **28** in the solid state; O–H–O bridges are indicated by the dotted lines between the stacks

Interestingly, a single *o*-methyl group is a steric protector sufficiently powerful to disfavor the formation of dinuclear 1,4-butanediol complexes in the γ -butyrolactone reactions almost completely. 2-Bromotoluene complex **14** therefore forms [(COD)(3-hydroxypropyl η^6 -2-tolyl ketone)Ru] (**31**) as the isolable main product. A dinuclear analogue to **28** and **30** can only be detected by mass spectrometry, as a small side product.

Electrophilic Substitution through *ortho*-Metalation of (Chloro- and fluoroarene)ruthenium Complexes

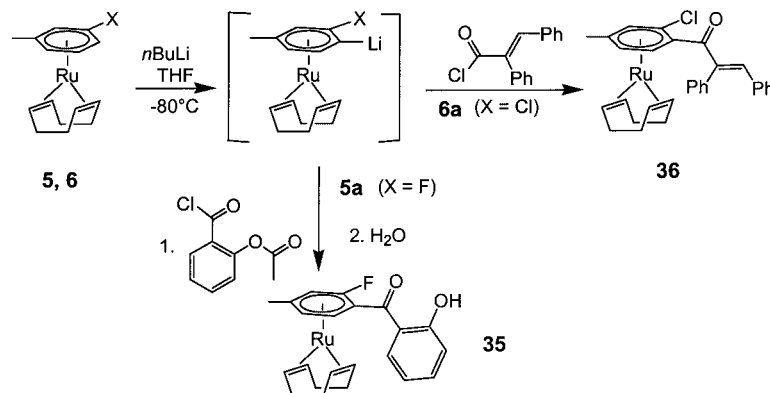
(Chloro- and fluoroarene)metal complexes follow a different reaction pathway when they are attacked by organolithium agents. The main route is no longer halogen/lithium

exchange, but *ortho*-metalation is observed instead.^[17] This type of reactivity was tested by treatment of *n*BuLi with [(COD)(η^6 -3-fluorotoluene)Ru] (**5**) and [(η^6 -3-chlorotoluene)(COD)Ru] (**6**). *o*-Acetylsalicyl chloride was treated with metalated fluoro derivative **5a**, and α -phenylcinnamoyl chloride with the corresponding chloro complex **6a**. (Scheme 7)

As in the case of the bromine/lithium exchange products, the *ortho*-metalation intermediates **5a** and **6a** allow effective introduction of electrophiles. The metalation takes place selectively at the less sterically hindered *o*-position with respect to the halogen substituent. As the chlorine and fluorine atoms remain in the complexes they might be usable a second time for subsequent modification of complexes **35** and **36**. In analogy to phenol complex **34**, the ester function of *o*-acetylsalicyl chloride is again split spontaneously in the reaction and the target phenolic side chain OH group is formed directly.

Conclusions

[(COD)(η^6 -haloarene)Ru] complexes are easily accessible by arene ligand substitution of [(COD)(η^6 -naphthalene)Ru] (**2**) by suitable mono- and dihaloarenes. The reaction works with F, Cl, Br, and I as arene ring substituents, and the incoming haloarene may have one or two halogen atoms and a maximum number of three substituents. Depending on the number and position of the halogen atom(s) and organyl substituent(s), the haloarenes form achiral or planar-chiral π -ligands. [(COD)(η^6 -haloarene)Ru] complexes are valuable starting materials for the introduction of arene ligand side chains with functional groups that would otherwise block the π -complexation of arene ligands to Ru⁰ or Ru^{II}. The bromine atom of [(η^6 -bromoarene)(COD)Ru] complexes is rapidly exchanged for a lithium atom when they are treated with *n*BuLi at low temperatures, but the chloro and fluoro derivatives undergo *ortho*-metalation under the same conditions. The re-



Scheme 7. Electrophilic substitution reaction by *ortho*-metalation

sulting lithioarene species react effectively with a great variety of chiral or achiral electrophiles to yield substituted $[(\eta^6\text{-arene})(\text{COD})\text{Ru}]$ complexes with donor functions such as OH or PR_2 groups in the side chains. Enantiopure complexes are obtained when achiral lithioarene complexes are combined with chiral electrophiles, but pairs of diastereomers are formed if the lithioarene ligand is a planar chiral species. Because of the high reactivity of the primary products, the combination of sterically unhindered lithioarene complexes and γ -butyrolactone results in the formation of dinuclear $[1,1\text{-bis}\{(\eta^6\text{-aryl})(\text{COD})\text{Ru}\}\text{-1,4-butanediol}]$ complexes, each with two $[(\eta^6\text{-aryl})(\text{COD})\text{Ru}]$ units linked by a common 1,4-butanediol side chain.

The new reaction sequences allow a completely new means of ligand design for (arene)ruthenium catalysts of interest, the selectivity and reactivity of which may now be controlled by highly variable side chains with σ -ligand properties of choice. This point is currently under investigation. In a subsequent paper we will report on the oxidation of some of the $(\eta^6\text{-arene})\text{Ru}^0$ complexes with the donor side chains reported here to form corresponding $(\eta^6\text{-arene})\text{Ru}^{\text{II}}$ species, the tethering of the donor function to the metal atom, and first insights into their potential as hydrogen-transfer catalysts.^[16]

Experimental Section

General: All reactions were carried out under dry, oxygen-free nitrogen. Solvents were purified by conventional methods, distilled, and stored under nitrogen. NMR spectra were recorded at close to room temperature with Jeol JNM-PMX 60, FT-JNM-EX 270, and FT-JNM-GX 270 spectrometers, with dimethylpolysiloxane and the solvent signals as internal standards. Mass spectra were recorded with a Varian MAT 212 spectrometer. Microanalyses were performed at the analytical department of the institute, on Carlo Erba Elemental Analyzers Mod. 1106 and Mod. 1108, for crystalline products only. Column chromatography (15×1 cm) was accomplished on neutral degassed alumina (Merck), deactivated with 5% degassed water. The starting materials $[(\text{COD})(\eta^6\text{-naphthalene})\text{Ru}]$ (**2**),^[12] $[(\eta^6\text{-bromobenzene})(\text{COD})\text{Ru}]$ (**13**),^[13] and $[(\eta^6\text{-2-bromotoluene})(\text{COD})\text{Ru}]$ (**14**)^[13] were prepared as reported in the literature.

Preparation of $[(\text{COD})(\eta^6\text{-haloarene})\text{Ru}]$ Complexes (General Procedure): $[(\text{COD})(\eta^6\text{-naphthalene})\text{Ru}]$ (**2**) and an excess of the haloarene were dissolved in THF and acetonitrile. After the mixture had been stirred at room temperature (room temp.) for 3 d, all volatile components were removed in vacuo at 45 °C. Filtering of the obtained oils through alumina/5% H_2O and recrystallization (if possible) yielded the products.

Bromine/Lithium Exchange and Electrophilic Substitution Reactions of $[(\eta^6\text{-Bromoarene})(\text{COD})\text{Ru}]$ Complexes (General Procedure): The bromoarene complex was dissolved in THF and cooled to -80 °C, and a solution of *n*-butyllithium in hexane was added by syringe. The reaction mixture was stirred for 10 min and a solution of the electrophile in THF was added at the same temperature. The mixture was then allowed to warm slowly to room temp. over 2 h. In the case of Li alkoxide intermediates, a small portion of degassed water was added by syringe to produce the OH groups. The mixture was stirred for a few minutes and the solvents were removed in vacuo. The residue was extracted with *n*-hexane and tolu-

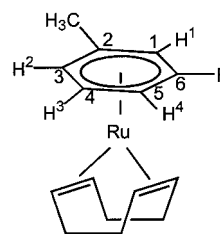
ene and the combined liquids were filtered through $\text{Al}_2\text{O}_3/5\%\text{H}_2\text{O}$. If necessary, the product was purified by column chromatography on $\text{Al}_2\text{O}_3/5\%\text{H}_2\text{O}$ with *n*-hexane as the mobile phase.

