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Coordination Chemistry of Ester-Functionalized Cp Ligands. The Atom-Economy Synthesis of Na[$C_5H_4CO_2(CH_2)_2OH$] and Solid State Structures of [Rh{$C_5H_4CO_2(CH_2)_2OH$}$(CO)_2$] and [Rh_2{μ-$(C_5H_4CO_2CH_2)_2$}$(NBD)_2$]

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The one-step synthesis of Na[$C_5H_4CO_2CH_2CH{=}CH_2$] (**1**) from NaCp and diallyl carbonate is presented together with a simple pathway for the synthesis of sodium hydroxyalkoxycarbonylcyclopentadienide, Na[$C_5H_4CO_2(CH_2)_2OH$] (**2**). The latter new reagent is obtained in high yield by reacting NaCp with 1,3-dioxolan-2-one (ethylene carbonate). When (±)-4-methyl-1,3-dioxolan-2-one [(±)-1,2-propylene carbonate] is used, the ring-opening reaction leads to a mixture of the two regioisomers Na[$C_5H_4CO_2CH_2CH(Me)OH$] (**3a**) and Na[$C_5H_4CO_2CH(Me)CH_2OH$] (**3b**) in a 7:3 ratio. Reactions of **1** and **2** with $FeCl_2$ and [Rh(L,L)Cl]$_2$ [L,L = CO or L,L = 2,5-norbornadiene (NBD)] lead to the respective metal complexes [Fe($C_5H_4CO_2CH_2CH{=}CH_2)_2$] (**4**), [Fe{$C_5H_4CO_2(CH_2)_2OH$}$_2$] (**5**), [Rh($C_5H_4CO_2CH_2CH{=}CH_2$)$(CO)_2$] (**6**), [Rh{$C_5H_4CO_2(CH_2)_2OH$}$(CO)_2$] (**7**), and [Rh{$C_5H_4CO_2(CH_2)_2OH$}(NBD)] (**8**). Additionally in the reaction of **2** with [Rh(L,L)Cl]$_2$ the diester-bridged dinuclear adducts [Rh_2{μ-$(C_5H_4CO_2CH_2)_2$}(L,L)$_2$] [L,L = CO (**9**); L,L = NBD (**10**)] are isolated. The reaction of **2** with MBr$(CO)_5$ (M = Mn, Re) leads to [M{$C_5H_4CO_2(CH_2)_2OH$}$(CO)_3$] [M = Mn (**11**); M = Re (**12**)] together with a complex mixture of unidentified metal carbonyls. The X-ray molecular structures of **7** and **10** are reported.

Introduction

In our investigation on the coordination ability of novel ester-functionalized Cp ligands we recently demonstrated that the disubstituted alkyl- and aryloxycarbonylcyclopentadienide anions [$C_5H_3(CO_2R)_2$-1,2]$^-$ [R = Me, Et, Ph] can be conveniently obtained by reacting the monosubstituted [$C_5H_4(CO_2R)$]$^-$ with the corresponding chloroformate ROC(O)Cl.[1]

To expand these studies, it was first necessary to widen the range of ester-monosubstituted cyclopentadienides available.[2] Therefore, we focused our attention on the synthesis of Cp ligands bearing, on the ester-containing side chain, an additional functional group that might be employed for anchoring their metal derivatives to an organic or inorganic matrix.

In this paper we describe the one-pot synthesis of Na[$C_5H_4CO_2CH_2CH{=}CH_2$] (**1**) from NaCp and diallyl carbonate previously obtained in two steps, starting from NaCp and allyl chloroformate followed by deprotonation of the resulting $C_5H_5CO_2CH_2CH{=}CH_2$ with Na.[3]

$$\text{NaCp} \quad + \quad (\text{RO})_2\text{CO} \quad \rightarrow \quad \text{Na}[\text{C}_5\text{H}_4\text{CO}_2\text{R}] + \text{ROH} \qquad (1)$$

$$\text{R} = \text{-CH}_2\text{CH}{=}\text{CH}_2 \qquad\qquad\qquad \mathbf{1}$$

Since in reactions involving organic carbonates (e.g., eq 1) part of these reagents are lost as alcohols, we decided to investigate the reactivity toward cyclic carbonates.

The reaction of NaCp with cyclic carbonates resulted in the exclusive formation of the novel β-hydroxyalkoxycarbonylcyclopentadienide Na[$C_5H_4CO_2(CHR)_2OH$] (R = H or Me). This ring-opening reaction represents an example of the atom-economy concept applied to the synthesis of multifunctionalized cyclopentadienyl ligands, and the main body of the next section is dedicated to

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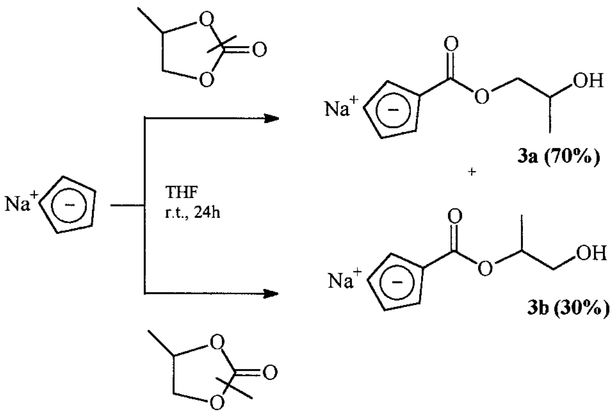
Scheme 1

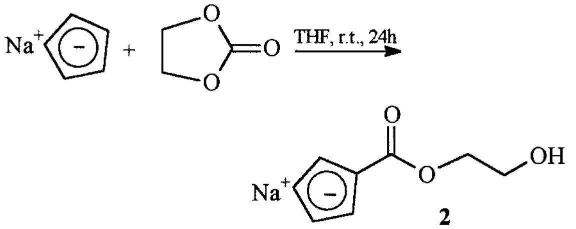


the discussion of the results of our investigation into these reactions, which allowed us to prepare metal-containing substituted Cp derivatives.

Results and Discussion

Ligands Synthesis. The Na[$C_5H_4CO_2CH_2CH{=}CH_2$] (**1**) has been prepared straightforwardly by reacting NaCp with a slight excess of diallyl carbonate in refluxing THF for 4 h (66%). The NMR spectra in [D_5]Pyr show for the Cp protons the expected AA′BB′ pseudotriplets pattern [^{1}H NMR δ 7.41 H(3,4), 6.62 H(2,5); corresponding ^{13}C NMR Cp signals at δ 112.8, 111.2, and 109.8] as well as the typical CKLM pattern for the allyl group in the pendant side chain.[3] The IR spectrum in THF (range 2300−1500 cm^{-1}) shows a broad band centered at 1614 cm^{-1} due to the conjugated C═O and C═C bonds of the Cp ring π system.

The reaction of NaCp with ethylene carbonate in tetrahydrofuran at room temperature leads (eq 2) to the β-hydroxyethoxycarbonylcyclopentadienide salt Na[$C_5H_4CO_2(CH_2)_2OH$] (**2**) in high yield (ca. 90%). The use of these easily available reagents has allowed us to maintain the hydroxy functionality on the side chain with a mechanism in which the deprotonation of the 1-substituted cyclopentadiene intermediate occurs intramolecularly.



