Chiral Arene Ruthenium Complexes, 2[◇]

A Diastereoselective Route to [(η^6-Benzyl Alcohol)(COD)Ru] Complexes

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Two preparative routes are reported that give access to the racemic series of planar chiral [(arene)(COD)Ru] derivatives containing η^6-bonded *o*-tolyl ketone or aldehyde arene units. The ketone and aldehyde functions of these have subsequently been reduced by *n*BuLi and PhLi, respectively. Hydrolysis converts the initially formed lithium salts into diastereomeric benzyl alcohol complexes in high yields. The formation of the new stereogenic centre is diastereoselective (88% de) for the aldehyde and diastereospecific for the ketone (de > 99%). Due to a sterically overcrowded situation, the rotation of the chiral side chain of [(COD)(η^6-*o*-tolyl-*tert*-butylphenylmethanol) Ru] (**7**) is hindered, as is the rotation of the phenyl and *tert*-butyl substituents. As a consequence, the hydroxyl group is fixed at a position close to the metal both in solution and in the solid state.

Introduction

Arene-ruthenium complexes have been shown to be catalytically active when the metal is in the oxidation states 0[2] and +2[3]. In combination with enantiomerically pure coligands, the ruthenium(II) species are excellent enantioselective hydrogen-transfer catalysts.[4] Arene-ruthenium(0) fragments are also believed to be the catalytically active species of such catalysts.[2] We, therefore, considered it worthwhile to develop the chemistry of chiral arene-ruthenium complexes. Due to high stability in both redox states,[5] the neutral complexes may be oxidized nearly quantitatively without breaking the arene-ruthenium bond.[2] Thus, access to a specific arene-ruthenium(0) complex directly leads to the corresponding arene-ruthenium(II) species. Thus, our efforts to date have been concentrated on Ru(0) compounds.

In a previous paper we reported on specific routes to C_1- or C_2-symmetric enantiomerically pure [(arene)(COD)Ru] complexes, which involved the addition of defined stereogenic centres to suitably coordinated arene ligands. In the case of planar chirality of the arene, the resulting mixture of diastereomers could be separated. The usefulness of [(arene)(COD)Ru] complexes has been demonstrated, in that all derivatives tested so far have been shown to be catalytically active at room temperature in the hydrogenation of C=C bonds.[1]

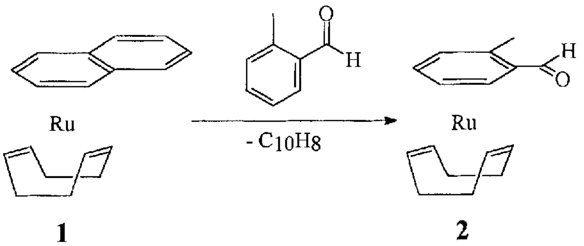
In this paper we report on the selective generation of a second stereogenic centre within a substituent of [(arene)-(COD)Ru] complexes containing planar chiral arene ligands.

As the new complexes have been designed as potential catalysts, we have introduced the stereogenic centre as close as possible to the metal. Benzyl alcohols as π ligands fulfill this condition in an ideal manner, especially if they carry bulky substituents at the benzyl position. These are repelled by the ruthenium atom and consequently the polar OH group is pushed into the vicinity of the coordination sphere of the metal atom. Following diastereoselective reduction experiments on planar chiral arene-chromium tricarbonyl complexes,[6] we obtained access to this class of compounds by reduction of π-coordinated planar chiral *o*-tolyl ligands bearing ketone or aldehyde functions. The side differentiation of the C=O double bond results from interactions with the coordinated metal and the adjacent methyl group.

Preparation of η^6-*o*-Tolyl Ketone and Aldehyde Ruthenium Complexes

Two routes give access to the racemic series of planar chiral [(arene)(COD)Ru] derivatives containing an η^6-bonded *o*-tolyl ketone or aldehyde arene unit. *o*-Tolyl aldehyde can be introduced directly by replacing the naphthalene ligand of [(COD)(η^6-naphthalene)Ru] (**1**)[7], thereby forming [(COD)(η^6-*o*-tolyl aldehyde)Ru] (**2**).

