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Coordination chemistry of ester-functionalized cp ligands: synthesis and catalytic activity of [Rh{$CpCO_2(CHPh)_2OH$}(NBD)] and [Rh{$CpCO_2(CH_2)_3OH$}(NBD)]

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Abstract

Two new sodium hydroxyalkoxycarbonylcyclopentadienide salts Na[*rac*-$CpCO_2(CHPh)_2OH$] (**1**) and Na[(*2S,3S*)-$CpCO_2(CHPh)_2OH$] (**2**) were prepared by reaction of NaCp with the five-membered cyclic carbonates *cis*-4,5-diphenyl-1,3-dioxolan-2-one and (4*S*,5*S*)-4,5-diphenyl-1,3-dioxolan-2-one. The reaction of these salts with $[Rh(NBD)Cl]_2$ gave [Rh{*rac*-$CpCO_2(CHPh)_2OH$}(NBD)] (**3**) and (−)-[Rh{(2*S*,3*S*)-$CpCO_2(CHPh)_2OH$}(NBD)] (**4**) whose catalytic activity in the hydroformylation of hex-1-ene and styrene has been investigated and compared with that of the previously reported rhodium complexes [Rh{$CpCO_2(CHR)_2OH$}(NBD)] (R = H, Me). In addition we also discuss some preliminary results regarding the behavior of these complexes in the hydrogenation of the same substrates. The reactivity of NaCp toward the six-membered cyclic carbonate 1,3-dioxan-2-one has also been studied and it has been found that the reaction leads to two cyclopentadienide anions $[CpCO_2(CH_2)_3OH]^-$ (**5**) and $[CpCO_2(CH_2)_3OC(O)O(CH_2)_3OH]^-$ (**6**) in amounts strictly dependent on the carbonate/NaCp stoichiometric ratio.

Keywords: Carbonyl-derived cyclopentadienyl ligands; Rhodium complexes; Hydroformylation; Hydrogenation

1. Introduction

In the course of our studies concerning the development of new ester-functionalized Cp ligands we have recently disclosed that the reaction of NaCp with aliphatic five-membered cyclic carbonates leads, in one step and high yields, to the formation of a variety of novel chiral and non-chiral hydroxy-functionalized alkoxycarbonylcyclopentadienides Na[$CpCO_2(CHR)_2OH$] (R = H, Me) (Scheme 1) [1].

The easy availability of such ligands provided a valuable route to rhodium complexes of the type [Rh{$CpCO_2(CHR)_nOH$}(L,L)] [R = H, Me; $n = 2$; L,L = 2CO, NBD] which showed to exert catalytic activity in the homogeneous hydroformylation of hex-1-ene and styrene [1c,1d].

Pursuing an extension of our studies, we now report the synthesis and catalytic activity of similar rhodium derivatives containing (i) an aromatic substituent (R = Ph) on the hydroxyalkoxycarbonyl pendant and (ii) a longer alkylene side chain ($n = 3$).

2. Results and discussion

2.1. Synthesis of Na[$CpCO_2(CHPh)_2OH$] and rhodium complexes

In order to obtain the title ligand we reacted NaCp with *cis*-4,5-diphenyl-1,3-dioxolan-2-one, easily available through transesterification of *meso*-1,2-diphenylethane-1,2-diol with diethyl carbonate in the presence of

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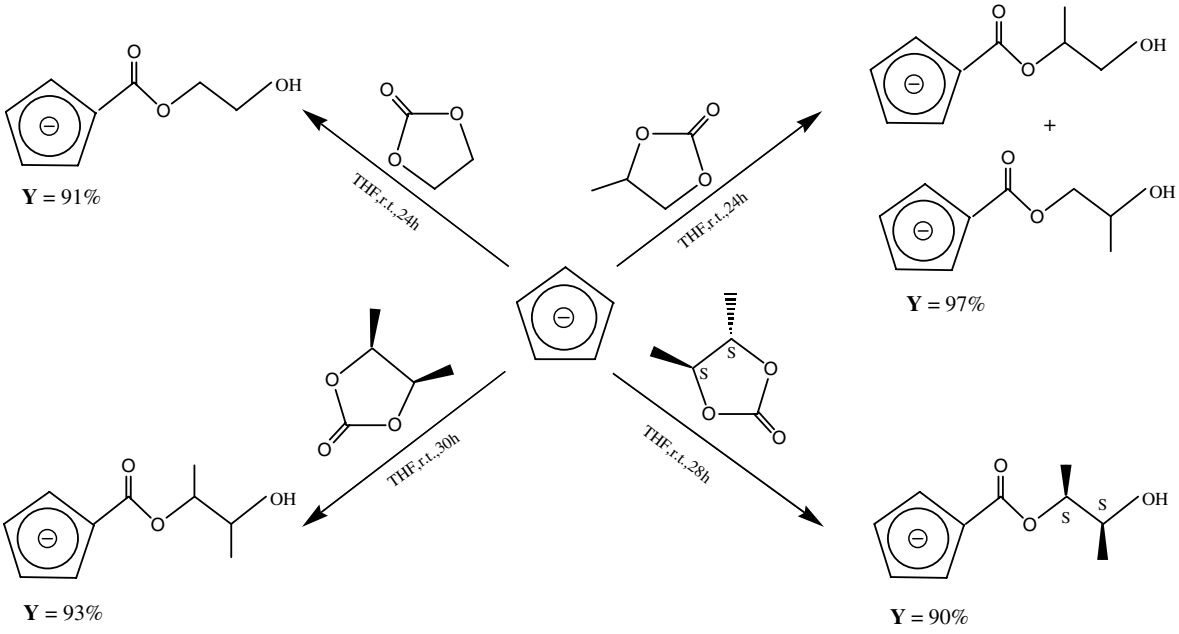
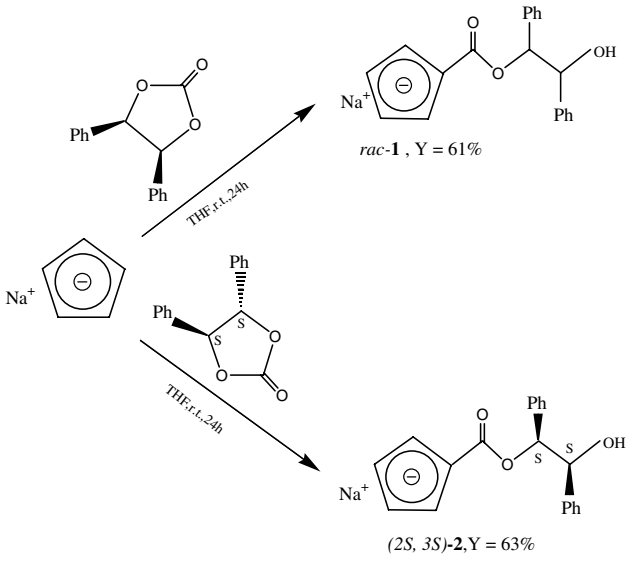


Scheme 1.

sodium methoxyde. Through our procedure the cyclic carbonate was converted into Na[*rac*-$CpCO_2(CHPh)_2$ OH] (**1**), a racemic mixture of the *2S,3R*-**1** and *2R,3S*-**1** enantiomers. Similarly, from optically active (−)(4*S*,5*S*)-(4,5)-diphenyl-1,3-dioxolan-2-one (prepared from (−)-(*1S,2S*)-1,2-diphenyl-ethane-1,2-diol) the enantiomerically pure Na[(*2S,3S*)-$CpCO_2(CHPh)_2OH$] (**2**) was obtained (Scheme 2). In both cases the yields (ca. 60%) were lower than that previously found with R = H, Me (ca. 90%).



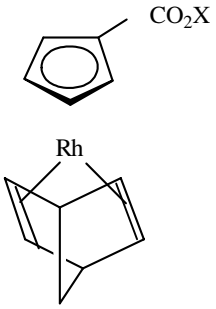
Scheme 2.

Due to the insolubility of the starting carbonates in diethyl ether the previously described work-up is not effective and a strict 1:1 ratio between the reagents must be employed in order to have a carbonate-free product. However, at least for the rhodium derivatives herein presented, this is not a crucial problem as the excess of carbonate can be easily separated by chromatography once the metal complex is obtained.

