

A Novel Cyclopentadienone and its Ruthenium and Iron Tricarbonyl Complexes

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Dedicated to Prof. Wolfgang Beck on the occasion of his 90th birthday.

A simple and efficient protocol allows the oxidation of the cyclopentadiene derivative 5H-dibenzo[e,h]-dibenzo[3,4:6,7]cyclohept[1,2-a]azulene (Cp^CH) provide according ketone Cp^CO. Comparable to the situation found for Cp^CH, the bending of the four annulated six-membered rings defines the C₂ symmetric molecular structure of Cp^CO. The cyclopentadienone Cp^CO readily reacts with [Ru₃(CO)₁₂] and [Fe₃(CO)₁₂] to generate tricarbonyl complexes of the type [(η⁴-Cp^CO)M(CO)₃]. In contrast

to [(η⁴-Cp^CO)Ru(CO)₃], the tricarbonyliron(0) complex is sensitive to oxygen and moisture. Refluxing [(η⁴-Cp^CO)Ru(CO)₃] in isopropanol makes the hydrido-bridged complex [(η⁴-Cp^CO)₂H]Ru₂(CO)₄ accessible, an analogue to Shvo's catalyst. Both ruthenium complexes and their ligand Cp^CO were characterized spectroscopically and by single crystal x-ray diffraction. The activity of [(η⁴-Cp^CO)Ru(CO)₃] was investigated for a series of transfer hydrogenation reactions.

Introduction

The oxidation of the cyclopentadienide anion with dioxygen normally leads to a complex mixture of compounds. However, the stabilizing influence of alkyl substituents at the Cp ring allows the isolation of some well-defined, oxidized Cp derivatives. In 1993 H. Sitzmann et al. were able to isolate 1,2,3,4-tetraisopropylcyclopentadienone by reacting the radical 1,2,3,4,5-penta-isopropylcyclopentadienyl - obtained by treatment of sodium 1,2,3,4,5-pentaisopropylcyclopentadienide with elemental bromine - in the presence of air.^[1] Just a few years later, R. Ramage et al. reported the synthesis of tetrabenzocyclopentadienone starting from the reaction of the corresponding sodium salt in tetrahydrofuran under aerobic conditions.^[2] On the other hand, 2,3,4,5-tetraphenylcyclopentadienone is accessible in a classical cyclisation reaction by the condensation of 1,3-diphenyl-2-propanone with 1,2-diphenylethane-1,2-

dione.^[3] Based on this ketone and other structurally related cyclopentadienones, a number of ruthenium and iron hydrido complexes could be prepared, which have found application as catalysts in transfer hydrogenation and dehydrogenation reactions.^[4]

The discovery of this new class of hydrido compounds dates back to observations made by Y. Shvo in the 1980ies during the catalytic oxidation of alcohols in the presence of triruthenium(0)dodecacarbonyl.^[5] They found an increase in activity by the addition of diphenylacetylene, which was at that time considered to act as a hydrogen acceptor. A few years later, the activating effect could be attributed to the in-situ formation of 2,3,4,5-tetraphenylcyclopentadienone by a [2 + 2 + 1] cycloaddition of two equivalents of diphenylacetylene and one equivalent of metal-bound carbon monoxide^[6] resulting primarily in the formation of the mononuclear tricarbonylruthenium(0) complex **1** (Scheme 1).

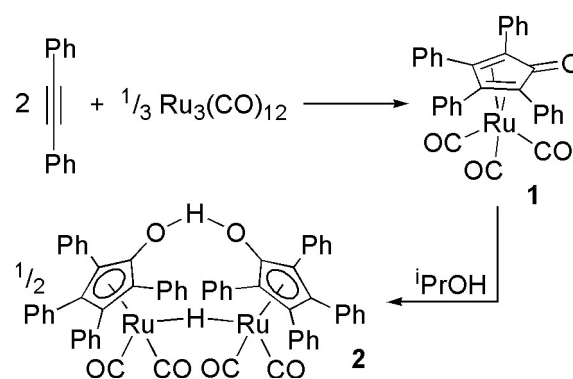
By treatment with isopropanol, the previously unknown, binuclear hydrido species **2** was obtained.^[7] Later, this air- and

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Scheme 1. Synthesis of Shvo's catalyst (2).

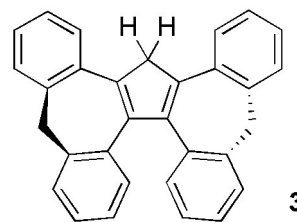
water-stable hydrido complex was given the name “Shvo catalyst”. Compared to other transition metal compounds that also catalyze the transfer of hydrogen atoms, the mechanism of transfer hydrogenation and dihydrogenation starting from the “Shvo catalyst” is unique, since it is based on a concerted uptake (or release) of two hydrogen atoms after dissociation of the complex into monomers.^[4c] This mechanism requires both, the metal center and the cyclopentadienone ligand. It therefore is considered as a bifunctional ligand-metal catalyst.^[4a,c,8] Hereby, the 18-VE hydrido species with a ruthenium center in the oxidation state +II represents the reducing agent (hydrogen donor), while the coordinatively unsaturated 16-VE carbonyl species with the ruthenium in the oxidation state ± 0 functions as the oxidant (hydrogen acceptor). The proportion of the two catalytically active species in equilibrium is specifically controlled by either the aid of an external hydrogen donor or hydrogen acceptor.^[4a]

Nowadays, the “Shvo catalyst” **2** is synthesized in a two-step process starting from 2,3,4,5-tetraphenylcyclopentadienone and $[\text{Ru}_3(\text{CO})_{12}]$ followed by a reaction with either an alcohol or an aqueous alkaline solution and subsequent protonation.^[4a] An alternative synthetic access is a one-step reaction of the two components in boiling methanol, which was developed by C. P. Casey et al.^[9]

Despite the high catalytic activity of Shvo-type complexes, only a few stereoselective catalyses involving enzymes were known for a long time, probably due to the lack of chiral versions of the cyclopentadienone ligand.^[4a,10] In 2010 Y. Yamamoto et al. synthesized a chiral catalyst, which provided a small enantiomeric excess of 21% in the transfer hydrogenation of acetophenone.^[11] In the following years, other chiral ruthenium tricarbonyl complexes appeared in the literature, all providing only little enantiomeric excess.^[12] A first improvement could be established in 2018 by X. Dou and T. Hayashi.^[13] Their planar-chiral catalyst had different substituents at the 2,5-positions of the cyclopentadienone ring. The enantiomeric mixture, which was formed by its coordination to the metal center, had to be separated before its application in catalysis by means of preparative chromatography using a chiral column. The subsequent reaction of the enantiomerically pure tricarbonyl complex in the presence of an alkaline solution gave the corresponding binuclear hydrido complexes which were structurally analogous to Shvo's catalyst and yielded ee values of up to 56% in the asymmetric transfer hydrogenation of ketones.

