Coordination Chemistry of Cyclopentadienyl Ester-Disubstituted Ligands. Synthesis and Solid State Structures of [Na([18]-crown-6)][$C_5H_3(CO_2Et)_2$-1,2] and [Mn{$C_5H_3(CO_2Ph)_2$-1,2}$(CO)_3$]

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The disubstituted alkyl- and aryloxycarbonylcyclopentadienides of sodium Na[$C_5H_3(CO_2R)_2$-1,2] [R = Me (**3a**), Et (**3b**), Ph (**3c**)] are obtained in a two-step synthesis. The known Na[$C_5H_4(CO_2R)$] [R = Me (**1a**), Et (**2b**)] and the hitherto unknown Na[$C_5H_4(CO_2Ph)$] (**1c**), prepared from NaCp and dialkyl- or diphenyl carbonate, are subsequently reacted with the corresponding chloroformates ROCOCl to give **3** contamined with variable amounts of 1,3 isomers. Treatment of **3b** with [18]-crown-6 affords the buff-colored crystalline salt [Na([18]-crown-6)][$C_5H_3(CO_2Et)_2$-1,2] (**4b**). Reactions of **4b** and **3c** with $MBr(CO)_5$ [M = Mn, Re] or $[RuCl_2(CO)_3]_2$ lead to the respective metal complexes [M{η^5-$C_5H_3(CO_2R)_2$-1,2}$(CO)_3$] [R = Et and M = Mn (**5b**) or Re (**6b**), R = Ph and M = Mn (**5c**)] and [Ru{$C_5H_3(CO_2Et)_2$-1,2}(CO)]$_2$ **(7b)**. The solid state structure of **4b** reveals ion pairs in which the anion adopts an idealized C_{2v} conformation and chelates the sodium (κ^2O,O'-coordination). The structure of [Mn{$C_5H_3(CO_2Ph)_2$-1,2}$(CO)_3$] (**5c**) confirms the expected η^5-coordination of the Cp ring and exhibits significant torsion angles between the Cp ring and carboxylate groups.

Introduction

Cyclopentadienyl ligands (Cp) have a wide range of applications in organometallic chemistry and catalysis. Replacements of one or more of the cyclopentadienyl ring hydrogens with different functional groups can change both electronic properties and range of applications of the related metal complexes.[1] This is especially true for Cp with attached carbonyl COX (X = OR, NHR) functionalities because they may offer different coordination modes, i.e., κ^2O,O'-chelation of the carbonyl oxygen atoms or η^5-coordination of the ring carbons, depending on the nature of the metal center.[2]

The chemistry of mono- or pentasubstituted-Cp rings with alkoxycarbonyl groups CO_2R (R = Me, Et) has been thoroughly developed and studied by Rausch[1a,3] and Bruce, respectively.[2a,4] However bisalkoxycarbonylcyclopentadienyl ligands have been scarcely, if at all, investigated due to the lack of selective, good yield syntheses. In 1959 Peter described the low-yield synthesis of sodium 1,2-di(methoxycarbonyl)cyclopentadienide from reaction of methyl chloroformate and sodium cyclopentadienide.[5] The subsequent NMR analysis showed that the product contained 20% of 1,3 isomer.[6] By analogy Arthurs[7a] described in detail the reaction of KC_5H_5 with MeOCOCl that gave a complex, time-dependent, mixture of bi- and trisubstituted cyclopentadienide salts together with several organic byproducts; these results were confirmed in a very recent work.[7b]

With the aim of investigating the chemistry of bisalkoxy- or bisaryloxycarbonylcyclopentadienyl ligands here we report their synthesis, and spectroscopic and X-ray crystallographic characterization. The coordinating properties are also presented and discussed.

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Results and Discussion

Synthesis and Characterization of $[C_5H_3(CO_2R)_2]^-$. Following what was previously reported on the synthesis of the polysubstituted-Cp-containing ester functionalities, we have used, as starting material, the monosubstituted Cp $[C_5H_4CO_2R]^-$ [R = Me (**1a**), Et (**1b**)], prepared as described by Rausch[3a,b] from sodium cyclopentadenide and dimethyl or diethyl carbonate (eq 1).

$$\mathrm{NaCp} + (\mathrm{RO})_2\mathrm{CO} \rightarrow \mathrm{Na}[\mathrm{C}_5\mathrm{H}_4\mathrm{CO}_2\mathrm{R}] + \mathrm{ROH} \quad (1)$$
$$\mathrm{R} = \mathrm{Me, Et}$$

We have prepared the new $Na[C_5H_4CO_2Ph]$ (**1c**) in a similar manner by reacting NaCp with diphenyl carbonate $(PhO)_2CO$ in tetrahydrofuran at room temperature. The substantial difference observed in the formation of **1c** is that the likely neutral intermediate, 1-substituted cyclopentadiene $C_5H_5CO_2Ph$, is in this case rapidly deprotonated by a second molecule of Cp and not by the concurrently produced phenoxide NaOPh [cf. $pK_a(C_5H_6) = 15$[1a] with $pK_a(PhOH) = 10$]. The overall reaction stoichiometry is shown in eq 2.

$$2\mathrm{NaCp} + (\mathrm{PhO})_2\mathrm{CO} \rightarrow \mathrm{Na}[\mathrm{C}_5\mathrm{H}_4\mathrm{CO}_2\mathrm{Ph}] + \mathrm{C}_5\mathrm{H}_6 + \mathrm{NaOPh} \quad (2)$$

1c is a light brown solid, stable in air and water for short periods and sparingly soluble in THF; it was characterized by NMR (D_2O and pyr-d_5) and IR spectroscopy as well as by the reaction with $FeCl_2$ that gave the new ferrocene derivative $[Fe\{C_5H_4CO_2Ph\}_2]$ (**2**). Noteworthy, the yield of **1c** is strictly dependent on the reaction time: short reaction times favor higher yields (3 h, 89%). After 20 h **1c** is obtained in about 20% yield, and after 2 days of stirring the yield drops to zero. This behavior is due to the instability in solution of **1c**: the pure product totally decomposes after 48 h of stirring in THF.

