Coordination Chemistry of Ester-Functionalized Cp Ligands. A Versatile Approach to the Chiral Hydroxyalkoxycarbonylcyclopentadienide $[C_5H_4CO_2(CHMe)_2OH]^-$. Synthesis, Structure, and Catalytic Activity of Rhodium(I) and Iron(II) Complexes

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The ring-opening reaction of *meso*-4,5-dimethyl-1,3-dioxolan-2-one or (4*S*,5*S*)-dimethyl-1,3-dioxolan-2-one with NaCp yields the sodium hydroxyalkoxycarbonylcyclopentadienides Na[*rac*-$C_5H_4CO_2(CHMe)_2OH$] (**1**) and Na[(1*S*,2*S*)-$C_5H_4CO_2(CHMe)_2OH$] (**2**). Complexes of rhodium and iron have been prepared, and the X-ray molecular structures of [Rh{(1*R*,2*S*)-$CpCO_2(CHMe)_2OH$}(NBD)] (**7**) and [Rh{(1*S*,2*S*)-$CpCO_2(CHMe)_2OH$}(NBD)] (**8**) are reported. The rhodium complexes are catalytically active in the hydroformylation of hex-1-ene. Heptanal is the prevailing product with a regioselectivity up to 70%, while the residual olefin is mainly isomerized.

Introduction

Transition metal complexes containing cyclopentadienyl ligands are widely employed due to the ability of these ancillary ligands to stabilize the metal in different oxidation states. Most of these compounds are extensively studied as catalysts in several reactions such as hydrogenation,[1] polymerization,[2] and hydroformylation.[3−7]

The efficiency of these complexes in catalytic reactions may be tuned by introducing functional groups into the cyclopentadienyl ring. Good results have recently been reported in the hydroformylation reaction using rhodium complexes containing methoxycarbonyl or methoxycarbonylmethylene substituents at the cyclopentadienyl ligand.[4−7]

As part of our ongoing project concerning the development of new ester-functionalized Cp ligands,[8] we have recently demonstrated that the reaction of NaCp with five-membered cyclic carbonates, such as ethylene carbonate and (±)-1,2-propylene carbonate, results in the exclusive formation of the novel *β*-hydroxyalkoxycarbonylcyclopentadienide Na[$C_5H_4CO_2(CH_2)_2OH$] when the former reagent is employed, while a racemic mixture of the two regioisomers Na[$C_5H_4CO_2CH_2CH(Me)OH$] and Na[$C_5H_4CO_2CH(Me)CH_2OH$] is obtained when the latter is used (Scheme 1).[8c]

The introduction of stereogenic centers on the side chain of these systems may assist in controlling the stereochemistry of reactions taking place at the metal center and therefore could eventually induce stereoselectivity in catalytic reactions.[9]

In this paper we describe how the above synthetic procedure has successfully been extended to *meso*-4,5-dimethyl-1,3-dioxolan-2-one and (4*S*,5*S*)-dimethyl-1,3-dioxolan-2-one, leading to Na[*rac*-$C_5H_4CO_2(CHMe)_2OH$] (**1**) and optically pure Na[(1*S*,2*S*)-$C_5H_4CO_2CH(CH_3)CH(CH_3)OH$] (**2**), respectively. The chiral unit is introduced

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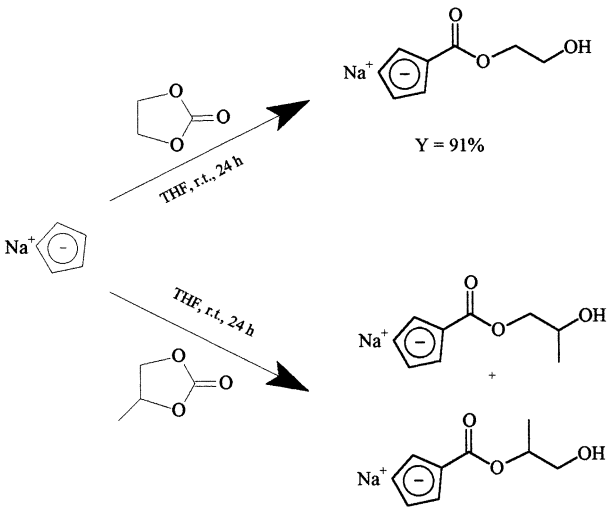
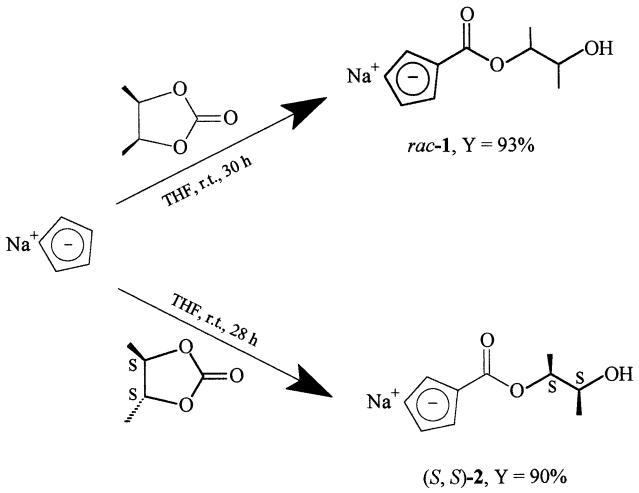
Scheme 1



Scheme 2



in one step so that multigram quantities of chiral Cp ligands can be readily prepared and used without further purification to synthesize organometallic complexes. The syntheses of related Rh(I) and Fe(II) derivatives are presented, and the absolute configuration is established on the basis of X-ray diffraction studies and circular dichroism (CD) spectroscopy.

As a final step of this investigation, we have studied the catalytic activity in the hydroformylation of hex-1-ene of the previously reported [Rh{$C_5H_4CO_2(CH_2)_2OH$}(L,L)] [L,L = 2CO, (**3**); L,L = NBD, (**4**)][8c] and of new rhodium complexes herein presented. The influence of some reaction parameters on the catalytic activity and selectivity of the reaction has also been tested.

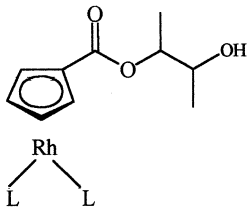
Results and Discussion

A. Ligands Synthesis. The starting material of our investigations is *meso*-4,5-dimethyl-1,3-dioxolan-2-one, easily available through transesterification of *meso*-2,3-butanediol with diethyl carbonate in the presence of sodium methoxide.[10] Through the synthetic procedure described in the previous section this cyclic carbonate is converted into Na[*rac*-$C_5H_4CO_2(CHMe)_2OH$] (**1**) (ca. 90% yield) by reaction with NaCp in tetrahydrofuran at room temperature.

Similarly, from optically active (4*S*,5*S*)-dimethyl-1,3-dioxolan-2-one (prepared from *2S*,*3S*-butanediol) the enantiomerically pure Na[(1*S*,2*S*)-$C_5H_4CO_2(CHMe)_2OH$] (**2**) is obtained in comparable yields (Scheme 2).