Scheme 1



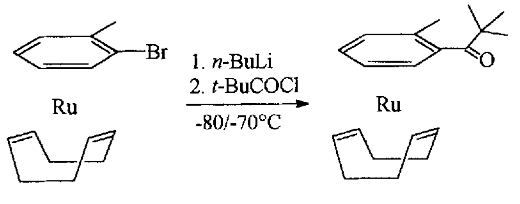
1 **2**

[◇] Part 1: Ref.[1].

Since naphthalene ligand exchange reactions of **1** only give good yields if the incoming arene ligand is applied in excess and the surplus material can be removed by distillation, this type of reaction is not very useful for *o*-tolyl ketones containing medium- or large-sized alkyl or aryl groups because of low vapour pressure. On the other hand, a bulky second substituent of the ketone ensures a strong interaction with the adjacent methyl group, thus the preconditions for a high diastereoselectivity of the reduction seemed to be best fulfilled by such a ligand. In analogy to the introduction of ester substituents by reacting lithiated ruthenium-arene complexes with alkyl chloroformates,[1] the η^6-aryl ketone unit can be formed by reacting organic acid chlorides with the lithiated complexes.

The bromine-lithium exchange of racemic [(COD)(η^6-*o*-tolyl bromide)Ru] (**3**) is accomplished within a few minutes at −80°C. Once this rapid lithiation process is complete, the electrophile pivaloyl chloride has to be added immediately at −70°C. The product [(COD)(η^6-*o*-tolyl *tert*-butyl ketone)Ru] (**4**) can be isolated in high yield.

Scheme 2

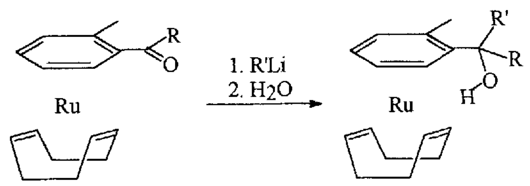


3 **4**

Diastereoselective Reduction

The η^6-*o*-tolyl complexes **2** and **4** were reacted with *n*BuLi and PhLi, respectively. Hydrolysis with degassed water converts the lithium salts into diastereomeric benzyl alcohols. Besides the coordinated *o*-tolyl and hydroxyl groups, the new stereogenic benzyl carbon atoms carry the incoming organyl group of the lithium reagent and a hydrogen atom or the *t*Bu substituent, depending on the nature of the precursor ruthenium complex.

Scheme 3



R = H **2**
R = *t*-Bu **4**

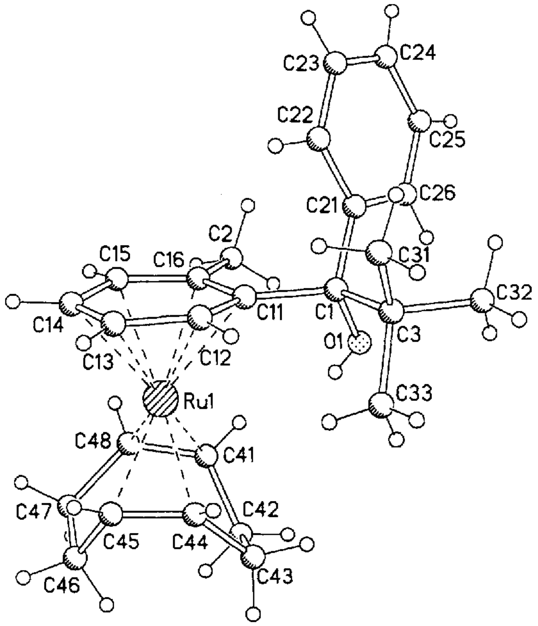
R = H, R' = Ph **5**
R = *t*-Bu, R' = *n*-Bu **6**
R = *t*-Bu, R' = Ph **7**

On the basis of NMR spectroscopic analysis of the crude products, the reduction is quantitative and the formation of the new stereogenic centre is diastereoselective in all cases. The diastereomeric excess (*de*) values are 88% in the case of **5** and greater than 99% for the *t*Bu derivatives **6** and **7**. Thus, the reduction of **4** may be classified as being diastereospecific.

Structural Investigation of 7

The molecular structure of [(COD)(η^6-*o*-tolyl-*tert*-butylphenylmethanol)Ru] (**7**) was determined by single-crystal X-ray diffraction. Both enantiomers are present in the unit cell, and are related by a centre of symmetry. The relative configuration of both stereogenic centres is shown in Figure 1. All hydrogen atoms of **7**, including that of the hydroxyl group, were localized in a difference Fourier synthesis and isotropically refined.