Although ruthenium-based Shvo-type catalysts usually exhibit high catalytic activity and stability, (chiral) iron tricarbonyl complexes have increasingly appeared in recent years since the economic advantage of these compounds outweighs the corresponding noble metal derivatives.^[12b]

One typical example is a C_2 -symmetric iron complex prepared in 2015 by U. Gennari et al. bearing a cyclopentadienone ligand, which was synthesized from enantiomerically pure BINOL.^[14] Its reaction with aqueous sodium hydroxide gave access to a monomeric hydrido complex, which use in the asymmetric transfer hydrogenation of acetophenone provided enantiomeric excesses of up to 77%. Furthermore, a series of enantiomerically pure iron complexes of the so-called “Knölker



Scheme 2. Molecular structure of $\text{Cp}^{\text{C}^{\text{H}}}$ (**3**).

type” was reported in recent years. They were synthesized from functionalized dialkynes and different iron carbonyl precursors in a $[2 + 2 + 1]$ cyclisation reaction.^[12,15]

Since some time we are investigating the coordination chemistry of the novel cyclopentadienyl-type ligand $\text{Cp}^{\text{C}^{\text{H}}}$ (**3**, Scheme 2), which is accessible in just a few steps from cheap dibenzosuberone.^[16]

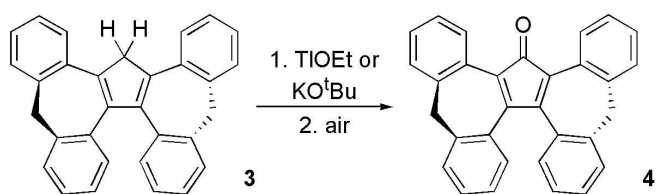
It turned out, that transition metal complexes of this ligand can be obtained as simple as those of the structurally related 1,2,3,4,5-pentaphenylcyclopentadienyl ligand, although it is by far less structurally flexible.^[16,17] During the course of these investigations, the formation of red-colored by-products was observed in a series of reactions. This was a first hint for the formation of the ketone $\text{Cp}^{\text{C}^{\text{O}}}$ (**4**). A few years before, we were able to isolate the structurally related ketone dibenzo[c,g]-fluorenone,^[18] which was the starting point for a series of publications on the organometallic chemistry of the ligand 7*H*-dibenzo[c,g]fluorenone (Dbf^{-1}).^[19] As Dbf^{-1} , $(\text{Cp}^{\text{C}})^{-1}$ is an intrinsically chiral cyclopentadienyl ligand. While its barrier of inversion ($\sim 85 \text{ kJ}\cdot\text{mol}^{-1}$) is much higher than the barrier of inversion of Dbf^{-1} ($\sim 20 \text{ kJ}\cdot\text{mol}^{-1}$), it is still too low to prevent slow racemization at room temp, which we were able to demonstrate by means of a detailed NMR spectroscopic study on two Cp^{C} ruthenium(II) complexes.^[20] It therefore seemed to be interesting to prove the formation of $\text{Cp}^{\text{C}^{\text{O}}}$ (**4**) and evaluate its organometallic chemistry in more detail.

Results and Discussion

Complex Synthesis and Characterization

Since the thallium(I) salt TlCp^{C} has turned out to be the most suitable precursor for the transfer of the $(\text{Cp}^{\text{C}})^{-}$ ligand to late, electron-rich transition metal centers,^[20] its reactivity towards oxygen was investigated first. Treatment of TlCp^{C} in THF with air leads to an intense red coloration of the solution (Scheme 3). After work-up, the ketone $\text{Cp}^{\text{C}^{\text{O}}}$ (**4**) could be isolated in almost quantitative yields.

Due to their toxicity, working with thallium(I) compounds should be avoided if possible. After some optimization of the reaction conditions, ketone **4** could also be obtained by treatment of the potassium salt KCp^{C} with air, however, in somewhat smaller yields of 90%. KCp^{C} was formed in equilibrium by the addition of KO^tBu in THF/toluene to a solution of



Scheme 3. Synthesis of Cp^CO (4).

Cp^CH in toluene. To avoid the excessive formation of by-products, 1.5 eq. of KO^tBu were found to be ideal. The minor amounts of by-products formed under these conditions can simply be removed by column chromatography.

The molecular structure of 4 was evaluated by means of NMR and IR spectroscopy (see the Supporting Information): The ¹H NMR spectrum of 4 shows the two typical doublets (4.02, 3.77 ppm) with large geminal H,H-coupling constants of about 13.5 Hz for the four methylene protons of the cycloheptatriene rings. A band at 1699 cm⁻¹ in the IR spectrum of 4 is assigned

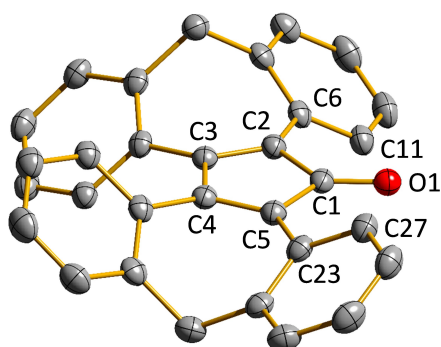
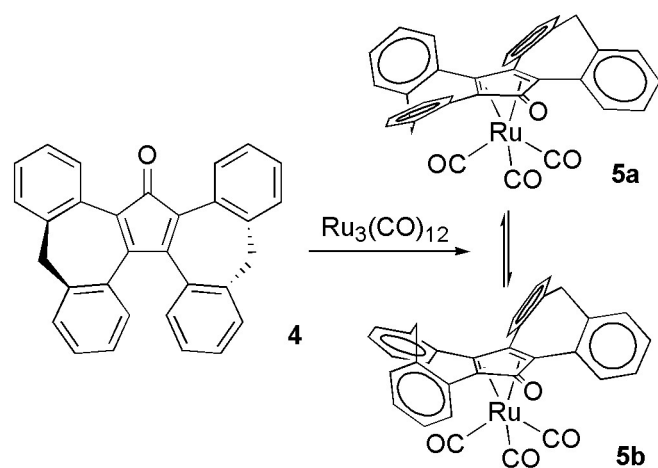


Figure 1. Molecular Structure of the ketone 4 in the solid state, hydrogen atoms are omitted for clarity. Characteristic bond lengths [Å] and dihedral angles [°]: O1–C1 1.2169(16), C1–C2 1.5057(18), C1–C5 1.5027(18), C2–C3 1.3586(18), C3–C4 1.5099(18), C4–C5 1.3605(19), C1–C2–C6–C11 30.8(2), C1–C5–C23–C27 31.1(2).



Scheme 4. Synthesis of the tricarbonylruthenium(0) complexes 5a and 5b.

to the stretching vibration of the conjugated carbonyl group. The molecular structure of 4 was finally elucidated by a single crystal X-ray diffraction analysis (Figure 1). Compound 4 displays the typical bond lengths of a conjugated, 2,3-unsaturated ketone with slightly elongated C=C double bonds (C2–C3 and C4–C5) and slightly shortened C–C single bonds (C1–C2, C1–C5, C3–C4). The bending of the two rings can be described best by two dihedral angles of about 30°.

Treatment of [Ru₃(CO)₁₂] with Cp^CO (4) in boiling toluene following a protocol developed by M. I. Bruce and J. R. Knight in 1967,^[21] provided the light yellow tricarbonyl complex [(η⁴-Cp^CO)Ru(CO)₃] in excellent yields of 93% (Scheme 4). The compound consists of a mixture of the two isomers 5a and 5b (see below). During the reaction, the evolution of carbon monoxide was observed.