As expected, the ring-opening reactions proceed without any racemization at the chiral carbon centers. This behavior has been confirmed by NMR experiments with the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$][11] and the characterization of the metal complexes synthesized (see next paragraph). The sodium salts *rac*-**1** and (1*S*,*2S*)-**2** are air- and moisture-sensitive light brown solids. The NMR spectra in [D_5]Pyr for *rac*-**1** and (1*S*,*2S*)-**2** show for the Cp protons H(3,4) and H(2,5) the two expected AA′BB′ pseudotriplets [^{1}H NMR δ 7.5−6.5; corresponding ^{13}C NMR Cp signals in the range δ 113−109], similar to those of the previously reported analogous systems.[8c] With regard to the spectral pattern of the β-hydroxyalkoxycarbonyl group in the pendant side chain, the NMR spectra for *rac*-**1** and (1*S*,2*S*)-**2** exhibit a single set of signals with very similar chemical shifts (see the Experimental Section), whereas the resonance due to the −OH group has never been observed. The IR spectrum in THF shows in both cases a ν(C═O) broad band around 1640 cm^{-1}.

B. Metal Complexes. We have tested first the synthetic utility of the sodium salts *rac*-**1** and (1*S*,*2S*)-**2** with the binuclear rhodium complex [Rh(L,L)Cl]$_2$ [L,L = 2CO or 2,5-norbornadiene (NBD)] and $FeCl_2$ to produce the corresponding half-sandwich and sandwich complexes. The metathetic reactions of *rac*-**1** and (1*S*,*2S*)-**2** with [Rh(L,L)Cl]$_2$ in THF at room temperature gave, after chromatography on silica gel, the corresponding yellow complexes [Rh{*rac*-$C_5H_4CO_2(CHMe)_2$-OH}(L,L)] [L,L = 2CO, (**5**); L,L = NBD, (**7**)] and [Rh{(1*S*,2*S*)-$C_5H_4CO_2(CHMe)_2OH$}(L,L)] [L,L = 2 CO, (**6**); L,L = NBD, (**8**)] (45−80% yields).



[L,L = 2 CO (*rac*)], **5**, Y = 47 %

[L,L = 2 CO (1*S*,*2S*)], **6**, Y = 45 %

[L,L = NBD (*rac*)], **7**, Y = 80 %

[L,L = NBD, (1*S*,*2S*)], **8**, Y = 64 %

All the above compounds are moisture- and air-stable and have been fully characterized by analytical and spectroscopic techniques. A detailed molecular structure of **7** and **8** has been determinated by X-ray diffraction.

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(11) The chiral shift reagent [Eu(hfc)$_3$] (Aldrich) was added in portions to [D_5]Pyr solutions of *rac*-**1** and (*S*,*S*)-**2** monitored by ^{1}H NMR after each addition. The addition was stopped when the C*H*OH resonance of *rac*-**1** split into two resonances separated by 0.1 ppm.

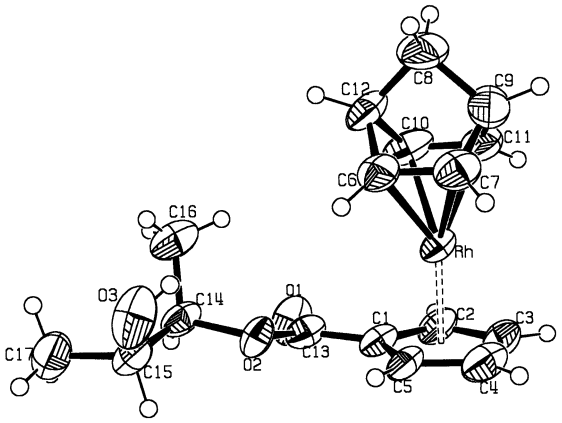


Figure 1. Molecular structure of [Rh(NBD){*rac*-$CpCO_2$-$(CHMe)_2OH$}] (**7**) showing the atomic numbering (thermal ellipsoids at 50% probability level).

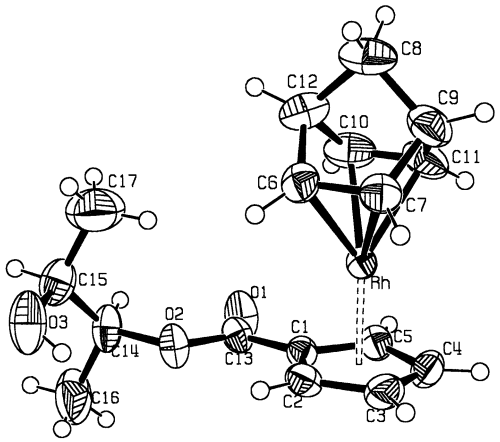


Figure 2. Molecular structure of (+)-[Rh(NBD){(1*S*,2*S*)-$CpCO_2(CHMe)_2OH$}] (**8**) showing the atomic numbering (thermal ellipsoids at 50% probability level).

The NMR and IR spectral properties of these materials are unexceptional.[8c,12,13] The NMR spectra of **5**, **6**, **7**, and **8** show only one set of resonances and are independent of time (days) and temperature (20−90 °C). Moreover, due to the presence of a chiral substituent, the four C−H units of the η-$C_5H_4R^*$ ring are inequivalent, giving four different groups of signals in the NMR spectra. This behavior, strongly affected by the nature of the ancillary ligands, is particularly evident when L,L = NBD.

It is noteworthy that, unlike what we have previously reported for the reactions of $Na[C_5H_4CO_2(CH_2)_2OH]$ with $[Rh(L,L)Cl]_2$,[8c] no evidence of diester-bridged dimers of the type $[Rh_2\{\mu\text{-}(C_5H_4CO_2CHMe)_2\}(L,L)_2]$ has been observed. The formation of this kind of complexes was due to a transesterification reaction among two molecules of the corresponding mononuclear complexes [Rh-$\{C_5H_4CO_2(CH_2)_2OH\}$(L,L)] catalyzed by the ligand itself. In the present case, the lack of dimers is explained with a decreased acidity of the secondary alcoholic function present on the side chain.

The molecular structure of the racemic species **7** is shown in Figure 1, and that of the chiral **8** in Figure 2. Relevant bond parameters are comparatively listed in Table 1. The stereogeometry in the coordination spheres of the rhodium atoms is very similar in the two molecules, and if the −CH(Me)CH(Me)OH appendages are not considered, both conform to an approximate C_s symmetry. The corresponding bond distances are strictly comparable and in accord with the idealized symmetry. The −C(O)O groups are approximately coplanar with the cyclopentadienyl rings [dihedral angles 22.6(3)° and 3.4(4)° in **7** and **8**, respectively], and the C(carboxylate)−C(ring) distances [1.450(8) and 1.463(4) Å in **7** and **8**, respectively] are only slightly longer than the average intra-ring C−C distance [1.424(4) Å in **8**]. This is a clear indication of the degree of conjugation between the C(O)O and C_5(ring) π orbitals.

