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Synthesis and characterization of substituted cyclopentadienide ligands that may form chelates or metal dimers

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Abstract

Nine different substituted cyclopentadienyl ligands, which have substituents that may either chelate or bridge to second metal center, have been prepared from nucleophilic substitution reactions of esters or alkyl halides with NaCp. The sodium or thallium salts of these ligands were isolated as solids and characterized by ^{1}H NMR. The alkyl halide and NaCp reaction proved to yield the purer salts of the ligands because of the milder reaction conditions. These salts were reacted futher with $Mn(CO)_5Br$ to form the corresponding manganese tricarbonyl derivatives (i.e. $(C_5H_4R)Mn(CO)_3$; where R = $C(O)CH_2OCH_3$, $C(O)CH_2SCH_3$, $C(O)CH_2CH_2SCH_3$, $CH_2CO_2CH_3$, $CH_2CO_2CH_2CH_3$, $CH_2CH_2CO_2CH_3$, $CH_2CH_2CO_2CH_2CH_3$, $CH_2CH_2O_2CCH_3$, and $CH_2CH_2OCH_3$) and $Na(C_5H_4C(O)CH_2OCH_3)$ was reacted with $Co_2(CO)_8$ to form $(C_5H_4C(O)CH_2OCH_3)Co(CO)_2$. The manganese and cobalt compounds were characterized by elemental analysis, IR, ^{1}H, and ^{13}C NMR spectra.

Keywords: Manganese; Carbonyl; Cyclopentadienyl; Cobalt; Thallium; Sodium

1. Introduction

The synthesis of substituted-cyclopentadienyl transition-metal complexes is of interest because of their potential uses in chemical technologies [1–5]. Two basic approaches have been used to synthesized a variety of these complexes. The first pathway is functionalization of the ring while it is a part of an organometallic compound. This approach works well with ferrocene [3,6] and a few other η^5-cyclopentadienyl metal compounds that are less reactive [5,7]. Most η^5-cyclopentadienyl metal compounds, however, will not just undergo ring substitution but other competing reactions occur under the reaction conditions of ring substitution. The second pathway involves the synthesis of the functionalized ligand followed by the formation of metal–ligand compound [2,8–11]. The second approach is the most versatile, since many different metal centers could form compounds with the functionalized ligands [12]. We chose the second approach for this work and synthesized the desired ligands by nucleophilic substitution reactions.

Our interests are in the development of new catalytic systems through variations of the ligands of known catalysts [13]. Two characteristics are important for the substituents of cyclopentadienyl metal compounds that we plan to study. The substituent must either have the ability to chelate or be able to form metal dimers. These properties should allow the synthesis of dimeric species, where the substituent bridges two metals, and of species that easily form coordinatively unsaturated compounds through the loss of chelation of the substituent. These types of compound are of interest in catalysis. In this paper we report the synthesis of several new functionalized cyclopentadienyl ligands and their transition metal complexes.

2. Results and discussion

The substituted cyclopentadienyl salts, MCpR (CpR = $C_5H_4R^-$, where R is the desired substituent and M is either Tl^+ or Na^+), were made by one of two synthetic pathways (see Scheme I and Scheme II).

Attempts to synthesize $NaC_5H_4C(O)(CH_2)_2OCH_3$ and $NaC_5H_4C(O)(CH_2)_2SCH_3$ using the method in Scheme I were successful, but the ^{1}H NMR spectra of these salts indicated that there were many impurities.

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The impurities in these salts complicated the synthesis of their manganese derivatives and isolation of the pure manganese derivatives was unsuccessful. The $NaC_5H_4C(O)(CH_2)_2SCH_3$ produced from Scheme II was purer than that produced from Scheme I and the manganese derivative of this ligand was easily obtained from the

Table 1
^1H, ^{13}C NMR and IR data of the synthesized transition metal complexes