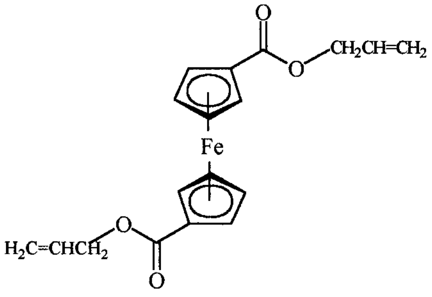
2 (2)

The sodium salt **2** is a light brown solid. The Cp ring NMR features are similar to those described above for **1**, two triplets at δ 4.55 and 4.05 (^3J = 4.9 Hz) for the β-hydroxyethoxycarbonyl unit protons. The resonance due to the −OH group was not observed. The IR spectrum in THF shows a ν(C═O) broad band at 1646 cm^{-1}.

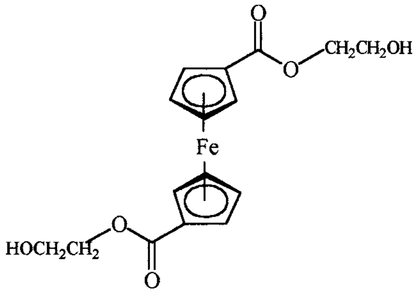
In the analogous reaction of NaCp with (±)-1,2-propylene carbonate (Scheme 1), the ring-opening reaction is not regiospecific and leads to the formation of the two regioisomers Na[$C_5H_4CO_2CH_2CH(Me)OH$] (**3a**) and Na[$C_5H_4CO_2CH(Me)CH_2OH$] (**3b**) in a 7:3 ratio, as estimated by ^{1}H NMR spectroscopy. Assignments for ^{1}H and ^{13}C chemical shifts for the 2-hydroxy-1-propyl moiety in **3a** and the 1-hydroxy-2-propyl in **3b** have unambiguously been confirmed by inverse gradient ^{1}H−^{13}C HSQC and HMBC NMR experiments.

The formation of **3a** as the main isomer may indicate that the secondary alcoholate anion $C_5H_5CO_2CH_2CH(Me)O^-$ rather than the primary one is the more favored intermediate; no significant change in the regioisomers ratio was observed by carrying out the reaction at −70 °C. The two regioisomers could not be separated, and their reactivity was not investigated. The above products **1**, **2**, and **3** are air- and moisture-sensitive and therefore can only be kept in air for short periods of time.

Synthesis and Characterization of Metal Complexes. The reactions of **1** and **2** with anhydrous $FeCl_2$ in THF at room temperature lead to [Fe{$C_5H_4CO_2CH_2CH{=}CH_2$}$_2$] (**4**) and [Fe{$C_5H_4CO_2(CH_2)_2OH$}$_2$] (**5**), isolated as air-stable red viscous oils.



4 (85%)



5 (38%)

The complexes **4** and **5** have previously been prepared via the usual route involving electrophilic aromatic-type substitution reactions. Compound **4**, prepared from 1,1′-bis(chloroformyl)ferrocene [Fe{C_5H_4COCl}$_2$] and allyl alcohol, has been employed as catalyst in polyesterification processes,[4] whereas the water-soluble [Fe{$C_5H_4CO_2(CH_2)_2OH$}$_2$] (**5**) had been previously synthesized by reacting [Fe{C_5H_4COCl}$_2$] with a refluxing solution of ethylene glycol in benzene for 48 h (this synthesis also led to substantial amounts of 2,5-dioxa[6](1,1′)ferrocenophane-1,6-dione).[5] Its use in solid composite propellants has recently been claimed in a German patent.[6] The present route, utilizing the reagents **1** and **2**, thus

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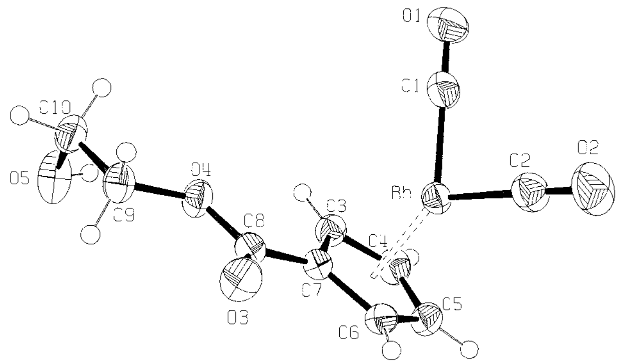


Figure 1. Molecular structure of $[Rh\{C_5H_4CO_2(CH_2)_2OH\}(CO)_2]$ (**7**) showing the atomic numbering (thermal ellipsoids at 50% probability level).

Table 1. Relevant Bond Distances (Å) and Angles (deg) for $[Rh\{C_5H_4CO_2(CH_2)_2OH\}(CO)_2]$ (7)

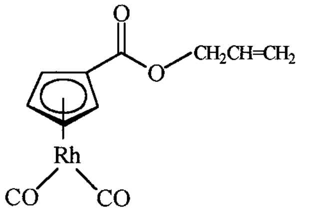
Rh−C(1)	1.857(2)	C(1)−O(1)	1.132(3)
Rh−C(2)	1.865(2)	C(2)−O(2)	1.135(3)
Rh−C(3)	2.245(2)	C(3)−C(4)	1.428(3)
Rh−C(4)	2.297(2)	C(3)−C(7)	1.429(3)
Rh−C(5)	2.283(2)	C(4)−C(5)	1.406(3)
Rh−C(6)	2.256(2)	C(5)−C(6)	1.433(3)
Rh−C(7)	2.292(2)	C(6)−C(7)	1.415(3)
C(7)−C(8)	1.462(3)	C(8)−O(3)	1.215(3)
C(8)−O(4)	1.337(2)	O(4)−C(9)	1.453(2)
C(10)−O(5)	1.408(3)	C(9)−C(10)	1.502(3)
C(1)−Rh−C(2)	88.8(1)	C(7)−C(8)−O(3)	124.7(2)
C(3)−C(7)−C(8)	127.9(2)	C(7)−C(8)−O(4)	111.6(2)
C(6)−C(7)−C(8)	125.0(2)	O(3)−C(8)−O(4)	123.7(2)
C(8)−O(4)−C(9)	116.8(2)	O(4)−C(9)−O(10)	106.5(2)
C(9)−C(10)−O(5)	112.4(2)		

represents a convenient alternative procedure recently disclosed by our group in a pending patent application.[7]

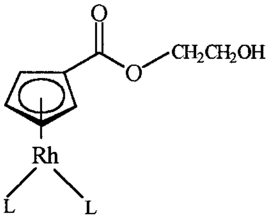
Because the previously reported characterization for **4** (elemental analysis, IR, color, and boiling point)[4] and **5** (color and physical state)[5] is limited, NMR, IR, and EI-MS mass spectra of these products are reported in detail in the Experimental Section. IR spectra in THF for **4** and **5** show a ν(C=O) band at 1720 cm^{-1}, a noticeable shift to higher wavenumbers upon metal coordination [cf. with the ν(C=O) of **1** and **2**]. NMR spectra of these complexes show similar resonances for the C_5H_4- moiety (^1H NMR δ = 4.8, 2H; 4.4, 2H; corresponding ^{13}C NMR Cp signals around 72 ppm) which are comparable with those of the previously reported $[Fe(C_5H_4CO_2Ph)_2]$.[1] In the case of **5** the triplet due to the OH proton is found at 3.49 ppm. The moderate yields obtained for **5** may be attributed to the formation of an insoluble organometallic polymeric material deriving from intermolecular transesterification reactions as found in the rhodium case (see next paragraph).