Figure 1. Molecular structure of **7** in the solid state[a] (one enantiomer)



[a]Selected bond lengths [pm] and bond angles [°]: Ru1−C11 226.5(3), Ru1−C12 226.3(3), Ru1−C13 223.8(3), Ru1−C14 224.0(3), Ru1−C15 224.8(3), Ru1−C16 223.4(3), Ru1−C41 215.7(3), Ru1−C44 214.8(3), Ru1−C45 215.6(3), Ru1−C48 213.6(3), Ru1···H1 308(5); O1−C1−C3 106.4(2), O1−C1−C11 107.2(2), C3−C1−C11 118.0(2), C11−C1−C21 107.7(2).

There are no unusually short intermolecular distances detectable in the unit cell, not even as a result of hydrogen bonding of the OH group. As a consequence, the details of the molecular structure have to be discussed mainly on the basis of intramolecular considerations.

As expected the benzyl carbon atom C1 is fixed in a rotational state, such that the hydroxyl group is close to and directed towards the metal. The Ru···H distance of 308(5) pm and the electronic saturation of the ruthenium atom, however, rule out a strong metal-hydrogen interaction. The phenyl substituent at C1 is in close contact with the methyl group C2 and is rotated orthogonal to it. This position minimizes the steric interactions between the two organyl substituents at C1 and the (COD)Ru fragment. The central carbon atom C3 and the methyl carbon C32 of the *t*Bu group are coplanar with the coordinated *o*-tolyl ligand and C3 is located in a transoid position with respect to the methyl group C2. The two methyl carbons C31 and C33 are located at similar distances from the plane of the ring [C31 130.0(3), C33 122.5(4) pm], leaving just enough space for the ring hydrogen atom H12 between them, as the bond angle C3−C1−C11 is widened to 118.0(2)°. The other bond angles at C1 are correspondingly reduced compared to the tetrahedral bond angle. To our surprise, this position of the *t*Bu group represents the transition state of the *t*Bu group passing the ring plane of the *o*-tolyl ligand. This means that the substituents at C1 create such an overcrowded situation that the bond rotations C1−C11 and C1−C3 are blocked, and thus the chiral side chain of **7** is conformationally fixed in the solid state.

Spectroscopic Properties in Solution

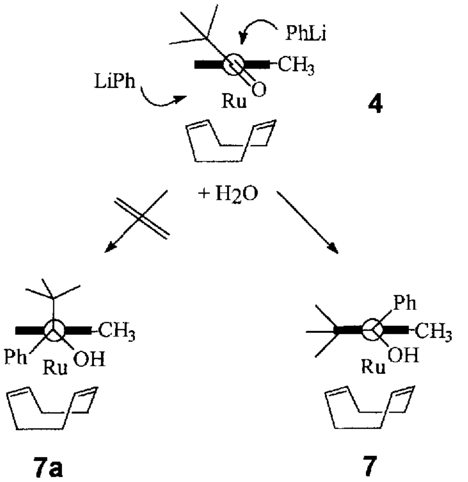
All spectra of the complexes in solution are consistent with their proposed C_1 symmetry. In contrast to the other compounds, the NMR signals of **7** are partly broadened or are unobservable close to room temperature, but at −50 and +70°C, respectively, slow and rapid exchange limits in the ^{1}H NMR spectra are reached. The broadening effect is seen only for the organyl substituents at the benzyl carbon atom C1. At low temperatures, we observe separated signals for the three methyl groups of the *t*Bu substituent ($\delta = 1.02$, 1.13 and 1.65) and the two *o*-hydrogen atoms of the phenyl group ($\delta = 6.66$ and 8.08). These coalesce to form one signal, respectively, at high temperature ($\delta_{tBu} = 1.30$; $\delta_{o\text{-}Ph} = 7.42$). Accordingly, the chemical shifts of the arene ligand protons, including that of the OH group are slightly temperature dependent in the investigated range ($\delta_{Ph} = 0.18$ to 0.36; $\Delta\delta_{OH} = -0.22$), whereas the COD multiplets remain at the same position. We interpret both findings as the consequence of sterically hindered rotations of the *t*Bu and phenyl substituents. If we take the structural features of **7** in the solid state as a model for the solvated molecule, H12 blocks the rotation of the *t*Bu group in a cogwheel-like manner and the phenyl is hindered by the methyl group of the *o*-tolyl unit. As a result, the bond rotation C11−C1 is also hindered, and indicates a conformational rigidity of the complete chiral side chain in solution. Therefore, the polar OH group preferentially resides in the vicinity of the coordination sphere of the ruthenium atom in solution as well as in the solid state.