Compound	^1H NMR [a] (ppm)	^{13}C NMR [a] (ppm)	IR [b] (cm^{-1})
$(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$ **I**	5.74 (t, 2 H, Cp) [c] 5.15 (t, 2 H, Cp) 4.34 (s, 2 H, $-CH_2-$) 3.39 (s, 3 H, $-OCH_3$)	224.3 (CO) [c] 195.2 ($-C(O)-$) 90.4 (C(1)) 88.2 (Cp, J_{CH} = 182 Hz) 85.3 (Cp, J_{CH} = 180 Hz) 76.0 ($-CH_2-$, J_{CH} = 142 Hz) 59.2 ($-OCH_3$, J_{CH} = 142 Hz)	2024(vs) 1935(vs) 1691(m)
$(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Co(CO)_2$ **II**	5.68 (t, 2 H, Cp) [c] 5.54 (t, 2 H, Cp) 4.40 (s, 2 H, $-CH_2-$) 3.40 (s, 3 H, $-OCH_3$)	193.2 ($-C(O)-$) [c] 98.2 (C(1)) 89.5 (Cp, J_{CH} = 181 Hz) 84.6 (Cp, J_{CH} = 181 Hz) 75.6 ($-CH_2-$, J_{CH} = 141 Hz) 58.9 ($-OCH_3$, J_{CH} = 142 Hz)	2029(vs) 1969(vs) 1690(m)
$(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_3$ **III**	5.75 (t, 2 H, Cp) [c] 5.15 (t, 2 H, Cp) 3.51 (s, 2 H, $-CH_2-$) 2.10 (s, 3 H, $-SCH_3$)	224.4 (CO) [c] 192.7 ($-C(O)-$) 91.4 (C(1)) 88.5 (Cp, J_{CH} = 182 Hz) 85.4 (Cp, J_{CH} = 181 Hz) 39.9 ($-CH_2-$, J_{CH} = 140 Hz) 15.6 ($-SCH_3$, J_{CH} = 139 Hz)	2027(s) 1938(s) 1671(m)
$(\eta^5\text{-}C_5H_4CH_2C(O)OCH_3)Mn(CO)_3$ **IV**	4.81 (s, 2 H, Cp) 4.66 (s, 2 H, Cp) 3.71 (s, 3 H, $-OCH_3$) 3.27 (s, 2 H, $-CH_2-$)	224.8 (CO) 170.6 ($-C(O)-$) 96.8 (C(1)) 84.2 (Cp, J_{CH} = 178 Hz) 82.2 (Cp, J_{CH} = 179 Hz) 52.4 ($-OCH_3$, J_{CH} = 147 Hz) 33.8 ($-CH_2-$, J_{CH} = 131 Hz)	2020(s) [d] 1935(s) 1745(m)
$(\eta^5\text{-}C_5H_4CH_2C(O)OCH_2CH_3)Mn(CO)_3$ **V**	4.81 (s, 2 H, Cp) 4.66 (s, 2 H, Cp) 4.15 (q, 2 H, $-OCH_2-$) 3.25 (s, 2 H, $-CH_2-$) 1.26 (t, 3 H, $-CH-_3$)	224.6 (CO) 169.9 ($-C(O)-$) 96.9 (C(1)) 83.9 (Cp, J_{CH} = 178 Hz) 81.9 (Cp, J_{CH} = 179 Hz) 61.2 ($-OCH_2-$, J_{CH} = 148 Hz) 33.8 ($-CH_2-$, J_{CH} = 131 Hz) 14.1 ($-CH_3$, J_{CH} = 127)	2020(s) [d] 1933(s) 1740(m)
$(\eta^5\text{-}C_5H_4CH_2CH_2C(O)OCH_3)Mn(CO)_3$ **VI**	4.63 (t, 2 H, Cp) 4.61 (t, 2 H, Cp) 3.67 (s, 3 H, -OCH_3) 2.61–2.47 (m, 4 H, $-(CH_2)_2-$)	224.5 (CO) 172.1 ($-C(O)-$) 104.2 (C(1)) 82.0 (Cp, J_{CH} = 177 Hz) 81.3 (Cp, J_{CH} = 179 Hz) 51.3 ($-OCH_3$, J_{CH} = 147 Hz) 34.5 ($-CH_2-$, J_{CH} = 130 Hz) 22.9 ($-CH_2-$, J_{CH} = 126)	2016(s) 1919(s) 1737(m)
$(\eta^5\text{-}C_5H_4CH_2CH_2C(O)OCH_2CH_3)Mn(CO)_3$ **VII**	4.63 (t, 2 H, Cp) 4.61 (t, 2 H, Cp) 4.12 (q, 2 H, $-OCH_2-$) 2.60–2.45(m, 4 H, $-(CH_2)_2$) 1.24 (t, 3 H, $-CH_3$)	224.9 (CO) 172.1 ($-C(O)-$) 104.8 (C(1)) 82.5 (Cp, J_{CH} = 178 Hz) 81.7 (Cp, J_{CH} = 179 Hz) 60.6 ($-OCH_2-$, J_{CH} = 147 Hz) 35.2 ($-CH_2-$, J_{CH} = 131 Hz) 23.3 ($-CH_2-$, J_{CH} = 131) 14.2 ($-CH_3$, J_{CH} = 127)	2017(s) 1921(s) 1732(m)

$$NaCp + CH_3O_2CR \xrightarrow[\text{reflux}]{THF} C_5H_5C(O)R + NaOCH_3$$
$$\longrightarrow NaCpC(O)R + HOCH_3$$

where R is CH_2OCH_3, CH_2SCH_3, $(CH_2)_2OCH_3$, and $(CH_2)_2SCH_3$

Scheme I.