The ring opening reactions proceeded without any racemization at the chiral carbon centers as confirmed by the nature of their metal complexes described below. The sodium salts *rac*-**1** and (*2S,3S*)-**2** are air and moisture sensitive light brown solids. Their NMR spectra in [D_5]Pyr showed, as expected, two AA′BB′ pseudotriplets for the Cp protons H(3,4) and H(2,5) [^{1}H NMR δ 7.5–6.5] and ^{13}C NMR Cp signals in the range δ 113–109 [1b,1c]. With regard to the spectral pattern of the β-hydroxyalkoxycarbonyl group –CO_2CH(Ph)CH(Ph)OH of the pendant side chain, the NMR spectra for *rac*-**1** and (2*S*,3*S*)-**2** exhibit a single set of signals with very similar chemical shifts (see Section 3); however, while in *rac*-1 the $^3J_{(CH,CH)}$ coupling constant between the two CH protons is 4.4 Hz, it rises to 6.7 Hz in (2*S*,3*S*)-**2**. This difference reflects a significative variation in the conformation and configuration of the side chains containing the two chiral centers that is retained in their rhodium complexes (see next). In addition, contrary to what found with analogous systems where the resonance of the –OH group has never been observed, with the help of a ^{1}H, ^{1}H-gCOSY correlation experiment, we located the OH proton resonance in the aromatic region around 7.40 ppm and found a $^3J_{(CH,OH)}$ coupling of ca. 4

Hz. The IR spectra of *rac*-**1** and (*2S,3S*)-**2** in THF show, in both cases, a ν(C═O) broad band around 1640 cm^{-1}.

The reactions of *rac*-**1** and (*2S,3S*)-**2** with $[Rh(NBD)Cl]_2$ in THF at r.t. gave, after chromatography on silica gel, the corresponding yellow, air and moisture stable, complexes [Rh{*rac*-$CpCO_2(CHPh)_2OH$}(NBD)] (**3**) and [Rh{(*2S,3S*)-$CpCO_2(CHPh)_2OH$}(NBD)] (**4**) (56–58% yields).



X =*rac*-CH(Ph)CH(Ph)OH (**3**)

X = (*2S,3S*)-CH(Ph)CH(Ph)OH (**4**)

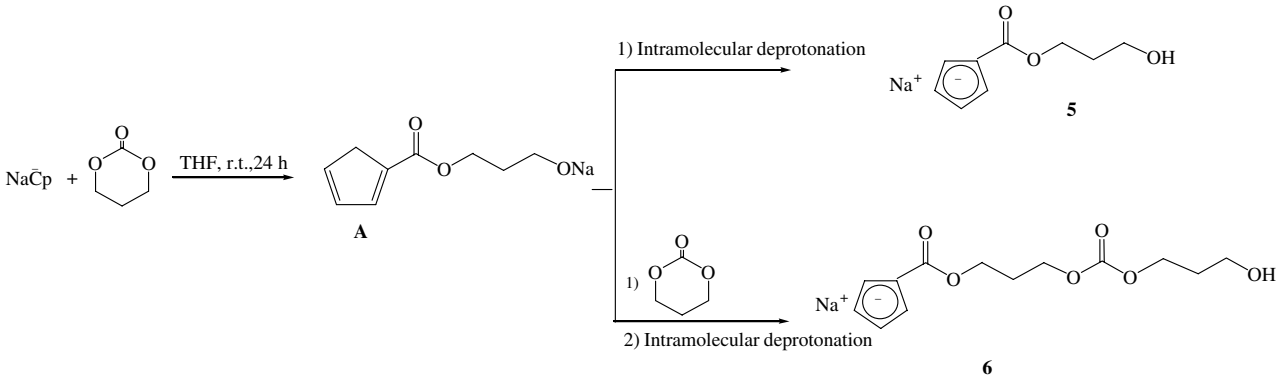
The NMR and IR spectral properties of these materials present features similar to those previously described [1b,1c]. We could not obtain suitable crystals for X-ray diffraction studies; however, the different $^3J_{(CH,CH)}$ coupling constants for *rac*-**3** and *S,S*-**4** (5.8 and 7.1 Hz, respectively) are consistent with those of the free ligands and in agreement with what previously found for [Rh{*rac*-$CpCO_2(CHMe)_2OH$}(NBD)] ($^3J_{(CH,CH)} = 3.5$ Hz) and [Rh{(*2S,3S*)-$CpCO_2(CHMe)_2OH$}(NBD)] ($^3J_{(CH,CH)} = 6.1$ Hz) [2]. It is worth mentioning that the X-ray diffraction studies of these latter complexes showed that the two molecules significant differ in the conformation and configuration of the –CH(Me)CH(Me)OH side chains containing the two chiral centers with dihedral angles equal to 68.4(3)° and 58.7(3)°, respectively.

2.2. Reaction of NaCp with 1,3-dioxan-2-one

The reaction between NaCp and the six-membered cyclic carbonate 1,3-dioxan-2-one carried out in THF at room temperature for 24 h, presented some significative differences compared to what observed for the just described five-membered ring case. The most informative feature came from the ^1H NMR spectrum of the reaction mixture in [D_5]Pyr which showed the appearance, in the cyclopentadienyl protons region (δ 7.40–6.60), of two sets of AA′BB′ multiplets whose relative intensities changed depending on the molar ratio of the reactants. In addition, the same trend was observed in the regions around 4 and 2 ppm where the resonances of the alkylene protons were expected. A parallel behavior was also found in the ^{13}C–{^1H} NMR spectra that presented three –C═O resonances of variable intensities at δ 168.8, 168.4 and 155.5 ppm and two sets of signals for the Cp ring carbons in the range δ 113–109 ppm. Finally, the IR spectrum in THF (range 2300–1500 cm^{-1}) exhibited two distinct ν(C═O) bands: a broad one centered at 1644 cm^{-1}, due to the conjugated C═O and C═C of the Cp ring π system and a sharp band at 1747 cm^{-1}, attributed to the presence of a non-conjugated –OC(O)O– group, with relative intensities depending on the carbonate/NaCp molar ratio employed.

We tentatively interpreted these findings with the presence of a mixture of two cyclopentadienide anions: the expected $[CpCO_2(CH_2)_3OH]^-$ (**5**) and the unexpected $[CpCO_2(CH_2)_3OC(O)O(CH_2)_3OH]^-$ (**6**). The product **5** derives from the intramolecular deprotonation of the likely intermediate **A** whereas **6** is formed from a nucleophilic attack of **A** on a second molecule of carbonate followed by deprotonation (Scheme 3).

Accordingly, Table 1 contains the products distribution, as determined by NMR analysis of the crude product, of the reaction carried out in the same conditions (THF, room temperature, reaction time 24 h) but with three different carbonate/NaCp ratios. The experiments showed that the higher is the carbonate/NaCp



Scheme 3.

Table 1
Reaction of NaCp with 1,3-dioxan-2-one: products distribution

Mixtures	1,3-Dioxan-2-one/NaCp	**5/6**	Yields of **5** (%)	Yields of **6** (%)
I	1.3	1.7	30	18
II	1.6	1.2	33	26
III	2.2	0.6	7	12

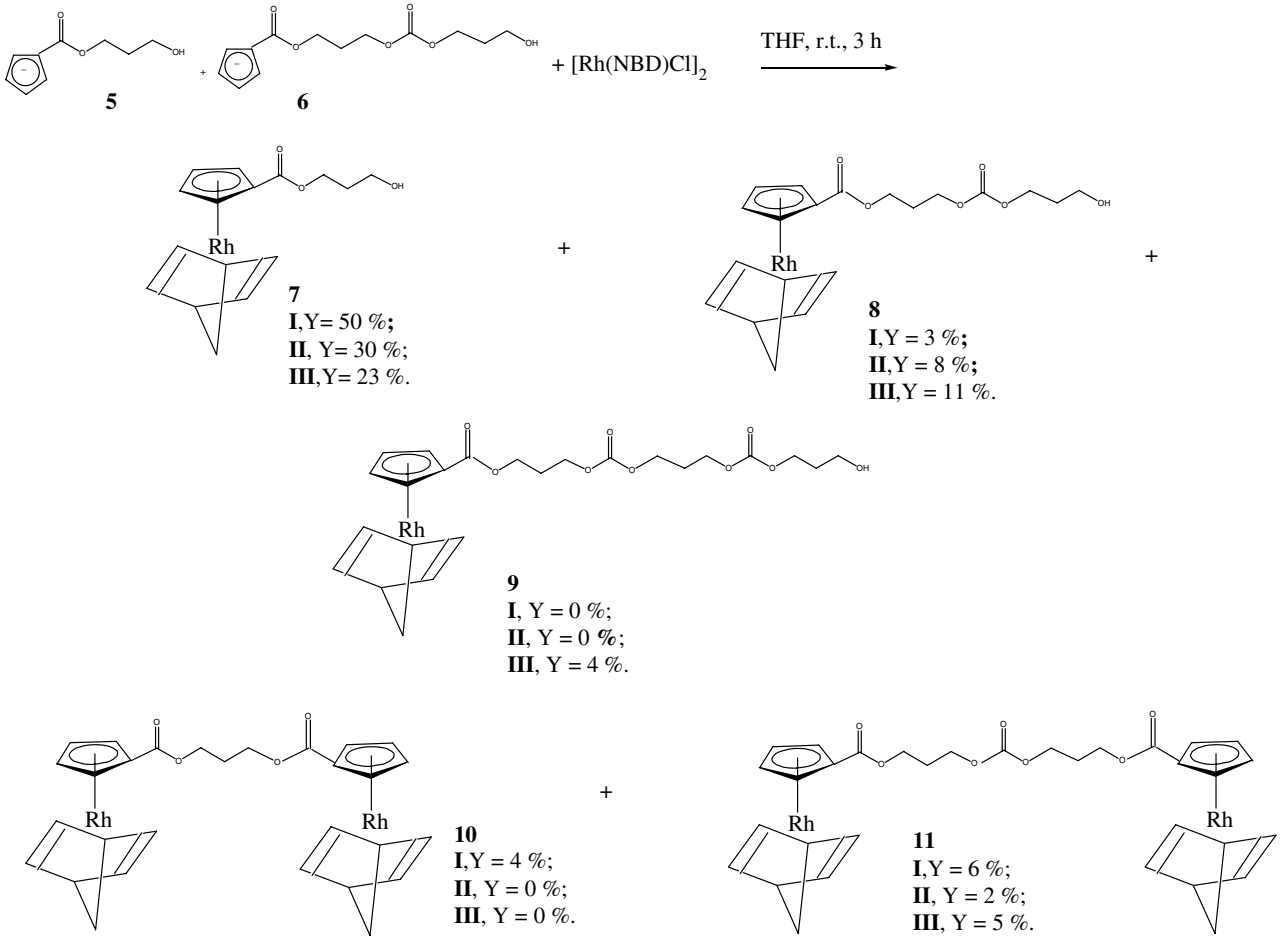
ratio, the lower the **5/6** ratio becomes and that while the total yield for **I** and **II** is ca. 50%, it drops to just 19% for **III**. It must be noted that when a 1:1 carbonate/NaCp ratio was employed the NMR spectra showed the presence of unreacted NaCp together with **5** and **6** in a ratio ca. 2/1 demonstrating that a competitive reaction involving the carbonate occurs. Finally, non-significant differences were observed in the products distribution varying the reaction times.