Due to lesser steric demand of the benzyl carbon atom substituents of **5** and **6**, no signal broadening is observed in their NMR spectra at room temperature. This does not necessarily mean a free rotation of the benzyl carbon atom, since a rapid pendulum movement of C1 and rotating substituents would result in the same spectroscopic situation.

Mechanistic Considerations

In the case of [(COD)(η^6-*o*-tolyl *tert*-butyl ketone)Ru] (**4**), the *tert*-butyl group is much bigger than the oxygen atom of the ketone, thus the minimization of the interactions between the bulky alkyl group, the adjacent methyl group, and the (COD)Ru fragment is the reason for the observed diastereospecificity of the reduction process. As for product **7**, the *t*Bu substituent of **4** cannot occupy positions at the same side of the *o*-tolyl ligand as the ruthenium atom and is tilted away from the methyl group. The organolithium reagent on the other hand must attack the carbonyl group from the distal side. As a result, the incoming alkyl or aryl group is introduced between the *t*Bu and methyl substituents and it remains in this position because of the hindered rotation of the side chain in the case of **7**.

Scheme 4



In contrast to **4**, the hydrogen atom of the aldehyde function of **2** is smaller than the oxygen and all considerations on the diastereoselectivity of its reduction are in favour of the opposite relative configurations of the two stereogenic centres of **5** in comparison to **7**. Since the interpretation of the spectra of **5** is not yet unequivocal in this respect, this point is under current investigation.

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Experimental Section

All reactions were performed in a dry, oxygen-free nitrogen atmosphere. Solvents were purified by conventional methods, distilled and stored under nitrogen. Unless otherwise stated, NMR spectra were recorded at around room temperature on Jeol FT-JNM-EX 270 and FT-JNM-LA 400 spectrometers, using dimethylpolysiloxane and solvent signals as internal standards. Mass spectra were recorded on a Varian MAT 212 spectrometer. Microanalyses were performed at the Analytical Department of the Institute, using a Carlo-Erba Elemental Analyser Model 1106. Column chromatography (15 × 1 cm) was accomplished with neutral degassed alumina (Merck), deactivated with 5% degassed water. [(COD)(η^6-naphthalene)Ru] (**2**)[7] and [(COD)(η^6-*o*-tolyl bromide)Ru] (**3**)[1] were prepared as reported previously.

[(COD)(η^6-o-Tolyl Aldehyde)Ru] (**2**): *o*-Tolylaldehyde (10 g, 0.08 mol) and acetonitrile (1 ml) were added to a solution of [(1,5-COD)(η^6-naphthalene)Ru] (**1**) (1.09 g, 3.23 mmol) in 40 ml of THF and the resulting mixture was stirred at room temperature for 2 d. Then, the solvent, the excess free ligand and naphthalene were removed in vacuo at 40°C. The residue was dissolved in a small amount of light petroleum ether/toluene (1:1) and chromatographed on Al_2O_3/5% H_2O using the same solvent mixture as eluent. After removal of the solvent, 531 mg (1.61 mmol, 50%) of pure,

red **2** was obtained and recrystallized from toluene. – ^{1}H NMR (399.65 MHz, C_6D_6): δ = 10.05 (s, 1 H, aldehyde H), 5.39 [t, 1 H, aryl H, ^3J(HH) = 5.5 Hz], 4.90 [d, 1 H, aryl H, ^3J(HH) = 6 Hz], 4.79 [t, 1 H, aryl H, ^3J(HH) = 5.7 Hz], 4.02 [d, 1 H, aryl H, ^3J(HH) = 5.5 Hz], 3.47–3.37 (m, 2 H, olef. COD H), 3.28–3.21 (m, 2 H, olef. COD H), 2.37–2.12 (m, 8 H, aliph. COD H), 1.86 (s, 3 H, CH_3). – ^{13}C NMR (100.4 MHz, C_6D_6): δ = 188.2 (C-carbonyl), 105.2 (C-aryl), 92.3 (C-aryl), 91.2 (C-aryl), 88.7 (C-aryl), 83.2 (C-aryl), 82.3 (C-aryl), 66.9 (COD olef.), 65.5 (COD olef.), 34.5 (COD aliph.), 33.7 (COD aliph.), 16.2 (CH_3). – IR (THF): $\tilde{\nu}$(CO) = 1683.91, 1669.94 cm^{-1}. – MS (EI, 70eV); *m/z:* 329 $[M]^+$. – $C_{16}H_{20}ORu$: calcd. C 58.34, H 6.12; found C 58.60, H 6.29.