$$NaCp + XR \xrightarrow{THF/-20°C} NaX + C_5H_5R$$
$$2C_5H_5R + 2Na \xrightarrow{THF/0°C} 2NaCpR + H_2$$
$$C_5H_5R + TlOC_2H_5 \xrightarrow{or} TlCpR + HOC_2H_5$$

where $R = CH_2CO_2CH_3$, $CH_2CO_2CH_2CH_3$, $(CH_2)_2CO_2CH_3$, $(CH_2)_2CO_2CH_2CH_3$, $(CH_2)_2OCH_3$, $(CH_2)_2O_2CCH_3$ when X = Br; $R = C(O)(CH_2)_2SCH_3$ when X = Cl.

Scheme II.

purer salt of the ligand. Although Scheme II requires an additional reaction step, we found that it generally gave us the purer salts of the ligands. The difference may be related to the milder reaction conditions used in Scheme II. All of the cyclopentadienyl salts were characterized by ^1H NMR.

The synthesis of $NaC_5H_4(CH_2)_2OCH_3$ was reported by Yanlong and coworkers [17]. They used the similar procedure as illustrated in Scheme II except they used 2-methoxyethyl tosylate where we used 2-methoxyethyl bromide. Since the bromide is commercially available and the NaBr by-product precipitates out of the THF reaction solution, the bromide is a more convenient starting material. The 2-methoxyethyl bromide reaction eliminates several steps when isolating the CpR product [17].

In Scheme II, Na sand, which is cheap and clean but takes several hours to deprotonate, can be used to form the salt of the ligand. Alternatively, $TlOCH_2CH_3$ is commercially available but more costly. Furthermore, the salts containing ester groups can react further to produce new substituents on the ring. $TlC_5H_4CH_2C(O)OCH_2CH_3$ and $TlC_5H_4(CH_2)_2C(O)OCH_2CH_3$ were isolated from solutions containing $TlC_5H_4CH_2C(O)OCH_3$ and $TlC_5H_4(CH_2)_2C(O)OCH_3$, respectively. The reaction occurred when the excess $TlOC_2H_5$ was given enough time to exchange the methoxide group of the substituent for an ethoxide (see Eq. (1)).

$$TlC_5H_4CH_2C(O)OCH_3 + TlOC_2H_5 \Leftrightarrow TlC_5H_4CH_2C(O)OCH_2CH_3 + TlOCH_3 \quad (1)$$

This reaction is fast because even after a short reaction time ($\sim$ 20 min) half of the $(C_5H_4CH_2C(O)OCH_3)^-$ would be converted to $(C_5H_4CH_2C(O)OCH_2CH_3)^-$. We did not attempt to separate the mixture of the two

Table 1 (continued)