σ -Lithiation and Electrophilic Substitution Reactions of $(\eta^6\text{-Chloro- and } \eta^6\text{-fluoroarene})\text{ruthenium Complexes (General Procedure):}$ The chloro- or fluoroarene complex was dissolved in THF and cooled to -80 °C, and a solution of *n*-butyllithium in hexane was added by syringe. After 5 min, a solution of the electrophile in THF was added at the same temperature, and the mixture was allowed to come to room temp. over 2 h. All volatile components were removed in vacuo. The residue was extracted with *n*-hexane and toluene and the product was purified by column chromatography on $\text{Al}_2\text{O}_3/5\%\text{H}_2\text{O}$ with *n*-hexane as the mobile phase.

$[(\text{COD})(\eta^6\text{-fluorobenzene})\text{Ru}]$ (3**):** Reaction mixture: $[(\text{COD})(\eta^6\text{-naphthalene})\text{Ru}]$ (**2**) (1300 mg, 3.84 mmol), fluorobenzene (10 mL, 106.6 mmol) in 20 mL of THF and 1 mL of acetonitrile. Yield 650 mg (2.12 mmol, 55%) of **3**. MS (FD+): $m/z = 306$ [M^+]. ^1H NMR (269.7 MHz, C_6D_6): $\delta = 5.14$ (dd, $^3J\{\text{H}_o\text{H}_m\} = 5.5$, $^3J\{\text{H}_o\text{F}\} = 2.7$ Hz, 2 H, H_o); 4.74 (td, $^3J\{\text{HH}\} = 5$, $^4J\{\text{H}_m\text{F}\} = 2.7$ Hz, 2 H, H_m); 4.20 (td, $^3J\{\text{H}_p\text{H}_m\} = 5$, $^3J\{\text{H}_p\text{F}\} = 3.8$ Hz, 1 H, H_p); 3.60 (m, 4 H, olefin. COD); 2.39 (m, 8 H, aliphatic. COD) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 138.0$ (d, $^1J\{\text{CF}\} = -271$ Hz, *ipso*-C); 86.1 (s, C_p); 81.1 (d, $^4J\{\text{CF}\} = 6$ Hz, C_m); 80.6 (d, $^3J\{\text{CF}\} = 22.4$ Hz, C_o); 61.6 (C olefin. COD); 33.0 (C aliphatic. COD) ppm. $\text{C}_{14}\text{H}_{17}\text{FRu}$ (305.2): calcd. C 55.1, H 5.6; found C 54.6, H 6.3.

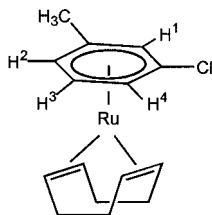
$[(\text{COD})(\eta^6\text{-1,3-difluorobenzene})\text{Ru}]$ (4**):** Reaction mixture: **2** (1300 mg, 3.84 mmol), 1,3-difluorobenzene (10 mL, 101.4 mmol) in 20 mL of THF and 1 mL of acetonitrile. Yield 510 mg (1.57 mmol, 41%) of **4**. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.61$ (s, 1 H, aromat. H); 4.76 (m, 1 H, aromat. H); 4.48 (m, 2 H, aromat. H); 3.57 (m, 4 H, olefin. COD); 2.24 (m, 8 H, aliphatic. COD) ppm. $\text{C}_{14}\text{H}_{16}\text{F}_2\text{Ru}$ (233.2): calcd. C 52.01, H 4.99; found C 52.19, H 5.35.

$[(\text{COD})(\eta^6\text{-3-fluorotoluene})\text{Ru}]$ (5**):** Reaction mixture: **2** (1300 mg, 3.84 mmol), 3-fluorotoluene (10 mL, 90.5 mmol) in 30 mL of THF and 1 mL of acetonitrile. Yield 930 mg (2.76 mmol, 72%) of **5**. MS (FD+): $m/z = 320$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.12$ (s, 1 H, H^1); 5.00 (d, $^3J\{\text{H}^2\text{H}^3\} = 5$ Hz, 1 H, H^2); 4.96 (td, $^3J\{\text{H}^2/4\text{H}^3\} = 5$, $^4J\{\text{H}^3\text{F}\} = 3$ Hz, 1 H, H^3); 4.00 (dd, $^3J\{\text{H}^4\text{H}^3\} = 5$, $^3J\{\text{H}^4\text{F}\} = 4.5$ Hz, 1 H, H^4); 3.38 (m, 4 H, olefin. COD); 2.28 (m, 8 H, aliphatic. COD); 1.57 (s, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 138.0$ (d, $^1J\{\text{CF}\} = -271$ Hz, C^6); 98.0 (d, $^3J\{\text{CF}\} = 6$ Hz, C^4); 87.3 (C^3); 80.6 (d, $^3J\{\text{CF}\} = 6$ Hz, C^2); 77.3 (d, $^2J\{\text{CF}\} = 22$ Hz, $\text{C}^{1/5}$); 76.5 (d, $^2J\{\text{CF}\} = 22$ Hz, $\text{C}^{1/5}$); 63.9, 63.4 (C olefin. COD); 34.5, 33.8 (C aliphatic. COD); 17.9 (C-methyl) ppm. $\text{C}_{15}\text{H}_{19}\text{FRu}$ (319.2): calcd. C 56.4, H 6.0; found C 56.3, H 6.2.



$[(\eta^6\text{-3-Chlorotoluene})(\text{COD})\text{Ru}]$ (6**):** Reaction mixture: **2** (1200 mg, 3.55 mmol), 3-chlorotoluene (10 mL, 84.6 mmol) in 10 mL of THF and 1 mL of acetonitrile. Yield 540 mg (1.61 mmol, 45%) of **6**. MS (FD+): $m/z = 336$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.36$ (s, 1 H, H^1); 5.31 (d, $^3J\{\text{H}^4\text{H}^3\} = 5$ Hz), 1 H, H^4 ; 4.96 (t, $^3J\{\text{H}^2/$

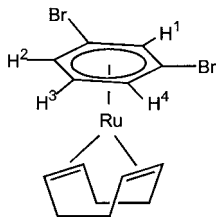
$^4\text{H}^3\} = 5 \text{ Hz}$, 1 H, H^3); 4.03 (d, $^3J\{\text{H}^2\text{H}^3\} = 5 \text{ Hz}$, 1 H, H^2); 3.44 (m, 4 H, olefin. COD); 2.37 (m, 8 H, aliphatic. COD); 1.67 (s, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 125.7$, 101.4, 100.4 (aromat. C), 88.7 (d, C-Cl), 84.7, 83.3 (aromat. C); 65.6, 64.8 (C olefin. COD); 34.2, 33.5 (C aliphatic. COD); 17.9 (C-methyl) ppm.



[(COD)(η^6 -1,4-dichlorobenzene)Ru] (7): Reaction mixture: **2** (180 mg, 0.53 mmol), 1,4-dichlorobenzene (735 mg, 5 mmol) in 10 mL of THF and 1 mL of acetonitrile. Yield 20 mg (0.06 mmol, 10%) of **7**. MS (EI, 70 eV): $m/z = 356 [\text{M}^+]$. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.05$ (s, 4 H, aromat. H); 3.50 (m, 4 H, olefin. COD); 2.30 (m, 8 H, aliphatic. COD) ppm. $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{Ru}$ (356.2): calcd. C 47.2, H 4.52; found C 46.06, H 4.38.

[(η^6 -2-Bromo-1,4-xylene)(COD)Ru] (8): Reaction mixture: **2** (500 mg, 1.5 mmol), 2-bromo-1,4-xylene (5 g, 27 mmol) in 25 mL of THF and 1 mL of acetonitrile. Yield 380 mg (0.96 mmol, 64%) of **8**. MS (FD+): $m/z = 394 [\text{M}^+]$. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.36$ (s, 1 H, aromat. H); 4.34 (d, $^3J = 8 \text{ Hz}$, 1 H, arom-H); 4.04 (d, $^3J = 8 \text{ Hz}$, 1 H, aromat. H); 3.35 (m, 2 H, olefin. COD); 3.03 (m, 2 H, olefin. COD); 2.2–2.4 (m, 8 H, aliphatic. COD); 1.95, 1.60 (s, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.7 MHz, C_6D_6): $\delta = 104.0$, 102.9, 92.4, 90.2, 86.0, 83.6 (aromat. C); 68.5, 66.6 (C olefin. COD); 35.0, 33.6 (C aliphatic. COD); 19.1, 17.8 (CH_3) ppm.