The formation of type **6** anion, never observed with five-membered cyclic carbonates, can be explained with (a) the intramolecular deprotonation of **A** requires the formation of a less favored nine-membered ring intermediate and (b), the higher reactivity of the six-membered cyclic carbonates compared to the five-membered ones due to a larger ring-strain energy (ca. 2.86 kcal/mol) [3].

The two salts **5** and **6** could not be separated and the mixtures **I**, **II** and **III** were reacted with $[Rh(NBD)Cl]_2$. The metathetic reactions in THF at r.t. gave several moisture and air stable yellow mono- and dinuclear complexes (Scheme 4), separated by chromatography on silica gel.

As it can be seen in Scheme 4 the complex $[Rh\{CpCO_2(CH_2)_3OH\}(NBD)]$ (**7**) is always the major product but, while with **I** the yield is 50%, similar to what usually found for these systems, it drops to 23% with **III** where a lower content of **5** is present. The formation of **8** confirmed the presence of **6** in all the anionic mixtures and the yield increased going from **I** to **III** due to the larger occurrence of **6**.

From Scheme 4 can also be observed that only when the anionic mixture **III** is employed, the isolation of small amounts of **9** was observed. The formation of **9** can be explained with the fact that, in the presence of a larger excess of carbonate, the reaction between NaCp and 1,3-dioxan-2-one proceeds further to give a product of the type $Na[CpCO_2\{(CH_2)_3OC(O)O\}_2(CH_2)_3OH]$,



Scheme 4.

deriving from a successive nucleophilic attack of the intermediate $C_5H_5CO_2(CH_2)_3OC(O)O(CH_2)_3O^-$ (analogous to **A**) on a third molecule of carbonate.

Finally, the dimeric products **10** and **11** are deriving from transesterification reactions catalyzed by the ligands similar to what already reported and described for [Rh{$CpCO_2(CH_2)_2OH$}(L,L)] [1b].

All the above compounds **7**–**11** have been fully characterized by standard analytical/spectroscopic techniques. The ^1H and ^{13}C NMR spectra in $CDCl_3$ of all the complexes depicted in Scheme 4 showed the expected resonances for the C_5H_4– and NBD moieties which are strictly comparable with those of the previously reported [Rh{$CpCO_2(CH_2)_2OH$}(NBD)] [1b].

All complexes showed in the IR spectra a strong ν(C═O) band at 1712 cm^{-1} for the Cp-linked ester group and a corresponding signal at δ 165 in the ^{13}C NMR spectra; in addition, complexes **8**, **9**, and **11** also showed a strong band at 1749 cm^{-1} and a parallel signal at δ 155.0, attributed to the –OC(O)O– group. The ESI-MS spectra showed the molecular ion peak $[M]^+$ for all the five complexes.

2.3. Catalytic activity

We have previously reported that the hydroformylation of olefins, in the presence of rhodium catalysts containing a β-hydroxyalkoxycarbonylcyclopentadienyl ligand, is affected by the nature of the substituents present on the lateral chain [1c,1d]. The new Rh(I) complexes **3**, **4** and **7**, herein synthesized, were tested in order to collect new evidences on the relation between the steric hindrance of the lateral chain and the catalytic activity of the corresponding rhodium complexes. The results are compared with those previously reported for [Rh{$CpCO_2(CHR)_2OH$}(NBD)] [R = H (**12**), Me (*rac*-**13**, *S,S*-**14**)]. The reaction conditions and the hydroformylation results are reported in Tables 2–4. In addition we also report some preliminary results regarding the behavior of these complexes in the hydrogenation of the same substrates.

2.3.1. Hydroformylation of hex-1-ene

Complexes *rac*-**3** and *S,S*-**4** are catalytically active in the hydroformylation and isomerization of hex-1-ene although the rates of these reactions are lower than those reported for *rac*-**13** and *S,S*-**14** having two methyl groups on the lateral chain therefore confirming that in the hydroformylation of hex-1-ene the presence of substituents on the side chain has a negative impact on the catalytic performances of the complexes. The data are summarized in Table 2, while in Table 3 are reported details regarding the yields of aldehydes and isomerized olefins.

Complex *rac*-**3** did not show any catalytic activity at 60 or 80 °C for 4 h (*entry 1* and *2*), however at 80 °C an

Table 2
Hydroformylation of hex-1-ene in the presence of [Rh(CpX)(NBD)] catalysts[a]

Entry	Catalyst code	X	T (°C)	Time (h)	Hex-1-ene (conversion %)	Aldehydes (yield %)	Regioselectivity (heptanal /aldehydes)(yield %)	Isomerized olefins (yield %)	Hydrocarbons (yield %)
1	**3**	*rac*-$CO_2(CHPh)_2OH$	60	4	0	0	-	0	0
2	**3**	*rac*-$CO_2(CHPh)_2OH$	80	4	0	0	-	0	0
3	**3**	*rac*-$CO_2(CHPh)_2OH$	80	24	99.1	61.8	54.6	36.8	0.5
4	**3**	*rac*-$CO_2(CHPh)_2OH$	80[c]	4	98.6	38.9	64.7	59.1	0.6
5	**3**	*rac*-$CO_2(CHPh)_2OH$	60[c]	4	37.1	23.0	69.0	13.0	1.1
6	**4**	(*S,S*)-$CO_2(CHPh)_2OH$	80	24	99.3	67.7	52.3	31.1	0.5
7[b]	**13**	*rac*-$CO_2(CHMe)_2OH$	60	4	43.2	22.6	67.7	20.8	0
8[b]	**13**	*rac*-$CO_2(CHMe)_2OH$	80	4	94.6	28.3	71.0	66.0	0.4
9[b]	**14**	(*S,S*)-$CO_2(CHMe)_2OH$	60	4	20.5	4.6	69.6	15.0	0.9
10	**7**	$CO_2(CH_2)_3OH$	60	4	69.4	36.5	69.6	32.9	0
11[b]	**12**	$CO_2(CH_2)_2OH$	60	4	98.8	70.2	68.1	28.1	0.5

[a] Reaction conditions: catalyst 20 μmol, hex-1-ene 2 mmol, THF 25 ml, p(CO) 15 bar, $p(H_2)$ 15 bar.
[b] See [1c,1d].
[c] The catalyst was pre-activated: a THF solution was heated up to 80°C for 24 h, under a $CO/H_2 = 1{:}1$ at 30 bar, then cooled to r.t. and the gases vented out. The substrate was introduced by suction into the vessel.

Table 3
Hydroformylation of hex-1-ene in the presence of [Rh(CpX)(NBD)] catalysts[a]

Entry	Catalyst code	T (°C)	Time (h)	Hexane (yield %)	Hex-1-ene (yield %)	*cis*-Hex-2-ene (yield %)	*trans*-Hex-2-ene (yield %)	*cis*-Hex-3-ene (yield %)	*trans*-Hex-3-ene (yield %)	Heptanal (yield %)	2-Methylhexanal (yield %)	2-Ethylpentanal (yield %)
3	**3**	80	24	0.5	0.9	10.7	17.7	1.6	6.8	33.8	28.1	0
4	**3**	80[c]	4	0.6	1.4	20.5	29.6	1.9	7.0	25.2	13.7	0
5	**3**	60[c]	4	1.1	62.9	3.5	8.6	0.8	0.1	15.8	7.1	
6	**4**	80	24	0.5	0.7	5.9	17.0	1.6	6.6	32.3	35.4	0
10	**7**	60	4	0	30.6	7.6	22.2	0.1	3.0	25.4	11.1	0
11[b]	**12**	60	4	0.5	1.2	9.7	14.5	0.7	3.1	47.9	22.4	0

[a] Reaction conditions: catalyst 20 μmol, hex-1-ene 2 mmol, THF 25 ml, p(CO) 15 bar, $p(H_2)$ 15 bar.
[b] See [1c,1d].
[c] The catalyst was pre-activated: a THF solution was heated up to 80 °C for 24 h, under a $CO/H_2 = 1{:}1$ at 30 bar, then cooled to r.t. and the gases vented out. The substrate was introduced by suction into the vessel.