The lower nucleophilic character of **1**, compared with the unsubstituted cyclopentadienide, did not allow further functionalization with dialkyl or diaryl carbonates; therefore the more reactive chloroformates had to be employed in order to obtain our target disubstituted molecules. Indeed, by treatment of **1** with the corresponding ROCOCl in a 2:1 molar ratio at room temperature in THF solvent, the disubstituted $[C_5H_3\{CO_2R\}_2]^-$ (**3**) was obtained in 80−90% yield together with dicyclopentadiene dicarboxylic ester $[C_5H_5CO_2R]_2$ (eq 3).

$$2\mathrm{Na}[\mathrm{C}_5\mathrm{H}_4\{\mathrm{CO}_2\mathrm{R}\}] + \mathrm{ROCOCl} \rightarrow$$
$$\mathrm{R} = \mathrm{Me, Et, Ph}$$
$$\mathrm{Na}[\mathrm{C}_5\mathrm{H}_3\{\mathrm{CO}_2\mathrm{R}\}_2] + 1/2[\mathrm{C}_5\mathrm{H}_5\mathrm{CO}_2\mathrm{R}]_2 + \mathrm{NaCl} \quad (3)$$

The ^1H NMR spectra in D_2O or pyridine-d_5 for **3** showed that the major, 1,2 isomers [R = Me (**3a**), Et (**3b**), Ph (**3c**)] were contaminated by the 1,3 form in amounts varying from ca. 5% (or less) when R = Ph, to 10% for R = Et, to a maximum of 20% for R = Me; no dependence was observed on reaction conditions, and the same ratios were observed carrying out the reaction at −78 °C. The $[C_5H_3(CO_2R)_2\text{-}1,2]^-$ anion can be regarded as a β-dicarbonyl system exhibiting further stabilization due to an additional fulvenoid mesomeric resonance form not present in the 1,3 isomers.[2b,c,4,8] While the separation of **3a**−**c** salts from the neutral byproduct $[C_5H_5CO_2R]_2$ was easily performed due to their different solubility in ether, the separation of the 1,2 from the 1,3 isomer was achieved exploiting the peculiar chelating properties of the *ortho* isomers. We discovered that, by adding an equimolar amount of [18]-crown-6 to **3b**, it was possible to precipitate the crown ether complex of the 1,2 isomer [Na([18]-crown-6)]-$[C_5H_3(CO_2Et)\text{-}1,2]$ (**4b**) as buff-colored, air-stable crystals soluble in chlorinated solvents. The NMR spectrum in $CDCl_3$ of **4b** (^1H NMR δ 6.92, d, 2H; 5.91, t, 1H; ^3J = 3.6 Hz; corresponding ^{13}C NMR Cp signals at δ 122.2, 111.5, and 109.8) is very similar to that of **3b** in D_2O. The IR absorptions in THF (range 2300−1500 cm^{-1}) of **3b** and **4b** are identical and show a strong broad band at 1680 cm^{-1} originating from the conjugated C═O and C═C system.[8d] In the solid state the ester carbonyl stretching frequency of **4b** occurs at 1695 cm^{-1}, a 32 cm^{-1} shift to higher frequency with respect to the uncoordinated **3b** (1663 cm^{-1}). This behavior, usually exhibited from enolate salts,[9] can be explained assuming that in solution **4b** does not retain the solid state structure due to the quite loose encapsulation of the sodium ion in the [18]-crown-6 (see further on). This method of separation allowed us to obtain a highly pure sample of **4b**, which in THF solution frees type **3** *ortho*-disubstituted Cp derivatives.

The nature of $[Na([18]\text{-crown-6})][C_5H_3(CO_2Et)_2\text{-}1,2]$ (**4b**) has been unambiguously ascertained by an X-ray diffraction study. The crystals contain ion pairs organized around the sodium cation that, although surrounded by the six oxygens of the crown ether, is exposed to the $\kappa^2 O,O'$-coordination of the more basic carbonyl oxygens of the anion (Figure 1). Relevant bond parameters concerning the anion are listed in Table 1. The anion adopts a conformation of C_{2v} idealized symmetry, if the ethyl appendages are ignored. The −C(O)O groups are almost coplanar with the Cp ring with dihedral angle for C(6)O(1)O(2) of 5.9(4)° and C(7)O(3)O(4) of 4.1(4)°. The C(ring)−C(carboxylate) distances are 1.430(4) and 1.421(4) Å for C(6) and C(7), respectively. These figures indicate significant double-bond character, comparable with that present in the Cp ring [C−C(ring) distances in the range 1.427−1.359(4) Å, average 1.39 Å]. The above distances can be compared with those found in $HC_5(CO_2Me)_5$,[8d] in which two adjacent $-CO_2Me$ groups "chelating" the proton are coplanar with the Cp ring and exhibit an average C(ring)−C(carboxylate) distance of 1.427 Å, while two such groups almost orthogonal to the Cp ring have an average C(ring)−C(carboxylate) distance of 1.493 Å.

The flat conformation of the anion allows efficient charge delocalization on the carbonylic oxygens and improves their basicity. In fact, these oxygens have a strong interaction with the sodium cation [average Na−

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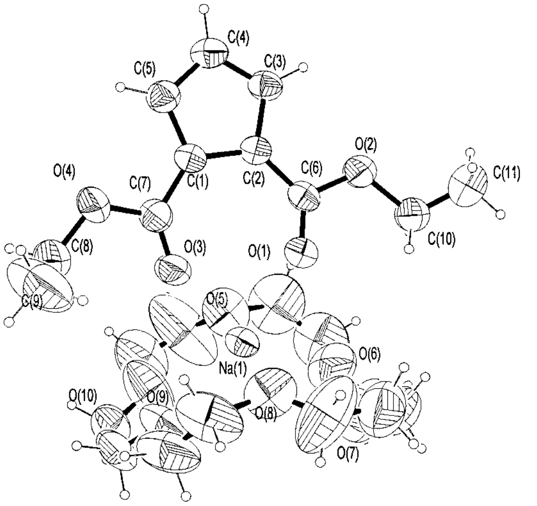


Figure 1. Molecular structure of [Na([18]-crown-6)][$C_5H_3(CO_2Et)$-1,2] (**4b**) showing the ionic pair and the atomic numbering (thermal ellipsoids at 20% probability level).