The reactions of **1** and **2** with $[Rh(L,L)Cl]_2$ [L,L = 2CO or L,L = 2,5-norbornadiene (NBD)] in THF at room temperature lead to the novel complexes $[Rh(C_5H_4CO_2CH_2CH{=}CH_2)(CO)_2]$ (**6**) and $[Rh\{C_5H_4CO_2(CH_2)_2OH\}(L,L)]$ [L,L = 2CO, (**7**); L,L = 2,5-norbornadiene, (**8**)] as the major products.

Complexes **6**, **7**, and **8** have been isolated after chromatography on silica gel. Derivative **6** is a yellow, air-stable oil, while **7** and **8** are air- and moisture-stable yellow crystalline compounds. The IR spectra in petroleum ether for **6** and **7** show a ν(C=O) at 1728 cm^{-1} and ν(C≡O) terminal carbonyl absorptions at 2058 and 1998 cm^{-1}, which are comparable to those of $[Rh(C_5H_4CO_2CH_3)(CO)_2]$ (2057 and 1997 cm^{-1} in hexane)[8] and, as expected, higher than those reported for the unsubstituted $[Rh(C_5H_5)(CO)_2]$ (2051, 1987 cm^{-1} in cyclohexane).[9] The ^1H NMR spectra for **6**, **7**, and **8** in $CDCl_3$ show the characteristic AA′BB′X pattern for the Cp ring protons analogous to related $[Rh(C_5H_4X)(L,L)]$ [X = CHO, CO_2R (R = Me, Et, Pr^i); L,L = ethylene or CO, L,L = 1,5-, 1,4-, 1,3-symmetrical dienes] complexes.[10]



6 (60%)



7 (41.5%), **8** (43%)

Complex **7** has been characterized by an X-ray diffraction study. An ORTEP drawing is shown in Figure 1, and relevant bond distances and angles are reported in Table 1. The molecule is asymmetric because the C_{2v} and C_s idealized symmetries of the fragments $Rh(CO)_2$ and $C_5H_4CO_2(CH_2)_2OH$ do not match. The actual molecular conformation seems dictated by the crystal packing. The cohesion energy is significantly influenced by an intermolecular hydrogen bond between the hydroxy group O(5)−H and the alkoxycarbonyl oxygen O(3) in the molecule related by translation along the *b* axis of the cell, so that an infinite chain is produced in that direction [O(5)···O(3) 2.93 Å, O(5)−H···O(3) 162.5°]. The geometry of the cyclopentadienyl ring is not affected by the $-C(O)O(CH_2)_2OH$ substituent with which conjugation of the π orbitals is expected and confirmed by the coplanarity of the C_5 and C(O)O groups [dihedral angle 5.7(3)°]. The C(Cp)−C(Cp) distances fall in a narrow range [1.408−1.433(3) Å], and the Rh−C(Cp) distances span a wider range [2.245−2.297(2) Å], as expected from their softer nature.

In the reactions of $Na[C_5H_4CO_2(CH_2)_2OH]$ (**2**) with $[Rh(L,L)Cl]_2$ the dinuclear side products **9** and **10** are also formed and subsequently isolated by chromatog-

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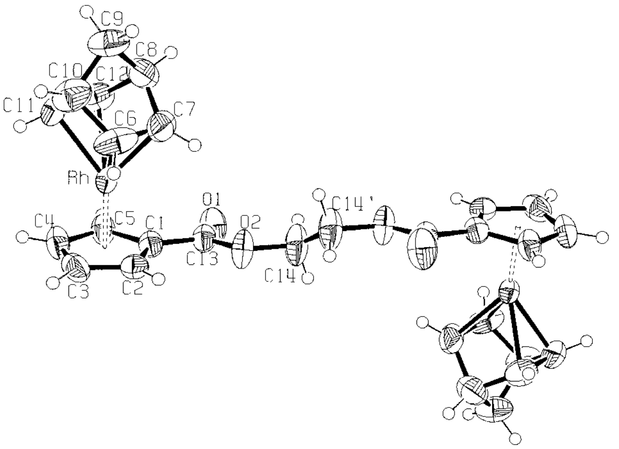
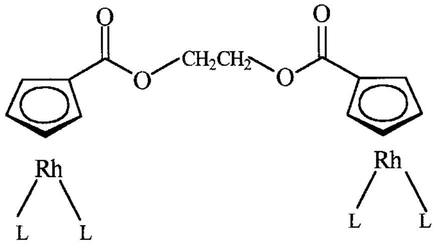


Figure 2. Molecular structure of $[Rh_2\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}(NBD)_2]$ (**10**) showing the atomic numbering of the crystallographically independent part of the molecule (thermal ellipsoids at 50% probability level).

raphy. These yellow diester-bridged dimers are derived



9 (L,L = CO, 11%) **10** (L,L = NBD, 14%)

from a transesterification type reaction between two molecules of the corresponding mononuclear complexes with elimination of a molecule of ethylene glycol. Accordingly, the reaction yields can be increased by raising the temperature and the ligand-to-metal ratio. The ^1H NMR spectra in $CDCl_3$ show only one single sharp resonance at δ 4.4 (corresponding ^{13}C signal at δ 62) for the diester bridge moiety. The EI-MS mass spectrum of **10** exhibits an intense molecular ion peak at m/z 634. The molecular structure of **10** has been confirmed by an X-ray diffraction study. An ORTEP drawing of the molecular geometry is shown in Figure 2, and bond distances and angles are listed in Table 2. The dinuclear compound lies on a crystallographic inversion center located at the midpoint of the C(14)−C(14′) bond. The constituent units of the dimeric C_p ligand are quite flat [dihedral angle between the Cp ring and C(O)O group 9.5(5)°], while the dihedral angle between O(1)−C(13)−O(2) and its symmetry equivalent is 62(1)°. The Rh−C(olefin) distances are in the range 2.125−2.147(5) Å. The Rh−C(Cp) distances are in the range 2.243−2.313(5) Å, and the C(Cp)−C(Cp) bonds are in the range 1.411−1.457(7) Å.

In addition when L,L = 2CO, small amounts of a red byproduct have been isolated by further eluting the chromatography column with Et_2O/acetonitrile (1:1). Although the spectroscopic data are not conclusive, an intense IR band at 1837 cm^{-1} may suggest the formation of a binuclear compound of the type $[Rh_2\{C_5H_4CO_2(CH_2)_2OH\}_2(CO)_2(\mu\text{-}CO)]$, in analogy to what is observed in the synthesis of $[Rh\{C_5H_4C(O)CH_3\}(CO)_2]$ and of $[Rh\{C_5H_4CO_2CH_2CH_3\}(CO)_2]$.[2d]

Table 2. Relevant Bond Distances (Å) and Angles (deg) for $[Rh_2\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}(NBD)_2]$ (10)