Table 1. Significant Bond Distances (Å) and Angles (deg) for 7 and 8

	7	**8**
Rh−C(1)	2.218(5)	2.261(3)
Rh−C(2)	2.238(4)	2.253(3)
Rh−C(3)	2.278(3)	2.275(3)
Rh−C(4)	2.283(5)	2.281(3)
Rh−C(5)	2.246(5)	2.233(3)
Rh−C(6)	2.109(6)	2.115(3)
Rh−C(7)	2.106(7)	2.114(3)
Rh−C(10)	2.096(7)	2.120(3)
Rh−C(11)	2.117(7)	2.126(3)
C(1)−C(2)		1.432(4)
C(2)−C(3)		1.425(5)
C(3)−C(4)		1.412(6)
C(4)−C(5)		1.422(5)
C(1)−C(5)		1.430(4)
C(6)−C(7)	1.39(1)	1.404(5)
C(7)−C(9)	1.50(1)	1.524(5)
C(8)−C(9)	1.54(1)	1.540(6)
C(8)−C(12)	1.52(1)	1.537(6)
C(9)−C(11)	1.50(1)	1.536(6)
C(10)−C(11)	1.39(1)	1.401(7)
C(6)−C(12)	1.53(1)	1.529(5)
C(10)−C(12)	1.51(1)	1.524(6)
C(1)−C(13)	1.450(8)	1.463(4)
C(13)− O(1)	1.206(9)	1.213(4)
C(13)− O(2)	1.330(8)	1.333(4)
C(14)−O(2)	1.481(8)	1.455(4)
C(14)−C(16)	1.48(1)	1.485(7)
C(14)−C(15)	1.51(1)	1.509(5)
C(15)−O(3)	1.413(9)	1.405(5)
C(15)−C(17)	1.50(1)	1.499(7)
H(3)···O(2)	2.60(2)	2.50(1)
C(1)−C(13)−O(2)	111.9(5)	111.4(3)
C(1)−C(13)−O(1)	123.0(6)	123.7(3)
C(13)−O(2)−C(14)	118.1(5)	118.7(3)
O(2)−C(14)−C(15)	104.4(5)	106.8(3)
O(2)−C(14)−C(16)	108.7(6)	109.0(4)
C(14)−C(15)−O(3)	111.9(6)	113.0(3)
C(14)−C(15)−C(17)	111.2(6)	112.1(5)

The two molecules significantly differ in the conformation and configuration of the −CH(Me)CH(Me)OH side chains containing two chiral centers [C(14) and C(15)]. The chiral atoms have opposite configuration in the racemic species **7**, and the α methyl [C(16)] is positioned on the same side of the NBD ligand (Figure 1). The chain conformation is different in the chiral species **8** (Figure 2), but, quite significantly, the area occupied by the α methyl in **7** [C(16)] is now occupied

(12) With regards to IR spectroscopy see: (a) Graham, P. B.; Rausch, M. D. *Organometallics* **1991**, *10*, 3049. (b) Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041.

(13) With regards to NMR see: (a) Bitterwolf, T. E.; Lott, K. A. *J. Organomet. Chem.* **1991**, *408*, 137. (b) Arthurs, M.; Karodia, H.; Sedgwick, M.; Morton-Blake, D. A.; Cardin, C. J.; Parge, H. *J. Organomet. Chem.* **1985**, *291*, 231. (c) Arthurs, M.; Gross, P.; Kubal, G.; Paniwnyk, L.; Curzon, E. *J. Organomet. Chem.* **1989**, *366*, 223. (d) Cesarotti, E.; Chiesa, A.; Ciani, G. F.; Sironi A.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1984**, 653. (e) Lindsay, C.; Cesarotti, E.; Adams, H.; Bailey, N. A.; White, C. *Organometallics* **1990**, *9*, 2594. (f) Suzuki, H.; Kakigano, T.; Fukui, H.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1994**, *473*, 295. (g) Erker, G.; Nolte, R.; Rainer, A.; Wilker, S.; Kruger, C.; Noe, R. *J. Am. Chem. Soc.* **1991**, *113*, 7594.

by the β methyl [C(17)]. Either conformation is stabilized by an O(3)−H···O(2) interaction (see Table 1); therefore one can assume that they persist out of the solid state. As reported in section **D,** the hindrance produced by the methyl groups can be considered responsible for the reduced catalytic activity observed for **7** and **8** with respect to **4**. In fact the same side chain $-CH_2CH_2OH$ was found flat in $[Rh(C_5H_4C(O)OCH_2CH_2OH)(CO)_2]$.[8c]

The reactions of *rac*-**1** and (1*S*,2*S*)-**2** with $[Rh(CO)_2Cl]_2$ form small amounts (av 7%) of red byproducts isolated by chromatography. Due to instability in solution (color changes from red to green overnight), a full characterization has not been possible; however an intense IR band at 1839 cm^{-1}, indicative of a bridging carbonyl ligand, and the ^1H NMR spectra suggest the formation of binuclear compounds of the type $[Rh_2\{C_5H_4CO_2(CHMe)_2OH\}_2(CO)_2(\mu\text{-}CO)]$, in analogy with what is already observed in related syntheses.[8c,12a,14] In the *rac*-**1** case the formation of a dinuclear compound has generated a 1:1 mixture of racemic and meso diastereoisomers.

The reaction of (1*S*,2*S*)-**2** with anhydrous $FeCl_2$ in THF has led to the corresponding ferrocene $[Fe\{(1S,2S)\text{-}C_5H_4CO_2(CHMe)_2OH\}_2]$ (**9**), obtained as a single enantiomer bearing homochiral ligands. As observed for the rhodium complexes, the presence of a chiral substituent makes the four C−H units of the two η-$C_5H_4R^*$ groups inequivalent.

Unlike what was found for the previously reported $[Fe\{C_5H_4CO_2(CH_2)_2OH\}_2]$, which has been prepared either via metalation of $[CpCO_2(CH_2)_2OH]^-$ with $FeCl_2$[8c] or via the usual electrophilic aromatic-type substitution route from $[Fe(C_5H_5)_2]$,[15] the preparation of the chiral ferrocene **9** via metalation of the corresponding Cp derivative confirms that the synthetic methodology here described represents a convenient and general procedure.

C. Circular Dichroism Spectroscopy. To examine the effect of the chiral chain on the metal-containing moiety, all the optically active complexes have been examined with circular dichroism spectroscopy. Figure 3 shows the UV−vis (a) and CD (b) spectra of the complexes **6**, **8**, and **9**, in which the Cotton effects determined by the stereogenic centers on the side chain of the Cp ring are weak. All the CD spectra show a well-defined morphology in the region 240−600 nm. The corresponding UV−vis spectra show as many transitions as the Cotton effects, some of which are not completely resolved in absorbance.