Compound	^1H NMR [a] (ppm)	^{13}C NMR [a] (ppm)	IR [b] (cm^{-1})
$(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)Mn(CO)_3$ **VIII**	4.69 (s, 2 H, Cp) 4.61 (t, 2 H, Cp) 3.47 (s, 2 H, $-CH_2-$) 3.33 (s, 3 H, $-OCH_3$) 2.48 (t, 2 H, $-CH_2-$)	225.1 (CO) 103.3 (C(1)) 83.3 (Cp, J_{CH} = 178 Hz) 81.5 (Cp, J_{CH} = 179 Hz) 72.7 ($-OCH_2-$, J_{CH} = 142 Hz) 58.6 ($-OCH_3$, J_{CH} = 138 Hz) 28.4 ($-CH_2-$, J_{CH} = 129)	2017(s) [d] 1925(s)
$(\eta^5\text{-}C_5H_4CH_2CH_2O_2CCH_3)Mn(CO)_3$ **IX**	4.57 (t, 2 H, Cp) 4.54 (t, 2 H, Cp) 4.06 (t, 2 H, $-CH_2O-$) 2.47 (t, 2 H, $-CH_2-$) 1.95 (s, 3 H, $-CH_3$)	224.6 (CO) 170.8 ($-O_2C-$) 101.7 (C(1)) 83.0 (Cp, J_{CH} = 177 Hz) 81.9 (Cp, J_{CH} = 179 Hz) 64.0 ($-OCH_2-$, J_{CH} = 149 Hz) 27.5 ($-CH_2-$, J_{CH} = 130 Hz) 20.9 ($-CH_3$, J_{CH} = 130)	2019(s) [d] 1931(s) 1744(m)
$(\eta^5\text{-}C_5H_4C(O)CH_2CH_2SCH_3)Mn(CO)_3$ **X**	5.33 (t, 2 H, Cp) 4.75 (t, 2 H, Cp) 2.68–2.81 (m, 4 H, $-(CH_2)_2-$) 2.03 (s, 3 H, $-SCH_3$)	222.7 (CO) 195.6 ($-C(O)-$) 91.2 (C(1)) 86.6 (Cp, J_{CH} = 180 Hz) 83.7 (Cp, J_{CH} = 182 Hz) 39.0 ($-C(O)CH_2-$, J_{CH} = 127 Hz) 28.0 ($-CH_2S-$, J_{CH} = 143 Hz) 15.9 ($-SCH_3$, J_{CH} = 138 Hz)	2033(s)[e] 1960(s) 1952(s) 1694(m)

[a] Resonances reported in ppm relative to the residual peaks of the solvent. $CDCl_3$ was used as the solvent unless noted. [b] Neat samples. [c] Acetone-d_6 was the solvent. [d] Benzen solution was the sample. [e] Cyclohexane solution was the sample.

thallium salts. Instead, we synthesized their manganese derivatives and then purified the two manganese compounds.

One can avoid the exchange reaction of Eq. (1) if Na sand is used as the deprotonation agent. If Na sand is used, then an additional problem is found. The protonated ligand can dimerize or the sodium salt of the ligand can react further with another ester group of a second ligand to form a dimer of ligands (see Eq. (2)).

$$NaC_5H_4CH_2C(O)OCH_3 + NaC_5H_4CH_2C(O)OCH_3 \longrightarrow Na_2(C_5H_4CH_2C(O)C_5H_3CH_2C(O)OCH_3) + CH_3OH \quad (2)$$

This reaction can take place during the synthesis of the ligand or during the synthesis of the metal complex of the ligand. Therefore it is better to avoid the sodium salts of the ligands where there is a reactive ester group present. The formation of the substituted organothallium salts is a better choice owing to their slightly lower ionic character as compared to the sodium analogues [8]. The exchange reaction (Eq. (1)) can be overcome if the $TlOCH_2CH_3$ is first converted to $TlOCH_3$, which is a white solid.

The synthesis of $TlC_5H_4CH_2C(O)OCH_3$ and $TlC_5H_4(CH_2)_2C(O)OCH_3$ using $TlOCH_3$ as the deprotonating agent always produced some TlCp. There are two possible sources of this impurity. First, there could be some unreacted HCp from the formation of NaCp (the first step in the reaction sequence). This possibility seems unlikely because every means was taken to remove the excess HCp under vacuum. We obtained a white solid, NaCp, during this evaporation. This solid was dry. The second possible source is from the deprotonation reaction (see Eq. 3).

$$2TlOCH_3 + 2C_5H_5R \longrightarrow Tl(C_5H_4R) + CH_3OH + TlCp + ROCH_3 \quad (3)$$

where $R = CH_2C(O)OCH_3$ or $(CH_2)_2C(O)OCH_3$

Eq. (3) illustrates the deprotonation and a substitution reaction, which leads to the formation of TlCp. In order to avoid the substitution reaction, the reaction was carried out at a low temperature.

The reason for synthesizing the substituted cyclopentadienyl ligands first was so that many different transition metal complexes of the ligand could be made and studied. In order to demonstrate this point, cobalt and manganese complexes of $C_5H_4C(O)CH_2OCH_3^-$ (i.e. **I** and **II**) were prepared and characterized (see Table 1 and Experimental section). Clearly compounds of these ligands are not limited to the $CpMn(CO)_3$ series. If there are limitations, they are probably due to the reagents involved in the synthetic procedure. There were very few differences in the chemical shifts of the protons and carbons in **I** and **II**. Both compounds yield apparent triplets for the ring protons with only a small difference in their chemical shifts (see Table 1). This difference is due to the metals in the compounds. The substituents on the rings yield similar chemical shifts for both the hydrogens in ^1H spectra and carbons in ^{13}C spectra.