Table 1. Relevant Bond Lengths [Å] and Angles [deg] for 4b

Na(1)−O(3)	2.309(3)	C(2)−C(6)	1.430(4)
Na(1)−O(1)	2.322(3)	C(3)−C(4)	1.381(5)
Na(1)−O(5)	2.504(4)	C(4)−C(5)	1.359(5)
Na(1)−O(9)	2.582(4)	C(6)−O(1)	1.202(3)
Na(1)−O(8)	2.693(5)	C(6)−O(2)	1.340(4)
Na(1)−O(10)	2.719(6)	C(7)−O(3)	1.198(4)
Na(1)−O(6)	2.736(5)	C(7)−O(4)	1.346(4)
Na(1)−O(7)	2.915(8)	C(8)−C(91)	1.407(9)
C(1)−C(5)	1.408(4)	C(8)−O(4)	1.429(5)
C(1)−C(7)	1.421(4)	C(8)−C(92)	1.442(9)
C(1)−C(2)	1.427(4)	C(10)−C(11)	1.350(6)
C(2)−C(3)	1.387(4)	C(10)−O(2)	1.472(5)
C(5)−C(1)−C(7)	124.1(3)	O(1)−C(6)−C(2)	129.2(3)
C(5)−C(1)−C(2)	1106.6(3)	O(2)−C(6)−C(2)	113.3(3)
C(7)−C(1)−C(2)	129.3(3)	O(3)−C(7)−O(4)	117.9(3)
C(3)−C(2)−C(1)	106.4(3)	O(3)−C(7)−C(1)	129.7(3)
C(3)−C(2)−C(6)	124.2(3)	O(4)−C(7)−C(1)	112.4(3)
C(1)−C(2)−C(6)	129.3(3)	C(91)−C(8)−O(4)	119.1(9)
C(4)−C(3)−C(2)	109.6(3)	O(4)−C(8)−C(92)	121.0(10)
C(5)−C(4)−C(3)	108.3(3)	C(11)−C(10)−O(2)	111.3(5)
C(4)−C(5)−C(1)	109.1(3)	C(6)−O(2)−C(10)	117.2(3)
O(1)−C(6)−O(2)	117.4(3)	C(7)−O(4)−C(8)	118.0(4)

O(carbonyl) distance 2.32 Å], to be compared with the Na−O(crown ether) ones, found in the range 2.504−2.914(4) Å. The just described geometry of the anion surely optimizes the total energy but at the cost of some intraligand tension, as demonstrated by the short O⋯O(carbonyl) contact [2.774(3) Å] (van der Waals radius ca. 1.5 Å) and by the wider inner C(carbonyl)−C(ring)−C(ring) angles [average 129.30°] with respect to the outer ones [average 124.17°]. Also the displacement of the carbonyl oxygens out of the Cp ring plane are not concerted rotations around the C(ring)−C(carboxyl) axes, but actually consist in a rotation around the C(1)−C(7) axis [distances from the ring plane O(4) +0.093(6) and O(3) −0.063(6) Å] and an out-of-plane tilting of the whole C(6)O(1)O(2) group [distances from the Cp plane C(6) +0.061(4), O(1) +0.124(6), and O(2) +0.133(6) Å]. In light of these facts one can hypothesize that the stable anion conformation, in the absence of a $\kappa^2 O,O'$-chelation, should not be a flat one (see below).

Synthesis and Characterization of Metal Complexes. To asses the synthetic utiliy of the disubstituted cyclopentadienide in the formation of transition metal complexes, we examined the reactions of [Na([18]-crown-6)][$C_5H_3(CO_2Et)$-1,2] (**4b**) and Na[$C_5H_3(CO_2Ph)$-1,2] (**3c**) with $MBr(CO)_5$ [M = Mn, Re] and $[RuCl_2(CO)_3]_2$ (Scheme 1). Due to the small amount of 1,3 isomer present in **3c** (see above) and the ease of crystallization of the related manganese complex (see next paragraph), it was used without treating it with a crown ether.

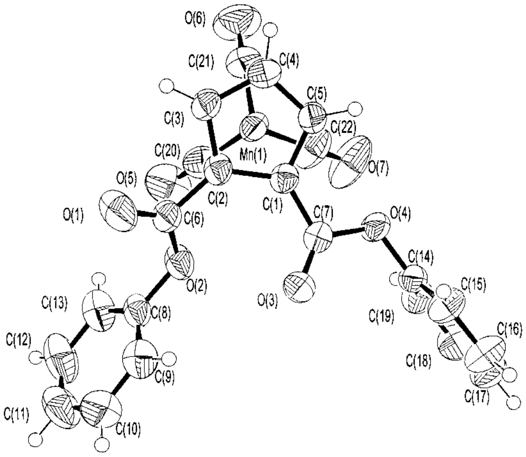
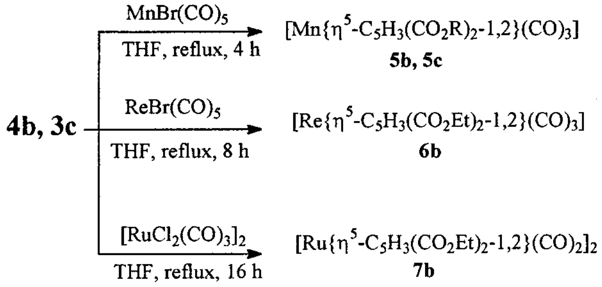


Figure 2. Molecular structure of [Mn{$C_5H_3(CO_2Ph)_2$-1,2}$(CO)_3$] (**5c**) showing the atomic numbering (thermal ellipsoids at 50% probability level).

Scheme 1



The reactions with $MnBr(CO)_5$ produced [Mn{η^5-$C_5H_3(CO_2R)_2$-1,2}$(CO)_3$] [R = Et (**5b**); R = Ph (**5c**)] in ca. 80% yields as a yellow oil (R = Et) and yellow crystals (R = Ph). The infrared spectra of **5b** [**5c**] in CH_2Cl_2 show ν(CO) terminal absorptions at 2037 [2040] and 1959 [1963] cm^{-1}. These values are, as expected, higher than those reported for [Mn{η^5-$C_5H_4(CO_2Et)$}$(CO)_3$] [IR(CH_2Cl_2) 2031, 1948][3d] but unexpectedly significantly higher than those in [Mn{$C_5(CO_2Me)_5$}$(CO)_3$] [IR (CH_2Cl_2) 2020, 1940], which are identical to those found for the unsubstituted complex [$Mn(C_5H_5)(CO)_3$].[10] This fact can be related to a significant charge delocalization on the two vicinal $-CO_2R$ groups in **5**.