[(COD)(η^6 -1,3-Dibromobenzene)Ru] (9): Reaction mixture: **2** (950 mg, 2.81 mmol), 1,3-dibromobenzene (10 mL, 82.8 mmol) in 50 mL of THF and 1 mL of acetonitrile. Yield 310 mg (0.7 mmol, 20%) of **9**. MS (FD+): $m/z = 444 [\text{M}^+]$. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.91$ (s, 1 H, H^1); 4.77 (t, $^3J\{\text{H}^2\text{H}^3\} = 6 \text{ Hz}$, 1 H, H^3); 4.68 (d, $^3J\{\text{H}^2\text{H}^3\} = 6 \text{ Hz}$, 2 H, H^2); 3.49 (m, 4 H, olefin. COD); 2.26 (m, 8 H, aliphatic. COD) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 93.0$, 89.2, 87.5, 86.3 (aromat. C); 69.8 (C olefin. COD); 34.6, 33.8 (C aliphatic. COD) ppm. $\text{C}_{14}\text{H}_{16}\text{Br}_2\text{Ru}$ (445.1): calcd. C 37.77, H 3.62; found C 38.37, H 3.71.



[(η^6 -1-Bromo-4-fluorobenzene)(COD)Ru] (10): Reaction mixture: **2** (1729 mg, 5.12 mmol), 1-bromo-4-fluorobenzene (10 g, 57 mmol) in 60 mL of THF and 1.5 mL of acetonitrile. Yield 512 mg (1.33 mmol, 26%) of **10**. MS (EI, 70 eV): $m/z = 384 [\text{M}^+]$. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.02$ (m, 2 H, aromat. H); 4.87 (m, 2 H, aromat. H); 3.55 (m, 4 H, olefin. COD); 2.30 (m, 8 H, aliphatic. COD) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.7 MHz, C_6D_6): $\delta = 126.0$, 88.7 (aromat. C), 86.0 (d, CF), 75.9, 75.7 (aromat. C); 67.8 (C olefin. COD); 34.0 (C aliphatic. COD) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, C_6D_6): $\delta = 88.7$ (aromat. C), 86.0 (d, CF), 75.9, 75.6 (aromat. C); 67.9 (C olefin. COD); 34.0 (C aliphatic. COD) ppm. $\text{C}_{14}\text{H}_{16}\text{BrFRu}$ (384.2): calcd. C 43.76, H 4.19; found C 43.29, H 4.01.

[(η^6 -1-Bromo-4-iodobenzene)(COD)Ru] (11): Reaction mixture: **2** (1400 mg, 4.1 mmol), 1-bromo-4-iodobenzene (10 g, 35.3 mmol) in 20 mL of THF and 1 mL of acetonitrile. Yield 420 mg (0.85 mmol, 21%) of **11**. MS (FD+): $m/z = 494 [\text{M}^+]$. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.22$ (d, $^3J = 5 \text{ Hz}$, 2 H, aromat. H); 5.12 (d, $^3J = 5 \text{ Hz}$, 2 H, aromat. H); 3.39 (s, 4 H, olefin. COD); 2.29 (m, 8 H, aliphatic. COD) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 97.0$, 96.2, 92.8, 91.9, 88.7 (aromat. C); 70.3 (C olefin. COD); 34.7 (C aliphatic. COD) ppm. $\text{C}_{14}\text{H}_{16}\text{BrIRu}$ (492.2): calcd. C 34.2, H 3.3; found C 34.4, H 3.1.

[(COD)(η^6 -4,4'-difluoro-1,1'-biphenyl)Ru] (12): Reaction mixture: **2** (960 mg, 2.84 mmol), 4,4'-difluoro-1,1'-biphenyl (2.03 g, 10.7 mmol) in 50 mL of THF and 1.5 mL of acetonitrile. Yield 1035 mg (2.59 mmol, 91%) of **12**. MS (FD+): $m/z = 399 [\text{M}^+]$. ^1H NMR (269.7 MHz, C_6D_6): $\delta = 6.99$ (m, 4 H, free aromat. H); 4.95 (dd, 2 H, coord. aromat. H, CHCF); 4.72 (dd, 2 H, coord. aromat. H); 3.35 (s, 4 H, olefin. COD); 2.28 (m, 8 H, aliphatic. COD) ppm.

[(COD)(diisopropyl- η^6 -phenylphosphane)Ru] (15): Reaction mixture: [(η^6 -bromobenzene)(COD)Ru] (**13**) (150 mg, 0.41 mmol) in 25 mL of Et_2O , *n*-butyllithium (0.24 mL, 0.6 mmol), and chlorodiisopropylphosphane (0.095 mL, 0.6 mmol). Yield 137 mg (0.34 mmol, 83%) of **15**. MS (EI, 70 eV): $m/z = 404 [\text{M}^+]$. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.45$ (t, 1 H, H_p); 4.63 (dd, $^3J\{\text{H}_m\text{H}_m\} = 6$, $^3J\{\text{H}_o\text{P}\} = 5 \text{ Hz}$, 2 H, H); 4.45 (t, 2 H, H_m); 3.67 (s, 4 H, olefin. COD); 2.15–2.40 (m, 8 H, aliphatic. COD), 1.81 (dh, $^2J\{\text{HP}\} = 1.5$, $^3J\{\text{HH}\} = 10.7 \text{ Hz}$, 2 H, CH isoprop.); 1.17 (dd, $^3J\{\text{HP}\} = 9.2$, $^3J\{\text{HH}\} = 6.7 \text{ Hz}$, 6 H, CH_3 isoprop.); 0.95 (dd, $^3J\{\text{HP}\} = 15.6$, $^3J\{\text{HH}\} = 6.7 \text{ Hz}$, 6 H, CH_3 isoprop.) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 98.1$ (d, $^1J\{\text{CP}\} = 29.72 \text{ Hz}$, *C-*ipso**); 89.4 (C^4), 88.3 (d, $^2J\{\text{CP}\} = 17.4 \text{ Hz}$, $\text{C}^{2/6}$); 84.4 (d, $^3J\{\text{CP}\} = 4.9 \text{ Hz}$, $\text{C}^{3/5}$); 62.5 (C olefin. COD); 33.9 (C aliphatic. COD); 22.6 (d, $J\{\text{CP}\} = 14.8 \text{ Hz}$, C isoprop.); 19.9 (d, $J\{\text{CP}\} = 16.6 \text{ Hz}$, C isoprop.); 19.4 (d, $J\{\text{CP}\} = 9 \text{ Hz}$, C isoprop.) ppm. ^{31}P NMR (109.6 MHz, C_6D_6): $\delta = 4.75$ (s) ppm.