In all transition metal complexes of (Cp^C)⁻¹ investigated before, the η⁵-coordinating ligand adopts a local C₂ symmetry, which minimizes the sterical interaction of the two “wings” of the ligand. This gives rise to four magnetically inequivalent methylene protons at the seven-membered rings of the ligand, leading to two independent AB spin systems and thus to four doublets in the ¹H NMR spectra of these complexes. In contrast, the ¹H NMR spectrum of [(η⁴-Cp^CO)Ru(CO)₃] shows, in addition to the expected four doublets of the methylene protons of the η⁴-coordinated Cp^CO ligand (local C₂ symmetry of the ligand in isomer 5a), two further doublets of minor intensity in the same region (see the Supporting Information). In the ¹³C NMR spectrum a second set of resonances could be identified, which suggests the presence of a second isomer 5b possessing an η⁴-coordinated Cp^CO ligand with a local C₅ symmetry. In particular, there are two resonances at 195.4 (5a) and 194.7 ppm (5b) for the metal-coordinated carbonyl ligands and two resonances for the Cp^CO carbonyl group (171.0 and 172.9 ppm). The latter are strongly high-field shifted compared to the signal of the carbonyl group of the free ligand 4 (199.4 ppm). This shielding effect can be attributed to the strong π-backbonding of the ruthenium(0) center into the empty π*-orbitals of the η⁴-coordinating 1,3-diene unit. In the C₅-symmetric isomer, there are only two magnetically independent methylene protons, which explains the additional AB spin system in the methylene region of the ¹H NMR spectrum. Integration of the methylene resonances calculates a ratio of 1:0.35 for the two isomers 5a and 5b. DFT calculations on (Cp^C)⁻¹ showed that the isomer with C₅ symmetry is about 35 kJ·mol⁻¹ higher in energy than the isomer with C₂ symmetry, which makes it impossible to see it in the NMR spectra. However, it must be present in equilibrium, because it has to be passed through during the racemization process of the ligand. The measured isomer ratio of 1:0.35 in the case of the ruthenium complex means that the racemic isomer 5a and the meso isomer 5b are energetically almost identical. This will be discussed in more detail below.

There are three absorptions at 2011, 2032 und 2084 cm⁻¹ in the IR spectrum of 5a/5b, which are assigned to the stretching vibrations of the carbonyl ligands and one absorption at 1630 cm⁻¹, which can be attributed to the stretching vibration of the Cp^CO carbonyl group. The latter one is strongly shifted to lower energy compared to the CO-absorption of the metal-free

Cp^cO ligand (1699 cm⁻¹) speaking for a severe lowering of the bond order in the carbonyl bond. This can be explained by the back-bonding from the ruthenium(0) site into the Cp^cO ligand that stabilizes the 4 π -electron configuration in the five-membered ring.

Single crystals suitable for an X-ray structure analysis of isomer **5b**, which seems to be less soluble than **5a**, were obtained by crystallization of a saturated *n*-hexane/ethyl acetate solution of equilibrium mixture of **5a** and **5b** at room temperature. Figure 2 shows the molecular structure of **5b** in the solid state. Compound **5b** crystallizes in the monoclinic space group *P*₂.

In complex **5b**, the ruthenium(0) center is coordinated by three carbonyl ligands and one η^4 -bound pentadienone ring. The η^4 -coordination is confirmed by four short Ru1–C bonds of approx. 2.202–2.234 Å and the long Ru1–C1 distance (2.491 Å). A striking feature of the molecular structure is the kinking of the C1=O1 keto group from the plane of the butadiene system with an angle of 19.2°. This behavior has already been observed in the solid state structures of other iron(0) and ruthenium(0) cyclopentadienone complexes and was explained in the 1960ies by N. A. Bailey and R. Mason and in the 1970ies by K. Hoffmann and E. Weiss by applying the Hückel molecular orbital model (HMO).^[22] Their calculations showed that the bending of the keto group away from the plane of the cyclobutadiene unit significantly favors the overlap of the occupied ligand orbitals of the coordinating cyclobutadiene fragment with the unoccupied orbitals of the metal atom. In addition, the bent carbonyl group promotes the energetic lowering of one of the two non-bonding molecular orbitals of the planar cyclobutadiene, thus enhancing π -backbonding through the occupied d-orbitals of the metal center. The bending of the C1=O1 carbonyl group out of the plane of the cyclobutadiene system also provides an explanation for the presence of isomer **5b**. The racemic

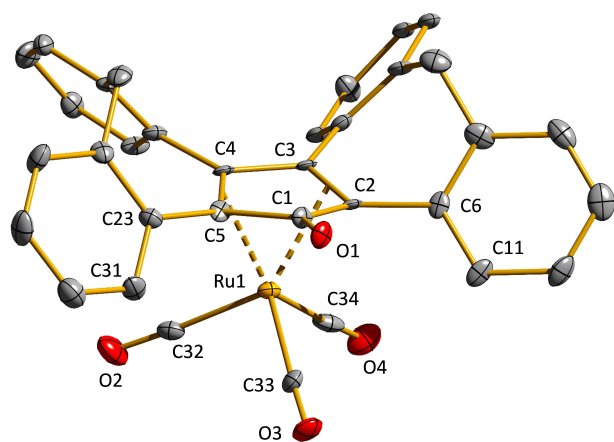


Figure 2. Molecular Structure of the tricarbonylruthenium(0) complex **5b** in the solid state, hydrogen atoms are omitted for clarity. Characteristic bond lengths [Å], angles [°] and dihedral angles [°]: Ru1–C1 2.49(1), Ru1–C2 2.22(1), Ru1–C3 2.23(1), Ru1–C4 2.20(1), Ru1–C5 2.21(1), Ru1–C32 1.96(1), Ru1–C33 1.94(1), Ru1–C34 1.92(2), O1–C1 1.22(1), O2–C32 1.12(2), O3–C33 1.13(1), O4–C34 1.15(2), C1–C2 1.48(2), C1–C5 1.50(2), C2–C3 1.45(2), C3–C4 1.47(2), C4–C5 1.45(2), C32–Ru1–C33 97.1(5), C32–Ru1–C34 91.9(5), C33–Ru1–C34 97.1(5), C1–C2–C6–C11 64.5(19), C1–C5–C23–C31 –62(2).

structure of **5a** (local C₂ symmetry of the Cp^cO ligand) on one hand decreases steric repulsions between the two “wings” of the Cp^cO ligand. On the other hand, there is an increase of steric interference between one of the wings and the carbonyl group.

In order to gain more insight into the energetic situation of the two stereoisomers, DFT calculations were carried out on the ruthenium complexes **5a** and **5b** as well as on their precursor Cp^cO (**4**), which was calculated in both, the C₂ symmetric form **4** and the C₅ symmetric form **4'**. Figure 3 summarizes the results.

The difference in energy between the two stereoisomers of the metal-free ligand Cp^cO (**4**) is nearly the same as calculated for the metal-free ligand Cp^cH (**3**) in the past.^[18] In contrast to this, the energy difference between the two isomeric ruthenium (0) complexes **5a** and **5b** is much smaller, which explains the presence of the resonances of both isomers in the NMR spectra. We assign the stabilization of the C₅ symmetric stereoisomer to the bending of the carbonyl group of the cyclopentadienone ring. The bending of both Cp^cO wings towards the metal center reduces steric interactions with the carbonyl group.

The two downwardly bent wings in **5b** lead to the largest twist of the ligand backbone obtained in a Cp^c compound to date, with a mean value of 63°. A strong π -backbonding from the electron-rich ruthenium(0) center into the non-occupied π^* -orbitals of the Cp^cO ligand is confirmed by largely widened C=C bonds (C2–C3: 1.45(2), C4–C5: 1.45(2) Å). The Ru1–C distances of the three C=O ligands arranged in a trigonal-pyramidal manner around the ruthenium(0) site are found between 1.92(2) and 1.96(1) Å and compare well with the bond lengths obtained by Shvo et al. for their structurally analogue complex.^[6c] In agreement with observations made by E. Weiss

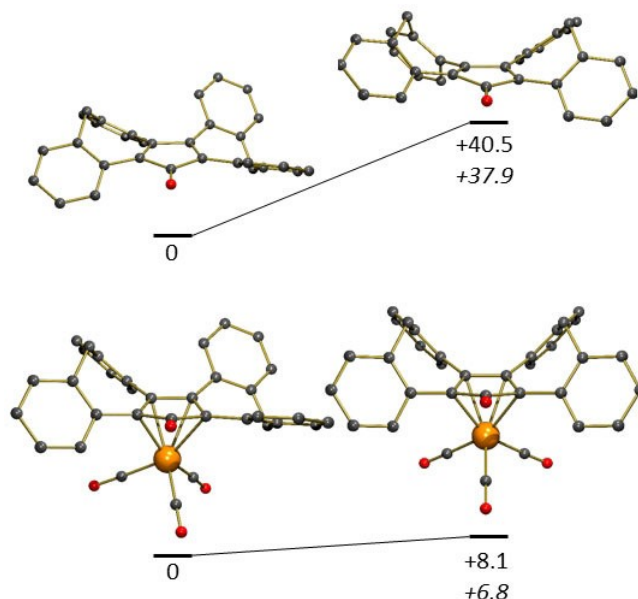


Figure 3. Calculated energy differences ($\Delta\Delta H$ and $\Delta\Delta G$, kJ/mol) between the stereoisomers of metal free Cp^cO (**4**, top) and the stereoisomeric metal complexes **5a** (bottom, left) and **5b** (bottom, right). The C₂ symmetric ligand structures are shown on the left and the C₅ symmetric ones on the right side.