The solid state structure of the neutral molecule [Mn{$C_5H_3(CO_2Ph)_2$-1,2}$(CO)_3$] (**5c**) is shown in Figure 2, and its bond parameters are listed in Table 2. Its main stereochemical feature is the regular η^5-coordination of the anion to the $Mn(CO)_3$ fragment. It is to be noted that, although a mirror plane of the C_{3v} $Mn(CO)_3$ fragment approximately matches a vertical plane of the Cp ring, the $-CO_2Ph$ substituents do not conform to this potential symmetry and the molecule is asymmetric in

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Table 2. Relevant Bond Lengths [Å] and Angles [deg] for 5c

Mn(1)−C(20)	1.777(3)	O(2)−C(6)	1.330(2)
Mn(1)−C(21)	1.789(3)	O(2)−C(8)	1.417(3)
Mn(1)−C(22)	1.794(3)	O(3)−C(7)	1.191(2)
Mn(1)−C(1)	2.133(2)	O(4)−C(7)	1.358(2)
Mn(1)−C(5)	2.137(2)	O(4)−C(14)	1.417(2)
Mn(1)−C(2)	2.141(2)	C(1)−C(5)	1.434(3)
Mn(1)−C(4)	2.158(2)	C(1)−C(2)	1.436(3)
Mn(1)−C(3)	2.162(2)	C(1)−C(7)	1.472(3)
O(5)−C(20)	1.160(3)	C(2)−C(3)	1.413(3)
O(6)−C(21)	1.150(3)	C(2)−C(6)	1.489(3)
O(7)−C(22)	1.141(3)	C(3)−C(4)	1.410(3)
O(1)−C(6)	1.179(3)	C(4)−C(5)	1.410(3)
C(5)−C(1)−C(2)	106.5(2)	O(3)−C(7)−O(4)	123.8(2)
C(5)−C(1)−C(7)	125.5(2)	O(3)−C(7)−C(1)	126.2(2)
C(2)−C(1)−C(7)	127.7(2)	O(4)−C(7)−C(1)	109.9(2)
C(3)−C(2)−C(1)	108.4(2)	C(6)−O(2)−C(8)	118.0(2)
C(3)−C(2)−C(6)	122.3(2)	C(7)−O(4)−C(14)	117.2(1)
C(1)−C(2)−C(6)	129.2(2)	O(5)−C(20)−Mn(1)	179.6(3)
O(1)−C(6)−O(2)	123.8(2)	O(6)−C(21)−Mn(1)	178.9(3)
O(1)−C(6)−C(2)	122.8(2)	O(7)−C(22)−Mn(1)	177.5(2)
O(2)−C(6)−C(2)	113.3(2)		

the crystal. The Mn−C(ring) distances are in the range 2.133−2.162(2) Å, average 2.15 Å. The small but significant differences in bond distances do not show any relation to the chemical nonequivalence of the carbon atoms and should be considered packing effects. Also the ring is quite regular [C−C distances in the range 1.410−1.436(3) Å, average 1.42 Å]. The average C−C(ring) bond length can be compared with that reported above in **4b** [average 1.39 Å]: a 0.03 Å elongation is a small but measurable effect of the ring−metal interaction.

A major structural difference between the present η^5-coordinated and the κ^2*O,O′*-chelated anion is found for the $-CO_2R$ substituents that are equivalent under C_{2v} idealized symmetry in **4b** and related by a quasi 5-fold rotation in **5c** (the C_5 ring axis). The conformation of $[C_5H_3(CO_2Ph)_2\text{-}1,2]^-$ is deprived of symmetry, and the intramolecular tension found in **4b** is partially alleviated [O(2)⋯O(3) contact 2.841(2) Å, inner and outer C(carboxyl)−C(ring)−C(ring) average angles 128.4° and 123.9°, respectively]. The −C(O)O groups are significantly rotated around their C(ring)−C(carboxylate) bond [21.5° around C(1)−C(7) and 35.6° around C(2)−C(6)], and some ring-carboxylate conjugation has been lost. Consistently, the C(ring)−C(carboxylate) distances [C(1)−C(7) 1.472 and C(2)−C(6) 1.489(3) Å, average 1.48 Å] are 0.06 Å longer than in **4b**, and the longer C(2)−C(6) distance corresponds to the higher torsion angle. The observed correlation between ring-carboxylate dihedral angles and C(ring)−C(carboxylate) bond distances shows that the π electron delocalization in the anion is reduced but not extinguished, in accord with the spectroscopic evidence.

Concerning the $Mn(CO)_3$ moiety, the average Mn−C and C−O distances are 1.79 and 1.15 Å, respectively. The structural parameters of **5c** should be compared with those in the unsubstituted $Mn(C_5H_5)(CO)_3$, the structure of which has been repeatedly reported with an increasing level of accuracy.[11a−c] The most recent low-temperature results[11c] are as follows: Mn−C(ring) 2.138, C−C(ring) 1.407, Mn−C(carbonyl) 1.793, C−O(carbonyl) 1.144 Å. They are in good agreement with the corresponding values in **5c**.

The ester carbonyl stretching frequency (THF), which occurs at 1680 cm^{-1} (**4b**) and 1706 cm^{-1} (**3c**) in the starting ligands, exhibits a ca. 40 cm^{-1} shift to higher frequency on complex formation 1722 [1742] cm^{-1} for the corresponding manganese derivatives **5b** [and **5c**] in agreement with the η^5 coordination of the ligand.[12] The ^1H NMR in $CDCl_3$ of **5b** shows for the C_5H_3 unit resonances at δ 5.60 (2H), 4.87 (1 H), at significantly higher field compared with the sodium salt **4b**. All the peaks are broad due to the presence of the quadrupolar ^{55}Mn, and lowering the temperature results only in further broadening. The same trend is observed in the ^{13}C spectra, where the corresponding resonances for the C_5H_3 unit are at δ 91.2 (*ipso*-C), 87.7(CH), 80.0 (CH).

The reaction of **4b** with $ReBr(CO)_5$ afforded the complex **6b**, which exhibits the same spectroscopic features as the manganese analogue. However, no comparison could be done with the pentasubstituted complex, as the reaction of $Tl[C_5(CO_2Me)_5]$ with $[ReCl(CO)_4]_2$ in acetonitrile was reported to give the $[C_5(CO_2Me)_5]^-$ salt of the cation $[Re(CO)_3(NCMe)_3]^+$ as the only product.[4]