Studies of the manganese compounds are in progress. We are studying the photolysis of these complexes, since these ligands contain substituents with atoms that can bond to a metal to form chelates.

3. Experimental

NMR spectra were recorded on a Varian VXR-300 NMR spectrometer and referenced to appropriate solvent resonances. IR spectra were recorded on a Mattson Galaxy 2020 FTIR with a resolution of 2 cm^{-1}. All column chromatography was with silica gel grade 643 (Aldrich). The solvents used in chromatography were used as received. Elemental analysis were carried out by either Desert Analytics of Tucson, Arizona, or Galbraith Laboratories, Inc of Knoxville, Tennessee.

All solvents were obtained from Fisher. The solvents were dried and distilled under argon before use unless otherwise noted. Methyl methoxyacetate, 2-bromoethyl acetate, methyl (methylthio)acetate, dicyclopentadiene, and thallous ethoxide were obtained from Aldrich. Methyl bromoacetate, 2-bromoethyl methyl ether, 3-methylthiopropionyl chloride, and methyl 3-bromopropionate were obtained from TCI America. Bromopentacarbonylmanganese was obtained from Strem. These chemicals were used without further purification.

3.1. Synthesis of $Na(C_5H_4C(O)CH_2OCH_3)$

Sodium sand is made by a reported procedure with 0.92 g (40 mmol) of sodium [14]. The toluene from the synthesis of the sodium sand was removed from the flask by cannula and replaced with THF. The flask was cooled to 0°C and 3.17 g (48 mmol) of freshly cracked cyclopentadiene were added [15]. The solution was stirred until all of the sodium had disappeared (~ 2 h). Methyl methoxyacetate (4.16 g, 40 mmol) was added to this solution by cannula and the solution refluxed for 5 h under Ar. After refluxing, solvent volume was reduced under vacuum to 50 ml and a precipitate formed. The solid was filtered with standard Schlenk techniques, and the precipitate was washed with pentane. The air sensitive tan solid was dried in vacuo and characterized by ^1H NMR. ^1H NMR ($DMSO-d_6$) δ 6.18 (br, 2 H, H(2,5)), 5.62 (br, 2 H, H(3,4)), 4.24 (s, 2 H, $-CH_2-$), 3.27 (s, 3 H, $-OCH_3$).

3.2. Synthesis of $Tl(C_5H_4C(O)CH_2OCH_3)$

THF (50 ml) was added by cannula to $Na(C_5H_4C(O)CH_2OCH_3)$ (5.0 g, 36.5 mmol) in a flask. The solution was cooled to −20°C and 3 ml of degassed water were added dropwise. The solution was stirred for 3 h. This solution was then added to a blender containing TlCl (8.75 g, 36.5 mmol), KOH (2.5 g), and water. The mixture was blended for 4 min at medium speed and the cream-white solid was separated by filtration. The solid was washed with two 25 ml portions of water, two 20 ml portions of diethyl ether, and a 10 ml portion of absolute ethanol. The solid was dried under vacuum and characterized by ^1H NMR. ^1H NMR (DMSO-d_6) δ 6.32 (t, 2 H, H(2,5)), 5.76 (t, 2 H, H(3,4)), 4.29 (s, 2 H, $-CH_2-$), 3.28 (s, 3 H, $-OCH_3$).

3.3. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$ (I)

The compound can be synthesized with either the sodium or thallium salt of the ligand. The thallium salt (0.249 g, 0.728 mmol) was placed in a argon purged reaction flask with 0.2 g of $Mn(CO)_5Br$ in 30 ml of THF. The mixture was stirred and refluxed for 5 h. After 5 h the solution was yellow-green and contained a tan solid. The mixture was filtered, and the solvent of the filtrate was evaporated under vacuum. The remaining sample was purified by column chromatography (diameter 2.5 cm, height 23 cm) using an ethyl acetate + pentane (1/4 ratio) mixture to elute the product. Solvent was removed under vacuum to yield a yellow liquid. Analytically pure sample was obtained after vacuum distillation (80°C at 0.1 mmHg). Yield of 39.8%. Found: C, 47.92; H, 3.37; Mn, 19.10; calcd.: C, 47.85; H, 3.29; Mn, 19.90.

3.4. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Co(CO)_2$ (II)

This compound was synthesized using $Na(C_5H_4C(O)CH_2OCH_3)$ and $Co_2(CO)_8$ as described previously for other $CpCo(CO)_2$ compounds [16]. The red liquid product was separated on an alumina column with diethyl ether + pentane elutant (yield 67.6%). An analytically pure sample was obtained by vacuum distillation at 67–68°C (0.1 mmHg). Found: C, 47.78; H, 3.62; Co, 23.11; calcd.: C, 47.64; H, 3.60; Co, 23.38.