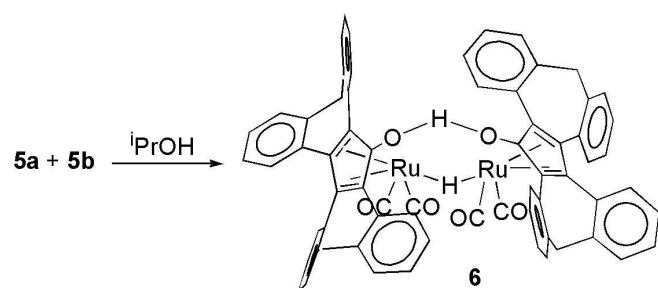
et al. and G. A. Sim the three carbonyl ligands arrange in a way that the extensions of the C=O bond vectors direct towards the centers with the highest electron density and thus not towards carbonyl carbon atom of the Cp^cO ligand.^[23]

When the mixture of the tricarbonyl ruthenium(0) complexes **5a** and **5b** was heated to reflux in isopropanol for 72 h, the binuclear ruthenium hydrido complex **6**, structurally analogous to Shvo's catalyst, was obtained under release of carbon monoxide (Scheme 5). In addition, to its function as a solvent, the alcohol also serves as a "hydrogen supplier" and is oxidized to acetone.

After removal of the solvent under vacuum and purification of the residue by slow diffusion of *n*-pentane into a saturated toluene solution of the raw product, compound **6** was isolated as a red crystalline solid with a yield of 39%. In the ¹H NMR spectrum of **6** (see the Supporting Information), there is a singlet resonance at -18.60 ppm integrating with a ratio of 1:8 with respect to the aliphatic signals. This resonance is assigned to the hydrido ligand bridging the two ruthenium centers. In the far low-field region at 14.01 ppm, there is a broad resonance that can be assigned to the proton bridging of the two oxygen atoms. In contrast to its ruthenium precursors **5a** and **5b**, there is no hint for a second configurational isomer, since only four partially superimposed doublets of totally eight protons belonging to the methylene units in the ligand backbone are observed. This suggests that the Cp^cO ligands of both ruthenium centers occupy local C₂ symmetry. Furthermore, there is no sign in the NMR spectra for diastereomers being present. Partially strongly unshielded signals of some aromatic protons are due to the ring currents of the numerous phenylene units within the two Cp^cO ligands.

In addition to the C–O stretching vibrations of the four carbonyl ligands (1945–2029 cm⁻¹), which are slightly shifted towards lower wavenumbers compared to compound **5b**, the C–O stretching vibrations of the two hydrogen-bridged carbonyl groups can be identified at 1524 and 1485 cm⁻¹ in the ATR-IR spectrum of compound **6**. The reduction of the C=O bond order is due to the aromatization of the five-membered Cp ring of the Cp^c ligand in compound **6**.

For the determination of the vibrations assigned to the Ru–H–Ru and O–H–O sites in the IR spectrum of compound **6**, quantum chemical calculations were carried out. To the best of our knowledge, no exact assignment of these bands in structurally analogous complexes has been made up to now.



Scheme 5. Synthesis of the homodinuclear ruthenium complex **6**.

The calculated values of the different CO bands agree very well with the experimentally obtained spectrum. In contrast, the calculations show a band for the O–H–O vibration at 2000 cm⁻¹ and a band for the Ru–H–Ru vibration at 1680 cm⁻¹, deviating from the measured IR spectrum. One reason for the deviation of the calculated from the measured IR spectrum can be attributed to the strong anharmonicity of these two vibrations, which is why they are not correctly determined by the harmonic calculation. Therefore, a reliable statement about the position of these bands in the experimental spectrum on the basis of the calculated spectrum is difficult. Compared to the harmonic calculation, both oscillations should be observed at lower energies and thus at lower wavenumbers.

The slow diffusion of *n*-pentane into a toluene solution of compound **6** gave crystals suitable for an X-ray structure analysis. Compound **6** crystallizes as red bricks in the monoclinic space group C2/c. Figure 4 shows the molecular structure of **6** in the solid state. The hydrido ligand bridging the two ruthenium centers is disordered across two positions.

The crystal structure analysis confirms the dinuclear structure of compound **6** with a bridging hydrido ligand and a bridging proton. It can be regarded as a heterodimer of the 18 VE ruthenium(II) species [(η⁵-Cp^cOH)Ru(CO)₂(H)] and the unsaturated 16 VE ruthenium(0) species [(η⁴-Cp^cO)Ru(CO)₂].^[4a,7b] The structural data also confirms the η⁵-coordination of the five-membered rings of the two Cp^cO ligands with almost identical Ru–C distances of all cyclopentadienide carbon atoms (2.191(3)–2.355(2) Å) as well as similar C–C distances within the cyclopentadienol rings (1.443(4)–1.459(4) Å), which is in contrast to the situation in **5b**. The value for the C1–O1 bond length 1.295(3) is exactly between a C–O single and double bond and confirms the loss of electron density as already observed in the

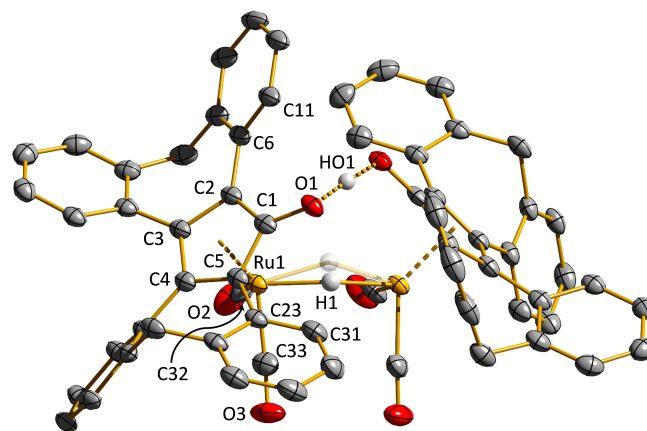


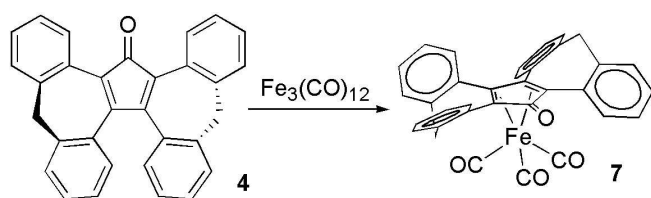
Figure 4. Molecular Structure of the dinuclear ruthenium complex **6** in the solid state, hydrogen atoms and a disordered molecule of *n*-pentane in the unit cell are omitted for clarity. The hydrido ligand is disordered across two positions. Characteristic bond lengths [Å], angles [°] and dihedral angles [°]: Ru1–C1 2.355(2), Ru1–C2 2.248(3), Ru1–C3 2.191(3), Ru1–C4 2.286(3), Ru1–C5 2.306(2), Ru1–C32 1.875(3), Ru1–C33 1.891(3), Ru1–H1_a 1.73(8), Ru1–H1 1.79(1), O1–C1 1.295(3), O2–C32 1.149(4), O3–C33 1.143(4), O1–HO1 1.233(3), C1–C5 1.459(4), C1–C2 1.451(5), C2–C3 1.449(4), C3–C4 1.445(5), C4–C5 1.443(4), C32–Ru1–H1 101(3), C32–Ru1–H1_a 85(3), C33–Ru1–H1 90(3), C33–Ru1–H1_a 106(3), Ru1–C32–O2 174.5(3), Ru1–C33–O3 173.8(3), C1–O1–HO1 116.0(13), C1–C2–C6–C11 43.8(4), C1–C5–C23–C31 20.6(4).