The η^5 coordination ability of the disubstituted ligand has been confirmed by the formation of the diruthenium complex $[Ru\{\eta^5\text{-}C_5H_3(CO_2Et)_2\text{-}1,2\}(CO)_2]_2$ (**7b**) obtained by reaction of **4b** with $[RuCl_2(CO)_3]_2$. The reaction occurs with an excess of **4b** in refluxing THF for about 16 h, and **7b** has been isolated as a dark yellow oil in >70% yield. The IR spectrum (Etp) of **7b** features the expected $\nu(C{\equiv}O)$ bands at 2032, 2024, 1992, 1964, 1812 cm^{-1} (cf. with IR (heptane) of $[Ru(C_5H_5)(CO)_2]_2$: 2020, 2010, 1973, 1944, 1794),[13] while the $\nu(C{=}O)$ for the ester carbonyl is at 1726 cm^{-1}. The ^1H NMR in $CDCl_3$ at room temperature shows for the C_5H_3 unit one set of signals at δ 5.82 (2H) and 5.35 (1H), while the ^{13}C NMR shows only one peak at δ 210.2 for the M-CO and peaks at δ 96.9 (*ipso*-C), 92.1 (CH), 89.8 (CH) for the cyclopentadienyl ring. A more detailed ^1H NMR study of complex **7b** in CD_2Cl_2 has shown a temperature dependence (−90 °C, +20 °C) of the chemical shift of the ring protons, without line broadening [H(2), H(4) δ 5.76 (+20 °C), 5.69 (−90 °C), $\Delta\delta = -0.07$ ppm; H(3) δ 5.24 (+20 °C), 5.36 (−90 °C), $\Delta\delta = +0.12$ ppm]. A similar behavior, involving the signals of the protons of complexes containing a cyclopentadienyl ring substituted with electron-withdrawing groups, has already been reported and was attributed to the loss of the symmetric η^5-delocalized bonding and adoption of a $(\eta^3 + \eta^2)$ localized structure.[14]

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Complexes **5b**,**c**, **6b**, and **7b** are stable to air and heat; for example the oils **5b** and **6b** can be distilled under vacuum ($p = 0.1$ mmHg) at 100 °C without decomposition.

Conclusions

The cyclopentadienyl ester-disubstituted ligands $[C_5H_3(CO_2R)_2\text{-}1,2]^-$ **3a**−**c** have been obtained from NaCp in a two-step sequence together with variable amounts of the 1,3 form. The **3b** derivative has been prepared free from the contaminating 1,3 isomer by addition of an equimolar amount of [18]-crown-6. The resulting crystalline salt, $[Na([18]\text{-crown-6})][C_5H_3(CO_2Et)_2\text{-}1,2]$ (**4b**), was structurally characterized by X-ray diffraction. The new $Na[C_5H_3(CO_2Ph)_2\text{-}1,2]$ (**3c**) was less contamined by the 1,3 isomer, and therefore no treatment with the crown ether was necessary. Unlike the direct reaction between NaCp and ROCOCl,[7] our method was more reproducibile and not dependent on reaction conditions such as temperature and reaction time.

4b and **3c** have been reacted with Mn, Re, and Ru carbonyl complexes. The η^5 derivatives $[M\{C_5H_3(CO_2R)_2\text{-}1,2\}(CO)_3]$ [R = Et, M = Mn (**5b)** or Re (**6b**); R = Ph, M = Mn (**5c**)] and $[Ru\{C_5H_3(CO_2Et)_2\text{-}1,2\}(CO)]_2$ **(7b**) have been prepared and the complex **5c** has been structurally characterized by X-ray diffraction. The IR comparison between the manganese adducts **5b**, **5c**, and $[Mn\{C_5(CO_2Me)_5\}(CO)_3]$ revealed that the disubstituted-ester ligands are more effective than the pentasubstituted ones in delocalizing the Cp ring charge.

Studies on the reactivity of **3** toward the more oxophilic lanthanide triflates $Ln(OTf)_3$ or group 4 metal halides MX_4 are in progress, and preliminary results indicate that a κ^2O,O'-chelation with the carbonyl oxygen atoms is favored, as found in the structurally characterized sodium salt **4b**.[15] Moreover the reported metal **5**, **6**, and **7** derivatives could be used as metalloligands in which the *ortho* ester act as (*O*,*O*′) coordinating groups toward oxophilic transition metals.

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 (^{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 and gHSQC 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; GC−MS analyses were performed using a Hewlett-Packard Model HP 5890B GC interfaced to a HP 5970 MSD.

The reagents $Na[C_5H_4CO_2R]$ (R = Me, Et)[3a,b] and $MBr(CO)_5$ (M = Mn, Re)[16] were prepared according to literature procedures; [18]-crown-6 (Aldrich) was crystallized from acetonitrile, and the adduct was kept under vacuum at 40 °C for 4 h and recrystallized from hexane; diphenyl carbonate (Aldrich) was crystallized from petrolum ether; $[Ru(CO)_3Cl_2]_2$ (Strem) and $FeCl_2$ (Aldrich) were used as purchased; and the chloroformates ROCOCl (Aldrich) were kept under argon on molecular sieves. 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.[17] Melting points were taken in sealed capillaries and were uncorrected.

$Na[C_5H_4CO_2Ph]$ (1c). To a solution of NaCp (7.2 g, 81.7 mmol) in THF (150 mL) was added solid $(PhO)_2CO$ (8.7 g, 40.9 mmol). After a few minutes the formation of a light brown precipitate was observed, the mixture was stirred at room temperature for 3 h, and then a large amount of Et_2O (200 mL) was added. The solid was filtered and further washed with diethyl ether to give 7.6 g (89%) of **1c** as a light brown solid. ^{1}H NMR (D_2O): δ 7.53−7.15 (m, 5H, Ph), 6.68 (m, 2H), 6.17 (m, 2H). ^{1}H NMR (Pyr-d_5): δ 7.51 (m, 2H, Cp), 7.28−7.07 (m, 5H, Ph), 6.72 (m, 2H). $^{13}C\{^1H\}$ NMR (pyr): δ 166.5 (C=O), 154.4 (*ipso*-C, Ph), 129.3 (*o*-Ph), 123.8 (*p*-Ph) 123.2 (*m*-Ph), 114.3 (CH, Cp), 112.8 (CH, Cp), 108.4 (*ipso*-C, Cp). IR (THF, cm^{-1}): ν(C=O) 1691 s, 1665 s, 1635 s. Anal. Calcd for $C_{12}H_9NaO_2$: C, 69.2; H, 4.33. Found: C, 69.6; H, 4.60. The filtrate was dried in vacuo: GC−MS analysis of the volatiles showed the presence of cyclopentadiene, while the IR and ^{1}H and ^{13}C NMR spectra of the solid residue showed the presence of NaOPh.[18]

$[Fe(C_5H_4CO_2Ph)_2]$ (2). To a suspension of **1c** (0.59 g, 2.84 mmol) in THF (20 mL) was added solid $FeCl_2$ (0.180 g, 1.42 mmol). The suspension was stirred at room temperature for 4 h. After concentration to a small volume the crude material was chromatographed on silica gel and eluted with a mixture of THF/CH_3CN in a 4:6 ratio to give 0.45 g (87%) of a dark orange product that can be crystallized from a double layer of CH_2Cl_2/Etp at −20 °C. ^{1}H NMR ($CDCl_3$): δ 7.28−7.14 (m, 10H, Ph), 5.05 (m, 2H), 4.60 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.1 (C=O), 150.6 (*ipso*-C), 129.4 (*o*-Ph), 125.7 (*p*-Ph) 121.7 (*m*-Ph), 73.3 (CH, Cp), 72.3 (CH, Cp), the *ipso*-C Cp carbon is hidden under the signals of the deuterated chloroform. IR (THF, cm^{-1}): ν(C=O) 1738 s. EIMS for $^{12}C_{24}1H_{18}56Fe^{16}O_4$ (*m*/*z*, %): 426 ($[M]^+$, 100), 333 ($[M]^+$ − OPh, 87). Mp: 143 °C. Anal. Calcd for $C_{24}H_{18}O_4Fe$: C, 67.6; H, 4.22. Found: C, 67.6; H, 4.23.