[(COD)(η^6-o-Tolyl tert-Butyl Ketone)Ru] (**4**): To a solution of [(COD)(η^6-*o*-tolyl bromide)Ru] (**3**) (250 mg, 0.66 mmol) in 10 ml of THF, 0.4 ml (1.0 mmol) of a 2.5 M solution of *n*-butyllithium in hexane was added via a syringe at −80°C. The reaction mixture was stirred for 10 min, 0.1 ml (1.0 mmol) of pivaloyl chloride was added at −70°C, and the mixture was allowed to warm to room temp. over a period of 2 h. The solvents were then removed in vacuo, the residue was extracted with light petroleum ether/toluene and the combined extracts were filtered through Al_2O_3/5% H_2O, yielding a yellow solution. Removal of the solvent in vacuo and redilution of the resulting yellow oil with petroleum ether allowed purification by column chromatography on Al_2O_3/5% H_2O. First by-products were eluted with light petroleum ether as a pale-yellow solution. [(COD)(η^6-*o*-tolyl *tert*-butyl ketone)Ru] (**4**) was eluted by toluene/light petroleum ether (1:1) as an orange solution. Evaporation of the solvent and recrystallization from *n*-heptane resulted in 231 mg (0.6 mmol, 91%) of pure, orange **4**. – ^{1}H NMR (269.6 MHz, C_6D_6): δ = 5.15 [t, 1 H, H-aryl, ^3J(HH) = 6 Hz], 4.65 [d, 1 H, aryl H, ^3J(HH) = 6 Hz], 4.55 [t, 1 H, aryl H, ^3J(HH) = 6 Hz], 4.40 [d, 1 H, aryl H, ^3J(HH) = 6 Hz],; 3.65–3.50 (m, 2 H, olef. COD H), 3.48–3.38 (m, 2 H, olef.-COD H), 2.40–2.10 (m, 8 H, aliph.-COD H), 1.70 (s, 3 H, CH_3), 1.07 (s, 9 H, CH_3-*tert*-butyl). – ^{13}C NMR (67.7 MHz, C_6D_6): δ = 208 (C-carbonyl), 104.5 (C-aryl), 97.7 (C-aryl), 86.0 (C-aryl), 85.4 (C-aryl), 84.4 (C-aryl), 81.9 (C-aryl), 64.6 (COD-olef.), 63.9 (COD-olef.), 45.2 (C-*tert*-butyl), 34.6 (COD-aliph.), 33.6 (COD-aliph.), 27.5 (CH_3-*tert*-butyl), 17.4 (CH_3-tolyl). – MS (EI, 70eV); *m/z:* 386 $[M]^+$. – $C_{20}H_{28}ORu$: calcd. C 62.31, H 7.32; found C 62.93, H 7.48.