^{13}C NMR spectrum and the associated decrease of the $\text{C}=\text{O}$ bond order caused by the aromatization of the five-membered ring and the proton-bridging of the two carbonyl groups.

The $\text{O1}-\text{OH1}$ distance of 1.232(3) Å is in the range of structurally analogous complexes,^[7] while the $\text{Ru1}-\text{H1}$ distance of 1.79(10) Å ($\text{Ru1}-\text{H1}^*$: 1.73(8) Å) is found slightly longer, which can be explained by the repulsion of the sterically demanding phenylene units. The $\text{C}-\text{O}$ bond lengths (1.143(4)–1.149(4) Å) of the four coordinating carbonyl ligands are somewhat widened compared to the values found for compound **5b**, which can be attributed to the weaker π -backbonding into the $\text{Cp}^{\text{C}}\text{O}$ ligands due to the η^5 -coordination of the electron-rich cyclopentadienide fragment. The twisting within the two $\text{Cp}^{\text{C}}\text{O}$ ligands is in the normal range with dihedral angles of 35.60(4) and 38.37(4)° of the front and with 40.81(4) and 41.78(4)° of the rear phenylene units. The two Cp^{C} ligands show the same helical chirality (homo-chiral dimer), which minimizes steric interaction between the two units. By having a closer look to the molecular structure, one can easily imagine, that there would be a strong steric repulsion of the Cp^{C} ligands in the heterochiral dimer. This explains, why there is no hint for the presence of such a stereoisomer in the NMR spectra of **6**.

Following a procedure published by M. Wills et al.,^[15] triirondecacarbonyl was reacted for 16 h with $\text{Cp}^{\text{C}}\text{O}$ in toluene at 80 °C and the iron(0) complex **7** could be isolated in moderate yields (Scheme 6).

In contrast to its ruthenium(0) congener, compound **7** is rather sensitive to air. Nevertheless, it could be fully characterized by means of NMR and IR spectroscopy as well as by elemental analysis. The ^1H NMR spectrum solely shows the typical four resonances of the methylene protons in the region between 4.43 and 3.25 ppm and no hint for two further resonances as in the case of the ruthenium complexes **5a** and **5b**. This proves that in the iron case the isomer with the local C_2 symmetry of the $\text{Cp}^{\text{C}}\text{O}$ ligand is preferred over the C_5 symmetric complex. We explain this observation by the shorter $\text{Fe}-\text{C}$ distances which lead to an increase of steric interference between the down-pointing wings of the ligand and the metal site. An increase of the difference of the free energy ($\Delta\Delta\text{G}$) by just a few kcal mol^{-1} will shift the equilibrium between the two isomers in a way that only one of them will be detectable by ^1H NMR spectroscopy. In the ^{13}C NMR spectrum of **7**, there are the expected 32 resonances. The signal of the carbonyl ligands is found at 209.9 ppm and the resonance of the carbonyl group in the $\text{Cp}^{\text{C}}\text{O}$ ligand is observed at 166.6 ppm. Intense bands at 2063, 2022 and 1992 cm^{-1} in the IR spectrum of **7** are assigned to the stretching vibrations of the carbonyl ligands. Another intense band, located at 1607 cm^{-1} , is assigned to the



Scheme 6. Synthesis of the tricarbonyliron(0) complex **7**.

carbonyl group of the $\text{Cp}^{\text{C}}\text{O}$ ligand. This band is even more shifted to lower energies as for the ruthenium complexes **5a** and **5b**, speaking for an even better back-bonding from the iron(0) site in **7**.

Catalysis

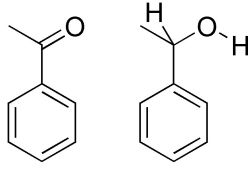
In the following, the catalytic activity of the mixture of compounds **5a** and **5b** in a series of hydrogen transfer reactions will be discussed and compared with that of $[(\eta^4-2,3,4,5\text{-tetraphenylcyclopentadienone})\text{Ru}(\text{CO})_3]$ (**1**). This precursor to Shvo's catalyst (**2**) was synthesized for this purpose according to a procedure published in the literature.^[5] In the presence of hydrogen-donating solvents used for reduction reactions it is converted in-situ to the active species. The same is true for the conversion of the mixture of **5a** and **5b** to **6**, which allows to avoid the low yield synthesis of **6**.

Bäckvall et al. described the catalytic transfer hydrogenation of aromatic imines to amines with Shvo's catalyst (**2**) and isopropanol as the hydrogen donor.^[24] We took *N*-benzylideneaniline as the substrate and reacted it under slightly modified conditions compared to the work of Bäckvall et al. (Table 1). Taking the first data points to determine the relative activity, it can be considered that the mixture of **5a** and **5b** is by a factor of 3–4 more active than **1**. It might be, that the more rigid structure of **5a** and **5b** compared to **1** favors the coordination of the substrate.

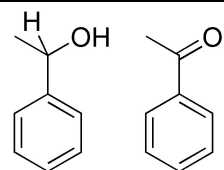
In contrast to the reduction of *N*-benzylideneaniline to *N*-benzylaniline, the reverse reaction using acetone as the hydrogen-accepting agent gave only conversions below 3% for both catalysts, even after 24 h. The catalytic reduction of acetophenone to 1-phenylethanol leads to equilibrium in between 24 h as does the reverse transfer dehydrogenation of 1-phenylethanol to acetophenone. Both catalysts show rather similar activities in these transformations (Table 2 and Table 3). In both cases, the activities of the mixture of **5a** and **5b** is comparable to the data measured for compound **1**, which may be due to the smaller molecular size of these substrates compared to *N*-benzylideneaniline.

Table 1. Catalytic transfer hydrogenation of <i>N</i> -benzylideneaniline. ^[a]				
Substrate	Product	Time [h]	5a and 5b	1
		0.5	26	7
		57	19	
		80	30	
		96	42	
		98	56	
		98	66	
		99	78	
		99	88	

[a] 1.0 mol% of catalyst, 1.00 mmol of *N*-benzylideneaniline, 3 mL of toluene/isopropanol (v:v=2:1), T=82 °C, conversion determined by GC analysis (int. standard: tetradecane).

Substrate	Product	Time [h]	5a + 5b	1
		2 h	2	3
		10	9	
		24	14	
		43	23	
		97	95	

[a] 1.0 mol% of catalyst, 1.00 mmol of acetophenone, 3 mL of isopropanol, T = 82 °C, conversion determined by GC analysis (int. standard: tetradecane).

Substrate	Product	Time [h]	5a and 5b	1
		2 h	31	28
		54	52	
		70	70	
		79	82	
		98	98	

[a] 1.0 mol% of catalyst, 1.00 mmol of acetophenone, 3 mL of actone, T = 56 °C, conversion determined by GC analysis (int. standard: tetradecane).