Rh−C(1)	2.300(4)	Rh−C(6)	2.131(5)
Rh−C(2)	2.244(5)	Rh−C(7)	2.125(5)
Rh−C(3)	2.289(5)	Rh−C(11)	2.140(5)
Rh−C(4)	2.277(5)	Rh−C(12)	2.147(5)
Rh−C(5)	2.312(5)	C(6)−C(7)	1.449(10)
C(1)−C(2)	1.457(7)	C(11)−C(12)	1.403(8)
C(2)−C(3)	1.429(7)	C(6)−C(10)	1.502(9)
C(3)−C(4)	1.410(8)	C(7)−C(8)	1.522(9)
C(4)−C(5)	1.432(7)	C(8)−C(9)	1.551(8)
C(5)−C(1)	1.438(7)	C(9)−C(10)	1.538(9)
C(1)−C(13)	1.477(7)	C(10)−C(11)	1.528(9)
C(13)−O(1)	1.197(6)	C(8)−C(12)	1.521(8)
C(13)−O(2)	1.346(6)		
O(2)−C(14)	1.453(6)		
C(14)−C(14′)	1.429(12)		
C(2)−C(1)−C(13)	128.3(4)	C(1)−C(13)−O(2)	111.1(4)
C(5)−C(1)−C(13)	124.7(5)	O(1)−C(13)−O(2)	123.5(5)
C(1)−C(13)−O(1)	125.4(5)	C(13)−O(2)−C(14)	116.7(4)

The reaction between $Na[C_5H_4CO_2(CH_2)_2OH]$ (**2**) and $MBr(CO)_5$ (M = Mn, Re) in THF rapidly occurs at room temperature. However we observe that an excess of ligand (ca. 5:1) is necessary for the complete conversion of the starting bromopentacarbonylmanganese and -rhenium and that the expected products $[M\{C_5H_4CO_2(CH_2)_2OH\}(CO)_3]$ (**11**, M = Mn; **12**, M = Re) are always obtained together with a complex mixture of metal carbonyl byproducts, whose real nature has not been established yet.

In the manganese case the infrared spectra in the carbonyl region of the crude material in THF presents, besides the bands assigned to **11** at 2028 (s), 1945 (vs) cm^{-1}, broad bands at 1975 (s), 1968 (s), 1896 (s), 1861 (s), and 1830 (m) cm^{-1}, while after chromatography a second yellow fraction eluted with acetonitrile shows completely different bands at 1993 (s), 1983 (s), 1963 (m), and 1936 (m). In the rhenium case instead, the byproducts observed in the IR of the crude material characterized by ν(CO) bands at 1998 (s) and 1878 (vs) cm^{-1} show the same spectra after chromatography. Complexes **11** and **12** have been isolated (although contaminated with organic material) by passing a THF solution of the crude product through a silica gel column using a THF/Etp mixture as eluent.

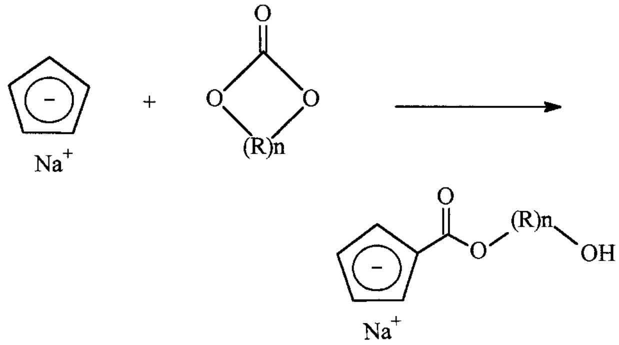
Conclusions

The described results indicate a general atom-economizing method for the synthesis of hydroxyalkoxycarbonylcyclopentadienide $Na[C_5H_4CO_2(CHR)_2OH]$ (R = H or Me). We expect that a wider variety of this type of multifunctionalized ligands can be prepared exploiting the reactivity of NaCp toward cyclic carbonates as shown in Scheme 2. In this direction cyclic chiral carbonates will be a future development of this work; moreover the easy availability of functionally substituted organo-iron and -rhodium derivatives provides valuable routes to organometallic derivatives, some of which are under investigation for testing their catalytic properties.

Experimental Section

Materials and Procedures. All reactions with organometallic reagents or substrates were carried out under argon

Scheme 2



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 Perkin-Elmer Spectrum 2000 FT-IR spectrometer. The routine NMR spectra (^{1}H, ^{13}C, DEPT) were always recorded using a Varian Gemini 300 instrument (^{1}H, 300.1; ^{13}C, 75.5 MHz), while the two-dimensional spectra (COSY, gHSQC, gHMBC experiments) were recorded using a Varian Mercury-VX 400 (^{1}H, 399.8; ^{13}C, 100.5 MHz) instrument. The spectra were referenced internally to residual solvent resonances and were recorded at 298 K for characterization purposes. Electron impact mass spectra were taken using a VG 7070E mass spectrometer. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. The reagents $MBr(CO)_5$ (M = Mn, Re) were prepared according to literature procedures;[11] ethylene carbonate (Aldrich) was crystallized from diethyl ether, and (±)-1,2-propylene carbonate and diallyl carbonate (Aldrich) were stored under argon on molecular sieves. $FeCl_2$, $[Rh(CO)_2Cl]_2$, and $[Rh(NBD)Cl]_2$ were used as purchased from Strem. Petroleum ether (Etp) 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.[12] Melting points were taken in sealed capillaries and were uncorrected.

$Na[C_5H_4CO_2CH_2CH{=}CH_2]$ (1). To a solution of NaCp (0.954 g, 10.8 mmol) in THF (20 mL) was dropwise added a solution of diallyl carbonate (2.4 mL, 16.7 mmol) in THF at room temperature. The mixture was stirred for 10 min at room temperature and then refluxed for 4 h. The reaction mixture 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 solid residue was washed with Et_2O to give 1.22 g (66%) of a light beige product. ^{1}H NMR (300.1 MHz, [D$_5$]Pyr): δ 7.41 (AA′BB′, ^3J(H,H) = 2.6 Hz, 2H; Cp), 6.62 (AA′BB′, ^3J(H,H) = 2.6 Hz, 2H; Cp), 6.05 (m, 1H; CH=), 5.30 (m, 1H; =CH$_{cis}$), 5.05 (m, 1H; =CH$_{trans}$), 4.80 (m, 2H; −OCH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_5$]Pyr): δ 168.0 (C=O), 135.9 (CH=), 115.6 (=CH$_2$), 112.8 (CH; Cp), 111.2 (CH; Cp), 109.4 (*ipso*-C; Cp), 62.9 (OCH$_2$). IR (THF): ν 1662 (m), 1644 (m), 1614 (s) cm^{-1} (C=O). Anal. Calcd for $C_9H_9NaO_2$: C, 62.80; H, 5.27. Found: C, 63.00; H, 5.56.