[(COD)(diisopropyl- η^6 -2-tolylphosphane)Ru] (16): Reaction mixture: [(η^6 -2-bromotoluene)(COD)Ru] (**14**) (185 mg, 0.48 mmol) in 25 mL of Et_2O , *n*-butyllithium (0.26 mL, 0.65 mmol), and chlorodiisopropylphosphane (0.10 mL, 0.65 mmol). Yield 174 mg (0.42 mmol, 86%) of **16**. MS (EI, 70 eV): $m/z = 417 [\text{M}^+]$. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.51$ (t, $^3J\{\text{H}_p\text{H}_m\} = \{\text{H}_p\text{H}_m\} = 6 \text{ Hz}$, 1 H, H_{pm}); 5.11 (d, $^3J\{\text{H}_m\text{H}_p\} = 6 \text{ Hz}$, 1 H, H_m); 5.10 (dd, $^3J\{\text{H}_o\text{H}_m\} = 6$, $^3J\{\text{H}_o\text{P}\} = 5 \text{ Hz}$, 1 H, H_o); 3.82 (t, $^3J\{\text{H}_m\text{H}_p\} = ^3J\{\text{H}_m\text{H}_o\} = 6 \text{ Hz}$, 1 H, H_{mp}); 3.43 (s, 4 H, H olefin. COD); 2.00–2.40 (m, 10 H, H aliphatic. COD, H isoprop.); 1.75 (s, 3 H, CH_3); 1.57 (dd, $^3J\{\text{HH}\} = 10.7$, $^3J\{\text{HP}\} = 18.8 \text{ Hz}$, 3 H, H isoprop. CH_3); 1.13 (dd, $^3J\{\text{HH}\} = 10.7$, $^3J\{\text{HP}\} = 14.8 \text{ Hz}$, 3 H, H isoprop. CH_3); 0.94 (dd, $^3J\{\text{HH}\} = 10.7$, $^3J\{\text{HP}\} = 14.8 \text{ Hz}$, 3 H, H isoprop. CH_3); 0.86 (dd, $^3J\{\text{HH}\} = 10.7$, $^3J\{\text{HP}\} = 10.3 \text{ Hz}$, 3 H, H isoprop. CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.7 MHz, C_6D_6): $\delta = 98.9$ (d, $^1J\{\text{CP}\} = 32.11 \text{ Hz}$, *C-*ipso**); 96.5 (d, $J\{\text{CP}\} = 26.2 \text{ Hz}$, aromat. C); 92.8 (d, $J\{\text{CP}\} = 2.78 \text{ Hz}$, aromat. C); 91.6 (d, $J\{\text{CP}\} = 2.71 \text{ Hz}$, aromat. C); 87.3, 79.7 (aromat. C); 62.9, 61.7 (C olefin. COD); 34.3; 33.5 (C aliphatic. COD); 25.2 (d, $J\{\text{CP}\} = 17.9 \text{ Hz}$, C isoprop.); 22.3 (d, $J\{\text{CP}\} = 13.7 \text{ Hz}$, C isoprop.); 22.1 (d, $J\{\text{CP}\} = 20.6 \text{ Hz}$, C isoprop.); 20.2 (d, $J\{\text{CP}\} = 15.2 \text{ Hz}$, C isoprop.); 19.8 (d, $J\{\text{CP}\} = 16.6 \text{ Hz}$, C isoprop.); 18.7 (d, $^3J\{\text{CP}\} = 5.6 \text{ Hz}$, CH_3 tolyl.); 18.3 (d, $J\{\text{CP}\} = 22.1 \text{ Hz}$, C isoprop.) ppm. ^{31}P NMR (109.6 MHz, C_6D_6): $\delta = -6.8$ (s).

[(COD)(di-*tert*-butyl- η^6 -phenylphosphane)Ru] (17): Reaction mixture: **13** (170 mg, 0.46 mmol) in 25 mL of Et_2O , *n*-butyllithium (0.24 mL, 0.6 mmol), and di-*tert*-butylchlorophosphane (0.11 mL,

0.6 mmol). Yield 156 mg (0.36 mmol, 78%) of **16**. MS (EI, 70 eV): $m/z = 432$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.55$ (t, $^3J\{\text{H}_p\text{H}_m\} = 6$ Hz, 1 H, H_p); 4.85 (dd, $^3J\{\text{H}_o\text{H}_m\} = 6$, $^3J\{\text{H}_o\text{P}\} = 5$ Hz, 2 H, H_o); 4.40 (t, 2 H, H_m); 3.55 (s, 4 H, H olefin. COD); 2.10–2.40 (m, 8 H, H aliphatic. COD); 1.25 (d, $^3J\{\text{HP}\} = 13.4$ Hz, 18 H, H-*t*Bu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.7 MHz, C_6D_6): $\delta = 100.2$ (d, $^1J\{\text{CP}\} = 13.8$ Hz, C-*ipso*); 91.8 (d, $^2J\{\text{CP}\} = 21.3$ Hz, C^{2/6}); 87.7 (s, C⁴); 85.1 (d, $^3J\{\text{CP}\} = 3.9$ Hz, C^{3/5}); 62.8 (C olefin. COD); 34.0 (C aliphatic. COD); 32.8 (d, $J\{\text{CP}\} = 22.8$ Hz, C-*t*Bu); 31.2 (d, $J\{\text{CP}\} = 13.6$ Hz, C-*t*Bu) ppm. ^{31}P NMR (109.6 MHz, C_6D_6): $\delta = 33.7$ (s) ppm. $\text{C}_{22}\text{H}_{35}\text{PRu}$ (431.6): calcd. C 61.26, H 8.17; found C 61.01, H 8.37.

[(COD)(diphenyl- η^6 -2-tolylphosphane)Ru] (18**):** Reaction mixture: **14** (250 mg, 0.65 mmol) in 20 mL of THF, *n*-butyllithium (0.32 mL, 0.8 mmol), and chlorodiphenylphosphane (0.15 mL, 0.8 mmol). Yield 230 mg (0.474 mmol, 73%) of **18**. MS (EI, 70 eV): $m/z = 486$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 7.7$ (dt, $^3J\{\text{HH}\} = 12$, $^3J\{\text{HP}\} = 5$ Hz, 2 H, aromat. H); 7.45 (dt, $^3J\{\text{HH}\} = 12$, $^3J\{\text{HP}\} = 13.7$ Hz, 2 H, aromat. H); 7.17–7.0 (m, 6 H, aromat. H). 5.47 (t, $^3J\{\text{H}_p\text{H}_m\} = ^3J\{\text{H}_p\text{H}_{m'}\} = 6$ Hz, 1 H, $\text{H}_{p/m}$); 4.73 (dd, $^3J\{\text{H}_o\text{H}_m\} = 6$, $^3J\{\text{H}_o\text{P}\} = 5$ Hz, 1 H, H_o); 4.65 (d, $^3J\{\text{H}_m\text{H}_p\} = 6$ Hz, 1 H, H_m); 4.05 (t, $^3J\{\text{H}_m\text{H}_p\} = ^3J\{\text{H}_m\text{H}_o\} = 6$ Hz, 1 H, $\text{H}_{m/p}$); 3.43 (s, 4 H, H olefin. COD); 2.25–2.40 (m, 8 H, H aliphatic. COD); 1.63 (s, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 137.5$, 136.3 (d, $^1J\{\text{CP}\} = 13.2$ Hz, aromat. C); 135.3 (d, $^2J\{\text{CP}\} = 20.7$ Hz, aromat. C^{2/6}); 133.6 (d, $^2J\{\text{CP}\} = 19.8$ Hz, aromat. C^{2/6}); 128.83 (d, $^3J\{\text{CP}\} = 6.6$ Hz, aromat. C^{3/5}); 128.6 (d, $^3J\{\text{CP}\} = 6.6$ Hz, aromat. C^{3/5}); 128.81, 128.5 (aromat. C⁴); 99.7 (d, $^1J\{\text{CP}\} = 24.8$ Hz, C^{1-*ipso*}); 96.1 (d, $^2J\{\text{CP}\} = 18.2$ Hz, aromat. C); 90.9 (d, $^2J\{\text{CP}\} = 3.3$ Hz, aromat. C); 90.1, 85.9, 84.1 (aromat. C); 64.1, 62.2 (C olefin. COD); 34.2 (C aliphatic. COD); 17.4 (d, $^3J\{\text{CP}\} = 19.7$ Hz, CH_3) ppm. ^{31}P NMR (109.6 MHz, C_6D_6): $\delta = -17.6$ (s) ppm.

[(COD)(η^6 -2-methylacetophenone)Ru] (19**):** MS (EI, 70 eV): $m/z = 343$ [M^+]. ^1H NMR (269.9 MHz, C_6D_6): $\delta = 4.95$ (t, 1 H, aromat. H); 4.77 (d, 1 H, aromat. H); 4.51 (t, 1 H, aromat. H); 4.40 (d, all $^3J_{\text{arom}} = 6$ Hz, 1 H, aromat. H); 3.45–3.35 (m, 2 H, H olefin. COD); 3.30–3.20 (m, 2 H, H olefin. COD); 2.40–2.10 (m, 8 H, H aliphatic. COD); 2.25 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 189.9$ (CO); 101.6; 93.0, 91.4; 88.7, 87.8, 82.4 (aromat. C); 65.6; 63.9 (C olefin. COD); 34.5, 33.4 (C aliphatic. COD); 28.5, 19.6 (C- CH_3) ppm. $\text{C}_{17}\text{H}_{22}\text{ORu}$, $M = 343.4$.