3.5. Synthesis of $Na(C_5H_4C(O)CH_2SCH_3)$

The method is similar to that described for $Na(C_5H_4C(O)CH_2OCH_3)$. ^1H NMR (DMSO-d_6) δ 6.11 (br, 2 H, H(2,5)), 5.64 (br, 2 H, H(3,4)), 3.35 (s, 2 H, $-CH_2-$), 1.98 (s, 3 H, $-SCH_3$).

3.6. Synthesis of $(\eta^5\text{-}C_5H_4C(O)CH_2SCH_3)Mn(CO)_3$ (III)

The procedure is similar to that described for $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$. The yield was 44.1%. Found: C, 44.60; H, 3.30; Mn, 17.27; S, 10.89; calcd.: C, 45.22; H, 3.10; Mn, 18.80; S, 10.97.

3.7. Synthesis of $Tl(C_5H_4CH_2C(O)OCH_3)$ and $Tl(C_5H_4CH_2C(O)OCH_2CH_3)$ as a mixture

Sodium cyclopentadienide (0.1 mol) was made as described earlier. The unreacted HCp was evaporated under vacuum and the NaCp was dissolved again in THF (60 ml). Methyl bromoacetate (15.33 g, 0.1 mol) was added to the THF solution of NaCp, and the mixture was stirred at −20°C for 2 h. The solid NaBr was filtered off, and the filtrate (containing $C_5H_5CH_2C(O)OCH_3$) stirred with 25 g of thallium(I) ethoxide for 12 h. The thallium salts were separated by filtration and dried under vacuum. Two thallium substituted-cyclopentadienides were identified by NMR. Some of the expected product, $Tl(C_5H_4CH_2C(O)OCH_3)$, exchanged the methoxide group with the excess ethoxide in solution. The two thallium salts were not separated. The mixture was reacted to form the mixture of manganese derivatives and the manganese compounds were separated. ^1H NMR (DMSO-d_6) for $Tl(C_5H_4CH_2C(O)OCH_3)$ δ 5.79 (t, 2 H, H(2,5)), 5.64 (t, 2 H, H(3,4)), 3.58 (s, 3 H, $-OCH_3$), 3.25 (s, 2 H, $-CH_2-$) and for $Tl(C_5H_4CH_2C(O)OCH_2CH_3)$ δ 5.79 (t, 2 H, H(2,5)), 5.64 (t, 2 H, H(3,4)), 4.03 (q, 2 H, $-OCH_2-$), 3.25 (s, 2 H, $-CH_2-$), 1.19 (t, 3 H, $-CH_3$).

3.8. Synthesis of $(\eta^5\text{-}C_5H_4CH_2C(O)OCH_3)Mn(CO)_3$ (IV) and $(\eta^5\text{-}C_5H_4CH_2C(O)OCH_2CH_3)Mn(CO)_3$ (V)

The mixture of thallium salts (2.5 g) was reacted with 2.01 g of bromopentacarbonylmanganese in 100 ml of THF. The mixture was refluxed in the absence of light for 5 h. The mixture was allowed to cool to room temperature before the thallium(I) bromide was separated by filtration. The solvent was removed from the filtrate and the liquid product was purified by chromatography (diameter 4 cm, height 40 cm) with ethyl acetate + benzene (1/19 ratio by volume). The solvent was removed from the fractions under vacuum and a mixture of the desired products was identified by ^1H NMR. The mixture was purified by a second column (diameter 2.5 cm, height 23 cm) with ethyl acetate + pentane elutant (7% ethyl acetate by volume). Two bands were not clearly observed during the chromatography, but the early fraction of the band and the late

fraction of the band contained pure compounds. The solvent of both fractions was evaporated under vacuum to yield two yellow liquids. The products, (η^5-$C_5H_4CH_2C(O)OCH_3$)$Mn(CO)_3$ (5.4% yield) and (η^5-$C_5H_4CH_2C(O)OCH_2CH_3$)$Mn(CO)_3$ (30.1% yield), were characterized individually.

For **IV**: Found: C, 48.25; H, 3.07; calcd.: C, 47.85; H, 3.29. For **V**: Found: C, 50.03; H, 3.68; Mn, 19.19; calcd.: C, 49.67; H, 3.82; Mn, 18.93.