$Na[C_5H_4CO_2(CH_2)_2OH]$ (2). To a solution of NaCp (6.93 g, 78.8 mmol) in THF (50 mL) was added solid ethylene carbonate (6.93 g, 78.8 mmol) and the reaction mixture stirred at room temperature for 24 h. After filtering the slightly turbid solution with a cannula, 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 12.5 g (90%) of **2** as a beige solid. ^{1}H NMR (300.1 MHz, [D$_5$]Pyr): δ 7.42 (AA′BB′, ^3J(H,H) = 3.0 Hz, 2H; Cp), 6.63 (AA′BB′, ^3J(H,H) = 3.0 Hz, 2H; Cp), 4.55 (t, ^3J(H,H) = 4.9 Hz, 2H; CO$_2$CH$_2$), 4.1 (t, ^3J (H,H) = 4.9 Hz, 2H; CH$_2$OH). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_5$]Pyr): δ 169.8 (C=O), 112.5 (CH; Cp); 111.5 (CH; Cp), 109.1 (*ipso*-C; Cp), 67.1 (CO$_2$*C*H$_2$), 64.0 (CH$_2$OH). ^{1}H NMR (300.1 MHz, [D$_8$]THF): δ 6.44 (AA′BB′, ^3J(H,H) = 3.0 Hz, 2H; Cp), 5.83 (AA′BB′, ^3J(H,H) = 3.0 Hz, 2H; Cp), 4.11 (t, 2H, ^3J(H,H) = 4.9 Hz; CO$_2$CH$_2$), 3.7 (t, ^3J(H,H) = 4.9 Hz, 2H; CH$_2$OH). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF): δ 169.4 (C=O), 112.0 (CH; Cp); 110.4 (CH; Cp), 108.4 (*ipso*-C; Cp), 65.2 (CO$_2$*C*H$_2$), 62.8 (CH$_2$OH). IR (THF): ν 1646 (s) cm^{-1} (C=O). Anal. Calcd for $C_8H_9NaO_3$: C, 54.6; H, 5.15. Found: C, 54.9; H, 4.90.

$Na[C_5H_4CO_2(CHR)_2OH]$ (3). (±)-1,2-Propylene carbonate (2.15 mL, 25 mmol) was dropped with a syringe into a solution of NaCp (2.14 g, 24.3 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred for 24 h. The solvent was 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 4.48 g (97%) of **3** as a beige solid. The NMR analysis of the solid in [D$_5$]Pyr showed it was a mixture of the two regioisomers $Na[C_5H_4CO_2CH_2CH(CH_3)OH]$ (**3a**) and $Na[C_5H_4CO_2CH(CH_3)CH_2OH]$ (**3b**) in ca. 7:3 ratio. ^{1}H NMR (399.8 MHz, [D$_5$]Pyr): δ 7.42 (AA′BB′, ^3J(H,H) = 3.0 Hz, 4H; Cp), 6.64 (AA′BB′, ^3J(H,H) = 3.0 Hz, 4H; Cp), 5,55 [m, 1H; CH-(**3b**)], 4.54 [m, 1H; C*H*$_a$H$_b$(**3a**)], 4.30 [m, 2H; CH(**3a**) + CH$_a$*H*$_b$-(**3a**)], 3.98 [m, 1H; C*H*$_a$H$_b$(**3b**)], 3.87 [m, 1H; CH$_a$*H*$_b$(**3b**)], 1.30 (d, ^3J(H,H) = 6 Hz, 6H; CH$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, [D$_5$]-Pyr): δ 169.3 [CO(**3b**)], 168.9 [CO(**3a**)], 113.1 (CH; Cp); 111.4 [CH; Cp(**3a**)], 111.3 [CH; Cp(**3b**)], 109.7 [*ipso*-C; Cp(**3b**)], 109.4 [*ipso*-C; Cp(**3a**)], 69.7 [CH(**3b**)**]**, 68.1 [CH$_2$(**3a**)**]**, 67.6 [CH$_2$(**3b**)], 66.9 [CH(**3a**), 20.7 [CH$_3$(**3a**)], 17.7 [CH$_3$(**3b**)]. IR (THF): ν 1646 (s) cm^{-1} (C=O). Anal. Calcd for $C_9H_{11}NaO_3$: C, 56.8; H, 5.83. Found: C, 56.3; H, 5.45.

$[Fe(C_5H_4CO_2CH_2CH{=}CH_2)_2]$ (4). To a solution of **1** (1.07 g, 6.22 mmol) in THF (30 mL) was added solid $FeCl_2$ (0.28 g, 2.21 mmol). The solution was stirred for 24 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 chromatographed on silica gel eluting with Et_2O to give 0.66 g (85%) of an orange viscous oil. The product was partially soluble in Etp, and from this solvent at −20 °C orange crystals melting at room temperature could be obtained. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 6.01 (m, 2H; CH=), 5.39 (d, ^3J(H,H) = 16.8 Hz, 2H; =CH$_{cis}$), 5.27 (d, ^3J(H,H) = 9.9 Hz, 2H; =CH$_{trans}$), 4.82 (AA′BB′, ^3J(H,H) = 2.1 Hz, 4H; Cp), 4.71 (d, ^3J(H,H) = 5.1 Hz, 4H; OCH$_2$), 4.40 (AA′BB′, ^3J(H,H) = 2.1 Hz, 4H; Cp). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 169.9 (C=O), 132.5 (−CH=), 118.0 (=CH$_2$), 72.8 (CH; Cp), 72.1 (*ipso*-C; Cp), 71.5 (CH; Cp), 64.9 (OCH$_2$). MS (70 eV, EI): *m/z* (%) 354 (85) [M]$^+$, 121 (58) [Fe(C$_5$H$_5$)]$^+$, 56 (48) [C$_3$H$_5$O]$^+$, 41 (100) [C$_3$H$_5$]$^+$. IR (THF): ν 1720 (s) cm^{-1} (C=O). Anal. Calcd $C_{18}H_{18}FeO_4$: C, 61.0; H, 5.12. Found: C, 61.4; H, 5.01.

$[Fe\{C_5H_4CO_2(CH_2)_2OH\}_2]$ (5). To a solution of **2** (1.10 g, 6.24 mmol) in THF (20 mL) was added solid $FeCl_2$ (0.40 g, 3.16 mmol). After stirring the suspension at room temperature for 24 h the solvent was removed and CH_2Cl_2 added. The suspension was filtered on a Celite pad and the orange filtrate chromatographed on silica gel. The product was obtained eluting with a Et_2O/acetonitrile mixture (1:1) as an orange viscous oil (38%). ^{1}H NMR (300.1, CDCl$_3$): δ 4.80 (AA′BB′, ^3J(H,H) = 2 Hz, 4H; Cp), 4.45 (AA′BB′, ^3J(H,H) = 2 Hz, 4H; Cp), 4.36 (m, 4H; CO$_2$CH$_2$), 3.91 (m, 4H; CH$_2$OH), 3.49 (t, ^3J(H,H) = 6 Hz, 2H; OH). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 171.1 (C=O), 72.8 (*ipso*-C; Cp), 72.5 (CH; Cp), 72.1 (CH; Cp), 66.3 (CO$_2$*C*H$_2$), 61.0 (CH$_2$OH). IR (THF): ν 1719 (s) cm^{-1} (C=O). IR (neat, CsI): ν 3401 (br) (OH), 2956 (m) (CH), 1710 (vs) (C=O), 1467 (s) (C=C), 1284 (s) (C−O), 1151 (s) (O−CH$_2$) cm^{-1}. MS (70 eV, EI): *m/z* (%) 362 (42) [M]$^+$, 344 (8) [M − H$_2$O]$^+$, 136 (36) [C$_5$H$_5$CO$_2$CH$_2$CH$_2$]$^+$, 93 (94) [C$_5$H$_5$COH]$^+$, 65 (100) [C$_5$H$_5$]$^+$. Anal. Calcd for $C_{16}H_{18}FeO_6$: C, 53.1; H, 5.01. Found: C, 53.4; H, 5.00.

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[11] Herrmann W. A. In *Synthetic Methods of Organometallics and Inorganic Chemistry*; Herrmann, W. A., Ed.; Georg Thieme Verlag: Stuttgart, 1997; Vol. 7.