Catalytic transfer hydrogenation reactions with the tricarbonyliron(0) complex **7** gave only poor conversions. We assign these findings to the high sensitivity of this compound.

Conclusion

We herein reported the synthesis of two new and catalytically active ruthenium complexes and one iron complex starting from the easily available cyclopentadienone ligand Cp^cO. The ruthenium complexes are structural analogues to Shvo's catalyst resp. its ruthenium(0) precursor. Structural characterization of [(η⁴-Cp^cO)Ru(CO)₃] revealed a pronounced bending of the Cp^cO carbonyl group away from the metal site, which is explained by the strong π-backbonding from the ruthenium(0) center into the C=C double bonds of the electron poor diolefin ligand. Both stereoisomers of [(η⁴-Cp^cO)Ru(CO)₃] are observable in its NMR spectra. While the dimeric complex [(η⁴-Cp^cO)₂H]Ru₂(μ²-H)(CO)₄ was fully characterized, the analogue iron complex could not be obtained. The activity of the new ruthenium complexes in base-free transfer hydrogenation of *N*-benzylideneaniline is higher compared to [(η⁴-Ph₄CpO)Ru(CO)₃], which we explain by the more rigid nature of the annulated Cp^cO ligand.

Experimental Section

All commercially available and not in-house produced chemicals were used without further purification for the synthesis of ligands and transition metal complexes. Purchases were made from the following suppliers: ABCR GmbH, Fisher Scientific GmbH, Merck KGaA and Strem Chemicals GmbH. Acquired compounds sensitive

to air or moisture were filled under exclusion of oxygen and water into suitable Schlenk tubes. The solvents dichloromethane, diethyl ether, *n*-pentane and toluene were dried using the MBraun MB-SPS solvent drying system and degassed by passing nitrogen for 10 min. Acetonitrile and tetrahydrofuran were dried according to standard methods.^[25] All reactions were carried out by using the Schlenk technique under an atmosphere nitrogen, unless otherwise stated. Glassware was heated three times with a heat gun under vacuum and refilled with dry nitrogen. When necessary, purification of compounds was carried out by column chromatography on the CombiFlash Rf200 instrument from Teledyne Isco with pre-packed RediSept® columns. For the sample preparation, the compounds were dissolved in dichloromethane and then mixed with silica. After removing the solvent under vacuum, the samples were placed on a pre-column. The elution was carried out with a mixture of *n*-hexane and ethyl acetate in adjusted ratios, whereby the solvent gradient was varied during the separation. NMR spectra were recorded by using the Avance 400 and 600 devices from Bruker Corporation at a temperature of 293 K (20 °C). Air- or moisture-sensitive compounds were measured under an inert gas atmosphere using an NMR tube with a Teflon cap from VWR International GmbH. The anhydrous deuterated solvents CD₃CN, C₆D₆, CDCl₃ and CD₂Cl₂ used were dried according to standard methods, recondensed and then stored under an inert gas atmosphere in suitable Schlenk tubes. The evaluation of the NMR spectra was carried out with the programme MestReNova 6.0.2-5475© of the company Mestrelab Research. The infrared spectra were recorded on the Perkin-Elmer FT-ATR-IR 100 spectrometer and on the JASCO FT/IR-4100 spectrometer with diamond-coated zinc selenide windows. The IR spectra were processed using the Perkin-Elmer Spectrum 6.3.5 software from and the OriginLab Corporation software OriginPro 8G. Elemental analyses were measured out in the Analytical Laboratory of the Department of Chemistry at the TU Kaiserslautern. Compounds sensitive to air or moisture were filled in a glove box into tin capsules and sealed under an atmosphere of argon. The measurement of the elemental analyses was carried with a Vario Micro Cube analyser from Elementar-Analysetechnik. Cp^cH (**1**) was synthesized according to procedures published in the literature.^[16]

Cp^cO (4) by oxidation of TICp^c: 2.00 g (3.35 mmol) of Cp^cTi^[20] were dissolved in 100 mL of dry THF and stirred under air at room temperature. The solution turned from orange to deep red within about 3 min. After 2 h, the solvent was removed and the residue was dissolved in 100 mL of dichloromethane. The suspension thus obtained was extracted twice with 30 mL of 2 M HCl and then with 30 mL of 2 M NaHCO₃. The organic phase was dried over MgSO₄ and the solvent was removed under vacuum. After recrystallisation from dichloromethane/diethyl ether, Cp^cO (**4**) was obtained as deep red crystals. Yield: 1.35 g (3.30 mmol, 99%) of red hygroscopic crystals. Elemental analysis calcd. for C₃₁H₂₀O·(H₂O)_{0.3} (413.89): C 89.96, H 5.02; found: C 90.04, H 5.12. For further spectroscopic characterization see below.

Cp^cO (4) by oxidation of KCp^c: 501 mg (1.27 mmol) of Cp^cH (**3**) were dissolved in 12 mL of hot toluene and were added to a solution of 225 mg (1.91 mmol) of potassium *tert*-butoxide dissolved in a mixture of 24 mL of dry toluene and 6 mL of dry THF. The mixture was stirred for 2 h at room temperature. Then the flask was opened and the mixture was stirred for another 18 h with exposure to air. The solvent was removed under reduced pressure, the residue was dissolved in 25 mL of chloroform and washed with 2 M HCl, a saturated solution of NaHCO₃ and water. The organic phase was dried over MgSO₄. Removing of the solvent gave a red solid, which was purified by column chromatography with ethyl acetate/hexane. Yield: 467 mg (90%) of a red hygroscopic solid. Elemental analysis calcd. for C₃₁H₂₀O·(H₂O)_{0.8} (422.91): C 88.04, H 5.15; found: C 88.13, H 5.05. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.87 (dd,

$^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 2H, H_{ar}), 7.46–7.32 (m, 10H, H_{ar}), 7.00 (td, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 0.9$ Hz, 2H, H_{ar}), 6.75 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H, H_{ar}), 4.02 (d, $^2J_{\text{HH}} = 13.0$ Hz, 2H, CH_2), 3.77 (d, $^2J_{\text{HH}} = 13.0$ Hz, 2H, CH_2). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 199.4 (CO), 152.8, 140.1, 139.4, 130.8, 130.7, 129.5, 129.3, 129.1, 128.8, 127.7, 127.6, 126.7, 126.5, 125.0, 42.2 (CH_2). IR (ATR, cm^{-1}): $\tilde{\nu}$ 3058w, 3018w, 2958w, 2950w, 2077w, 2005m, 1996m, 1980m, 1968m, 1959m, 1810m, 1699vs, 1596m, 1569w, 1548w, 1480m, 1430m, 1369m, 1332m, 1322m, 1299m, 1275m, 1160m, 1133m, 1115m, 1073m, 1040m, 984m, 950m, 906m, 881m, 837m, 800m, 776m, 765m, 740s, 720s, 708m, 663m.