$Na[C_5H_3(CO_2Me)_2]$ (3a). To a solution of $Na[C_5H_4(CO_2Me)]$ (20.3 g, 139 mmol) in THF was added dropwise MeOCOCl (37 mL, 69.5 mmol) in 10 mL of THF at room temperature. After stirring for 2 h the dark red suspension was filtered on a Celite pad and the solvent was removed in vacuo, and after keeping the solid under vacuum at ca. 80 °C for 4 h, the residue was thoroughly washed with diethyl ether to give 11.8 g (83%) of a light brown solid. ^{1}H NMR (D_2O): δ 6.75 (d, $^3J = 3.6$, 2H), 5.95 (t, $^3J = 3.6$, 1H), 3.75 (s, 6H). ^{1}H NMR (Pyr-d_5): δ 7.66 (d, $^3J = 3.6$, 2H), 6.49 (t, $^3J = 3.6$, 1H), 3.56 (s, 6H). $^{13}C\{^1H\}$ NMR (Pyr-d_5): δ 168.2 (C=O), 124.3 (CH), 112.2 (*ipso*-C, Cp), 111.1 (CH), 50.1 (OCH_3). The ^{1}H NMR (Pyr) spectrum showed the presence of the 1,3 isomer (up to a maximum of 20% observed): δ 8.26 (t, $^4J = 2.1$, 1H), 7.33 (d, $^4J = 2.1$, 1H), 3.56 (s, 6H). IR (THF): ν(C=O) 1687 s. IR (KBr, cm^{-1}): ν(C=O) 1663 vs, ν(C−O) 1284 s, $\nu(C{-}OCH_2)$ 1082 s. Anal. Calcd. for $C_9H_9NaO_4$: C, 52.9; H, 4.41. Found: C, 52.6; H, 4.80. The NMR, GC−MS, and EIMS analysis (*m*/*z*, %): 124 ($^1/_2[M]^+$), of the

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ether washings showed the presence of dicyclopentadiene dicarboxylic ester $(C_5H_5CO_2Me)_2$.[5,19]

$Na[C_5H_3(CO_2Et)_2]$ (3b). To a solution of $Na[C_5H_4(CO_2Et)]$ (11.6 g, 72 mmol) in THF was added dropwise EtOCOCl (3.5 mL, 3.76 mmol) in 10 mL of THF at room temperature. After stirring for 2 h the dark red suspension was filtered on a Celite pad and the solvent was removed in vacuo, and after keeping the solid under vacuum at ca. 80 °C for 4 h the residue was thoroughly washed with diethyl ether to give 7.15 g (85%) of a light brown solid. ^1H NMR (D_2O): δ 6.78 (d, $^3J = 3.6$, 2H), 5.97 (t, $^3J = 3.6$, 1H), 4.25 (q, $^3J = 7.2$, 4H), 1.32 (t, $^3J = 7.2$, 6H). ^1H NMR (Pyr-d_5): δ 7.69 (d, $^3J = 3.6$, 2H), 6.50 (t, $^3J = 3.6$, 1H), 4.11 (q, $^3J = 7.2$, 4H), 1.11 (t, $^3J = 7.2$, 6H). $^{13}C\{^1H\}$ NMR (Pyr): δ 167.8 (C═O), 124.3 (CH), 112.5 (*ipso*-C, Cp), 110.8 (CH), 58.2 (OCH_2CH_3), 15.0 (OCH_2CH_3). The ^1H NMR (Pyr-d_5) spectrum showed the presence of the 1,3 isomer (up to a maximum of 10% observed): δ 8.21 (t, $^4J = 2.1$, 1H), 7.33 (d, $^4J = 2.1$, 1H), 4.31 (q, $^3J = 7.2$, 4H), 1.19 (t, $^3J = 7.2$, 6H). IR (THF, cm^{-1}): ν(C═O) 1680 s. IR (KBr, cm^{-1}): ν(C═O) 1663 vs, ν(C−O) 1284 s, $\nu(C-OCH_2)$ 1082 s. Anal. Calcd. for $C_{11}H_{13}NaO_4$: C, 56.9; H, 5.60. Found: C, 57.3; H, 4.57. The NMR, GC−MS, and EIMS analysis (*m*/*z*, %): 138 ($^1/_2[M]^+$), of the ether washings showed the presence of dicyclopentadiene dicarboxylic ester $(C_5H_5CO_2Et)_2$.

$Na[C_5H_3(CO_2Ph)_2$-1,2] (3c). To a suspension of $Na[C_5H_4(CO_2Ph)]$ (7.0 g, 33.6 mmol) in THF was added dropwise PhOCOCl (2.1 mL, 16.8 mmol) in 10 mL of THF at room temperature. After stirring for 2 h the volatiles were removed under reduced pressure; the dark red solid was kept under vacuum at 80 °C for 4 h and then thoroughly washed with diethyl ether (3 × 50 mL). The ether of the combined washings was removed in vacuo: the resulting sticky crude material was found to contain the desired product **3c** contamined with the dimer $(C_5H_5CO_2Ph)_2$. The final purification was accomplished by redissolving the oily mixture in a small volume of ether and adding Etp: the resulting precipitate was triturated for one night to give 4.45 g (81%) of a light brown solid. ^1H NMR of **3c** (pyr): δ 7.95 (d, $^3J = 3.6$, 2H), 7.32−7.14 (m, 10 H), 6.59 (t, $^3J = 3.6$, 1H). $^{13}C\{^1H\}$ NMR (pyr): δ 165.7 (C═O), 153.6 (*ipso*-Ph), 129.4 (*o*-Ph), 127.3 (CH, Cp) 124.6 (*p*-Ph), 123.5 (*m*-Ph), 112.7 (CH, Cp), 111.5 (*ipso*-C, Cp); a poorly resolved triplet at δ 8.55 was assigned to the 1,3 isomer (5% or less of the total product). IR (THF, cm^{-1}): ν(CO) 1706 s. Anal. Calcd. for $C_{19}H_{13}NaO_4$: C, 69.5; H, 3.96. Found: C, 69.8; H, 4.00. The dimer $(C_5H_5CO_2Ph)_2$ was characterized by NMR, GC−MS, and EIMS analysis (*m*/*z*, %): 186 ($^1/_2[M]^+$).