[(COD)(*tert*-butyl η^6 -phenyl ketone)Ru] (20**):** Reaction mixture: **13** (240 mg, 0.65 mmol) in 20 mL of THF, *n*-butyllithium (0.31 mL, 0.78 mmol), and pivalyl chloride (0.1 mL, 0.78 mmol). Yield 252 mg (0.68 mmol, 94%) of **20**. MS (EI, 70 eV): $m/z = 372$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.17$ (t, $J\{\text{H}_p\text{H}_m\} = 5.4$ Hz, 1 H, H_p); 5.16 (d, $J\{\text{H}_o\text{H}_m\} = 6.3$ Hz, 2 H, H_o); 4.16 (t, 2 H, H_m); 3.21 (m, 4 H, H olefin. COD); 1.92 (s, 8 H, H aliphatic. COD), 1.06 (s, 9 H, H *t*Bu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): 203.6 (CO); 91.7, 87.8, 87.3, 84.4 (aromat. C); 65.2 (C olefin. COD); 44.1 (C_{quart} *t*Bu); 34.1 (C aliphatic. COD); 29.1 (C *t*Bu) ppm. $\text{C}_{19}\text{H}_{26}\text{ORu}$ (371.5): calcd. C 61.43, H 7.05; found C 61.96, H 7.42.

[(COD)(*tert*-butyl η^6 -2-tolyl ketone)Ru] (21**):** Reaction mixture: **14** (207 mg, 0.54 mmol) in 20 mL of THF, *n*-butyllithium (0.25 mL, 0.6 mmol), and pivalyl chloride (0.075 mL, 0.6 mmol). Yield 191 mg (0.49 mmol, 91%) of **21**. MS (EI, 70 eV): $m/z = 386$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.15$ (t, 1 H, aromat. H); 4.65 (d, 1 H, aromat. H); 4.55 (t, 1 H, aromat. H); 4.40 (d, all $J = 6$ Hz, 1 H, aromat. H); 3.65–3.50 (m, 2 H, H olefin. COD); 3.48–3.38 (m, 2 H, H olefin. COD); 2.40–2.10 (m, 8 H, H aliphatic. COD);

1.70 (s, 3 H, CH_3); 1.07 (s, 9 H, CH_3 *t*Bu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.7 MHz, C_6D_6): $\delta = 208$ (CO); 104.5, 97.7, 86.0, 85.4, 84.4, 81.9 (aromat. C); 64.6, 63.9 (C olefin. COD); 45.2 (C_{quart} *t*Bu); 34.6, 33.6 (C aliphatic. COD); 27.5 (CH_3 *t*Bu); 17.4 (CH_3 tolyl) ppm. $\text{C}_{20}\text{H}_{28}\text{ORu}$ (385.5): calcd. C 62.31, H 7.32; found C 62.93, H 7.48.

[(COD)(4-*tert*-butylphenyl η^6 -phenyl ketone)Ru] (22**):** Reaction mixture: **13** (264 mg, 0.72 mmol) in 20 mL of THF, *n*-butyllithium (0.34 mL, 0.86 mmol), and 4-*tert*-butylbenzoyl chloride (0.17 mL, 0.86 mmol). Yield 202 mg (0.45 mmol, 67%) of **22**. MS (EI, 70 eV): $m/z = 448$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 8.22$ (d, $J\{\text{H}^{6/9}\text{H}^{7/8}\} = 8.0$ Hz, 2 H, $\text{H}^{6/9}$); 7.33 (d, $J\{\text{H}^{6/9}\text{H}^{7/8}\} = 8.0$ Hz, 2 H, $\text{H}^{7/8}$); 5.48 (d, $J\{\text{H}_o\text{H}_m\} = 6.2$ Hz, 2 H, H_o); 5.38 (t, $J\{\text{H}_p\text{H}_m\} = 5.7$ Hz, 1 H, H_p); 4.53 (t, 2 H, H_m); 3.55 (m, 4 H, H olefin. COD); 2.25 (m, 8 H, H aliphatic. COD), 1.28 (s, 9 H, H *t*Bu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.70 MHz, C_6D_6): $\delta = 194.8$ (CO); 155.0, 136.7, 129.7; 125.4, 93.3, 88.3, 87.5, 84.6 (aromat. C); 64.9 (C olefin. COD); 34.9 (C_{quart} *t*Bu); 33.8 (C aliphatic. COD); 31.1 (C-*t*Bu) ppm.

(–)-[(COD)(camphanoyl η^6 -phenyl ketone)Ru] (23**):** Reaction mixture: **13** (300 mg, 0.8 mmol) in 15 mL of THF, *n*-butyllithium (0.3 mL, 0.75 mmol), and (1*S*)-(–)-camphanoyl chloride (177 mg, 0.8 mmol). Yield 160 mg (0.34 mmol, 43%) of **23**. MS (FD+): $m/z = 468$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 6.0$ (d, $^3J\{\text{HH}\} = 6$ Hz, 1 H, H_o); 5.5 (m, 2 H, $\text{H}_{o/p}$); 4.55 (t, $^3J\{\text{H}_m\text{H}_p\} = 6$ Hz, 1 H, H_m); 3.58 (m, 4 H, H olefin. COD); 2.24 (m, 8 H, H aliphatic. COD); 0.97, 0.88 (s, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, C_6D_6): $\delta = 194.3$ (CO); 177.7, 129.3, 128.5, 125.6, 96.6 (aromat. *ipso*-C); 91.0, 90.9, 90.4, 87.5, 86.1 (aromat. C); 66.3, 65.5 (C olefin. COD); 34.2, 33.8 (C aliphatic. COD); 16.9, 9.7 (CH_3) ppm. $\text{C}_{24}\text{H}_{30}\text{O}_3\text{Ru}$ (467.6): calcd. C 61.65, H 6.46; found C 59.44, H 6.66. $[\alpha]_D^{25} = -312$, $[\alpha]_D^{578} = -152$, $[\alpha]_D^{633} = -92$ (25 °C, toluene).

[(COD){1-phenyl-2-(η^6 -2-tolyl)ethanol}Ru] (24a, b**):** Reaction mixture: **14** (500 mg, 1.3 mmol) in 100 mL of THF, *n*-butyllithium (0.6 mL, 1.5 mmol), and (*R*)-(+)-styrene epoxide (0.18 mL, 1.5 mmol). Yield 169 mg (0.4 mmol, 31%) of **24a** and **24b** as a 1:1 mixture of diastereomers. MS (EI, 70 eV): $m/z = 422$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 7.16$ (d, $J = 14.8$ Hz, 2 H, aromat. H); 7.14 (d, $J = 14.8$ Hz, 2 H, aromat. H); 7.03–6.87 (m, 6 H, aromat. H); 5.12 (t, $^3J\{\text{H}_p\text{H}_m\} = ^3J\{\text{H}_p\text{H}_{m'}\} = 8$ Hz, 1 H, H_p); 5.00 (t, $^3J\{\text{H}_{p2}\text{H}_{m2}\} = ^3J\{\text{H}_{p2}\text{H}_{m'2}\} = 8$ Hz, 1 H, H_{p2}); 4.55 (d, $J = 8$ Hz, 1 H, aromat. H); 4.5–4.38 (m, 2 H, aromat. H); 4.27 (d, 1 H, aromat. H); 4.10 (d, $^3J\{\text{HH}\} = 3$ Hz, 1 H, OH); 4.02 (m, 2 H, aromat. H); 3.62 (d, $^3J\{\text{HH}\} = 3$ Hz, 1 H, OH); 3.25–3.05, 3.00–2.90 [m, 4 H, H olefin. COD, COD(2)]; 2.45–1.85 [m, 20 H, H aliphatic. COD, COD(2), H aliphatic. CH_2 and CH_2 (2)]; 1.35 (s, 3 H, CH_3); 1.34 [s, 3 H, CH_3 (2)] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.7 MHz, C_6D_6): $\delta = 144.8$, 129.2, 128.6, 127.8, 127.4, 126.2, 126, 101.3, 101.1, 100.5, 97.4, 91.2, 90.4, 88.0, 87.5, 86.3, 86.1, 86.0, 84.5 (aromat. C); 73.2, 72.5 (C-alcohol); 62.9, 62.3, 61.3, 61.1 (C olefin. COD); 41.8, 41.0 (C aliphatic. CH_2); 34.6; 34.5, 33.7, 33.6 (C aliphatic. COD); 17.0, 16.5 (CH_3) ppm.