$\{(\eta^4\text{-Cp}^{\text{C}}\text{O})\text{Ru}(\text{CO})_3\}$ (5a + 5b, two stereo isomers): 818 mg (2.00 mmol) of ketone **4** and 450 mg (0.70 mmol) of $\text{Ru}_3(\text{CO})_{12}$ were stirred at 120 °C in 15 mL of toluene for 72 h. During this time, a beige solid precipitated. The precipitate was filtered off and washed three times with 15 mL of *n*-pentane. The light beige crude product was purified by precipitation from a saturated solution in dichloromethane with *n*-pentane and finally dried under vacuum. Yield: 1.10 g (93%) of a colorless solid. Elemental analysis calcd. for $\text{C}_{34}\text{H}_{20}\text{O}_4\text{Ru}$ (593.59): C 68.80, H 3.40; found: C 68.45, H 3.47%. Isomer **5a**. ^1H NMR (400 MHz, CD_2Cl_2): δ 9.26–9.18 (m, 1H, H_{ar}), 7.76 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, H_{ar}), 7.48 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H, H_{ar}), 7.43–7.21 (m, 9H, H_{ar}), 7.14 (d, $^3J_{\text{HH}} = 7.2$ Hz, 1H, H_{ar}), 7.02 (dd, $^3J_{\text{HH}} = 7.5$ Hz, 2H, H_{ar}), 6.92 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H, H_{ar}), 4.39–4.27 (m, 2H, CH_2), 4.20 (d, $^2J_{\text{HH}} = 13.7$ Hz, 1H, CH_2), 3.80 (d, $^2J_{\text{HH}} = 13.7$ Hz, 1H, CH_2). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 195.4 ($3 \times \text{CO}$), 171.0 (C1), 142.9, 142.6, 142.1, 140.4, 135.4, 134.9, 134.6, 131.0, 130.7, 130.0, 129.9, 129.9, 129.9, 129.8, 129.6, 129.0, 128.9, 128.9, 128.8, 128.3, 127.4, 127.4, 127.3, 127.1, 110.1 (C2, C5), 95.2 (C2, C5), 85.4 (C3, C4), 81.0 (C3, C4), 44.4 (CH_2), 41.6 (CH_2). Isomer **5b**. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.92–7.86 (m, 2H, H_{ar}), 7.53 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2H, H_{ar}), 7.43–7.21 (m, 12H, H_{ar}), 4.12 (d, $^2J_{\text{HH}} = 13.4$ Hz, 2H, CH_2), 3.66 (d, $^2J_{\text{HH}} = 13.5$ Hz, 2H, CH_2). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 194.7 ($3 \times \text{CO}$), 172.9 (C1), 144.7, 143.3, 134.7, 132.1, 130.5, 129.2, 128.4, 127.9, 127.7, 126.8, 126.4, 126.1, 106.8 (C2), 83.1 (C3), 41.6 (CH_2). IR (ATR, cm^{-1} , isomers **5a** and **5b**): $\tilde{\nu} = 3114\text{w}$, 3071w, 3023w, 3019w, 2944w, 2919w, 2903w, 2848w, 2084vs, 2032vs, 2011vs ($3 \times \nu_{\text{C=O}}$), 1630vs ($\nu_{\text{C=O}}$), 1605m, 1491m, 1254m, 1441m, 1385w, 1324w, 1287w, 1200w, 1164w, 1138w, 1076w, 1041w, 1000w, 865w, 845w, 804w, 755s, 733s, 718.

$\{(\eta^5\text{-Cp}^{\text{C}}\text{O}_2\text{H})[\text{Ru}(\text{CO})_2]_2(\mu\text{-H})\}$ (6): 400 mg (0.67 mmol) of the mixture of **5a** and **5b** were stirred at 85 °C in 25 mL of degassed 2-propanol for 72 h. During this time the starting material almost completely dissolved. After cooling to room temperature, the reaction mixture was filtered and the solvent was removed under vacuum. The crude product was purified by slow diffusion of *n*-pentane into a saturated solution in toluene. Yield: 164 mg (39%) of red crystals. Elemental analysis calcd. for $\text{C}_{66}\text{H}_{42}\text{O}_6\text{Ru}_2$ (1133.18): C 69.95, H 3.74; C 70.24, H 3.47%. ^1H NMR (600 MHz, CD_2Cl_2): δ 14.01 (s, 1H, O–H–O), 8.47 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H, H_{ar}), 7.54 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, H_{ar}), 7.46 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, H_{ar}), 7.41–7.36 (m, 4H, H_{ar}), 7.33 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H, H_{ar}), 7.31–7.28 (m, 4H, H_{ar}), 7.27–7.20 (m, 4H, H_{ar}), 7.19–7.12 (m, 3H, H_{ar}), 7.03 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H, H_{ar}), 6.97 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H, H_{ar}), 6.87–6.82 (m, 4H, H_{ar}), 6.58 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, H_{ar}), 4.47 (d, $^2J_{\text{HH}} = 13.2$ Hz, 2H, CH_2), 4.27 (d, $^2J_{\text{HH}} = 13.6$ Hz, 4H, CH_2), 3.73 (d, $^2J_{\text{HH}} = 13.8$ Hz, 2H, CH_2), –18.60 (s, 1H, Ru–H–Ru). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 202.2 (CO), 200.0 (CO), 146.6 (C1), 143.2, 142.7, 142.0, 140.6, 134.6, 133.3, 131.9, 130.6, 130.6, 130.4, 129.7, 129.5, 129.3, 129.3, 129.1, 128.7, 128.5, 128.4, 128.2, 127.9, 127.3, 126.9, 126.9, 125.8, 103.5 (C2 bzw. C5), 95.6 (C2 bzw. C5), 92.5 (C3 bzw. C4), 86.1 (C3 bzw. C4), 43.7 (CH_2), 41.6 (CH_2). IR (ATR, cm^{-1}): $\tilde{\nu}$ 3058w, 3029w, 1956w, 2920w, 2846w, 2029s, 2001s, 1979s, 1964s, 1945s ($5 \times \nu_{\text{C=O}}$), 1672bw, 1603w, 1573w, 1524m, 1485m, 1453m, 1437m, 1398m, 1327w, 1272w, 1217w, 1196w, 1158w, 1142w, 1041w, 954w, 876w, 839w, 766s, 750s, 732s, 718s, 686m.

$\{(\eta^4\text{-Cp}^{\text{C}}\text{O})\text{Fe}(\text{CO})_3\}$ (7): 700 mg (171 mmol) of $\text{Cp}^{\text{C}}\text{O}$ (**4**) and 900 mg (1.79 mmol) of $\text{Fe}_3(\text{CO})_{12}$ were dissolved in 15 mL of toluene. The

mixture was heated for 17.5 h to 80 °C. After cooling to room temperature it was filtered over Celite®. The solvent was removed under reduced pressure and the solid residue was redissolved in 5 mL of dichloromethane. The volume of the solution was reduced to 2 mL and 25 mL of *n*-pentane were added to precipitate the product, which was isolated by filtration, washed five times with 15 mL of *n*-pentane and dried under vacuum. Yield: 479 mg (51%) of an orange-brown solid. Elemental analysis calcd. for $\text{C}_{34}\text{H}_{20}\text{O}_4\text{Fe} \cdot (\text{CH}_2\text{Cl}_2)_{0.3}$ (616.33): C 71.79, H 3.62; found: C 71.91, H 3.80%. ^1H NMR (400.13 MHz, CDCl_3): δ 9.97 (1H, H_{ar}), 8.21 (1H, H_{ar}), 7.35 (1H, H_{ar}), 7.08–6.97 (m, 9H, H_{ar}), 6.88–6.84 (m, 2H, H_{ar}), 6.68–6.60 (m, 2H, H_{ar}), 4.43 (d, $^3J_{\text{HH}} = 13.5$ Hz, 1H, CH_2), 3.82–3.74 (m, 2H, CH_2), 3.25 (d, $^3J_{\text{HH}} = 12.0$ Hz, 1H, CH_2). ^{13}C NMR (100.61 MHz, CDCl_3): δ 209.9 (C=O), 166.6 (C=O), 142.6, 142.2, 141.5, 140.5, 135.2, 133.3, 132.5, 131.6, 130.5, 130.1, 130.0, 129.7, 129.6, 129.5, 129.3, 129.1, 128.9, 128.7, 128.5, 127.6, 127.5, 127.4, 126.4, 125.8, 104.9, 91.8, 89.0, 83.6, 43.9, 41.0. IR (ATR, cm^{-1}): $\tilde{\nu}$ 3057w, 3023w, 2954w, 2924w, 2886w, 2838w, 2348w, 2063s, 2022s, 1992s ($3 \times \nu_{\text{C=O}}$), 1707m, 1691m, 1607s ($\nu_{\text{C=O}}$), 1483m, 1435m, 1383m, 1323w, 1267m, 1216w, 1192w, 1159w, 1143w, 1118w, 1045w, 996w, 955w, 874w, 849w, 809m, 768s, 760s, 751s, 743s, 735m, 718s, 710m.