Table 4
Hydroformylation of styrene of [Rh(CpX)(NBD)] catalysts[a]

Entry	Catalyst code	X	T (°C)	Time (h)	Conversion (yield %)	2-Phenylpropanal (yield %)	3-Phenylpropanal (yield %)	Ethylbenzene (yield %)	Regioselectivity (2-phenylpropanal/total aldeydes) (yield %)
12[b]	**12**	$CO_2(CH_2)_2OH$	80	4	53.1	30.0	23.1	0	56.4
13	**7**	$CO_2(CH_2)_3OH$	80	4	51.6	26.5	25.1	0	51.4
14	**3**	*rac*-$CO_2(CHPh)_2OH$	60	4	11.2	10.1	1.1	0	90.0
15	**3**	*rac*-$CO_2(CHPh)_2OH$	80	4	64.0	47.0	21.0	0	67.1
16	**4**	(*S,S*)-$CO_2(CHPh)_2OH$	60	4	6.7	6.7	0	0	100
17	**4**	(*S,S*)-$CO_2(CHPh)_2OH$	60	24	10.1	10.1	0	0	100
18	**4**	(*S,S*)-$CO_2(CHPh)_2OH$	80	4	42.1	21.4	20.5	0.2	51.1
19	**4**	(*S,S*)-$CO_2(CHPh)_2OH$	80	24	99.9	50.7	48.1	1.1	51.3
20[b]	**13**	*rac*-$CO_2(CHMe)_2OH$	80	4	51.5	26.4	25.1	0	51.1
21[b]	**14**	(*S,S*)-$CO_2(CHMe)_2OH$	80	4	30.0	23.5	6.5	0	78.4

[a] Reaction conditions: catalyst 20 μmol, styrene 2 mmol, THF 25 ml, p(CO) 15 bar, $p(H_2)$ 15 bar.
[b] See [1c,1d].

almost complete conversion (99.1%) of hex-1-ene has been reached after 24 h, with an aldehyde yield of 61.8% (*entry 3*). This behavior suggested that an activation of the catalyst at 80 °C is necessary before starting a catalytic cycle. This hypothesis was supported by a test where the catalyst *rac*-**3** was pre-activated at 80 °C for 24 h under CO/H_2 (1/1, 30 bar). The solution was then cooled down to room temperature, the gases vented and hex-1-ene (substrate/catalyst = 100/1) added. The autoclave was re-pressurized with 30 bar of CO/H_2 (1/1) and heated up to 80 °C (*entry 4*) for 4 h obtaining an almost complete conversion of hex-1-ene and a slightly higher regioselectivity. In these latter conditions, however, the yields of aldehydes and isomerized olefins were very different from those obtained in the reaction performed at 80 °C for 24 h (*entry 3*). If the hydroformylation, after the same pre-activation procedure, is carried out at 60 °C for 4 h, a 37.1% conversion was obtained (*entry 5*). These data confirmed our hypothesis on the required pre-activation of the catalyst and they also showed that different rhodium active species must be present either using or not the pre-activated catalyst. Furthermore, the pre-activated catalysts were more active in the isomerization than in the hydroformylation. The regioselectivity of the reaction performed without catalyst pre-activation is lower than that obtained with the pre-activated one. The catalytic activity of *rac*-**3** in the hydroformylation and isomerization of hex-1-ene was similar to that shown by *S,S*-**4**: the conversion [99.1% (*entry 3*) and 99.3% (*entry 6*), respectively] and yield of aldehydes [61.8% and 67.7%, respectively] are almost the same. These results are significantly different from those previously reported for the racemic and chiral rhodium complexes *rac*-**13** and *S,S*-**14**, having two methyl groups on the lateral chain (*entry 7*, *8 and 9*), indicating a different steric influence of the phenyl groups with respect to the methyl ones.

The hydroformylation of hex-1-ene is also affected by the length of the lateral chain on the cyclopentadienyl ligand: the presence of three methylene groups on the side arm of **7** decreases its catalytic activity with respect to **12**. In fact the correlation of the data obtained with the catalysts **7** and **12** showed that the olefins conversion drops from 98.8 (**12**, *entry 11*) to 69.4% (**7**, *entry 10*). The reduction of the catalytic activity is mainly reflected in the hydroformylation. In fact, the yield of aldehydes goes down from 70.2% to 36.5%, while the regioselectivity remains almost unchanged. On the contrary, the isomerization slightly increases from 28.1% to 32.9%. The complex **7** showed a slightly lower activity in the isomerization of hex-1-ene than in the hydroformylation. In these conditions, the hydrogenation of the starting olefin is almost absent.

2.3.2. Hydroformylation of styrene

The catalytic activity of these catalysts in the hydroformylation of styrene showed significant differences with respect to the results obtained with the aliphatic substrate just described (Table 4). The most remarkable difference concerned the reaction temperature.

Complexes *rac*-**3** and *S,S*-**4** hydroformylated styrene after 4 h at 60 °C with low conversions but very high (**3**, *entry 14*) or complete (**4**, *entry 16*) regioselectivities toward 2-phenylpropanal. With regard to *S,S*-**4**, *entry 17* shows that when the reaction time was raised up to 24 h, a low increase of the conversion was obtained (10.1 %), while the regioselectivity remained unchanged. However, in both cases (*entry 16* and *17*), the enantiomeric excess of 2-phenylpropanal was not higher than 3%. With the same complex at 80 °C for 4 h, the conversion of styrene has been increased up to 42.1% (*entry 18*) and it was almost complete (99.9%, *entry 19*) after 24 h, however in both cases the regioselectivity (51%) is remarkably lower than that found at 60 °C.

Moreover with respect to the influence of the substituents on the side chain, the results obtained running the reaction for 4 h, at 80 °C showed that in the presence of two Ph groups the catalytic activity of the rhodium complexes is higher than that of the analogous systems with two Me groups (*rac*-**3** vs. **13**, *entries 15* and *20*; *S,S*-**4** vs. **14**, *entries 18* and *21*). Conversely at this temperature the regioselectivity is slightly affected by the steric hindrance of the lateral chain and remained in the range 51–79%.

The length of the lateral chain of the cyclopentadienyl ligand did not affect the catalytic activity of these rhodium complexes in the hydroformylation of styrene: complex **7** showed an almost identical catalytic activity (*entry 13*) to that shown by **12** (*entry 12*) with a 51.6% conversion.

2.3.3. Catalytic activity in the hydrogenation: preliminary results

The rhodium cyclopentadienyl catalysts described so far did not hydrogenate alkenes in the hydroformylation conditions nevertheless, with the aim of testing their catalytic activity in the absence of CO, we have performed the hydrogenation of hex-1-ene and styrene. In this paper we report some preliminary results regarding the catalytic activity of **12**, **3**, (respectively bearing R = H, Ph on the side chain) in comparison with the unsubstituted [Rh(Cp)(NBD)] (**15**). The reaction conditions and the hydrogenation results are reported in Tables 5 and 6.

As usually found for rhodium complexes [4], compounds **3** and **12** resulted to be more active in the hydrogenation than in the hydroformylation of hex-1-ene and styrene. Working at 20 °C under 15 bar of H_2 for 4 h in the presence of **12** (for hex-1-ene and styrene) and **3** (for hex-1-ene only) an almost complete conversion was reached, while in the hydroformylation higher temperatures (>60 °C) or longer times were required to obtain these results. Nevertheless the hydrogenation reaction

Table 5
Hydrogenation of hex-1-ene in the presence of [Rh(CpX)(NBD)] catalysts[a]

Entry	Catalyst code	X	T (°C)	$p(H_2)$ (bar)	Hexane (conversion %)
22	**12**	$CO_2(CH_2)_2OH$	20	15	97.6
23	**3**	*rac*-$CO_2(CHPh)_2OH$	20	1	0
24	**3**	*rac*-$CO_2(CHPh)_2OH$	20	15	99.0
25	**3**	*rac*-$CO_2(CHPh)_2OH$	40	15	100
26	**3**	*rac*-$CO_2(CHPh)_2OH$	60	15	100
27	**15**	H	20	15	97.1

[a] Reaction conditions: catalyst 20 μmol, hex-1-ene 2 mmol, THF 25 ml, time 4 h.