[Na([18]-crown-6)][$C_5H_3(CO_2Et)_2$-1,2] (4b). To a solution of **3b** (3.7 g, 16 mmol) in THF (20 mL) was added [18]-crown-6 (4.1 g, 15.5 mmol). After 30 min the slightly turbid suspension was filtered and the solution concentrated to a small volume in vacuo. A large quantity of Et_2O was added, and the solution was cooled at −20 °C, yielding buff-colored crystals of **4b** (three crops, 5.6 g, 70%). ^1H NMR ($CDCl_3$): δ 6.92 (d, $^3J = 3.6$, 2H), 5.91 (t, $^3J = 3.6$, 1H), 4.16 (q, $^3J = 7.2$, 4H), 3.64 (s, 24H), 1.28 (t, $^3J = 7.2$, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.2 (C═O), 122.2 (CH, Cp), 111.5 (*ipso*-C, Cp), 109.8 (CH, Cp), 69.5 ([18]-crown-6), 57.9 (OCH_2CH_3), 14.9 (OCH_2CH_3). IR (THF, cm^{-1}): ν(CO) 1680 s. IR(KBr, cm^{-1}): ν(C═O) 1695 s, ν(C−O) 1258 s, $\nu(C-OCH_2)$ 1108 vs, 1058 s. Mp: 144 °C (dec). Anal. Calcd for $C_{23}H_{37}NaO_{10}$: C, 55.6; H, 7.46. Found: C, 55.5; H, 7.45. The complex was also characterized by an X-ray diffraction study.

[Mn{$C_5H_3(CO_2Et)_2$-1,2}$(CO)_3$] (5b). To a solution of $MnBr(CO)_5$ (1.80 g, 6.55 mmol) in ca. 30 mL of THF was added [Na([18]-crown-6)][$C_5H_3(CO_2Et)_2$-1,2] as a solid (3.25 g, 6.72 mmol). The mixture was refluxed for 4 h and then chromatographed on silica gel using 1Etp/1CH_2Cl_2 as eluent to give 2.11 g (81%) of **5b** as an air- and moisture-stable yellow oil. ^1H NMR ($CDCl_3$): δ 5.33 (br, 2H), 4.70 (br, 1H), 4.30 (br, 4H), 1.34 (br, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 222.3 (C≡O), 164.0 (C═O), 91.2 (*ipso*-C, Cp), 87.7 (CH, Cp), 80.0 (CH, Cp), 61.9 (OCH_2CH_3), 14.0 (OCH_2CH_3). IR (THF, cm^{-1}): ν(C≡O) 2034 s, 1953 vs, ν(C═O) 1727 m. IR (CH_2Cl_2 cm^{-1}): ν(C≡O) 2037 s, 1959 vs, ν(C═O) 1722 m. IR(neat, CsI, cm^{-1}): ν(C≡O) 2033 s, 1954 vs, ν(C═O) 1726 s, ν(C−O) 1259 s, $\nu(C-OCH_2)$ 1078. EIMS for $^{12}C_{14}1H_{13}55Mn^{16}O_7$ (*m*/*z*, %): 348 ($[M]^+$, 21), 264 ($[M]^+ - 3CO$, 92), 220 ($[Mn\{C_5H_3(CO_2Et)_2\}]^+ - CO_2$, 100), 176 ($[Mn\{C_5H_3(CO_2Et)_2\}]^+ - 2CO_2$, 86), 119 ($[MnCp]^+$, 58). Anal. Calcd for $C_{14}H_{13}MnO_7$: C, 48.3; H, 3.75. Found: C, 48.5; H, 3.79.

[Mn{$C_5H_3(CO_2Ph)_2$-1,2}$(CO)_3$] (5c). To a solution of $MnBr(CO)_5$ (0.25 g, 1.1 mmol) in ca. 30 mL of THF was added $Na[C_5H_3(CO_2Ph)_2]$ as a solid (0.35 g, 1.1 mmol). After refluxing the mixture for 4 h the solvent was removed in vacuo and CH_2Cl_2 was added. The suspension was filtered on a Celite pad, and the resulting yellow solution was concentrated to a small volume and layered with Etp. After 3 days at −20 °C, 0.44 g (93%) of yellow crystals of **5c** were obtained. ^1H NMR ($CDCl_3$): δ 7.41−7.16 (m, 10H, Ph), 5.61 (br, 2H), 4.89 (br, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 221.8 (C≡O), 162.6 (C═O), 150.3 (*ipso*-C, Ph), 129.5 (*o*-Ph), 126.3 (*p*-Ph), 121.4 (*m*-Ph), 89.9 (*ipso*-C, Cp), 88.9 (CH, Cp), 81.0 (CH, Cp). IR (THF, cm^{-1}): ν(C≡O) 2036 s, 1957 vs, ν(C═O) 1747 m. IR (CH_2Cl_2, cm^{-1}): 2040 s, 1962 vs, 1742 m. IR (KBr, cm^{-1}): ν(C≡O) 2040 s, 1972 vs, 1942 vs, ν(C═O) 1739 s, ν(C−O) 1259 s, $\nu(C-OCH_2)$ 1078 m. EIMS for $^{12}C_{22}1H_{13}55Mn^{16}O_7$ (*m*/*z*, %): 444 ($[M]^+$, 8), 360 ($[M]^+ - 3CO$, 55), 119 ($[MnCp]^+$, 100). Mp: 112 °C. Anal. Calcd for $C_{22}H_{13}MnO_7$: C, 59.5; H, 2.93. Found: C, 59.5; H, 2.94. The complex was also characterized by an X-ray diffraction study.