The CD spectrum of the rhodium complex **8** consists of three positive Cotton effects at λ = 248, 278, 373 nm ($\Delta\epsilon$ = +1.56, +0.48, +0.13 M^{-1} cm^{-1}, respectively) and a negative one at λ = 322 nm ($\Delta\epsilon$ = −0.09), whereas the CD spectrum of the rhodium complex **6** shows three positive Cotton effects at λ = 271, 313, 455 nm ($\Delta\epsilon$ = +0.10, +0.20, +0.013 M^{-1} cm^{-1}, respectively) and a negative one at λ = 381 nm ($\Delta\epsilon$ = −0.009 M^{-1} cm^{-1}).

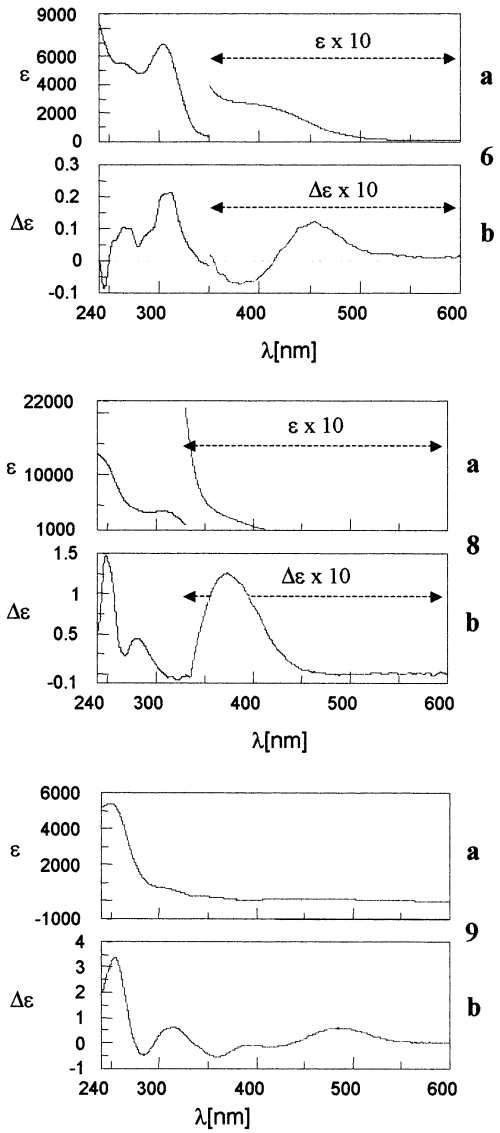


Figure 3. Absorption (a) and CD (b) spectra of $[Rh(CO)_2\{(1S,2S)\text{-}CpCO_2(CHMe)_2OH\}]$ (**6**), $[Rh(NBD)\{(1S,2S)\text{-}CpCO_2(CHMe)_2OH\}]$ (**8**), $[Fe\{(1S,2S)\text{-}C_5H_4CO_2(CHMe)_2OH\}_2]$ (**9**) in 3×10^{-4} to 10^{-3} M in $CHCl_3$.

The CD spectrum of the ferrocene complex **9** consists of three positive Cotton effects at λ = 255, 315, 484 nm ($\Delta\epsilon$ = +3.37, +0.64, +0.60 M^{-1} cm^{-1}, respectively) and three negative ones at λ = 284, 360, 421 nm ($\Delta\epsilon$ = −0.49, −0.56, −0.16 M^{-1} cm^{-1}, respectively).[16]

D. Catalytic Activity in the Hydroformylation of Hex-1-ene. A preliminary test on the catalytic activity of the complexes reported below in the hydroformylation of hex-1-ene has been performed. The reaction conditions and the hydroformylation results are reported in Table 2.

A functionalyzed substituent on the cyclopentadienyl moiety affects the catalytic activity of the complexes tested. The results obtained using **4** and **10** show that the presence of a β-hydroxyalkoxycarbonyl substituent

(14) Jones, S. S.; Rausch, M. D.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *396*, 279. Bitterwolf, T. E.; Lott, K. A.; Rest, A. J. *J. Organomet. Chem.* **1991**, *408*, 137.

(15) Izumi, T.; Tezuka, T.; Yusa, S.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2435. Mackowiak, H.-P.; Gottlieb, K.; Jungbluth, H.; Neitsch, H. (Dynamit Nobel G.m.b.H.), PCT Int. Appl. EP 2600, 1998 [*Chem. Abstr.* **1998**, *130*, 15540].

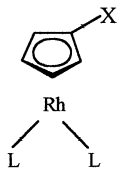
(16) Cesarotti, E.; Chiesa, A.; Ciani, G. F.; Sironi A.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1984**, 653. Carmona, D.; Vega, C.; Lahoz, F. J.; Atencio, R.; Oro, L. A.; Lamata, M. P.; Viguri, F.; San Josè, E. *Organometallics* **2000**, *19*, 2273. Ramsden, J. A.; Milner, J. D.; Adams, H.; Bailey, N. A.; Smith, A. J.; White, C. *Organometallics* **1995**, *14*, 2575. Cicogna, F.; Colonna, M.; Houben, J. L.; Ingrosso, G.; Marchetti, F. *J. Organomet. Chem.* **2000**, *593−594*, 251.

Table 2. Hydroformylation of Hex-1-ene[a]

catalyst	conversion (%)	aldehydes (yield %)	hydrocarbons (yield %)	isomerized olefins (yield %)	regioselectivity (heptanal/total aldehydes) (%)
3	76.8	49.1	1.1	26.7	69.5
4	98.8	70.2	0.5	28.1	68.1
7	43.2	22.6	0	20.8	67.7
8	20.5	4.6	0.9	15.0	69.6
10	21.5	2.7	5.6	13.2	74.8

[a] Catalyst 20 μmol, hex-1-ene 2 mmol, THF 25 mL, *T* 60 °C, *p*(CO) 15 bar, *p*(H_2) 15 bar, reaction time 4 h.

on the cyclopentadienyl ligand in **4** increases considerably its catalytic activity. As reported in Table 2, the olefin conversion increases from 21.5% in the presence of **10** to 98.8% with **4**. This increment is reflected in a higher amount of hydroformylation products (70.2% compared with 2.7%) and isomerized olefins (28.1% vs 13.2%) but in lower olefin hydrogenation (0.5% compared with 5.6%) and regioselectivity (from 68.1% to 74.8%, respectively).



L,L = 2CO, X = -$CO_2CH_2CH_2OH$ (**3**);

L,L = NBD, X = -$CO_2CH_2CH_2OH$ (**4**);

L,L = NBD, X = (*dl*)-$CO_2CH(Me)CH(Me)OH$ (**7**);

L,L = NBD, X = (*S,S*)-$CO_2CH(Me)CH(Me)OH$ (**8**);

L,L = NBD, X = H (**10**).