Table 6
Hydrogenation of styrene in the presence of [Rh(CpX)(NBD)] complexes[a]

Entry	Catalyst code	X	T (°C)	$p(H_2)$ (bar)	Ethylbenzene (conversion %)
28	**12**	$CO_2(CH_2)_2OH$	20	15	100
29	**12**	$CO_2(CH_2)_2OH$	20	5	0
30	**12**	$CO_2(CH_2)_2OH$	40	1	0.2
31	**12**	$CO_2(CH_2)_2OH$	20	5[b]	4.0
32	**3**	*rac*-$CO_2(CHPh)_2OH$	20	15	2.5
33	**3**	*rac*-$CO_2(CHPh)_2OH$	30	15	7.7
34	**3**	*rac*-$CO_2(CHPh)_2OH$	40	15	100
35	**3**	*rac*-$CO_2(CHPh)_2OH$	60	15	100
36	**13**	*rac*-$CO_2(CHMe)_2OH$	20	15	6.4
37	**15**	H	20	15	8.1

[a] Reaction conditions: catalyst 20 μmol, styrene 2 mmol, THF 25 ml, time 4 h.
[b] The catalyst **12** was pre-activated: a THF solution was heated up to 20 °C for 4 h under/$H_2 = 20$ bar, then the gases was vented out. The substrate was introduced by suction into the vessel.

required hydrogen under pressure to take place: more than 5 bar of hydrogen are necessary (**3**, *entry 23*; **12**, *entry 29*).

In our opinion, the relatively high pressure of hydrogen required is necessary to maintain the active catalyst. To confirm this hypothesis a solution of **12** was stirred under 15 bar of hydrogen for 4 h at 20 °C. The hydrogen was then vented, styrene was added and the solution stirred again under 5 bar of hydrogen for 4 h at 20 °C: a 4% conversion was observed (*entry 31*). We can consequently assume that a hydrogen pressure higher than 5 bar is required to perform the catalytic cycle. This behavior was confirmed by the fact that running the same reaction with **12** at higher temperature (40 °C) under a 1 bar of hydrogen only a 0.2% conversion was obtained (*entry 30*).

Contrary to what observed in the hydroformylation, the presence of different groups on the lateral chain of the cyclopentadienyl ligand did not affect the hydrogenation of hex-1-ene. Furthermore, we observed that also the unsubstituted rhodium cyclopentadienyl complex **15** gave a 97.1% conversion (*entry 27*).

The presence of a lateral chain on the cyclopentadienyl ligand did affect the catalytic activity of the rhodium complexes in the hydrogenation of styrene. While **12** showed a complete conversion at 20 °C and 15 bar of H_2 (*entry 28*), **15** showed, in the same conditions only 8.1% conversion (*entry 37*). On the other hand, an increase of the steric encumbrance on the lateral chain reduces the catalytic activity as shown by the data reported in Table 6 for the complexes **12** (conversion 100%, *entry 28*), *rac*-**13** (conversion 6.4%, *entry 36*), and *rac*-**3** (conversion 2.5%, *entry 32*). An analogous behavior was observed in the hydroformylation of olefins catalyzed by the same complexes [1c,1d]. In particular, the presence of two phenyl groups on the lateral chain of the cyclopentadienyl ligand strongly decreases the catalytic activity of the corresponding rhodium complex and a reaction temperature of 40 °C is required to reach a complete conversion after 4 h.

The observation that in the course of the hydroformylation reaction a very low hydrogenation of the substrate takes place, allow us to draw the conclusion that the presence of CO strongly inhibits the formation of a rhodium hydride complex and consequently the hydrogenating activity of these catalysts.

In order to shed light on the real nature and structure of the active catalytic species, high pressure NMR and IR studies in hydroformylation ($CO/H_2 = 1/1$, 30 bar) and hydrogenation (H_2, 15 bar) conditions are under investigation. Preliminary results obtained using the rhodium complexes [Rh{$CpCO_2CH_2CH_2OH$}(L,L)] (L,L = 2CO, NBD) showed that the integrity of the starting Cp–Rh moiety is maintained throughout the

experiments. However so far we did not succeed in determining the nature of the rhodium species formed during the catalytic cycle.

3. Conclusions

In the first part of this paper we have presented an extension of our previously described procedure to obtain chiral and non-chiral hydroxy-functionalized alkoxycarbonylcyclopentadienides $Na[CpCO_2(CHR)_2OH]$ and synthesized the novel ligands **1** and **2**. We have also demonstrated that the above procedure applied to six-membered cyclic carbonates such as 1,3-dioxan-2-one leads to the unselective formation of a mixture of at least two anionic cyclopentadienide systems in a ratio strictly dependent on the carbonate/NaCp stoichiometric ratio.

In the second part we have examined the catalytic activity in the hydroformylation of hex-1-ene and styrene of the novel rhodium complexes **3**, **4**, and **7** and compared with that of previously reported analogous complexes $[Rh\{CpCO_2(CHR)_2OH\}(NBD)]$ (R = H, Me). The present studies have confirmed that the catalytic activity of these complexes is strongly affected by the nature of the substituents present on the lateral chain. Finally, preliminary results showed that the same effect is present in the hydrogenation of styrene.

4. Experimental

4.1. Materials and procedures for the syntheses

All reactions with organometallic reagents or substrates were carried out under argon or nitrogen 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 or with a Perkin–Elmer mod. 1760-X instrument. The NMR spectra were recorded using Varian Gemini XL 300 (^{1}H, 300.1; ^{13}C, 75.5 MHz), Varian Mercury-Plus VX 400 (^{1}H, 399.9; ^{13}C, 100.6 MHz), Varian Inova 600 (^{1}H, 599.7, ^{13}C, 150.8 MHz) instruments. The spectra were referenced internally to residual solvent resonances, and were recorded at 298 K for characterization purposes. EI-MS spectra were taken using a VG 7070E mass spectrometer. ESI-MS analyses were performed by direct injection of methanol solutions of the metal complexes using a WATERS ZQ 4000 mass spectrometer. A GC Shimadzu GC-14A, equipped with a flame ionization detector (FID), and integrator Shimadzu C-R4A was used to evaluate the hydroformylation products, while a GC Perkin–Elmer mod. 8320, equipped with a FID detector, was employed to analyze the composition of the residual hexenes. A GC-MS Shimadzu QP 5050 instrument was used to verify the identity of the products obtained. A 150 ml Parr autoclave was employed for the catalytic tests. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument.

The reagents (−)(*1S,2S*)-1,2-diphenyl-1,2-ethanediol [5], *cis*-4,5-diphenyl-1,3-dioxolan-2-one [6], (−)(4*S*,5*S*)-4,5-diphenyl-1,3-dioxolan-2-one [6], and 1,3-dioxan-2-one [7] were prepared according to the literature procedures; *meso*-1,2-diphenyl-ethane-1,2-diol (Aldrich), $[Rh(NBD)Cl]_2$ (Strem) were used as purchased. The complexes **12** [1b,8], *rac*-**13**, *S,S*-**14** [1c] were prepared as previously described. Petroleum ether (Etp) refers to a fraction having b.p. 60–80 °C. The THF (RPE C. Erba) used in the catalytic experiments was dried by refluxing over Na/K under nitrogen atmosphere, distilled (b.p. 65 °C) and stored under nitrogen. Hex-1-ene (Aldrich), eluted through an Al_2O_3 column and distilled, had b.p. 64 °C. Styrene (Aldrich), distilled prior to use, had b.p. 145 °C. Silica gel was heated at about 200 °C while a slow stream of a dry nitrogen was passed through it [9]. Melting points were taken in sealed capillaries and were uncorrected.

4.1.1. Preparation of $Na[rac\text{-}C_5H_4CO_2(CHPh)_2OH]$ (*1*)

To a solution of NaCp (0.56 g, 6.36 mmol) in THF (25 ml) solid *meso*-4,5-diphenyl-1,3-dioxolan-2-one was added (1.53 g, 6.38 mmol) at room temperature. The mixture was stirred for 24 h, the volatiles were removed under vacuum and the residue kept under vacuum at 60 °C for 2 h. The resulting solid was washed with Et_2O to give 1.29 g of **1** (61%) as a beige solid. ^{1}H NMR gCOSY (599.7 MHz, [D$_5$]Pyr): $\delta = 7.74$–7.55 (m, Ph), 7.46 (AA′BB′, $^3J_{H,H} = 2.9$ Hz, 2H; Cp), 7.39 (d, $^3J_{CH,OH} = 4.2$ Hz, 1H; OH); 7.36-7.10 (m, Ph), 6.70 (d, $^3J_{CH,CH} = 4.4$ Hz, 1H; CO_2CH), 6.65 (AA′BB′, $^3J_{H,H} = 2.9$ Hz, 2H; Cp), 5.50 (dd, $^3J_{H,H} = 4.4$ Hz, $^3J_{CH,OH} = 4.2$ Hz, 1H; C*H*OH), ^{13}C–{^{1}H} gHSQC NMR (150.8 MHz, [D$_5$]Pyr): $\delta = 167.8$ (C=O), 143.0 (*ipso*-C; Ph), 141.1 (*ipso*-C; Ph), 128.4, 128.2, 127.8, 127.7, 127.2, 127.0 (Ph), 113.3 (CH; Cp), 111.5 (CH; Cp), 109.7 (*ipso*-C; Cp), 77.7 (CHOH), 77.2 (CO_2CH). IR (THF, cm^{-1}) ν(C=O) 1673 (bs), 1619 (bs). Anal. Calc. for $C_{20}H_{17}NaO_3$: C, 73.2; H, 5.22. Found: C, 73.6; H, 5.00%.