[Re{$C_5H_3(CO_2Et)_2$-1,2}$(CO)_3$] (6b). To a solution of $ReBr(CO)_5$ (0.51 g, 1.26 mmol) in ca. 30 mL of THF was added [Na([18]-crown-6)][$C_5H_3(CO_2Et)_2$-1,2] as a solid (0.625 g, 1.26 mmol). The mixture was refluxed for 8 h and then chromatographed on silica gel (eluting mixture 1Etp/1CH_2Cl_2) to give 0.47 g (70%) of **6b** as a light yellow oil. ^1H NMR ($CDCl_3$): δ 5.85 (d, $^3J = 3.0$, 2H), 5.29 (t, $^3J = 3.0$, 1H), 4.31 (q, $^3J = 7.2$, 4H), 1.33 (t, $^3J = 7.2$, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 191.3 (C≡O), 162.6 (C═O), 94.7 (*ipso*-C, Cp), 88.8 (CH, Cp), 82.5 (CH, Cp), 62.2 (OCH_2CH_3), 13.9 (OCH_2CH_3). IR (THF, cm^{-1}): ν(C≡O) 2034 s, 1941 vs, ν(C═O) 1730 m. IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2037 s, 1947 vs, ν(C═O) 1724 m. IR (neat, CsI, cm^{-1}): ν(C≡O) 2033 s, 1941 vs, ν(C═O) 1733 s, ν(C−O) 1259 s, $\nu(C-OCH_2)$ 1082 m. EIMS for $^{12}C_{14}1H_{13}16O_7187Re$ (*m*/*z*, %): 480 ($[M]^+$, 100), 396 ($[M]^+ - 3CO$, 25), 324 ($[Re\{C_5H_3CO_2Et\}]^+$, 38). Anal. Calcd for $C_{14}H_{13}O_7Re$: C, 35.0; H, 2.71. Found: C, 35.4; H, 2.75.

[Ru{$C_5H_3(CO_2Et)_2$-1,2}(CO)]$_2$ (7b). To a solution of $[Ru(CO)_3Cl_2]_2$ (0.41 g, 0.81 mmol) in ca. 30 mL of THF was added [Na([18]-crown-6)][$C_5H_3(CO_2Et)_2$-1,2] (2.18 g, 4.40 mmol). The solution was refluxed, and the progress of the reaction was monitored by infrared spectroscopy. After 15 h, when the absorption at 2128 cm^{-1} due to a carbonyl stretching of $[RuCl_2(CO)_3]_2$ had disappeared, the reaction mixture was cooled to room temperature. The solvent was removed under vacuum and the solid washed three times with ether. The combined washings were concentrated to a small volume and then cromatographed on silica gel. The ruthenium complex was eluted with acetonitrile, and evaporation of the solvent produced 0.46 g (77%) of **7b** as a dark yellow-orange oil. ^1H NMR ($CDCl_3$): δ 5.76 (d, $^3J = 3.0$, 2H), 5.25 (t, $^3J = 3.0$, 1H), 4.29 (q, $^3J = 7.2$, 4H), 1.32 (t, $^3J = 7.2$, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 210.2 (C≡O), 162.9 (C═O), 96.9 (*ipso*-C, Cp), 92.1 (CH), 89.8 (CH), 62.0 (OCH_2CH_3), 14.0 (OCH_2CH_3). IR (THF, cm^{-1}): ν(CO) 2018 s, 1985 s, 1959 s, 1805 s, 1726 s. IR (neat, CsI, cm^{-1}): ν(C≡O) 2018 s, 1985 s, 1961 s, 1802 s, ν(C═O) 1717 s, ν(C−O) 1286 s, 1253 s, $\nu(C-OCH_2)$ 1072 m. Anal. Calcd for $C_{26}H_{26}O_{12}Ru_2$: C, 42.5; H, 3.54. Found: C, 42.6; H, 3.58.

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Table 3. Crystal Data and Details of Structure Refinement for Complexes 4b and 5c

	4b	**5c**
empirical formula	$C_{23}H_{37}NaO_{10}$	$C_{22}H_{13}MnO_7$
fw	496.52	444.02
temp (K)	293	293
wavelength (Å)	0.71069	0.71069
cryst syst	monoclinic	monoclinic
space group	$\mathrm{P2_1/n}$	$P2_1/n$
unit cell dimens	$a = 12.619(2)$ Å $b = 14.620(3)$ Å $c = 14.805(3)$ Å $\beta = 91.96(3)°$	$a = 10.133(2)$ Å $b = 10.415(2)$ Å $c = 18.864(4)$ Å $\beta = 103.94(3)°$
volume (Å^3)	2729.8	1932.2
Z	4	4
$F(000)$	1064	904.0
cryst size (mm)	0.53 × 0.55 × 0.42	0.25 × 0.31 × 0.28
max θ for data collection	33.5°	36.5°
no. of reflns collected	27 159	22 564
no. of obsd ind reflns	1917	3027
no. of params	322	271
goodness-of-fit on F^2	1.03	0.97
final R indices [$I > 2\sigma(I)$]	0.085	0.053
R indices (all data)	0.26	0.16
largest diff peak and hole (e Å^{-3})	0.26, −0.15	0.54, −0.30

X-ray Crystallography. Crystals of **4b** and **5c** suitable for the X-ray single-crystal studies were precipitated from THF/diethyl ether for **4b** and CH_2Cl_2/Etp for **5c**. Diffraction intensities were collected at room temperature on a Bruker 2K SMART-CCD diffractometer using graphite monochromated Mo Kα radiation. The data were collected using 0.3° wide ω scans with a crystal-to-detector distance of 5.0 cm and corrected for absorption empirically using the SADABS routine. Crystal data and details of structure refinement are reported in Table 3.

Data collections nominally covered a full sphere of reciprocal space for both complexes with 30 and 20 s exposure time per frame for **4b** and **5c**, respectively. Five independent data collections were performed for **4b** on crystals from different crystallization batches both at room temperature and at 223 K, trying to overcome the weak diffraction power of the samples. All the structure models showed high thermal motion of the crown-ether counterion. None of the different experiments improved thermal motion information significantly, so that we concluded that this was an intrinsic crystal characteristic probably due to the quite loose encapsulation of the sodium ion in the [18]-crown-6. Therefore, the set of data with the highest number of observed reflections was used for structure solving and refinement.

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 geometrically positioned [C−H 0.96 Å] and refined "riding" on their corresponding carbon atoms. For **4b**, one of the two ethyl appendages was found affected by positional disorder over two orientations for the methyl C(9) group. Refinement of the relative contribution to each orientation converged to an occupancy factor ratio of approximately 70:30.

Refinement converged at a final $R = 0.085$, wR2 = 0.24, $S = 1.03$ for **4b**, $R = 0.052$, wR2 = 0.14, $S = 0.974$ for **5c**.

Molecular graphics were prepared using ORTEP3 for WindowsNT.[21]

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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 **4b** and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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