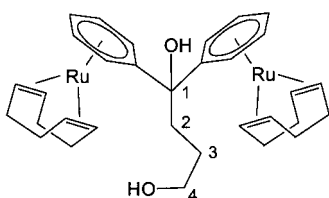
[(COD)(dimethyl- η^6 -phenylmethanol)Ru] (25**):** Reaction mixture: **13** (220 mg, 0.59 mmol) in 20 mL of THF, *n*-butyllithium (0.35 mL, 0.88 mmol), and acetone (0.06 mL, 0.88 mmol). Yield 132 mg (0.38 mmol, 65%) of **25**. MS (EI, 70 eV): $m/z = 346$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.29$ (t, $J\{\text{H}_p\text{H}_m\} = 5.4$ Hz, 1 H, H_p); 4.60 (d, $J\{\text{H}_o\text{H}_m\} = 5.7$ Hz, 2 H, H_o); 4.14 (t, 2 H, H_m); 3.17 (m, 4 H, H olefin. COD); 1.94 (m, 8 H, H aliphatic. COD), 1.23 (s, 6 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): $\delta = 115.2$, 86.1, 85.7, 84.8 (aromat. C); 70.8 (C alcohol); 60.2 (C olefin. COD); 34.1 (C aliphatic. COD); 31.3 (CH_3) ppm.

[(COD)(η^6 -phenylcyclohexanol)Ru] (26**):** Reaction mixture: **13** (350 mg, 0.91 mmol) in 20 mL of THF, *n*-butyllithium (0.44 mL,

1.1 mmol), and cyclohexanone (0.11 mL, 1.1 mmol). Yield 242 mg (0.63 mmol, 69%) of **26**. MS (EI, 70 eV): $m/z = 386$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.32$ (t, $J\{\text{H}_p\text{H}_m\} = 5.5$ Hz, 1 H, H_p); 4.63 (d, $J\{\text{H}_o\text{H}_m\} = 6.0$ Hz 2 H, H_o); 4.14 (t, 2 H, H_m); 3.18 (m, 4 H, H olefin. COD); 1.95 (m, 8 H, H aliph. COD); 1.68 (m, 4 H, H aliph. cyclohexane); 1.28 (m, 6H, H aliph. cyclohexane) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): $\delta = 116.2$, 86.2, 85.8, 85.1 (aromat. C); 70.1 (C alcohol.); 60.1 (C olefin. COD); 39.2 (C aliph. cyclohexane); 34.3 (C aliph. COD); 26.1 (C aliph. cyclohexane); 22.8 (C aliph. cyclohexane) ppm.

[(COD)(3-hydroxypropyl η^6 -phenyl ketone)Ru] (27**):** Reaction mixture: **13** (380 mg, 1.03 mmol) in 30 mL of THF, *n*-butyllithium (0.44 mL, 1.1 mmol), and γ -butyrolactone (88.7 mg, 1.03 mmol). Yield 80 mg (0.21 mmol, 21%) of **27** and 150 mg (0.23 mmol, 45%) of **28**. MS (FD+): $m/z = 374$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.31$ (d, $^3J\{\text{HH}\} = 6$ Hz, 2 H, H_o); 5.24 (t, $^3J\{\text{HH}\} = 6$ Hz; 1 H, H_p); 4.52 (t, $^3J\{\text{HH}\} = 6$ Hz, 1 H, H_m); 3.45 (m, 2 H, CH_2OH); 3.40 (m, 4 H, H olefin. COD); 2.59 (t, 2 H, CH_2CO); 2.10 (m, 8 H, H aliph. COD); 1.88 (quint, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): $\delta = 199.0$ (CO); 91.3, 88.8, 86.8, 82.9 (aromat. C); 64.4 (C olefin. COD); 62.1 (COH); 34.5 (CCO); 33.9 (C aliph. COD); 27.7 (CH_2) ppm.

Data for 1,1-Bis[(COD)(η^6 -phenyl)Ru]-1,4-butanediol (28**):** MS (FD+): $m/z = 662$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.52$ (t, $^3J = 6$ Hz, 2 H, aromat. H); 5.21 (d, 2 H, aromat. H); 5.03 (d, 2 H, aromat. H); 4.39 (tt, all $^3J = 6$ Hz, 4 H, aromat. H); 3.4 (m, 4 H, $\text{H}^{2/4}$; 8 H, H olefin. COD); 2.20 (m, 16 H, H aliph. COD); 1.79 (m, 2 H, H^3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): $\delta = 114.5$, 86.5, 85.8, 85.7, 84.8 (aromat. C); 75.2 (C^1); 63.2 (C^4); 61.3, 61.1 (C olefin. COD); 40.5 (C^2); 34.3, 34.2 (C aliph. COD); 27.6 (C^3) ppm.

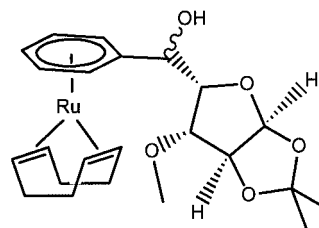


[(COD)(η^6 -4-fluorophenyl 3-hydroxypropyl ketone)Ru] (29**):** Reaction mixture: **10** (353 mg, 0.92 mmol) in 45 mL of THF, *n*-butyllithium (0.58 mL, 0.92 mmol), and γ -butyrolactone (79 mg, 0.92 mmol). Yield 140 mg (0.36 mmol, 40%) of **29** and 50 mg (0.07 mmol, 16%) of **30**. MS (FD+): $m/z = 392$ [M^+]. ^1H NMR (269.71 MHz, C_6D_6): $\delta = 5.39$ (dd, 2 H, aromat. H); 5.02 (dd, 2 H, aromat. H); 3.54 (m, 4 H, H olefin. COD); 3.54 (t, 2 H, CH_2OH); 2.58 (t, 2 H, CH_2CO); 2.25 (m, 8 H, H aliph. COD); 1.86 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, C_6D_6): $\delta = 197.9$ (CO); 139.8, 135.8, 92.1 (aromat. C); 82.8 (d, CF); 77.3, 77.0 (aromat. C) 66.8 (C olefin. COD); 61.8 (COH); 34.8 (CCO); 33.8 (C aliph. COD); 27.3 (CH_2) ppm.

Data for [1,1-bis[(COD)(η^6 -4-fluorophenyl)Ru]-1,4-butanediol] (30**):** MS (FD+): $m/z = 697$ [M^+], 488 [$M - \text{Ru}(\text{COD})$] $^+$. ^1H NMR (269.71 MHz, C_6D_6): $\delta = 5.02$ (m, 2 H, aromat. H); 4.95 (m, 2 H, aromat. H); 4.90 (m, 2 H, aromat. H); 4.74 (m, 2 H, aromat. H); 3.66 (m, 8 H, H olefin. COD); 3.23 (q, 2 H, H_3); 2.32 (m, 16 H, H aliph. COD); 2.11 (t, 2 H, H_3); 1.68 (m, 2 H, H_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, C_6D_6): $\delta = 143.6$, 139.6, 116.0 (aromat. C); 80.8, 79.8 (d, C-F); 74.7, 74.4, 73.1 (aromat. C); 72.7 (C^1); 63.9, 63.7 (C olefin. COD); 62.8 (C^4); 40.1 (C^2); 34.2, 33.6 (C aliph. COD); 26.6 (C^3) ppm.