The presence of methyl substituents on the lateral chain on the cyclopentadienyl ligand reduces the catalytic activity. The results obtained show that the conversion of the starting olefin decreases from 98.8% (using **4**) to 43.2% (with **7**), the aldehydes from 70.2% to 22.6%, and the isomerized olefins from 28.1% to 20.8%, while the regioselectivity (68.1% and 67.7%, respectively) and the amount of hexane (0.5% and 0.0%) remain almost unaltered. This behavior may be attributed to the high encumbrance of the lateral chain of the cyclopentadienyl group.

These data are confirmed by the different catalytic activity among the racemic complex **7** and one of its diastereoisomers, the *S,S* complex **8**. The racemic complex **7** shows a higher olefin conversion (43.2% and 20.5%, respectively), hydroformylation (22.6% and 4.6%), and isomerization yield (20.8% vs 15.0%) but almost the same regioselectivity (69.6% vs 67.7%) and hydrogenation yield (0.9% vs 0%).

The ancillary ligand affects the catalytic activity of the complexes as shown by the data obtained using **4** and **3**. The complex containing the NBD ligand, **4**, gives higher conversion (98.8%) than **3**, containing a CO ligand (76.8%). As a consequence, a higher yield of aldehydes (70.2% and 49.1%, respectively), almost the same olefin isomerization (28.1% vs 26.7%) but always a low amount of hexane (0.5−1.1%) and almost the same regioselectivity (68.1−69.5%) were obtained. These data are an indication that a different catalytically active intermediate was formed using **3** or **4** as catalyst precursor.

As a conclusion, compounds **3**, **4**, **7**, **8**, and **10** are catalytically active in the hydroformylation of hex-1-ene. The parallel isomerization of the olefin takes place to a lesser extent, while hydrogenation reactions are practically absent. The main product is always the linear aldehyde. Compound **4** shows the best catalytic activity and a good regioselectivity. An analogous regioselectivity has been obtained using the Wilkinson catalyst in the same conditions.[17] These catalysts show a higher activity than analogous Rh cyclopentadienyl complexes reported in a previous paper.[5]

Finally it must be pointed out that the complexes under investigation are catalytically active in the isomerization of hex-1-ene under a CO/H_2 atmosphere. In these conditions it is possible to assume that a hydride intermediate is not formed in the preliminary step of the catalytic process, therefore excluding the well-established addition−elimination mechanism.

Experimental Section

Materials and Procedures. All reactions with organometallic reagents or substrates were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. The prepared derivatives were characterized by elemental analysis and spectroscopic methods. The IR spectra were recorded with a FT-IR spectrometer Perkin-Elmer Spectrum 2000. The routine NMR spectra (^1H, ^{13}C, DEPT) were always recorded using a Varian Gemini 300 instrument (^1H, 300.1; ^{13}C, 75.5 MHz), while the two-dimensional spectra (gHSQC) were recorded using a Varian Mercury-VX 400 (^1H, 399.8; ^{13}C, 100.5 MHz) instrument. The spectra were internally referenced to residual solvent resonances and recorded at 298 K for characterization purposes. Electron impact mass spectra were taken using a VG 7070E mass spectrometer. A GC Shimadzu GC-14A equipped with a flame ionization detector (FID) and an elaboration system Shimadzu C-R4A was used to evaluate the hydroformylation products, while a GC Perkin-Elmer model 8320 equipped with a FID detector was employed to detect the residual olefin composition. A GC-MS Shimadzu QP 5050 instrument was employed to test the identity of the products obtained. Elemental analyses were performed on a Thermo-Quest Flash 1112 Series EA instrument. Melting points were taken in sealed capillaries and were uncorrected. Optical rotations were measured with a Perkin-Elmer 341 polarimeter. CD and UV−vis spectra in the region 240−800 nm were recorded on a Jasco J-810 spectropolarimeter using $CHCl_3$ as a solvent and generally with concentrations of 10^{-2}−10^{-3} mol L^{-1} in 1, 0.1, and 0.01 cm path length cells; the short-wavelength limit was determined by the strong absorption of the solvent.

The reagents *meso*-4,5-dimethyl-1,3-dioxolan-2-one and (4*S*,5*S*)-dimethyl-1,3-dioxolan-2-one were prepared according to literature procedures;[10] $FeCl_2$, $[Rh(CO)_2Cl]_2$, and $[Rh(NBD)Cl]_2$ were used as purchased from Strem. Petroleum ether (Etp)

(17) Pino, P.; Piacenti, F.; Bianchi, M. *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; J. Wiley & Sons: New York, 1977; Vol. 2, p 175.

refers to a fraction of bp 60−80 °C. Silica gel was heated at about 200 °C while a slow stream of a dry nitrogen was passed through it.[18] Hex-1-ene (Aldrich) was passed through an Al_2O_3 column and distilled under nitrogen and had a bp 64 °C.

Na[*rac*-$C_5H_4CO_2$(CHMe)$_2$OH] (1). To a solution of NaCp (0.87 g, 9.9 mmol) in THF (ca. 50 mL) was added *meso*-4,5-dimethyl-1,3-dioxolan-2-one (1.0 mL, 9.9 mmol) in THF at room temperature. The mixture was stirred for 30 h, the volatiles were removed under vacuum, and the residue was kept under vacuum at 60 °C for 2 h. The resulting solid was washed with Et_2O to give 1.86 g (93%) of **1** as a beige solid. ^{1}H NMR (300.1 MHz, [D$_5$]Pyr): δ 7.34 (AA′BB′, ^3J(H,H) = 2.7 Hz, 2H; Cp), 6.57 (AA′BB′, ^3J(H,H) = 2.7 Hz, 2H; Cp), 5.41 (m, 1H; CO_2CH), 4.15 (m, 1H; $CHOH$), 1.42 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 1.40 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_5$]Pyr): δ 168.8 (C=O), 112.8 (CH; Cp), 111.2 (CH; Cp), 109.8 (*ipso*-C; Cp), 76.6 (CO_2CH), 70.8 (CHOH), 19.2 (CH_3), 17.3 (CH_3). IR (THF, cm^{-1}): ν(C=O) 1637 (bs). Anal. Calcd for $C_{10}H_{13}NaO_3$: C, 58.8; H, 6.37. Found: C, 58.4; H, 6.28.

Na[(1*S*,2*S*)-$C_5H_4CO_2$(CHMe)$_2$OH] (2). To a solution of pure (4*S*,5*S*)-dimethyl-1,3-dioxolan-2-one (1.19 g, 10.2 mmol) in THF (ca. 30 mL) was added solid NaCp (0.90 g, 10.2 mmol). The mixture was stirred at room temperature for 28 h, the solvent was removed under vacuum, and the residue was kept under vacuum at 60 °C for 2 h. The resulting solid was washed with Et_2O to give 1.87 g (90%) of **2** as a beige solid. ^{1}H NMR (300.1 MHz, [D$_5$]Pyr): δ 7.41 (AA′BB′, ^3J(H,H) = 2.7 Hz, 2H; Cp), 6.64 (AA′BB′, ^3J(H,H) = 2.7 Hz, 2H; Cp), 5.38 (m, 1H; CO_2CH), 4.14 (m, 1H; $CHOH$), 1.33 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 1.31 (d, ^3J(H,H) = 7.5 Hz, 3H; CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_5$]Pyr): δ 168.7 (C=O), 113.0 (CH; Cp), 111.2 (CH; Cp), 109.9 (*ipso*-C; Cp), 71.8 (CO_2CH), 70.4 (CHOH), 19.7 (CH_3), 16.8 (CH_3). IR (THF, cm^{-1}): ν(C=O) 1645 (s). Anal. Calcd for $C_{10}H_{13}NaO_3$: C, 58.8; H, 6.37. Found: C, 59.1; H, 6.31.