[(COD)(η^6-o-Tolylphenylmethanol)Ru] (**5**): Phenyllithium was prepared in 20 ml of THF by reacting bromobenzene (157 mg, 1.0 mmol) and 0.4 ml (1.0 mmol, 2.5 M) of *n*-butyllithium in hexane at −80°C. At −50°C, a solution of [(COD)(η^6-*o*-tolyl aldehyde)Ru] (**2**) (250 mg, 0.75 mmol) in 10 ml of THF was added and the mixture was allowed to warm to room temp. over a period of 1 h. Then, 1 ml of degassed water was slowly added by means of a syringe. After stirring the mixture overnight, the solvents were removed in vacuo, the residue was extracted with toluene/light petroleum ether and chromatographed on Al_2O_3/5% H_2O, yielding an orange solution upon elution with toluene. Evaporation of the solvent yielded 259 mg (0.63 mmol, 85%) of **5** as an orange oil. – Main diastereomer: ^{1}H NMR (399.65 MHz, C_6D_6): δ = 7.51 [d, 2 H, phenyl H_o, ^3J(HH) = 6.4 Hz], 7.21 [t, 2 H, phenyl H_m, ^3J(HH) = 7.0 Hz], 7.10 [t, 1 H, phenyl H_p, ^3J(HH) = 6.1 Hz], 5.64 [d, 1 H, benzyl H, ^3J(HH) = 3.2 Hz], 5.43 [t, 1 H, aryl H, ^3J(HH) = 5 Hz], 4.95 [d, 1 H, aryl H, ^3J(HH) = 5.6 Hz], 4.36 [d, 1 H, aryl H, ^3J(HH) = 5.3 Hz[, 4.21 [t, 1 H, aryl H, ^3J(HH) = 5.1 Hz], 3.51–3.46 (m, 2 H, olef.-COD H), 3.29–3.16 (m, 2 H, olef.-COD H), 3.01 [d, 1 H, OH, ^3J(HH) = 3.2 Hz], 2.40–2.20 (m, 8 H, aliph.-COD H), 1.65 (s, 3 H, CH_3). – ^{13}C NMR (100.4 MHz, C_6D_6): δ = 143.6 (C-phenyl), 129.0 (C-phenyl), 128.0 (C-phenyl), 127.4 (C-phenyl), 112.0 (C-aryl), 99.4 (C-aryl), 89.2 (C-aryl), 86.7 (C-aryl), 86.4 (C-aryl), 86.0 (C-aryl), 70.0 (C-OH), 63.2 (COD-olef.), 60.8 (COD-olef.), 35.1 (COD-aliph.), 34.7 (COD-aliph.), 16.8 (CH_3). – MS (FD, 2kV); *m/z:* 407 $[M]^+$ $C_{22}H_{26}ORu$.

[(COD)(η^6-o-Tolyl-n-butyl-tert-butylmethanol)Ru] (**6**): To a solution of [(COD)(η^6-*o*-tolyl *tert*-butyl ketone)Ru] (**4**) (200 mg, 0.52 mmol) in 50 ml of THF, 0.4 ml (1.0 mmol) of a 2.5 M solution of *n*-butyllithium was added via a syringe at −50°C. The mixture was allowed to warm to room temp. over a period of 2 h, 1 ml of degassed water was added, and the solution was stirred overnight. The solvents were then removed in vacuo, the residue was extracted with toluene and the combined extracts were filtered through Al_2O_3/5% H_2O, yielding a yellow solution. Evaporation of the solvent resulted in 214 mg (0.48 mmol, 93%) of **6** as a yellow oil. – ^{1}H NMR (399.65 MHz, C_6D_6): δ = 5.42 [t, 1 H, aryl H, ^3J(HH) = 6 Hz], 5.13 [t, 1 H, aryl H, ^3J(HH) = 5.6 Hz], 4.78 [d, 1 H, aryl H, ^3J(HH) = 6 Hz], 3.51–4.45 (m, 3 H, aryl H, olef.-COD H), 3.12–3.08 (m, 2 H, olef.-COD H), 2.41–1.93 (m, 12 H, aliph.-COD H, aliph.-*n*-butyl H), 1.89 (s, 3 H, CH_3-tolyl), 1.68 (s, 1 H, OH), 1.61–1.31 (m, 2 H, aliph.-*n*-butyl H), 1.03 (t, H-CH_3-*n*-butyl, ^3J = 7.3 Hz), 0.93 (s, 9 H, CH_3-*tert*-butyl). – ^{13}C NMR (100.4 MHz, C_6D_6): δ = 110.3 (C-aryl), 104.2 (C-aryl), 92.1 (C-aryl), 87.4 (C-aryl), 83.5 (C-aryl), 80.8 (C-alcohol*), 80.6 (C-aryl*), 63.8 (COD-olef.), 60.5 (COD-olef.), 41.2 (C-*tert*-butyl), 36.7 (C-*n*-butyl), 34.8 (COD-aliph.), 32.9 (COD-aliph.), 26.8 (C-*n*-butyl), 27.5 (C-*tert*-butyl), 24.0 (C-*n*-butyl), 20.7 (CH_3-tolyl), 14.3 (CH_3-*n*-butyl). (* = assignments not unequivocal). – MS (EI, 70eV); *m/z:* 443 $[M]^+$ $C_{24}H_{38}ORu$.