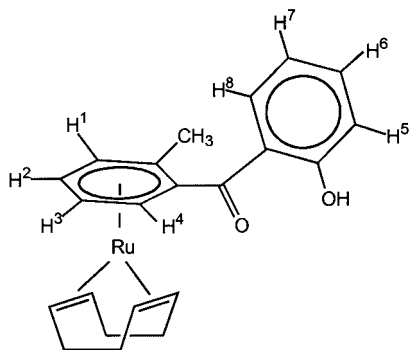
[(COD)(3-hydroxypropyl η^6 -2-tolyl ketone)Ru] (31**):** Reaction mixture: **14** (180 mg, 0.47 mmol) in 20 mL of THF, *n*-butyllithium (0.3 mL, 0.48 mmol), and γ -butyrolactone (0.036 mL, 0.47 mmol). Yield 80 mg (0.21 mmol, 44%) of **31**. MS (FD+): $m/z = 388$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.36$ (t, $^3J\{\text{HH}\} = 8$ Hz, 1 H, aromat. H); 4.82 (d, $^3J\{\text{HH}\} = 8$ Hz, 1 H, aromat. H); 4.43 (t, $^3J\{\text{HH}\} = 8$ Hz, 1 H, aromat. H); 4.31 (t, $^3J\{\text{HH}\} = 8$ Hz, 1 H, aromat. H); 3.42 (m, 2 H, CH_2OH); 3.37 (m, 2 H, H olefin. COD); 3.20 (m, 2 H, H olefin. COD); 2.72 (m, 1 H, CH_2CO); 2.63 (m, 1 H, CH_2CO); 2.19 (m, 8 H, H aliph. COD); 2.02 (s, 3 H, CH_3); 1.86 (quint, 2 H, CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): $\delta = 202.3$ (CO); 101.3, 93.2, 91.6, 88.6, 87.6, 82.3 (aromat. C); 65.7, 64.0 (C olefin. COD); 62.17 (CH_2OH); 37.1 (CH_2CO); 34.4, 33.6 (C aliph. COD); 27.8 (CH_2); 19.6 (CH_3) ppm.

[(COD){(6-methoxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)(η^6 -phenyl)methanol}Ru] (32a**, **32b**):** Reaction mixture: **13** (455 mg, 1.24 mmol) in 15 mL of THF, *n*-butyllithium (0.75 mL, 1.2 mmol), and 1,2-*O*-isopropylidene-3-*O*-methyl- α -D-xylopentodialdofuranose-(1,4) (250 mg, 1.24 mmol). Yield 290 mg (0.59 mmol, 48%) of **32a**, **32b**. MS (FD+): $m/z = 490$ [M^+]. ^1H NMR (399.65 MHz, C_6D_6): $\delta = 5.91$ (d, $^3J\{\text{HH}\} = 4$ Hz, 1 H, aromat. H); 5.84 (d, $^3J\{\text{HH}\} = 4$ Hz, 1 H, aromat. H); 5.51 (d, $^3J\{\text{HH}\} = 5$ Hz, 2 H, aromat. H); 5.36 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 5.19 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.87 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.84 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.79 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.70 (d, $^3J\{\text{HH}\} = 5$ Hz, 2 H, aromat. H); 4.54 (d, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.47 (td, $^3J\{\text{HH}\} = 4$ Hz, 2 H, aromat. H); 4.43 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.34 (d, $^3J\{\text{HH}\} = 4$ Hz, 1 H, aromat. H); 4.26 (d, $^3J\{\text{HH}\} = 4$ Hz, 1 H, aromat. H); 4.10 (t, $^3J\{\text{HH}\} = 5$ Hz, 1 H, aromat. H); 4.05 (d, $^3J\{\text{HH}\} = 3$ Hz, 2 H, aromat. H); 3.46 (d, $^3J\{\text{HH}\} = 3$ Hz, 2 H, aromat. H); 3.58–3.33 (m, 4 H, H olefin. COD); 3.20 (s, 3 H, H OMe); 3.01 (s, 1 H, OH); 2.83 (s, 3 H, H OMe); 2.81 (d, $J\{\text{HH}\} = 7$ Hz, 1 H, HOH); 2.38–2.05 (m, 8 H, H aliph. COD); 1.40 (d, 3 H, H isoprop. *endo*); 1.11 (d, 3 H, H isoprop. *exo*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, C_6D_6): $\delta = 112.0$, 111.8 (aromat. C); 110.0, 106.0 (isoprop. C); 106.0 (d, C-OH); 88.7, 87.7, 87.6, 87.4, 87.0, 86.6, 86.5 (aromat. C); 85.4, 84.9, 84.8 (C furanose); 84.5 (aromat. C); 84.2 (C furanose); 83.9, 83.7 (aromat. C); 82.4, 82.0, 71.2, 69.5 (C furanose); 61.4, 60.6 (C olefin. COD); 58.2, 57.0 (COMe); 34.8, 34.3 (C aliph. COD); 27.4, 27.3, 26.7, 26.6 (CH_3 isoprop.) ppm.

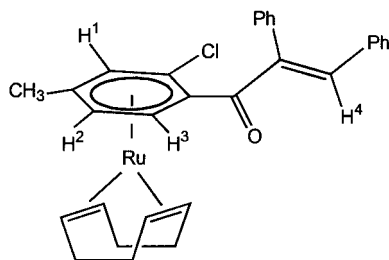


[(COD)(menthyl η^6 -1,4-xylylene-2-carboxylate)Ru] (33a** and **33b**):** Reaction mixture: **8** (380 mg, 0.96 mmol) in 10 mL of THF, *n*-butyllithium (0.5 mL, 1.25 mmol), and (–)-menthyl chloroformate (0.3 mL, 1.3 mmol). Yield 200 mg (0.4 mmol, 42%) of **33a** and **33b**. MS (FD+): $m/z = 497$ [M^+]. ^1H NMR (269.6 MHz, C_6D_6): $\delta = 5.52$ (s, 1 H, aromat. H); 5.13 (m, 1 H, ester H); 4.88 (dt, 1 H, aromat. H); 4.75 (dt, 1 H, aromat. H); 4.32 (t, 1 H, aromat. H); 4.04 (t, 1 H, aromat. H); 3.48 (m, 2 H, H olefin. COD); 3.14 (m, 2 H, H olefin. COD); 2.2–2.4 (m, 8 H, H aliph. COD); 0.7–1.7 (19 H, menthyl) ppm.

[(COD)(*o*-hydroxyphenyl η^6 -2-tolyl ketone)Ru] (34): Reaction mixture: **14** (300 mg, 0.79 mmol) in 30 mL of THF, *n*-butyllithium (0.32 mL, 0.79 mmol), and *o*-acetylsalicyl chloride (156 mg, 0.79 mmol). Yield 200 mg (0.47 mmol, 60%) of **34**. MS (FD+): $m/z = 422$ [M⁺]. ¹H NMR (399.65 MHz, [D₈]THF): $\delta = 12.62$ (s, 1 H, phenol. H); 8.50 (d, ³ $J\{H^5H^6\} = 8$ Hz, 1 H, H⁵); 7.08 (t, ³ $J\{H^{5/8}H^{6/7}\} = 8$ Hz, 1 H, H^{6/7}); 7.01 (d, ³ $J\{H^7H^8\} = 8$ Hz, 1 H, H⁸); 6.56 (t, ³ $J\{H^{5/8}H^{6/7}\} = 8$ Hz, 1 H, H^{6/7}); 5.24 (t, ³ $J\{H^2H^{1/3}\} = 5.5$ Hz), 1 H, H²; 4.78 (d, ³ $J\{H^4H^3\} = 5.5$ Hz, 1 H, H⁴); 4.60 (d, ³ $J\{H^1H^2\} = 5.5$ Hz, 1 H, H¹); 4.31 (t, ³ $J\{H^3H^{2/4}\} = 5.5$ Hz, 1 H, H³); 3.48 (m, 4 H, H olefin. COD); 2.38 (m, 8 H, H aliphatic. COD); 1.63 (s, 3 H, CH₃) ppm. ¹³C{¹H} NMR (100.40 MHz, [D₈]THF): $\delta = 201.8$ (CO); 163.7 (C-OH); 136.8, 134.0, 120.6, 118.8, 118.4 (aromat. C); 99.4 (*ipso*-C); 96.0 (π -tolyl-C); 89.4, 88.6, 85.0, 83.6 (arom-C), 65.3 (C olefin. COD); 64.3; 34.1 (C aliphatic. COD); 33.5; 17.2 (CH₃) ppm.