3.9. Synthesis of $Tl(C_5H_4CH_2C(O)OCH_3)$

Sodium cylcopentadienide (37.8 mmol) was made as described earlier. The unreacted HCp was evaporated under vacuum. The white NaCp was dissolved again in THF (150 ml) and cooled down to −70°C; 5.88 g methyl bromoacetate (38.4 mmol) were added and the reaction mixture was stirred for 2 h at a temperature under −60°C. The reaction mixture was then transferred into another 3-neck round bottom flask where there was 9.0 g $TlOCH_3$ (42.38 mmol) previously prepared from the reaction of $TlOCH_2CH_3$ and CH_3OH. The reaction mixture was stirred for another 2 h at −60°C and then filtered at room temperature. The volume of the filtrate was reduced to about 15 ml and 25 ml of pentane were added slowly. After it was thoroughly stirred, the pentane washing solution was decanted. The yellow sticky substance was washed by pentane three additional times and a light yellow solid was obtained. The obtained $Tl(C_5H_4CH_2C(O)OCH_3)$ contained ~10% of TlCp (based on the ^{1}H NMR spectrum). **IV** can be synthesized from this thallium salt as described previously.

3.10. Synthesis of $Tl(C_5H_4CH_2CH_2C(O)OCH_3)$ and $Tl(C_5H_4CH_2CH_2C(O)OCH_2CH_3)$ as a mixture

Thallium salt mixture was synthesized from NaCp and methyl 3-bromopropionate, as described for the mixture of $Tl(C_5H_4CH_2C(O)OCH_3)$ and $Tl(C_5H_4CH_2C(O)OCH_2CH_3)$. ^{1}H NMR (DMSO-$d_6$) For $Tl(C_5H_4CH_2CH_2C(O)OCH_3)$ δ 5.75 (s, 2 H, H(2,5)), 5.59 (s, 2 H, H(3,4)), 3.58 (s, 3 H, $-OCH_3$), 2.73–2.63 (m, 4 H, $-CH_2CH_2-$) and for $Tl(C_5H_4CH_2CH_2C(O)OCH_2CH_3)$ δ 5.75 (s, 2 H, H(2,5)), 5.59 (s, 2 H, H(3,4)), 4.05 (q, 2 H, $-OCH_2-$), 2.73 − 2.63 (m, 4 H, $-CH_2CH_2-$), 1.18 (t, 3 H, $-CH_3$).

3.11. Synthesis of (η^5-$C_5H_4CH_2CH_2C(O)OCH_3$)$Mn(CO)_3$ (VI) and (η^5-$C_5H_4CH_2CH_2C(O)OCH_2CH_3$)$Mn(CO)_3$ (VII)

The compounds were synthesized as discussed for (η^5-$C_5H_4CH_2C(O)OCH_3$)$Mn(CO)_3$ and (η^5-$C_5H_4CH_2C(O)OCH_2CH_3$)$Mn(CO)_3$. The crude product was chromatographed twice as descibed previously to obtain the two pure compounds. The products, (η^5-$C_5H_4CH_2CH_2C(O)OCH_3$)$Mn(CO)_3$ (31.6% yield) and (η^5-$C_5H_4CH_2CH_2C(O)OCH_2CH_3$)$Mn(CO)_3$ (47.3% yield), were characterized individually. For **VI**: Found: C, 49.92; H, 3.87; calcd.: C, 49.67; H, 3.82. For **VII**: Found: C, 51.20; H, 4.30; calcd.: C, 51.33; H, 4.31.

3.12. Synthesis of $Tl(C_5H_4CH_2CH_2C(O)OCH_3)$

Similar procedure to that described for $Tl(C_5H_4CH_2C(O)OCH_3)$ but the mixture of NaCp and methyl bromopropionate was stirred under −60°C for 19 h before being deprotonated by $TlOCH_3$. The obtained $Tl(C_5H_4CH_2CH_2C(O)OCH_3)$ contained ~23% TlCp (determined from ^{1}H NMR spectrum). **VI** can be synthesized from this thallium salt using a procedure described previously.

3.13. Synthesis of $Na(C_5H_4CH_2CH_2OCH_3)$

2-Bromoethyl methyl ether (15.71 g, 0.11 mol) was added to 0.1 moles NaCp in 60 ml THF, and the mixture was stirred at −20°C for 2 h. The solid NaBr was filtered off, and the filtrate (containing $C_5H_5CH_2CH_2OCH_3$) was reacted with Na sand (0.1 mol). The volume of THF was reduced to ~50 ml and the sodium salt was separated by filtration. The vacuum dried solid was characterized by NMR. ^{1}H NMR (DMSO-d_6) δ 5.37 (br, 2 H, H(2,5)), 5.20 (br, 2 H, H(3,4)), 3.35 (t, 2 H, $-CH_2-$), 3.21 (s, 3 H, $-OCH_3$), 2.61 (t, 2 H, $-CH_2-$).

