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Wittig and Reformatsky chemistry of the formyl and acetyl derivatives of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$

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Abstract

Formyl and acetyl derivatives of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(\eta^5\text{-}C_5H_5)Re(CO)_3$ react with the Wittig reagent CH_2PPh_3 to form vinyl and 2-propenyl derivatives, respectively. Reaction of the same formyl and acetyl derivatives with the Reformatsky complex formed from ethyl bromoacetate and zinc yields the expected hydroxy esters in good yield. Dehydration of these alcohols gives the corresponding ethyl propenoate and ethyl butenoate products in excellent yield. All compounds have been fully characterized by IR, ^1H and ^{13}C NMR, mass spectrometry and elemental analysis.

Molecules which have potential application as nonlinear optical materials are typically characterized by extensive π-electron conjugation, charge transfer ability, and acentric crystal structures [1]. There is a growing recognition that structurally tailored organometallic complexes have promise in these applications [2]. With the exception of the work by Frazier and co-workers, who have examined (arene)chromiumtricarbonyl compounds, studies of optical nonlinearity in organometallic complexes have focused on ferrocene and its derivatives because of the extensive organic chemistry that is available for the structural elaboration of ferrocene. We believe that the wide range of electronic properties available to arene and cyclopentadienyl and metal complexes would make it possible to fine tune nonlinear optical behavior by judicious selection of the metal and secondary ligands.

In addition to their interest as nonlinear optical materials, organometallic species with conjugated side chains are potential monomers for the formation of

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organometallic polymers. The application of vinylcyclopentadienyl metal compounds and styrenechromiumtricarbonyl have been discussed in recent reviews [3].

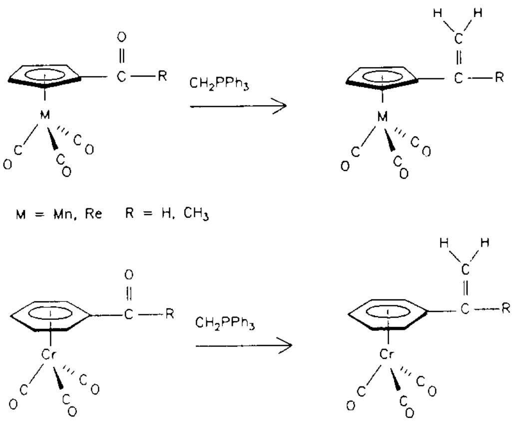
We have for some time been concerned with the development of ring functionalized arene and cyclopentadienyl organometallic compounds. In contrast to the rich organic chemistry of ferrocene, very few workers have examined the organic chemistry of functional groups on arene or cyclopentadienyl metal carbonyl compounds. Some publications have described Wittig reactions for (benzaldehyde)chromiumtricarbonyl, while none have been reported for the cyclopentadienylmanganesetricarbonyl or cyclopentadienylrheniumtricarbonyl series [4]. Arsonium ylides have been employed by Mioskowski and co-workers for the synthesis of vinylic epoxide derivatives of (benzaldehyde)chromiumtricarbonyl [5]. Federic and Toma [6] have reported a Michael addition to (formylcyclopentadienyl)manganesetricarbonyl. To our knowledge, no Reformatsky chemistry has been reported for organometallic compounds other than ferrocene. We wish to describe our recent work on the elaboration of formyl and acetyl groups on organometallic complexes of $(\eta^6\text{-RC}_6\text{H}_5)\text{Cr(CO)}_3$, where R = CHO (**1a**) and R = COCH_3 (**1b**), $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn(CO)}_3$, where R = CHO (**2a**) and R = COCH_3 (**2b**) and $(\eta^5\text{-RC}_5\text{H}_4)\text{Re(CO)}_3$, where R = CHO (**3a**) and R = COCH_3 (**3b**) using Wittig and Reformatsky reagents. After submission of this paper, we became aware of the studies by Miller *et al.* [7], on the Wittig chemistry of (acetylcyclopentadienyl)manganesetricarbonyl and acetylferrocene which are presented in the preceding paper.

Results and discussion

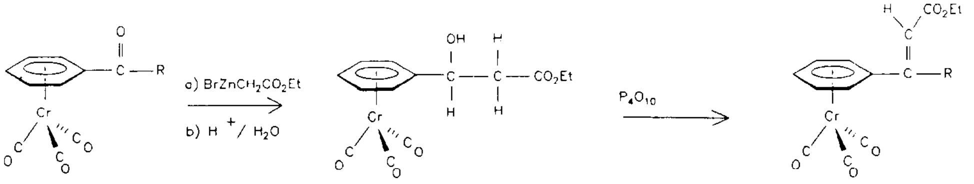
Vinylsubstituted organometallic complexes have been examined because of their application in the formation of organometallic containing polymers. For cyclopentadienylmanganesetricarbonyl, the vinyl group is typically introduced by dehydration of 1-(cyclopentadienylmanganesetricarbonyl)-ethan-1-ol, which is itself prepared by reduction of (acetylcyclopentadienyl)manganesetricarbonyl [8]. Styrene chromium tricarbonyl is prepared by direct metallation of styrene [9].