[12] Perrin, D. D.; Armarego, W. L. F.; Perrin D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

$\mathrm{[Rh(C_5H_4CO_2CH_2CH{=}CH_2)(CO)_2]}$ (6). To a solution of **1** (0.22 g, 1.28 mmol) in THF (50 mL) was added solid $\mathrm{[Rh(CO)_2Cl]_2}$ (0.18 g, 0.46 mmol). The solution was stirred for 24 h at room temperature. The solvent was removed under vacuum, and $\mathrm{CH_2Cl_2}$ was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Using $\mathrm{Et_2O}$ as eluent 0.086 g of **6** (60%) was obtained as a yellow oil. ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 5.96 (m, 1H; CH$=$), 5.95 (AA′BB′, ^3J(H,H) $=$ 2.1 Hz, 2H; Cp), 5.63 (AA′BB′X, ^3J(H,H) $=$ 2.1 Hz, J(H,Rh) $=$ 0.9 Hz, 2H; Cp), 5.36 (m, 1H; $=\mathrm{CH_{cis}}$), 5.26 (m, 1H; $=\mathrm{CH_{trans}}$), 4.70 (m, 2H; $\mathrm{OCH_2}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 188.8 (d, J(C,Rh) $=$ 83 Hz; $\mathrm{C{\equiv}O}$), 162.9 ($\mathrm{C{=}O}$), 132.0 (CH$=$), 118.0 ($=\mathrm{CH_2}$), 92.2 (*ipso*-C; Cp), 91.4 (d, J(C,Rh) $=$ 3.6 Hz, CH; Cp), 87.9 (d, J(C,Rh) $=$ 3.7 Hz, CH; Cp), 65.2 ($\mathrm{OCH_2}$). IR (Etp): ν 2058 (s) ($\mathrm{C{\equiv}O}$), 1998 (s) ($\mathrm{C{\equiv}O}$), 1728 (m) ($\mathrm{C{=}O}$) cm^{-1}. IR (THF): ν 2050 (s) ($\mathrm{C{\equiv}O}$), 1987 (s) ($\mathrm{C{\equiv}O}$), 1718 (m) ($\mathrm{C{=}O}$) cm^{-1}. MS (70 eV, EI): m/z (%) 308 (14) $\mathrm{[M]^+}$, 280 (23) $\mathrm{[M - CO]^+}$, 252 (41) $\mathrm{[M - 2CO]^+}$, 196 (52) $\mathrm{[Rh(C_5H_4COH)]^+}$, 168 (100) $\mathrm{[Rh(C_5H_5)]^+}$, 103 (35) $\mathrm{[Rh]^+}$, 41 (61) $\mathrm{[C_3H_5]^+}$. Anal. Calcd for $\mathrm{C_{11}H_9O_4Rh}$: C, 42.9; H, 2.94. Found: C, 42.6; H, 2.96.

$\mathrm{[Rh\{C_5H_4CO_2(CH_2)_2OH\}(CO)_2]}$ (7) and $\mathrm{[Rh_2\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}(CO)_2]}$ (9). To a solution of **2** (0.5 g, 2.84 mmol) in THF (50 mL) was added solid $\mathrm{[Rh(CO)_2Cl]_2}$ (0.390 g, 1.003 mmol). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, and $\mathrm{CH_2Cl_2}$ was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Eluting with $\mathrm{Et_2O}$ a first yellow fraction (0.062 g, 0.11 mmol, 11%) was collected and identified as $\mathrm{[Rh_2\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}(CO)_2]}$ (**9**). ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 5.94 (AA′BB′, ^3J(H,H) $=$ 2.2 Hz, 4H; Cp), 5.63 (AA′BB′X, ^3J(H,H) $=$ 2.2 Hz, J(H,Rh) $=$ 0.8 Hz, 4H; Cp), 4.45 (s, 4H; $\mathrm{CO_2CH_2}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 188.7 (d, J(C,Rh) $=$ 84 Hz; $\mathrm{C{\equiv}O}$), 163.0 ($\mathrm{C{=}O}$), 97.9 (*ipso*-C; Cp), 91.6 (d, J(C,Rh) $=$ 3.7 Hz, CH; Cp), 88.0 (d, J(C,Rh) $=$ 3.7 Hz; Cp), 62.2 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$). IR (THF): ν 2051 (s) ($\mathrm{C{\equiv}O}$), 1988 (vs) ($\mathrm{C{\equiv}O}$), 1719 (s) ($\mathrm{C{=}O}$) cm^{-1}. IR (Etp): ν 2058 (s) ($\mathrm{C{\equiv}O}$), 1998 (vs) ($\mathrm{C{\equiv}O}$), 1731 (s) ($\mathrm{C{=}O}$) cm^{-1}. MS (70 eV, EI): m/z (%) 534 (16) $\mathrm{[M - CO]^+}$, 347 (100) $\mathrm{[Rh(C_5H_4CO_2CH_2)_2]^+}$. Anal. Calcd for $\mathrm{C_{18}H_{12}O_8Rh_2}$: C, 38.5; H, 2.15. Found: C, 38.7; H, 2.17.

The major product **7** was obtained by further eluting with $\mathrm{Et_2O}$. Yellow crystals (0.260 g, 41.5%) were obtained overnight from a double layer of $\mathrm{Et_2O}$/Etp at -20 °C. ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 5.94 (AA′BB′, ^3J(H,H) $=$ 2.1 Hz, 2H; Cp), 5.64 (AA′BB′X, ^3J(H,H) $=$ 2.1 Hz, J(H,Rh) $=$ 0.9 Hz, 2H; Cp), 4.34 (m, 2H; $\mathrm{CO_2CH_2}$), 3.89 (m, 2H; $\mathrm{CH_2OH}$), 2.09 (t, ^3J(H,H) $=$ 6.3 Hz, 1H; OH). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 188.6 (d, J(C,Rh) $=$ 84 Hz; $\mathrm{C{\equiv}O}$), 163.7 ($\mathrm{C{=}O}$), 97.9 (d, J(C,Rh) $=$ 4.7 Hz, *ipso*-C; Cp), 91.7 (d, J(C,Rh) $=$ 2.4 Hz, CH; Cp), 88.0 (d, J(C,Rh) $=$ 2.4 Hz; Cp), 66.4 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$), 61.3 ($\mathrm{CH_2OH}$). IR (THF): ν 2050 (s) ($\mathrm{C{\equiv}O}$), 1987 (vs) ($\mathrm{C{\equiv}O}$), 1718 (s) ($\mathrm{C{=}O}$) cm^{-1}. IR (Etp): ν 2059 (s) ($\mathrm{C{\equiv}O}$), 1999 (vs) ($\mathrm{C{\equiv}O}$), 1729 (s) ($\mathrm{C{=}O}$) cm^{-1}. MS (70 eV, EI): m/z (%) 312 (15) $\mathrm{[M]^+}$, 284 (25) $\mathrm{[M - CO]^+}$, 256 (54) $\mathrm{[M - 2CO]^+}$, 196 (54) $\mathrm{[Rh(C_5H_4COH)]^+}$, 168 (100) $\mathrm{[Rh(C_5H_5)]^+}$, 103 (35) $\mathrm{[Rh]^+}$. Anal. Calcd for $\mathrm{C_{10}H_9O_5Rh}$: C, 38.5; H, 2.88. Found: C, 38.7; H, 2.90. Mp $=$ 70 °C. The complex was also characterized by an X-ray diffraction study.