[(COD)(η^6-o-Tolyl-tert-butylphenylmethanol)Ru] (**7**): Phenyllithium was prepared in 20 ml of THF by reacting bromobenzene (234 mg, 1.5 mmol) and 0.6 ml (1.5 mmol, 2.5 M) of *n*-butyllithium in hexane at −80°C. At −50°C, a solution of [(COD)(η^6-*o*-tolyl *tert*-butyl ketone)Ru] (**4**) (210 mg, 0.54 mmol) in 10 ml THF was added and the mixture was allowed to warm to room temp. over a period of 1 h. Then, 1 ml of degassed water was added slowly by means of a syringe. After stirring the mixture overnight, the solvents were removed in vacuo, the residue was extracted with toluene/light petroleum ether and chromatographed on Al_2O_3/5% H_2O, yielding a yellow solution upon elution with toluene. Evaporation of the solvent and recrystallization from toluene resulted in 231 mg (0.50 mmol, 92%) of pure, yellow **7**. – ^{1}H NMR (slow exchange limit, 223 K, 399.65 MHz, [D_8]toluene): δ = 8.08 [d, 1 H, H_o-phenyl, ^3J(HH) = 7.6 Hz], 7.13–6.92 (m, 3 H, phenyl H), 6.66 [d, 1 H,phenyl H_o, ^3J(HH) = 7.6 Hz], 5.56 [t, 1 H, aryl H, ^3J(HH) = 5.2 Hz], 5.23 [d, 1 H, aryl H, ^3J(HH) = 6.4 Hz], 4.12 [d, 1 H, aryl H, ^3J(HH) = 5.4 Hz], 3.76 [t, 1 H, aryl H, ^3J(HH) = 5.4 Hz], 3.74 (s, 1 H, OH), 3.21 (s, 4 H, olef.-COD H), 2.42–2.26 (m, 8 H, aliph.-COD H), 1.65 (s, 3 H, CH_3-*tert*-butyl), 1.13 (s, 3 H, CH_3-*tert*-butyl), 1.02 (s, 3 H, CH_3-*tert*-butyl), 0.99 (s, 3 H, CH_3-tolyl). – ^{13}C NMR (100.4 MHz, C_6D_6): δ = 144.5 (C-phenyl), 129.1 (C-phenyl), 126.5 (C-phenyl), 126.1 (C-phenyl), 114.2 (C-aryl), 96.1 (C-aryl), 94.9 (C-aryl), 82.7 (C-aryl*), 81.4 (C-aryl*), 81.0 (C-OH*), 62.1 (COD-olef.), 61.9 (COD-olef.), 39.7 (C, *tert*-butyl), 35.3 (COD-aliph.), 33.2 (COD-aliph.), 26.8 (broad, C-*tert*-butyl), 25.7 (broad, C-*tert*-butyl), 19.1 (CH_3, aryl). (* = assignments not unequivocal). – MS (EI, 70eV); *m/z:* 463 $[M]^+$. – $C_{26}H_{34}ORu$: calcd. C 67.35, H 7.34; found C 67.94, H 7.71.

Crystal Structure Determination: Suitable crystals of **7** were taken directly out of the mother liquor. Data were collected on a Siemens P4 diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator (Table 1). The crystal structure was solved by direct methods (SHELXS-86[8]) and refined using SHELXL-93 programmes.[9] Non-hydrogen atoms were refined an-

Table 1. Crystal data of **7**

Empirical formula	$C_{26}H_{34}ORu$
Colour, form	orange quader
Size (mm)	0.7 x 0.5 x 0.4
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å)	a = 12.406(5) b = 12.443(5) c = 14.340(6) β = 107.25(4)
Volume (Å^3)	2114(2)
Z	4
Molecular mass	463.42
Density (calcd.)	1.457 gcm^{-3}
Absorption coefficient	0.755 mm^{-1}
Absorption correction	none
Number of refined parameters	398
$F^{(000)}$	968.0
Reflections measured	6460
Independent reflections	4610
Goodnesss-of-fit at F^2	1.260
$R1$	0.0270
wR_2	0.0974
Residual electron density eÅ^{-3}	max. 1.288 min. −1.239

isotropically; the hydrogen atoms were taken from a difference Fourier synthesis and refined anisotropically. Other experimental details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100095. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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