4.1.2. Preparation of $Na[(2S,3S)\text{-}C_5H_4CO_2(CHPh)_2OH]$ (*2*)

To a solution of NaCp (0.61 g, 6.93 mmol) in THF (25 ml), solid 4*S*, 5*S*-diphenyl-1,3-dioxolan-2-one (1.67 g, 6.96 mmol) was added at room temperature. The mixture was stirred at room temperature for 24 h, the solvent removed under vacuum and the residue kept under vacuum at 60 °C for 2 h. The resulting solid was washed with Et_2O and **2** (1.45 g, 63%) was obtained as a

beige solid. ^{1}H NMR gCOSY (599.7 MHz, [D$_5$]Pyr): = 7.51 (AA′BB′, $^3J_{H,H}$ = 2.9 Hz, 2H; Cp), 7.49–7.46 (m, Ph, OH overlapped peaks), 7.27–7.05 (m, Ph), 6.70 (d, $^3J_{H,H}$ = 6.7 Hz, 1H; CO_2CH), 6.68 (AA′BB′, $^3J_{H,H}$ = 2.9 Hz, 2H; Cp), 5.48 (dd, $^3J_{CH,CH}$ = 6.7 Hz, $^3J_{CH,OH}$ = 4.1 Hz, 1H; C*H* OH); ^{13}C–{^{1}H} NMR gHSQC (150.8 MHz, [D$_5$]Pyr): δ = 168.9 (C=O), 143.0 (*ipso*-C; Ph), 140.7 (*ipso*-C; Ph), 128.4, 128.3, 127.8, 127.7, 127.3, 127.1 (Ph), 113.5 (CH; Cp), 111.7 (CH; Cp), 109.6 (*ipso*-C; Cp), 77.7 (CHOH), 77.6 (CO_2CH). IR (THF, cm^{-1}) ν(C=O) 1673 (bs), 1619 (bs). Anal. Calc. for $C_{20}H_{17}NaO_3$: C, 73.2; H, 5.22. Found: C, 73.5; H, 5.23%.

4.1.3. Preparation of [Rh(NBD){rac-CpCO$_2$(CHPh)$_2$-OH}] (3)

To a solution of **1** (1.13 g, 3.44 mmol) in THF (30 ml), solid [Rh(NBD)Cl]$_2$ (0.65 g, 1.41 mmol) was added. The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum and CH_2Cl_2 was added. The yellow suspension was first filtered on a celite pad and then chromatographed on silica gel. Eluting with Et$_2$O/Etp 1:1 a yellow fraction 0.79 g (56%) was collected and identified as the product **3**. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 10H; Ph), 6.00 (d, $^3J_{H,H}$ = 5.8 Hz, 1H; CO_2CH Ph), 5.44 (m, 1H; Cp), 5.38 (m, 1H; Cp), 5.29 (m, 1H; Cp), 5.27 (m, 1H; Cp), 5.00 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{CH,OH}$ = 3.7 Hz, 1H; C*H*OH), 3.18 (m, 2H, H$_{1,4}$; NBD), 3.14 (m, 4H, H$_{2,3,5,6}$; NBD), 2.26 (d, $^3J_{CH,OH}$ = 3.7 Hz, 1H; OH), 0.98 (t, $^3J_{CH,CH}$ = 1.5 Hz, 2H, H$_7$; NBD); ^{13}C–{^{1}H} NMR gHSQC (100.6 MHz, $CDCl_3$): δ = 164.9 (C=O), 139.7 (*ipso*-C; Ph), 137.2 (*ipso*-C; Ph), 128.2, 128.0, 127.9, 127.4, 127.2 (Ph), 91.7 (d, $J_{C,Rh}$ = 3.8 Hz, *ipso*-C; Cp), 88.4 (d, $J_{C,Rh}$ = 3.4 Hz, CH; Cp), 86.1 (d, $J_{C,Rh}$ = 4.0 Hz, CH; Cp), 86.0 (d, $J_{C,Rh}$ = 4.0 Hz, CH; Cp), 78.4 (CO_2CH), 76.7 (CHOH), 57.5 (d, $J_{C,Rh}$ = 6.8 Hz, C$_7$; NBD), 46.7 (d, $J_{C,Rh}$ = 2.9 Hz, C$_{1,4}$; NBD), 32.7 (d, $J_{C,Rh}$ = 8.0 Hz, =CH; NBD), 32.5 (d, $J_{C,Rh}$ = 8.0 Hz, =CH; NBD). IR (THF, cm^{-1}) ν(C=O) 1713 (s). Anal. Calc. for $C_{27}H_{25}O_3Rh$: C, 64.8; H, 5.03. Found: C, 64.8; H, 5.05%. ESI-MS [M + Na]$^+$ = 523 *m*/*z*; m.p. = 164–166 °C.

4.1.4. Preparation of (−)-[Rh(NBD){(2S,3S)CpCO$_2$-(CHPh)$_2$OH}] (4)

To a solution of **2** (0.62 g, 1.89 mmol) in THF (30 ml), solid [Rh(NBD)Cl]$_2$ (0.36 g, 0.78 mmol) was added. The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum and CH_2Cl_2 was added. The yellow suspension was first filtered on a celite pad and then chromatographed on silica gel. Eluting with Et$_2$O/Etp = 1/1 a yellow fraction was collected and identified as the product **8** (yellow solid, 0.45 g, 58%). $[\alpha]_D^{19.0} = -17.6$ (c = 0.63, $CHCl_3$). ^{1}H NMR (399.9 MHz, $CDCl_3$): δ = 7.26–7.18 (m, 10H; Ph), 5.98 (d, $^3J_{H,H}$ = 7.1 Hz, 1H; CO_2CHPh), 5.58 (m, 1H; Cp), 5.53 (m, 1H; Cp), 5.40 (m, 1H; Cp), 5.37 (m, 1H; Cp), 5.00 (dd, $^3J_{H,H}$ = 7.1 Hz, $^3J_{CH,OH}$ = 3.0 Hz 1H; C*H*OH), 3.32 (m, 2H, H$_{1,4}$; NBD), 3.26 (m, 4H, H$_{2,3,5,6}$; NBD), 2.83 (d, $^3J_{CH,OH}$ = 3.3 Hz, 1H; OH), 0.96 (t, $^3J_{H,H}$ = 1.5 Hz, 2H, H$_7$; NBD); ^{13}C–{^{1}H} NMR gHSQC (100.6 MHz, $CDCl_3$): δ = 165.0 (C=O), 139.1 (*ipso*-C; Ph), 137.2 (*ipso*-C; Ph), 128.0, 127.9, 127.8, 127.2, 127.1 (Ph), 91.6 (d, $J_{C,Rh}$ = 4.9 Hz, *ipso*-C; Cp), 88.6 (d, $J_{C,Rh}$ = 3.2 Hz, CH; Cp), 88.5 (d, $J_{C,Rh}$ = 4.1 Hz, CH; Cp), 86.1 (d, $J_{C,Rh}$ = 4.0 Hz, CH; Cp), 86.0 (d, $J_{C,Rh}$ = 4.0 Hz, CH; Cp), 85.9 (d, $J_{C,Rh}$ = 4.0 Hz, CH; Cp), 79.5 (CO_2CH), 77.2 (CHOH), 57.5 (d, $J_{C,Rh}$ = 7.2 Hz, C$_7$; NBD), 46.7 (d, $J_{C,Rh}$ = 2.4 Hz, C$_{1,4}$; NBD), 32.8 (d, $J_{C,Rh}$ = 10.6 Hz, =CH; NBD), 32.6 (d, $J_{C,Rh}$ = 10.6 Hz, =CH; NBD). IR (THF, cm^{-1}): ν(C=O) 1704 (s). Anal. Calc. for $C_{27}H_{25}O_3Rh$: C, 64.8; H, 5.03. Found: C, 64.7; H, 5.04%. ESI-MS [M + Na]$^+$ = 523 *m*/*z*; m.p. = 150–151 °C.