[Rh(CO)$_2${*rac*-CpCO$_2$(CHMe)$_2$OH}] (5). To a solution of **1** (0.22 g, 1.078 mmol) in THF (ca. 50 mL) was added solid $[Rh(CO)_2Cl]_2$ (0.160 g, 0.411 mmol). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, and CH_2Cl_2 was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Eluting with Et_2O a first oily yellow fraction was collected and identified as the major product **5** (0.132 g, 47%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 5.91 (AA′BB′, ^3J(H,H) = 2.2 Hz, 2H; Cp), 5.59 (AA′BB′X, ^3J(H,H) = 2.2 Hz, J(H,Rh) = 0.9 Hz, 2H; Cp), 4.92 (m, 1H; CO_2CH), 3.87 (m, 1H; $CHOH$), 2.39 (d, ^3J(H,H) = 2.4 Hz, 1H; OH), 1.23 (d, ^3J(H,H) = 6.3 Hz, 3H; CO_2CHCH_3), 1.16 (d, ^3J(H,H) = 6.3 Hz, 3H; CH_3CHOH). ^{13}C-{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 188.7 (d, J(C,Rh) = 84 Hz; C≡O), 163.0 (C=O), 98.2 (*ipso*-C; d, J(C,Rh) = 3.6 Hz; Cp), 91.5 (d, J(C,Rh) = 3.7 Hz, CH; Cp), 91.4 (d, J(C,Rh) = 4.9 Hz, CH; Cp), 88.1 (d, J(C,Rh) = 2.5 Hz; Cp), 88.0 (d, J(C,Rh) = 2.5 Hz; Cp), 74.7 (CO_2CH), 69.6 ($CHOH$), 18.0 (CO_2CHCH_3), 14.5 (CH_3CHOH). IR (THF, cm^{-1}): ν(C≡O) 2050 (vs), 1986 (vs), ν(C=O) 1715 (s); MS (70 eV, EI): *m*/*z* (%) 340 (15) [M]$^+$, 312 (28) [M − CO]$^+$, 284 (40) [M − 2CO]$^+$, 212 (35) [$RhC_5H_4CO_2$]$^+$, 195 (32) [RhC_5H_4CO]$^+$, 168 (100) [RhC_5H_5]$^+$, 103 (28) [Rh]$^+$. Anal. Calcd for $C_{12}H_{13}O_5Rh$: C, 42.3; H, 3.82. Found: C, 42.1; H, 3.83.

By further eluting with a 9:1 mixture of Et_2O/CH_3CN a second red oily fraction was collected (16 mg, 6%) and identified as an 1:1 mixture of the two diastereoisomers *rac*-[Rh_2{$C_5H_4CO_2$(CHMe)$_2$OH}$_2$(CO)$_2$(μ-CO)] and *meso*-[Rh_2{$C_5H_4CO_2$(CHMe)$_2$OH}$_2$(CO)$_2$(μ-CO)], which are unstable in solution (the color changed from red to green overnight). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 6.11, 6.04, 5.96, 5.90, 5.69, 5.66, 5.63, 5.60 (m, 1H each; Cp), 5.07 (m, 2H; CO_2CH), 3.98 (m, 2H; $CHOH$), 2.55, 2.41 (d, ^3J(H,H) = 4.5 Hz, 1H each; OH), 1.28, 1.27 (d, 3H each; ^3J(H,H) = 6.6 Hz CO_2CHCH_3), 1.22, 1.21 (d, 3H each, ^3J(H,H) = 6.6 Hz, CH_3CHOH). IR (THF, cm^{-1}): ν(C≡O) 2026 (s), 1993 (vs), ν(μ(C=O)) 1839 (s), ν(C=O) 1713 (s).

[Rh(CO)$_2${(1*S*,2*S*)-CpCO$_2$(CHMe)$_2$OH}] (6). To a solution of **2** (0.43 g, 2.10 mmol) in THF (ca. 30 mL) was added solid $[Rh(CO)_2Cl]_2$ (0.27 g, 0.70 mmol). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, and CH_2Cl_2 was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Eluting with Et_2O an oily orange fraction was collected and identified as the major product **6** (0.214 g, 45%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 5.92 (m, 2H; Cp), 5.60 (AA′BB′X, ^3J(H,H) = 2.2 Hz, J(H,Rh) = 0.9 Hz, 2H; Cp), 4.86 (m, 1H; CO_2CH), 3.80 (m, 1H; $CHOH$), 2.27 (bs, 1H; OH), 1.24 (d, ^3J(H,H) = 6.3 Hz, 3H; CO_2CHCH_3), 1.18 (d, ^3J(H,H) = 6.3 Hz, 3H; CH_3CHOH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 188.7 (d, J(C,Rh) = 84 Hz; C∞O), 163.0 (C=O), 98.1 (d, J(C,Rh) = 3.6 Hz, *ipso*-C; Cp), 91.5 (d, J(C,Rh) = 3.7 Hz, CH; Cp), 91.4 (d, J(C,Rh) = 3.7 Hz, CH; Cp), 88.0 (d, J(C,Rh) = 2.4 Hz; Cp), 87.9 (d, J(C,Rh) = 3.7 Hz; Cp), 74.8 (CO_2CH), 69.9 ($CHOH$), 18.8 (CO_2CHCH_3), 15.7 (CH_3CHOH). IR (THF, cm^{-1}): ν(C≡O) 2050 (vs), 1986 (vs), ν(C=O) 1715 (s). MS (70 eV, EI): *m*/*z* (%) 340 (14) [M]$^+$, 312 (26) [M − CO]$^+$, 284 (44) [M − 2CO]$^+$, 212 (19) [$RhC_5H_4CO_2$]$^+$, 195 (19) [RhC_5H_4CO]$^+$, 168 (100) [RhC_5H_5]$^+$, 103 (9) [Rh]$^+$. Anal. Calcd for $C_{12}H_{13}O_5Rh$: C, 42.3; H, 3.82. Found: C, 42.4; H, 3.80.