Further elution with $\mathrm{Et_2O}$/acetonitrile (1:1) resulted in a red band, which produced a dark red oil upon removal of the solvent (0.04 g). ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 6.00 (AA′BB′, ^3J(H,H) $=$ 2.2 Hz, 2H; Cp), 5.66 (AA′BB′X, ^3J(H,H) $=$ 2.1 Hz, J(H,Rh) $=$ 0.8 Hz, 2H; Cp), 4.38 (m, 2H; $\mathrm{CO_2CH_2}$), 3.90 (m, 2H; $\mathrm{CH_2OH}$), 2.59 (t, ^3J(H,H) $=$ 6.2 Hz, 1H; OH). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$, major peaks): δ 189.1 (d, J(C,Rh) $=$ 84 Hz; $\mathrm{C{\equiv}O}$), 164.4 ($\mathrm{C{=}O}$), 97.1 (*ipso*-C; Cp), 93.3 (CH; Cp), 91.3 (CH; Cp), 66.5 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$), 61.1 ($\mathrm{CH_2OH}$). IR (THF): ν 2026 (s) ($\mathrm{C{\equiv}O}$), 1994 (vs) ($\mathrm{C{\equiv}O}$), 1837 (s) (μ-$\mathrm{C{\equiv}O}$), 1717 (s) ($\mathrm{C{=}O}$) cm^{-1}. In the EI-MS spectra the peak with highest m/z was found at 312, corresponding to the molecular fragment $\mathrm{[Rh\{C_5H_4CO_2(CH_2)_2OH\}(CO)_2]^+}$, and the fragmentation pattern is identical to that reported for the mononuclear compound.

$\mathrm{[Rh\{C_5H_4CO_2(CH_2)_2OH\}(NBD)]}$ (8) and $\mathrm{[Rh_2\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}(NBD)_2]}$ (10). To a solution of **2** (0.43 g, 2.44 mmol) in THF (50 mL) was added solid $\mathrm{[Rh(NBD)Cl]_2}$ (0.40 g, 0.868 mmol). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, and $\mathrm{CH_2Cl_2}$ was added. The suspension was first filtered on a Celite pad and then chromatographed on silica gel. Eluting with $\mathrm{Et_2O}$ a first yellow fraction was collected and identified as $\mathrm{[Rh_2\{\mu\text{-}(C_5H_4CO_2CH_2)_2\}(NBD)_2]}$ (**10**). Yellow crystals (0.080 g, 0.126 mmol, 14%) have been obtained from a double layer of $\mathrm{CH_2Cl_2}$/Etp at -20 °C. ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 5.54 (AA′BB′X, ^3J(H,H) $=$ 2.2 Hz, J(H,Rh) $=$ 0.5 Hz, 4H; Cp), 5.34 (AA′BB′X, ^3J(H,H) $=$ 2. Hz, J(H,Rh) $=$ 0.8 Hz, 4H; Cp), 4.48 (s, 4H; $\mathrm{CO_2CH_2}$), 3.33 (m, 12H; NBD), 0.97 (t, ^3J(H,H) $=$ 1.4 Hz, 4H, NBD). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 165.9 ($\mathrm{C{=}O}$), 91.5 (d, J(C,Rh) $=$ 4.9 Hz, *ipso*-C; Cp), 88.3 (d, J(C,Rh) $=$ 3.7 Hz, CH; Cp), 86.2 (d, J(C,Rh) $=$ 3.7 Hz; Cp), 62.0 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$), 57.4 (d, J(C,Rh) $=$ 7.3 Hz, $\mathrm{C_7}$, NBD), 46.7 (d, J(C,Rh) $=$ 2.5 Hz, $\mathrm{C_{1,4}}$; NBD), 32.5 (d, J(C,Rh) $=$ 9.8 Hz, $\mathrm{C_{2,3,5,6}}$; NBD). IR (THF): ν 1715 (s) ($\mathrm{C{=}O}$) cm^{-1}. MS (70 eV, EI) m/z (%): 634 (86) $\mathrm{[M]^+}$, 542 (33) $\mathrm{[M - NBD]^+}$, 347 (35) $\mathrm{[Rh\{C_5H_4CO_2(CH_2)_2O\}(NBD)]^+}$, 259 (40) $\mathrm{([Rh(C_5H_5)(C_7H_7)]^+}$, 194 (100) $\mathrm{[Rh(C_7H_7)]^+}$, 168 (71) $\mathrm{[Rh(C_5H_5)]^+}$. Anal. Calcd for $\mathrm{C_{28}H_{28}O_4Rh_2}$: C, 53.0; H, 4.42. Found: C, 53.1; H, 4.44. Mp $=$ 198 °C (dec). The complex was also characterized by an X-ray diffraction study.

The major product **8** was obtained by further eluting with $\mathrm{Et_2O}$. Yellow crystals (0.260 g, 43%) have been obtained overnight from a double layer of $\mathrm{Et_2O}$/Etp at -20 °C. ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 5.54 (AA′BB′X, ^3J(H,H) $=$ 2.2 Hz, J(H,Rh) $=$ 0.4 Hz, 2H; Cp), 5.36 (AA′BB′X, ^3J(H,H) $=$ 2. Hz, J(H,Rh) $=$ 0.9 Hz, 2H; Cp), 4.36 (m, 2H; $\mathrm{CO_2CH_2}$), 3.88 (m, 2H; $\mathrm{CH_2OH}$), 3.34 (m, 6H, CH; NBD), 2.30 (t, ^3J(H,H) $=$ 6.0 Hz, 1H; OH), 0.99 (t, ^3J(H,H) $=$ 1.4 Hz, 2H, $\mathrm{CH_2}$; NBD). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 166.7 ($\mathrm{C{=}O}$), 91.2 (d, J(C,Rh) $=$ 4.9 Hz, *ipso*-C; Cp), 88.5 (d, J(C,Rh) $=$ 3.7 Hz, CH; Cp), 86.1 (d, J(C,Rh) $=$ 4.9 Hz; Cp), 65.8 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$), 61.8 ($\mathrm{CH_2OH}$), 57.5 (d, J(C,Rh) $=$ 6.1 Hz, $\mathrm{C_7}$; NBD), 46.8 (d, J(C,Rh) $=$ 2.5 Hz, $\mathrm{C_{1,4}}$; NBD), 32.6 (d, J(C,Rh) $=$ 9.7 Hz, $\mathrm{C_{2,3,5,6}}$; NBD). IR (THF): ν 1711 (s) ($\mathrm{C{=}O}$) cm^{-1}. MS (70 eV, EI): m/z (%) 348 (98) $\mathrm{[M]^+}$, 303 (41) $\mathrm{[M - CH_2CH_2OH]^+}$, 259 (68) $\mathrm{[M - CO_2(CH_2)_2OH]^+}$, 194 (58) $\mathrm{[Rh(C_7H_7)]^+}$, 168 (88) $\mathrm{[Rh(C_5H_5)]^+}$, 142 (79) $\mathrm{[Rh(C_3H_3]^+}$, 103 (100) $\mathrm{[Rh]^+}$, 91 (70) $\mathrm{[(C_7H_7)]^+}$. Anal. Calcd for $\mathrm{C_{15}H_{17}O_3Rh}$: C, 51.7; H, 4.88. Found: C, 51.7; H, 4.89. Mp $=$ 85 °C.