4.1.5. Reactions of NaCp with 1,3-dioxan-2-one

Synthesis of ***I***. To a solution of NaCp (2.00 g, 19.0 mmol) in THF (25 ml), solid 1,3-dioxan-2-one (2.49 g, 24.4 mmol) was added and the reaction mixture stirred at room temperature for 24 h. The suspension was filtered on a celite pad and the solvent removed under vacuum. After keeping the solid under vacuum at 60 °C for 2 h, the residue was washed with Et$_2$O to give 2.05 g of an inseparable mixture of **5** (30%) and **6** (18%) (determined by NMR analysis of the crude product) obtained as a beige solid. For **5**: ^{1}H NMR (300.1 MHz, [D$_5$]Pyr): δ = 7.40 (AA′BB′, $^3J_{H,H}$ = 3.0 Hz, 2H; Cp), 6.64 (AA′BB′, $^3J_{H,H}$ = 3.0 Hz, 2H, Cp), 4.56 (t, $^3J_{H,H}$ = 6.0 Hz, 2H; CO_2CH_2), 3.93 (t, $^3J_{H,H}$ = 5.5 Hz, 2H; CH_2OH), 2.03 (m, 2H, $CH_2CH_2CH_2$); ^{13}C–{^{1}H} NMR (75.5 MHz, [D$_5$]Pyr): δ = 168.8 (C=O), 112.9 (CH; Cp); 111.2 (CH; Cp), 109.6 (*ipso*-C; Cp), 65.6 (CO_2CH_2), 58.5 (CH_2OH), 29.5 (CH_2). IR (THF, cm^{-1}) ν = 1644 (s) (C=O). For **6**: ^{1}H NMR (300.1 MHz, [D$_5$]Pyr): δ = 7.36 (AA′BB′, $^3J_{H,H}$ = 3.0 Hz, 2H; Cp), 6.60 (AA′BB′, $^3J_{H,H}$ = 3.0 Hz, 2H; Cp), 4.56 (t, $^3J_{H,H}$ = 6.0 Hz, 2H; CO_2CH_2,), 4.35 (t, $^3J_{H,H}$ = 6.3 Hz, 2H; $CH_2OC(O)O$), 4.32 (t, $^3J_{H,H}$ = 6.3 Hz, 2H; $OC(O)OCH_2$), 3.93 (t, $^3J_{H,H}$ = 5.5 Hz, 2H; CH_2OH), 2.03 (m, 4H; $CH_2CH_2CH_2$); ^{13}C–{^{1}H} NMR (75.5 MHz, [D$_5$]Pyr): δ = 168.4 (C=O), 155.5 (OC(O)O), 112.7 (CH; Cp), 111.2 (CH; Cp), 109.4 (*ipso*-C; Cp), 65.6 (CO_2CH_2), 59.1 ($CH_2OC(O)O$), 59.0 ($OC(O)OCH_2$), 58.5 (CH_2OH), 34.3 (CH_2), 29.5 (CH_2). IR (THF, cm^{-1}) ν = 1748 (s) (OC(O)O), 1644 (s) (C=O).

Synthesis of ***II***. To a solution of NaCp (1.13 g, 10.7 mmol) in THF (25 ml), solid 1,3-dioxan-2-one (1.74 g, 17.1 mmol) was added and the reaction mixture stirred at room temperature for 24 h. The suspension was filtered on a celite pad and the solvent removed under vacuum. After keeping the solid under vacuum at 60 °C for 2 h, the residue was washed with Et$_2$O to give 1.48 g of an inseparable mixture of **5** (33%) and **6** (26%)

(determined by NMR analysis of the crude product) as a beige solid.

*Synthesis of **III***. To a solution of NaCp (0.62 g, 5.97 mmol) in THF (25 ml), solid 1,3-dioxan-2-one (1.34 g, 13.1 mmol) was added and the reaction mixture stirred at room temperature for 24 h. The suspension was filtered on a celite pad and the solvent removed under vacuum. After keeping the solid under vacuum at 60 °C for 2 h, the residue was washed with Et_2O to give 0.29 g of an inseparable mixture of **5** (7%) and **6** (12%) (determined by NMR analysis of the crude product) as a beige solid.

Rhodium(I) derivatives . By reacting the three mixtures **I**, **II**, or **III** with $[Rh(NBD)Cl]_2$ several mono- and dinuclear yellow complexes were obtained in yields depending on the starting mixtures employed.

(a) To a solution of 0.28 g of **I** in THF (25 ml), solid $[Rh(NBD)Cl]_2$ (0.20 g, 0.43 mmol) was added. 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 a mixture of Et_2O/Etp (1:1) a first fraction (0.012 g, 0.019 mmol, 4%) was collected as a yellow solid and identified as $[Rh_2\{\mu\text{-}(CpCO_2(CH_2)_3CO_2Cp)\}(NBD)_2]$ (**10**). ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 5.54$ (AA′BB′, $^3J_{H,H} = 2.4$ Hz, 4H; Cp), 5.36 (AA′BB′, $^3J_{H,H} = 2.4$ Hz, 4H; Cp), 4.39 (t, $^3J_{H,H} = 6.3$ Hz, 4H; CO_2CH_2), 3.34 (m, 12H; NBD), 2.13 (quintet, $^3J_{H,H} = 6.3$ Hz, 2H; CH_2), 0.99 (t, $^3J_{H,H} = 1.4$ Hz, 4H; NBD); ^{13}C–$\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 166.1$ (C═O), 91.5 (*ipso*-C; Cp), 88.3 (d, $J_{C,Rh} = 3.4$ Hz; Cp), 86.0 (d, $J_{C,Rh} = 4.0$ Hz; Cp), 60.4 (CO_2CH_2), 57.5 (d, $J_{C,Rh} = 6.8$ Hz, C_7; NBD), 46.8 (d, $J_{C,Rh} = 2.3$ Hz, $C_{1,4}$; NBD), 32.4 (d, $J_{C,Rh} = 10.2$ Hz, $C_{2,3,5,6}$; NBD), 28.6 (s, $CH_2CH_2CH_2$). IR (THF, cm^{-1}): $\nu = 1712$ (s) (C═O); ESI-MS $[M + Na]^+ = 671$ m/z. Anal. Calc. for $C_{29}H_{30}O_4Rh_2$: C, 53.7; H, 4.66. Found: C, 53.6; H, 4.68%; m.p. = 126 °C.

Further eluting with the same solvent mixture a second yellow fraction (0.021 g, 6%) was collected and a yellow crystalline solid identified as $[Rh_2\mu\text{-}(CpCO_2(CH_2)_3OC(O)O(CH_2)_3O_2CCp)\}(NBD)_2]$ (**11**). ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 5.50$ (AA′BB′X, $^3J_{H,H} = 2.1$ Hz, $^3J_{H,Rh} = 0.6$ Hz, 4H; Cp), 5.35 (AA′BB′X, $^3J_{H,H} = 2.1$ Hz, $^3J_{H,Rh} = 0.9$ Hz, 4H; Cp), 4.31 (m, 8H; CO_2CH_2, $OC(O)OCH_2$), 3.33 (m, 12H; NBD), 2.08 (m, 4H; CH_2), 0.99 (t, $^3J_{H,H} = 1.4$ Hz, 4H; NBD); ^{13}C–$\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 165.9$ (C═O), 155.0 (OC(O)O), 91.5 (*ipso*-C; Cp), 88.3 (d, $J_{C,Rh} = 3.7$ Hz, CH; Cp), 86.0 (d, $J_{C,Rh} = 3.7$ Hz, CH; Cp), 64.7 ($OC(O)OCH_2$), 60.1 (CO_2CH_2), 57.5 (d, $J_{C,Rh} = 6.1$ Hz, C_7; NBD), 46.7 (d, $J_{C,Rh} = 2.4$ Hz, $C_{1,4}$; NBD), 32.4 (d, $J_{C,Rh} = 10.9$ Hz, $C_{2,3,5,6}$; NBD), 28.4 (s, $CH_2CH_2CH_2$). IR (THF, cm^{-1}): $\nu = 1749$ (s) (OC(O)O), 1712 (s) (C═O); ESI-MS $[M + Na]^+ = 773$ m/z. Anal. Calc. for $C_{33}H_{36}O_7Rh_2$: C, 52.8; H, 4.80. Found: C, 53.0; H, 4.82%; m.p. = 80 °C.