[(COD)(η^6 -1-{2-fluoro-4-tolyl} *o*-hydroxyphenyl ketone)Ru] (35): Reaction mixture: **5** (550 mg, 1.7 mmol) in 30 mL of THF, *n*-butyllithium (0.68 mL, 1.7 mmol), and *o*-acetylsalicyl chloride (300 mg, 1.5 mmol). Yield 300 mg (0.68 mmol, 40%) of **35**. MS (FD+): $m/z = 440$ [M⁺]. ¹H NMR (300.13 MHz, C₆D₆): $\delta = 12.46$ (s, 1 H, phenol. H); 8.81 (m, 1 H, aromat. H); 7.06 (m, 2 H, aromat. H); 6.66 (m, 1 H, aromat. H); 4.50 (dd, ³ $J\{HH\} = 6$, $J\{HF\} = 3$ Hz, 1 H, aromat. H); 4.41 (dd, ³ $J\{HH\} = 6$, $J\{HF\} = 3$ Hz, 1 H, aromat. H); 4.27 (d, ³ $J\{HF\} = 4$ Hz, 1 H, aromat. H); 3.54 (m, 4 H, H, olefin. COD); 2.18 (m, 8 H, H aliphatic. COD); 1.72 (s, 3 H, CH₃) ppm. ¹³C{¹H} NMR (75.47 MHz, C₆D₆): $\delta = 197.2$ (CO); 163.4 (C-OH); 137.4, 134.2 (aromat. C); 127.3 (¹ $J\{CF\} = -271$ Hz, π -aromat. C); 120.8, 118.8, 118.6 (aromat. C); 99.4 (³ $J\{CF\} = 6$ Hz, π -aromat. C); 89.2 (d, ² $J\{CF\} = 17$ Hz, π -aromat. C); 79.7 (³ $J\{CF\} = 2$ Hz, π -aromat. C); 85.0 (π -aromat. C); 75.2 (d, π -aromat. C, ² $J\{CF\} = 22$ Hz); 67.6 (C olefin. COD); 33.5 (C aliphatic. COD); 18.3 (CH₃) ppm.



[(η^6 -1-{2-chloro-4-tolyl}-2,3-diphenylprop-2-en-1-one)(COD)Ru] (36): Reaction mixture: **6** (275 mg, 0.82 mmol) in 20 mL of THF, *n*-butyllithium (0.36 mL, 0.9 mmol), and α -phenylcinnamoyl chloride (218 mg, 0.9 mmol). Yield 180 mg (0.33 mmol, 41%) of **36**. MS (FD+): $m/z = 542$ [M⁺]. ¹H NMR (399.65 MHz, C₆D₆): $\delta = 7.93$ (s, 1 H, olefin. H); 7.1 (m, 10 H, phenyl. H); 5.25 (d, ³ $J\{H^2H^3\} = 5.5$ Hz, 1 H, H²); 5.03 (s, 1 H, H¹); 4.10 (d, ³ $J\{H^2H^3\} = 5.5$ Hz, 1

H, H³); 3.59 (m, 4 H, H olefin. COD); 2.25 (m, 8 H, H aliphatic. COD); 1.68 (s, 3 H, CH₃) ppm. ¹³C{¹H} NMR (100.40 MHz, C₆D₆): $\delta = 193.8$ (CO); 142.3, 141.4, 138.1, 136.7, 136.6, 135.7, 130.9, 130.7, 129.5, 129.4, 129.1, 128.7, 128.7, 125.9 (phenyl. C, olefin. C); 102.2, 101.9, 99.4, 88.8, 86.2, 83.4 (aromat. C); 70.2, 68.4 (C olefin. COD); 34.5, 33.8 (C aliphatic. COD); 18.4 (CH₃) ppm.

Crystal Structure Determinations: Suitable crystals of **10**, **11**, **28**, and **30** were taken directly from the mother liquor. Data were collected with a Siemens P4 diffractometer for **10**, **11**, and **28** and with a Nonius KappaCCD for **30**, with use of Mo- K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structures were solved by direct methods and refined by use of the SHELXTL 5.03[18] programs for **10** and **28**, and SHELXTL NT 5.10[19] for **11** and **30**. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms are either geometrically positioned (**10** and **28**) or their positions were derived from a difference Fourier map and refined with a fixed common isotropic displacement parameter (**11** and **30**). Other experimental details are given in Tables 2 and 3. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-186921 (**10**), -186922 (**11**), -186923 (**28**), and -186924 (**30**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ca.ac.uk].

Table 2. Crystallographic data for **10** and **11**

	10	11
Empirical formula	C ₁₄ H ₁₆ BrFRu	C ₁₄ H ₁₆ BrIRu
Formula mass	384.25	492.15
Color, shape	yellow, plate	yellow, needle
Size [mm]	0.90×0.52×0.10	0.70×0.35×0.20
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> ₂ /c	<i>P</i> ₂ /n
<i>a</i> [Å]	13.003(1)	14.702(2)
<i>b</i> [Å]	8.316(1)	6.369(2)
<i>c</i> [Å]	12.586(1)	16.062(3)
β [°]	110.04(1)	113.14(1)
Volume [Å ³]	1278.6(2)	1383.0(5)
<i>Z</i>	4	4
ρ_{calc} [g·cm ⁻³]	1.996	2.364
μ [mm ⁻¹]	4.337	6.230
<i>T</i> [K]	294(2)	200(2)
Absorption correction	ψ -scan	ψ -scan
<i>T</i> _{min} / <i>T</i> _{max}	0.017/0.059	0.049/0.120
<i>F</i> (000)	752	928
Reflections measured	3606	4362
Independent reflections	2795	3335
Observed reflections	2063	2630
$[F_o \geq 4\sigma(F)]$		
No. refined parameters	202	154
Goodness-of-fit on <i>F</i> ²	1.029	1.077
<i>R</i> ₁ [$F_o \geq 4\sigma(F)$]	0.0550	0.0585
<i>wR</i> ₂ (all data)	0.1470	0.1766
Max/min resid. density [e·Å ⁻³]	1.034/−1.487	3.007/−3.076

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Table 3. Crystallographic data for **28** and **30**

	28	30
Empirical formula	C ₃₂ H ₄₂ O ₂ Ru ₂	C ₃₉ H ₄₈ F ₂ O ₂ Ru ₂ ^[a]
Formula mass	660.80	788.91 ^[a]
Color, shape	Yellow, block	Yellow, block
Size [mm]	0.75×0.38×0.30	0.28×0.24×0.15
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	8.725(4)	36.1071(6)
<i>b</i> [Å]	14.455(5)	8.9293(2)
<i>c</i> [Å]	23.190(9)	21.7669(4)
α [°]	107.14(2)	90.0
β [°]	90.76(4)	112.294(1)
γ [°]	106.38(4)	90.0
Volume [Å ³]	2667(2)	6493.3(2)
<i>Z</i>	4	8
$\rho_{\text{calcd.}}$ [g·cm ⁻³]	1.646	1.614
μ [mm ⁻¹]	1.161	0.977
<i>T</i> [K]	200(2)	100(2)
Absorption correction	ψ -scan	multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.501/0.712	0.701/0.769
<i>F</i> (000)	1352	3232
Reflections measured	13619	33917
Independent reflections	11365	9246
Observed reflections	8342	6534
[<i>F</i> _o ≥ 4σ(<i>F</i>)]		
No. refined parameters	663	544
Goodness-of-fit at <i>F</i> ²	1.093	1.011
<i>R</i> ₁ [<i>F</i> _o ≥ 4σ(<i>F</i>)]	0.0636	0.0346
<i>wR</i> ₂ (all data)	0.1723	0.0728
Max/min resid. density [e·Å ⁻³]	2.608/−1.175	0.604/−0.590

^[a] Includes one molecule of solvent (toluene).

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