$\mathrm{[Mn\{C_5H_4CO_2(CH_2)_2OH\}(CO)_3]}$ (11). To a solution of $\mathrm{MnBr(CO)_5}$ (0.52 g, 1.89 mmol) in THF (50 mL) was added solid $\mathrm{Na[C_5H_4CO_2CH_2CH_2OH]}$ (1.66 g, 9.45 mmol). After 1 h the IR spectra in THF of the reaction mixture showed the following bands: 2027 (s), 1975 (s), 1968 (s), 1944 (vs), 1896 (s), 1861 (s), 1830 (m) cm^{-1}. After filtration on a Celite pad the orange filtrate was reduced to a small volume under vacuum and chromatographed on a silica gel column. Eluting with 1:1 THF/Etp, the product **11** was obtained as a yellow oil (0.33 g). A yield was not calculated since, despite several attempts of purification, the product resulted always contamined with organic byproducts, presumably Cp-oligomers. ^{1}H NMR (300.1 MHz, $\mathrm{CDCl_3}$): δ 5.52 (br, 2H; Cp), 4.90 (br, 2H; Cp), 4.17 (br, 2H: $\mathrm{CO_2CH_2}$), 3.69 (br, 2H; $\mathrm{CH_2OH}$), 3.30 (br, 1H; OH). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 222.9 ($\mathrm{C{\equiv}O}$), 166.8 ($\mathrm{C{=}O}$), 88.9 (CH; Cp), 85.6 (*ipso*-C; Cp), 85.0 (CH; Cp), 67.4 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$), 60.9 ($\mathrm{CH_2OH}$). IR (THF): ν 2028 (s) ($\mathrm{C{\equiv}O}$), 1945 (vs) ($\mathrm{C{\equiv}O}$), 1728 (s) ($\mathrm{C{=}O}$) cm^{-1}. MS (70 eV, EI): m/z (%) 292 (14) $\mathrm{[M]^+}$, 208 (56) $\mathrm{[M - 3CO]^+}$, 164 (80) $\mathrm{[Mn\{C_5H_4(CH_2)_2\}OH)]^+}$, 55 (100) $\mathrm{[Mn]^+}$. A second yellow band was eluted with acetonitrile, and after evaporation of the solvent the resulting solid resulted to be sparingly soluble in THF and the IR (THF) showed main bands at 1993 (s), 1983 (s), 1963 (m), and 1936 (m) cm^{-1}; the NMR in $\mathrm{CD_3OD}$ did not reveal

Table 3. Crystal Data and Details of Structure Refinement for Complexes 7 and 10

	7	**10**
empirical formula	$C_{10}H_9O_5Rh$	$C_{28}H_{28}O_4Rh_2$
fw	312.08	634.32
temp (K)	293	293
wavelength (Å)	0.71069	0.71069
cryst syst	monoclinic	tetragonal
space group	$C2/c$, no. 15	$P4_2/n$, no. 86
unit cell dimens	$a = 19.091(1)$ Å $b = 5.7689(3)$ Å $c = 19.414(1)$ Å $\beta = 92.54(2)°$	$a = 20.135(3)$ Å $b = 20.135(3)$ Å $c = 6.002(1)$ Å
volume (Å^3)	2136.0(2)	2433.6(7)
Z	8	4
$F(000)$	1232	1272
cryst size (mm)	0.17 × 0.25 × 0.35	0.15 × 0.15 × 0.35
max θ for data collection	30°	25°
no. of reflns collected	26 862	20 634
no. of obsd ind reflns	3114	2111
no. of params	148	155
goodness-of-fit on F^2	1.07	1.07
final R indices $[I > 2\sigma(I)]$ (R_1 and wR_2)	0.029, 0.069	0.048, 0.122
R indices (all data) (R_1 and wR_2)	0.031, 0.070	0.054, 0.126
largest diff peak and hole/e Å^{-3}	0.64, −0.97	0.713, −1.09

the presence of cyclopentadienyl rings and the EI-MS spectra did not provide any useful information.

[Re{$C_5H_4CO_2(CH_2)_2OH$}(CO)$_3$] (12). To a solution of ReBr(CO)$_5$ (0.57, 1.40 mmol) in THF (50 mL) was added solid Na[$C_5H_4CO_2CH_2CH_2OH$] (1.24 g, 7.02 mmol). After 1 h the IR spectra in THF of the reaction mixture showed the following broad bands: 2029 (s), 1994 (vs), 1936 (s), 1879 (vs) cm^{-1}. The mixture was stirred for 3 h and then filtered on a Celite pad. The orange filtrate was reduced to a small volume and chromatographed on a silica gel column. Eluting with 2:1 THF/Etp, the product **12** was obtained as a yellow oil (0.18 g). Like in the manganese case, a yield was not calculated since we did not succeed in obtaining a pure compound. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 6.05 (AA′BB′, ^3J(H,H) = 2.4 Hz, 2H; Cp), 5.39 (AA′BB′, ^3J(H,H) = 2.4 Hz, 2H; Cp), 4.8−4.0 (m. 4H; $CO_2CH_2CH_2OH$); ^{13}C{^{1}H} (75.5 MHz, CDCl$_3$): δ 193.6 (C≡O), 166.5 (C=O), 90.5 (CH; Cp), 89.1 (*ipso*-C; Cp) 86.9 (CH; Cp), 66.8 (CO_2CH_2), 61.0 (CH_2OH). IR (THF): ν 2029 (s) (C≡O), 1936 (vs) (C≡O), 1726 (s) (C=O) cm^{-1}. MS (70 eV, EI): m/z (%) 424 (17) [M]$^+$, 406 (9) [M − OH]$^+$, 340 (6) [M − 3CO]$^+$, 294 (10) [Re($C_5H_4CO_2$)]$^+$, 154 (17) [$C_5H_5CO_2C_2H_4OH$)]$^+$, 93 (100) [C_5H_4COH]$^+$. A second yellow band was eluted with acetonitrile; after evaporation of the solvent the resulting solid resulted to be sparingly soluble in THF, and the IR(THF) showed main bands at ν = 1998 (s), 1878 (vs). The NMR in CD$_3$OD of the unknown product did not reveal the presence of cyclopentadienyl rings, and the EI-MS spectra did not provide any useful information.

X-ray Crystallography. Crystals of **7** and **10** suitable for X-ray diffraction studies were precipitated from petroleum ether. 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 using graphite-monochromated Mo Kα radiation. The data were collected using 0.3° wide ω scans, crystal-to-detector distance of 5.0 cm, and corrected for absorption empirically using the SADABS routine. Data collections nominally covered a full sphere of reciprocal space for both complexes with 10 and 30 s exposure time per frame for **7** and **10**, respectively. Despite repeated attempts the crystals of **10** were of low quality and did not diffract above $\theta = 25°$.

Both structures were solved by direct methods and refined on F^2 by full matrix least squares calculations using the SHELXTL/PC package.[13] 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 0.75 Å] and refined “riding” on their corresponding carbon atoms. Refinement converged at a final $R = 0.0289$, $wR_2 = 0.069$, $S = 1.07$ for **7**, $R = 0.048$, $wR_2 = 0.122$, $S = 1.07$ for **10**.

Molecular graphics were prepared using ORTEP3 for WindowsNT.[14]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC_167226 and CCDC_167227. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44)1223 336033; e-mail deopist@ccdc.cam.ac.uk).

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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 **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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