The major product $[Rh\{C_5H_4CO_2(CH_2)_3OH\}(NBD)]$ (**7**) was obtained eluting with Et_2O. Yellow crystals (0.158 g, 50%) have been obtained by evaporation of Et_2O. ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 5.47$ (AA′BB′X, $^3J_{H,H} = 2.1$ Hz, $^3J_{H,Rh} = 0.6$ Hz, 2H; Cp), 5.34 (AA′BB′X, $^3J_{H,H} = 2.1$ Hz, $^3J_{H,Rh} = 0.9$ Hz, 2H; Cp), 4.37 (t, $^3J_{H,H} = 6.0$ Hz, 2H; CO_2CH_2), 3.75 (m, 2H; CH_2-OH), 3.32 (m, 6H, CH; NBD), 2.66 (t, $^3J_{H,H} = 6.0$ Hz, 1H; OH), 1.92 (m, 2H; CH_2), 0.97 (t, $^3J_{H,H} = 1.4$ Hz, 2H, CH_2; NBD); ^{13}C–$\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 166.8$ (C═O), 91.5 [d, $J_{C,Rh} = 4.9$ Hz, *ipso*-C; Cp], 88.5 (d, $J_{C,Rh} = 3.6$ Hz, CH; Cp), 85.9 (d, $J_{C,Rh} = 4.9$ Hz; CH; Cp), 60.6 ($CpCO_2CH_2$), 59.0 (CH_2OH), 57.4 (d, $J_{C,Rh} = 7.3$ Hz, C_7; NBD), 46.7 (d, $J_{C,Rh} = 2.5$ Hz, $C_{1,4}$; NBD), 32.6 (d, $J_{C,Rh} = 10.8$ Hz, $C_{2,3,5,6}$; NBD), 32.2 (s, CH_2). IR (THF, cm^{-1}): $\nu = 1711$ (s) (C═O). EI-MS (70 eV): m/z (%): 362 (100) $[M]^+$, 303 (47) $[M\text{-}CH_2CH_2CH_2OH]^+$, 259 (68) $[M\text{-}CO_2(CH_2)_3OH]^+$, 194 (47) $[Rh(C_7H_7)]^+$, 168 (67) $([Rh(C_5H_5)]^+$, 103 (18) $[Rh]^+$. Anal. Calc. (%) for $C_{16}H_{19}O_3Rh$: C, 53.0; H, 5.29. Found: C, 53.0; H, 5.28%; m.p. = 62 °C.

Finally by further elution with Et_2O, a fourth yellow oily fraction was collected and identified as $[Rh\{C_5H_4CO_2(CH_2)_3OC(O)O(CH_2)_3OH\}(NBD)]$ (**8**) (0.013 g, 3%). ^1H NMR gCOSY (599.7 MHz, $CDCl_3$): $\delta = 5.49$ (AA′BB′, $^3J_{H,H} = 2.1$ Hz, 2H; Cp), 5.34 (AA′BB′, $^3J_{H,H} = 2.1$ Hz, 2H; Cp), 4.31 (m, 6H; $CpCO_2$-$CH_2CH_2CH_2OC(O)O$, $OC(O)OCH_2CH_2CH_2OH$), 3.74 (m, 2H; CH_2OH), 3.32 (m, 6H, CH; NBD), 2.09 (m, 2H, $CpCO_2CH_2CH_2CH_2OC(O)O$), 1.93 (m, 3H, OC(O)-$OCH_2CH_2CH_2OH$, OH overlapping resonances), 0.98 (t, $^3J_{H,H} = 1.4$ Hz, 2H; CH_2, NBD); ^{13}C–$\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, gHSQC): $\delta = 166.0$ (C═O), 155.4 (OC(O)O), 91.7 (d, $J_{C,Rh} = 4.8$ Hz, *ipso*-C; Cp), 88.3 (d, $J_{C,Rh} = 3.7$ Hz, CH; Cp), 86.0 (d, $J_{C,Rh} = 3.7$ Hz; CH; Cp), 64.9, 64.8 ($OC(O)OCH_2$), 60.0 ($C_5H_4CO_2CH_2$), 59.0 (CH_2OH), 57.5 (d, $J_{C,Rh} = 7.0$ Hz, C_7; NBD), 46.7 (d, $J_{C,Rh} = 2.4$ Hz, $C_{1,4}$; NBD), 32.5 (d, $J_{C,Rh} = 10.2$ Hz, $C_{2,3,5,6}$; NBD), 31.6 (s, $CH_2CH_2CH_2OH$), 28.4 (s, $CH_2CH_2CH_2OC(O)O$). IR (THF, cm^{-1}): $\nu = 1748$ (s) (OC(O)O), 1712 (s) (C═O); ESI-MS $[M + Na]^+ = 487$ m/z. Anal. Calc. for $C_{20}H_{25}O_6Rh$: C, 51.7; H, 5.43. Found: C, 51.8; H, 5.44%.

(b) To a solution of 0.20 g of **II** in THF (25 ml), solid $[Rh(NBD)Cl]_2$ (0.160 g, 0.35 mmol) was added. Using the same work up described in *(a)*, the following complexes were obtained (in elution order): $[Rh_2\{\mu\text{-}(CpCO_2(CH_2)_3OC(O)O(CH_2)_3O_2CCp)\}(NBD)_2]$ (**11**) (0.011 g, 2%), $[Rh\{CpCO_2(CH_2)_3OH\}(NBD)]$ (**7**) (0.077 g, 30%) $[Rh\{CpCO_2(CH_2)_3OC(O)O(CH_2)_3OH(NBD)]$ (**8**) (0.024 g, 8%).

(c) To a solution of 0.28 g of **III** in THF (25 ml), solid $[Rh(NBD)Cl]_2$ (0.190 g, 0.41 mmol) was added. Using the same work up described for (a) the following complexes were obtained (in elution order): $[Rh_2\{\mu\text{-}(CpCO_2(CH_2)_3OC(O)O(CH_2)_3O_2CCp)\}(NBD)_2]$ (**11**)

(0.014 g, 5%) [Rh{$CpCO_2(CH_2)_3OH$(NBD)] (**7**) (0.069 g, 23%), [Rh{$CpCO_2(CH_2)_3OC(O)O(CH_2)_3OH$}(NBD)] (**8**) (0.042 g, 11 %). By further elution with Et_2O a fifth yellow oily fraction was collected and the product identified as the complex [Rh{$CpCO_2[(CH_2)_3OC(O)O]_2(CH_2)_3OH$}(NBD)] (**9**) (0.026 g, 4%). ^{1}H NMR gCOSY (599.7 MHz, $CDCl_3$): $\delta = 5.50$ (AA′BB′, $^3J_{H,H} = 2.1$ Hz, 2H; Cp), 5.35 (AA′BB′X, $^3J_{H,H} = 2.1$ Hz, $^3J_{H,Rh} = 0.9$ Hz, 2H; Cp), 4.30 (m, 6H; $CpCO_2CH_2CH_2CH_2OC(O)O$, $OC(O)OCH_2CH_2CH_2OH$), 4.25 (m, 4H; $OC(O)OCH_2CH_2CH_2OC(O)O$), 3.74 (m, 2H; CH_2OH), 3.33 (m, 6H; CH, NBD), 2.09 (m, 2H, $CpCO_2CH_2CH_2CH_2OC(O)O$), 2.03 (m, 2H; $OC(O)OCH_2CH_2CH_2OC(O)O$), 1.92 (m, 2H; $OC(O)OCH_2CH_2CH_2OH$), 1.84 (t, $^3J_{H,H} = 6.0$ Hz, 1H; OH), 0.99 (t, $^3J_{H,H} = 1.3$ Hz, 2H; CH_2, NBD); ^{13}C–{^{1}H} NMR gHSQC (150.8 MHz, $CDCl_3$): $\delta = 166.0$ (C═O), 155.4 ($OC(O)O$), 155.0 ($OC(O)O$), 91.6 (d, $J_{C,Rh} = 4.6$ Hz, *ipso*-C; Cp), 88.3 (d, $J_{C,Rh} = 4.0$ Hz, CH; Cp), 86.0 (d, $J_{C,Rh} = 4.0$ Hz; CH; Cp), 65.0, 64.8, 64.3, 64.2 ($OC(O)OCH_2$), 60.1 ($C_5H_4CO_2CH_2$), 58.9 (CH_2OH), 57.5 (d, $J_{C,Rh} = 6.8$ Hz, C_7; NBD), 46.7 (d, $J_{C,Rh} = 2.3$ Hz, $C_{1,4}$; NBD), 32.5 (d, $J_{C,Rh} = 10.2$ Hz, $C_{2,3,5,6}$; NBD), 31.6 ($CH_2CH_2CH_2OH$), 28.3, 28.0 ($CH_2C\ H_2CH_2$). IR (THF, cm^{-1}): $\nu = 1750$ (s) (OC(O)O), 1711 (s) (C═O); ESI-MS $[M + Na]^+ = 589$ m/z. Anal. (%) for $C_{24}H_{31}O_9Rh$ Calc.: C, 50.9; H, 5.52. Found: C, 51.0; H, 5.50.

4.2. Catalysis

The catalytic 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 the selected rhodium complex and 2 mmol of substrate 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 the gases at the required pressure. The reaction mixture was stirred and heated at the prefixed temperature for the established time. After cooling the autoclave to r.t., the gases were vented and the solution collected. The reaction products were analyzed by GC. 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 and hydrogenation products. The oven was kept 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 up 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 hexenes: the column was kept at 130 °C for 32 min, heated with a rate of 30 °C/min up to 200 °C and kept at this temperature for 16 min. A 2 m FFAP packed column ('Free Fatty Acids Phase' supported on Chromosorb G AW-DMCS 5%) was used to analyze the styrene hydroformylation and hydrogenation products; the column was kept at 40 °C for 15 min, then heated with a rate of 5 °C/min up to 140 °C and kept at this temperature for 40 min.

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