Catalysis: All catalytic reactions were carried out in crimp-cap vials purchased from VWR International GmbH with a total volume of 20 mL. After the addition of a small magnetic stirring bar and the required amount of catalyst (see the foots of Tables 1–3), the vial was closed with a crimp-cap equipped with a teflon-coated rubber seal. The atmosphere in the vial was exchanged by applying vacuum and flooding with dinitrogen. The required amount of substrate and 100 mL of tetradecane (internal standard) dissolved in the required amount of solvent were added to the catalyst with a syringe. The vial was positioned in a pre-heated aluminum block and the mixture was heated to the required temperature. Samples of 0.2 mL were taken with a syringe at the reaction times given in Tables 1–3. In the case of the imine hydrogenation, the samples were filtered over a few mm of MgSO_4 and a few mm of Celite in a small glass column ($d = 0.4$ mm) with dichloromethane as the solvent. For the work-up of the phenylethanol dehydrogenation resp. the acetophenone hydrogenation, the samples were filtered over a few mm of MgSO_4 and a few mm of alumina in a small glass column ($d = 0.4$ mm) with ethylacetate as the solvent. Conversions were determined by gas chromatography.

X-ray structure analyses: Crystal data and refinement parameters are collected in Table 4. Data of **4** were collected at low temperatures (150 K) using ω -scans on an Oxford Gemini Ultra Diffractometer with dual fine-focus sealed X-ray tubes. Cu– $K\alpha$ radiation with wavelength 1.54184 Å was used. The structure was solved using direct methods (SHELXS), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.^[26] Semi-empirical absorption correction from equivalents was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model. **5a** and **6**: A single crystal was mounted on a MiTeGen Dual Thickness MicroMount™ with Fomblin Y oil and transferred to a N_2 cold stream (100 K) by an OXFORD CRYOSYSTEMS 700 low temperature system. Data were collected at low temperatures (100 K) using ϕ - and ω -scans on a BRUKER D8 Venture system equipped with dual μS microfocus sources and a PHOTON100 detector. Mo– $K\alpha$ radiation with wavelength 0.71073 Å and a collimating Quazar multilayer mirror were used. Semi-empirical absorption corrections from equivalents were calculated with SADABS-2016/2 (**6**) and TWINABS (**5a**).^[27] The space groups were determined using XPREP^[28] through analysis of the Laue symmetry and systematic absences. The structures were solved with SHELXT.^[29] Structures were refined by full-matrix least-squares based on F^2 using SHELXL^[30] and

Table 4. Crystallographic data, data collection and refinement.

	4	5b	6
emp. formula	C ₃₁ H ₂₀ O	C ₃₄ H ₂₀ O ₄ Ru	C ₇₁ H ₅₄ O ₆ Ru ₂
formula weight	408.47	593.57	1205.28
crystal size [mm]	0.414 × 0.292 × 0.069	0.882 × 0.303 × 0.018	0.304 × 0.245 × 0.105
T [K]	150(2)	100(2)	102(2)
λ [Å]	1.54184	0.71073	0.71073
crystal system	triclinic	monoclinic	monoclinic
space group	P-1	Pc	C2/c
a [Å]	8.9319(6)	11.0524(4)	24.6139(9)
b [Å]	9.8790(6)	8.1172(3)	13.5771(5)
c [Å]	12.6924(9)	14.6458(6)	19.7794(11)
α [°]	73.256(6)	90	90
β [°]	81.130(6)	109.496(2)	126.7830(10)
γ [°]	75.499(5)	90	90
V [Å ³]	1034.23(13)	1238.61(8)	5294.0(4)
Z	2	2	4
ρ _{calcd.} [g cm ⁻³]	1.312	1.592	1.512
μ [mm ⁻¹]	0.600	0.674	0.629
F(000)	428	600	2464
θ-range [°]	3.651–62.772	1.955–27.103	2.562–26.729
refl. coll.	6271	2809	48790
indep. refl.	3287 [R _{int} = 0.0240]	2809	5624 [R _{int} = 0.0470]
data/restr./param.	3287/0/289	2809/383/329	5624/84/386
final R indices [I > 2σ(I)] ^[a]	0.0361, 0.0854	0.0471, 0.1037	0.0332, 0.0785
R indices (all data)	0.0401, 0.0886	0.0635, 0.1121	0.0447, 0.0846
absol. structure parameter	–	0.06(5)	–
Goof ^[b]	1.066	1.051	1.041
Δρ _{max/min} (e · Å ⁻³)	0.156/–0.233	1.903/–1.116	1.049/–0.663

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $\omega R2 = [\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega F_o^2]^{1/2}$. [b] $Goof = [\sum \omega(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$.

SHELXL^[31] as a graphical interface. All structures were checked for a higher symmetry using PLATON.^[32] All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms attached to carbon atoms were assigned to idealized positions and given thermal parameters equal to either 1.2 times the thermal displacement parameters or 1.5 times (methyl groups) of the atoms to which they were attached. The bond distances were restrained to idealized distances. The positions of hydrogen atoms attached to other atoms were taken from the Fourier synthesis and refined freely. Constraints to idealize the bond distances have not been applied to those atoms. Similarity restraints on 1,2 distances were used to model disorder components. U_{ij} components of disordered atoms were restrained with similar ADP restraints. Refinement Details: **5a** crystallized as non-merohedral twin in the monoclinic space group Pc with one complex molecule in the asymmetric unit. The twin ratio refined to 0.38465 (esd. 0.00367). **6** crystallized in the monoclinic space group C2/c with half a complex molecule and one free pentane solvent molecule in the asymmetric unit. Crystallographic symmetry generates the full complex molecule that contains a Ru–H–Ru bridge. This bridging hydrogen atom was modeled across two positions with a fixed occupancy of 50%.

Deposition Numbers 2101873 (for **4**), 2101874 (for **5b**), and 2101875 (for **6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

DFT calculations: The calculations on the energy differences ($\Delta\Delta H$ and $\Delta\Delta G$) between the stereoisomers of Cp^cO (**4**) and its tricarbonylruthenium(0) complex were carried out with the program Gaussian16^[33] using the gradient corrected exchange-correlation functional B3LYP^[34] in combination with the 6-311G* basis set for C, H and O^[35] and for ruthenium, the Stuttgart RSC 1997 ECP basis set was applied.^[36] Theoretical calculations on the IR spectrum

of compound **6** were carried out using the quantum chemical program packages Gaussian^[33] and Turbomole^[37] with the functional B3LYP^[34] and the basis set def2-TZVP^[38] including dispersion correction (D3, Becke-Johnson damping).^[39] The basis sets were obtained from the EMSL/PNNL Basis Set Exchange site.^[40] Full geometry optimizations were carried out in C₁ symmetry using analytical gradient techniques and the resulting structures were confirmed to be true minima by diagonalization of the analytical Hessian Matrix. The thermodynamic corrections were obtained from the frequency calculations. The starting geometries were taken from a solid-state structure.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Catalysis · Hydrogen transfer · Iron · Pentadienone ligand · Ruthenium

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