By further eluting with a 9:1 mixture of Et_2O/CH_3CN a second red oily fraction was collected (36 mg, 8%) and identified as [Rh_2{(1*S*,2*S*)-$C_5H_4CO_2$(CHMe)$_2$OH}$_2$(CO)$_2$(μ-CO)], which is unstable in solution (the color changed from red to green overnight). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 6.10, 5.91, 5.67, 5.60 (m, 2H each; Cp), 4.93 (m, 2H; CO_2CH), 3.82 (m, 2H; $CHOH$), 2.53 (bs, 2H; OH), 1.28 (d, ^3J(H,H) = 6.6 Hz, 6H; CO_2CHCH_3), 1.23 (d, ^3J(H,H) = 6.6 Hz, 6H; CH_3CHOH). IR (THF, cm^{-1}): ν(C≡O) 2026 (s), 1993 (vs), ν(μ-(C=O)) 1839 (s), ν(C=O) 1713 (s).

[Rh(NBD){*rac*-CpCO$_2$(CHMe)$_2$OH}] (7). To a solution of **1** (0.270 g, 1.32 mmol) in THF (ca. 30 mL) was added solid $[Rh(NBD)Cl]_2$ (0.214 g, 0.46 mmol). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, and CH_2Cl_2 was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Eluting with Et_2O a first yellow fraction was collected and identified as the major product **7**. Yellow crystals (0.279 g, 80%) were obtained from a double layer of Et_2O/Etp at −20 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 5.52 (m, J(H,Rh) = 0.6 Hz, 1H; Cp), 5.47 (m, J(H,Rh) = 0.6 Hz, 1H; Cp), 5.36 (m, J(H,-Rh) = 0.6 Hz, 1H; Cp), 5.29 (m, J(H,Rh) = 0.6 Hz, 1H; Cp), 5.00 (m, 1H; CO_2CH), 3.90 (m, 1H; $CHOH$), 3.30 (m, 6H; NBD), 2.46 (d, ^3J(H,H) = 4.8 Hz, 1H; OH), 1.26 (d, ^3J(H,H) = 6.6 Hz, 3H; CO_2CHCH_3), 1.21 (d, ^3J(H,H) = 6.6 Hz, 3H; $CH(CH_3)OH$), 0.96 (m, 2H; NBD). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 165.8 (C=O), 91.7 (d, J(C,Rh) = 4.8 Hz, *ipso*-C; Cp), 88.4 (d, J(C,-Rh) = 3.7 Hz, CH; Cp), 88.3 (d, J(C,Rh) = 3.7 Hz, CH; Cp), 86.0 (d, J(C,Rh) = 3.6 Hz, CH; Cp), 85.8 (d, J(C,Rh) = 4.9 Hz, CH; Cp), 73.8 (CO_2CH), 69.8 ($CHOH$), 57.4 (d, J(C,Rh) = 6.1 Hz, C_7; NBD), 46.6 (d, J(C,Rh) = 2.4 Hz, $C_{1,4}$; NBD), 32.6 (d, J(C,Rh) = 9.8 Hz, 2CH; NBD), 32.3 (d, J(C,Rh) = 10.9 Hz, 2CH; NBD), 17.9 (CO_2CHCH_3), 14.9 ($CH(CH_3)OH$). IR (THF, cm^{-1}): ν(C=O) 1707 (s). MS (70 eV, EI): *m*/*z* (%) 376 (91) [M]$^+$, 303 (76) [$Rh(C_7H_8)C_5H_4CO_2$]$^+$, 287 (25) [$Rh(C_7H_8)C_5H_4CO$]$^+$, 259 (100) [$Rh(C_7H_7)C_5H_5$]$^+$, 194 (69) [RhC_7H_7]$^+$, 168 (78) [RhC_5H_5]$^+$. Anal. Calcd for $C_{17}H_{21}O_3Rh$: C, 54.1; H, 5.59. Found: C, 54.3; H, 5.61. Mp = 58 °C. The complex was also characterized by an X-ray diffraction study.

(+)-[Rh(NBD){(1*S*,2*S*)-CpCO$_2$(CHMe)$_2$OH}] (8). To a solution of **2** (0.28 g, 1.37 mmol) in THF (ca. 30 mL) was added solid $[Rh(NBD)Cl]_2$ (0.19 g, 0.41 mmol). The solution was stirred for 3 h at room temperature. The solvent was removed

(18) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.
(19) Sheldrick, G. M. *SADABS*, University of Göttingen, to be published.

under vacuum, and CH_2Cl_2 was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Eluting with Et_2O a first yellow fraction was collected and identified as the major product **8** (yellow solid, 0.22 g, 71%). Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation from Et_2O. $[\alpha]_D^{19.0}$ +13.4 (*c* 0.62, $CHCl_3$). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 5.53 (m, *J*(H,Rh) = 0.6 Hz, 1H; Cp), 5.47 (m, *J*(H,Rh) = 0.9 Hz, 1H; Cp), 5.37 (m, *J*(H,Rh) = 0.6 Hz, 1H; Cp), 5.28 (m, *J*(H,Rh) = 0.6 Hz, 1H; Cp), 4.90 (m, 1H; CO_2CH), 3.80 (m, 1H; $CHOH$), 3.31 (m, 6H; NBD), 2.35 (d, ^3J(H,H) = 5.1 Hz, 1H; −OH), 1.27 (d, ^3J(H,H) = 6.6 Hz, 3H; CO_2CHCH_3), 1.23 (d, ^3J(H,H) = 6.6 Hz, 3H; $CH(CH_3)OH$), 0.95 (m, 2H; NBD). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 165.7 (C=O), 91.7 (d, *J*(C,Rh) = 3.6 Hz, *ipso*-C; Cp), 88.5 (d, *J*(C,Rh) = 3.6 Hz, CH; Cp), 88.3 (d, *J*(C,Rh) = 3.7 Hz, CH; Cp), 86.0 (d, *J*(C,Rh) = 4.8 Hz, CH; Cp), 85.8 (d, *J*(C,Rh) = 4.9 Hz, CH; Cp), 74.1 (CO_2CHCH_3), 70.2 ($CH(CH_3)OH$), 57.4 (d, *J*(C,Rh) = 7.3 Hz, C_7; NBD), 46.7 (d, *J*(C,Rh) = 2.4 Hz, $C_{1,4}$; NBD), 32.6 (d, *J*(C,Rh) = 9.8 Hz, 2CH; NBD), 32.3 (d, *J*(C,Rh) = 10.9 Hz, 2CH; NBD), 18.9 (CO_2CHCH_3), 16.3 ($CH(CH_3)OH$). IR (THF, cm^{-1}): ν(C=O) 1707 (s). MS (70 eV, EI): *m*/*z* (%) 376 (94) $[M]^+$, 303 (65) $[Rh(C_7H_8)C_5H_4CO_2]^+$, 287 (20) $[Rh(C_7H_8)C_5H_4CO]^+$, 259 (100) $[Rh(C_7H_7)C_5H_5]^+$, 194 (66) $[RhC_7H_7]^+$, 168 (74) $[RhC_5H_5]^+$. Anal. Calcd for $C_{17}H_{21}O_3Rh$: C, 54.1; H, 5.59. Found: C, 54.0; H, 5.58. Mp = 97 °C. The complex was also characterized by an X-ray diffraction study.