3.14. Synthesis of (η^5-$C_5H_4CH_2CH_2OCH_3$)$Mn(CO)_3$ (VIII)

$Na(C_5H_4CH_2CH_2OCH_3)$ (0.798 g; 5.5 mmol) and 1.5 g of bromopentacarbonylmanganese in 100 ml of THF were refluxed for 5 h. The solid NaBr was separated by filtration, and the solvent removed from the filtrate under vacuum. The yellow-brown liquid was purified by chromatography (diameter 4 cm and height of 40 cm) with an ethyl acetate + benzene elutant (1/19 by volume). The solvent was removed from the desired fraction to yield a pure yellow liquid (31.5% yield). (Found: C, 50.44; H, 4.20; Mn, 21.54; calcd.: C, 50.40; H, 4.23; Mn, 20.96).

3.15. Synthesis of $Tl(C_5H_4CH_2CH_2OC(O)CH_3)$

NaCp (0.1 mol in 60 ml THF) was reacted with 2-bromoethyl acetate at −20°C as described for $Na(C_5H_5CH_2CH_2OCH_3)$. The solid sodium bromide was separated by filtration, and the $C_5H_5CH_2CH_2O_2CCH_3$ reacted with $TlOC_2H_5$. The yellow-brown solid

was filtered and vacuum dried. ^{1}H NMR (DMSO-d_6) δ 5.76 (t, 2 H, H(2,5)), 5.67 (t, 2 H, H(3,4)), 3.50 (t, 2 H, $-CH_2O-$), 2.54 (t, 2 H, $-CH_2O-$), 1.99 (s, 3 H, $-CH_3$); a resonance for TlCp impurity was present.

3.16. Synthesis of $(\eta^5$-$C_5H_4CH_2CH_2O_2CCH_3)Mn(CO)_3$ (IX)

Bromopentacarbonylmanganese (1.67 g, 6.1 mmol) was reacted with 2.0 g of $Tl(C_5H_4CH_2CH_2OC(O)CH_3)$ in 100 ml of THF. The mixture was refluxed for 5 h, cooled, and the TlBr was separated by filtration. The solvent was removed under vacuum, and the yellow liquid was purified by chromatography (diameter 4 cm, height 40 cm) with 5% ethyl acetate in benzene as the elutant. This column separated unreacted bromopentacarbonylmanganese. $CpMn(CO)_3$ was separated on a second column (diameter 2.5 cm height 23 cm) with benzene as the eluting solvent. After evaporation of the solvent, a yellow liquid remained (4.54% yield). Found: C, 50.03; H, 3.86; Mn, 18.46; calcd.: C, 49.67; H, 3.82; Mn, 18.93.

3.17. Synthesis of $Na(C_5H_4C(O)CH_2CH_2SCH_3)$

K sand (1.72 g) was prepared in THF in a manner similar to that for the Na sand. The K sand in THF was cooled to -20°C, and 2.90 g of HCp were added. After stirring for 3 h no K remained, and a white precipitate was obtained. 3-Methylthiopropionyl chloride (6.09 g) was added to the solution and the white precipitate slowly disappeared to yield a brown solution. The brown solution was then reacted with Na sand (1.01 g) at 0°C over 4.5 h. The solvent was removed under vacuum, and a light brown solid mixture was obtained (it contained the product and the chloride salt). The solid was characterized by ^{1}H NMR. ^{1}H NMR (DMSO-d_6) δ 6.12 (t, 2 H, H(2,5)), 5.60 (d, 2 H, H(3,4)), 2.70–2.62 (m, 4 H, $-CH_2CH_2-$), 2.04 (s, 3 H, $-SCH_3$).

3.18. Synthesis of $(\eta^5$-$C_5H_4C(O)CH_2CH_2SCH_3)Mn(CO)_3$ (XI)

Similar procedure to that desribed for $(\eta^5$-$C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$. The product was isolated by column chromatography with benzene as the elutant. The yield was 45.9%. Found: C, 48.20; H, 3.68; Mn, 16.64; S, 10.09; calcd.: C, 47.07; H, 3.62; Mn, 17.94; S, 10.47.

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