(+)-[Fe{(*S*,*S*)-CpCO$_2$(CHMe)$_2$OH}$_2$] (7). To a solution of **2** (0.46 g, 2.25 mmol) in THF (30 mL) was added solid $FeCl_2$ (0.13 g, 1.03 mmol). The solution was stirred for 8 h at room temperature. The solvent was removed under vacuum, and CH_2Cl_2 was added; the red suspension was first filtered on a Celite pad and then cromatographed on silica gel. Eluting with Et_2O a red solid was collected and identified as **9** (0.22 g, 51%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 4.91 (m, 1H; CO_2CH), 4.80 (m, 1H; Cp), 4.75 (m, 1H; Cp), 4.46 (m, 1H; Cp), 4.39 (m, 1H; Cp), 3.83 (m, 1H; $CHOH$), 3.39 (m, 1H; OH), 1.27 (d, ^3J(H,H) = 6.6 Hz, 3H; CO_2CHCH_3), 1.23 (d, ^3J(H,H) = 6.6 Hz, 3H; $CH(CH_3)OH$). $^{13}C\{^1H\}$ NMR (gHSQC, 100.5 MHz, $CDCl_3$): δ 170.6 (C=O), 75.5 (CO_2CH), 72.8 (*ipso*-C; Cp), 72.7 (CH; Cp), 72.5 (CH; Cp), 72.4 (CH; Cp), 71.1 (CH; Cp), 69.7($CHOH$), 19.1 (CO_2CHCH_3), 16.6 ($CH(CH_3)OH$). IR (THF, cm^{-1}): ν(C=O) 1716 (s). MS (70 eV, EI): *m*/*z* (%) 418 (100) $[M]^+$, 346 (33) $[Fe(C_5H_4CO_2H)(C_5H_4CO_2CH(CH_3)CH(CH_3)OH)]^+$, 274 (59) $[Fe(C_5H_4CO_2H)_2]^+$, 165 (36) $[FeC_5H_4CO_2H]^+$. Anal. Calcd for $C_{20}H_{26}O_6Fe$: C, 57.4; H, 6.22. Found: C, 57.6; H, 6.21. Mp = 93 °C. $[\alpha]_D^{19.0}$ +132.4 (*c* 0.68, $CHCl_3$).

X-ray Crystallography. Crystals of **7** and **8** suitable for the X-ray diffraction studies were precipitated from Et_2O. Crystal data and details of structure refinement are reported in Table 3. Diffraction intensities were collected at room temperature on a Bruker AXS SMART 2000 CCD diffractometer. The data were collected using 0.3° wide ω scans and a crystal-to-detector distance of 5.0 cm and corrected for absorption empirically using the SADABS routine.[19] Data collections nominally covered a full sphere of reciprocal space for both complexes with 30 s exposure time per frame for both **7** and **8**. Despite repeated attempts the crystals of **7** were of low quality and did not significantly diffract above θ = 20°; therefore a limited set of diffraction intensities was observed. Both structures were solved by direct methods and refined on F^2 by full matrix least-squares calculations using the SHELXTL/PC package.[20] Thermal vibrations were treated anisotropically; H atoms were experimentally located but geometrically positioned [C−H 0.93 and 0.97 Å for aromatic and aliphatic distances; O−H 0.82 Å] and refined "riding" on their corresponding carbon atoms. Refinement converged at a final R = 0.056, wR_2 = 0.142, S = 1.03 for **7**, R = 0.036, wR_2 = 0.096, S = 0.94 for **10**. Flack parameter for **8** was −0.02(4) for the correct absolute structure. Molecular graphics were prepared using ORTEP3 for WindowsNT.[21] Due to the low number of observations accessible for **7**, its structure model is affected by quite high estimated standard errors, and a rigid body refinement has been applied to the cyclopentadienyl ring (C−C distances 1.42 Å). On the contrary, the structure model of **8** is highly reliable because the observations-to-parameters ratio is as high as 28.5.

Table 3. Crystal Data and Details of Structure Refinement for Complexes 7 and 8

	7	**8**
empirical formula	$C_{17}H_{21}O_3Rh$	$C_{17}H_{21}O_3Rh$
fw	376.25	376.25
temp (K)	293	293
wavelength (Å)	0.71069	0.71069
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$, no. 14	$P2_12_12_1$, no. 19
unit cell dimens	a = 15.299(1) Å b = 5.8840(3) Å c = 17.803(1) Å β = 102.12(1)°	a = 5.816(1) Å b = 13.977(3) Å c = 19.434(4) Å
volume (Å^3)	1566.9(1)	1579.8(6)
Z	4	4
F(000)	768	768
cryst size (mm)	0.18 × 0.20 × 0.32	0.15 × 0.24 × 0.40
max θ for data collection	20°	32°
no. of reflns collected	4882	18 017
no. of obsd ind. reflns	1464	5505
no. of params	182	193
goodness-of-fit on F^2	1.07	0.94
final R indices [$I > 2\sigma(I)$] (R_1 and wR_2)	0.056, 0.142	0.036, 0.096
R indices (all data) (R_1 and wR_2)	0.057, 0.145	0.037, 0.098
largest diff peak and hole (e Å^{-3})	0.59, −0.53	0.54, −1.28

Hydroformylation of Hex-1-ene: General Procedure. The reactions were carried out in a 150 mL stainless steel Parr autoclave stirred with a self-sealing packing gland and electrically thermostated (±1 °C). A solution of 0.02 mmol of complexes **3**, **4**, **7**, **8**, and **10** and 2 mmol of hex-1-ene in 25 mL of THF was prepared in a Schlenk tube and transferred into the autoclave by suction. The autoclave was pressurized at room temperature with a 1:1 CO/H_2 mixture at 30 bar. The reaction mixture was stirred and heated at 60 °C for 4 h. After cooling the autoclave to room temperature, the gases were vented and the solution was collected. The reaction products were analyzed by gas chromatography. Sometimes GC−MS spectra were collected to confirm the nature of the products obtained. A PPG column (polypropylene glycol supported on Chromosorb W LB-550 X) was used to analyze the hex-1-ene hydroformylation products, keeping the oven at 35 °C for 5 min, then heated at a rate of 5 °C/min up to 50 °C and kept at this temperature for 2 min, then heated to 100 °C, with a rate of 1 °C/min and kept at this temperature for 60 min. A Chrompack capillary column Al_2O_3/Na_2SO_4 PLOT (length 50 m, diameter 0.45 mm) was used to analyze the residual olefin composition of the hex-1-ene hydrofomylation: the column was kept at 130 °C for 32 min, heated at a rate of 30 °C/min up to 200 °C, and kept at this temperature for 16 min.

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Supporting Information Available: A listing of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. Crystallographic files, in CIF format, for both complexes **7** and **8.** This material is available free of charge via the Internet at http://pubs.acs.org.

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