We have found that reaction of $\text{CH}_2\text{=PPh}_3$ (from $\text{CH}_3\text{PPh}_3\text{Br}$ and n-butyl lithium) with **1a**, **2a** or **3a** according to the procedure of Wittig and Schoellkopf [10] results in the formation of the corresponding vinyl derivatives, whereas reaction with **1b**, **2b** or **3b** yields the 1-methylvinyl derivatives. These reactions are summarized in Scheme 1. All products were recovered in good to very good yield and have been fully characterized using IR, ^{1}H and ^{13}C NMR, mass spectroscopy and elemental analysis. The vinyl proton resonances form a characteristic ABX pattern for the formulation $\text{RH}_\text{X} = \text{CH}_\text{A}\text{H}_\text{B}$, where H_A is *Z* to the organometallic moiety. (Vinylcyclopentadienyl)manganesetricarbonyl and styrenechromiumtricarbonyl prepared by this route are identical to samples prepared by published procedures. We believe that this route is superior to the dehydration route for (vinylcyclopentadienyl)manganesetricarbonyl as it avoids the high temperature flash distillation which leads to thermal polymerization. We have also utilized appropriate Wittig reagents for the synthesis of butadiene substituted derivatives of this series of metal complexes [11].

The Reformatsky reaction is an excellent method for the introduction of β-hydroxy esters into compounds [12]. We have examined the reaction of ethyl



Scheme 1.



Scheme 2.

bromoacetate with the formyl and acetyl complexes described above, and have found that the corresponding β-hydroxy esters are produced in very good yield from these reactions. These reactions are summarized in Scheme 2.

^{1}H NMR spectra of the β-hydroxy esters are consistent with the assigned structures. Of particular interest is the observation that the two geminal protons, H_A and H_B of $(CO)_3Re[\eta^5\text{-}C_5H_4CH_X(OH)CH_AH_BCO_2CH_2CH_3]$ are magnetically inequivalent and couple with H_X on the hydroxy bearing with coupling constants of 4.0 and 8.6 Hz. Models suggest that hydrogen bonding between the alcohol and the ester carbonyl will fix the relative geometry of the hydrogens on these two carbons (Fig. 1) so that one pair has a dihedral angle of 45° while the second has a dihedral angle of about 165°. The hydrogen bonding creates a

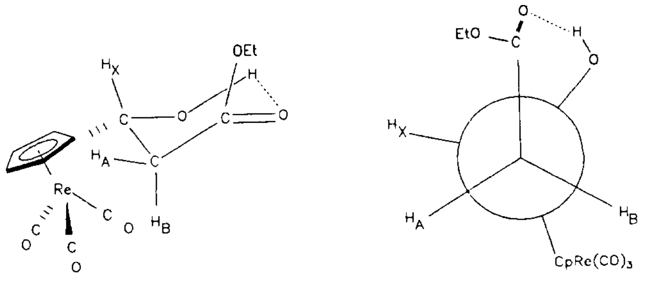


Fig. 1.

six-membered ring which assumes a chair conformation. The coupling constants predicted by the Karplus relationship are in excellent agreement with the observed values [13].

Dehydration of the hydroxypropionate esters with P_4O_{10} in refluxing benzene gave the expected acrylic esters in excellent yield. Again, all compounds have been fully characterized. HPLC and NMR analyses of the reaction products from these dehydrations indicated that only a single isomer was produced in these reactions. Coupling constants between the vinyl protons of these compounds are about 16 Hz which is in the range expected for an *E* isomer. Similar dehydration of the 3-hydroxybutyrate esters gave a single alkene product which we believe to be the *E* isomer with the organometallic moiety *trans* to the ester group. The 1.2 Hz (Re) and 1.5 Hz (Cr) coupling constants observed between the methyl and vinyl hydrogen are suggestive, but not diagnostic, of an *E* relationship between these two groups.

The remarkable ease with which these model compounds can be elaborated using Wittig and Reformatsky techniques to give conjugated derivatives strongly suggests that this methodology can play an important role in the synthesis of compounds for the study of nonlinear optical properties.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on an IBM NR-300 MHz NMR spectrometer or a JEOL FX-90Q NMR spectrometer and referenced to appropriate solvent resonances. IR spectra were recorded on a Bio-Rad Qualimatic FTIR with a resolution of 2 cm^{-1}. HPLC analyses were conducted on a GowMac HPLC with a silica gel column using 30% THF in petroleum ether as an eluant. Mass spectra were recorded by Dr. Garry Knerr using a VG 7070 HS mass spectrometer using direct insertion. Elemental analyses were carried out by Desert Analytics of Tucson, Arizona.

All solvents were dried and distilled under nitrogen. Preparative column chromatography was carried out using nitrogen flushed solvents and neutral (CAMAG) alumina. Methyltriphenylphosphonium bromide was purchased from Alfa, Inc. n-Butyl lithium and ethyl bromoacetate were purchased from Aldrich. **1a** [14], **1b** [15], **2a**, **2b**, **3a** and **3b** [16] were prepared by published procedures. All yields are the highest yields obtained with only modest effort being directed toward establishing optimal conditions.

Synthesis of (vinylcyclopentadienyl)manganesetricarbonyl $(\eta^5\text{-}C_5H_4C_2H_3)Mn(CO)_3$

A solution of n-butyl lithium (1.4 mmol) in anhydrous ethyl ether was added to a suspension of finely powdered CH_3PPh_3Br (0.500 g, 1.4 mmol), in ethyl ether (10 mL), and the resulting yellow solution was stirred for 4 h at room temperature. **2b** (0.325 g, 1.4 mmol), in ethyl ether (10 mL) was added dropwise, and the cloudy solution was heated under reflux overnight. The solution was cooled to room temperature, filtered and the solvent removed at 0°C using a rotary evaporator. The resulting residue was chromatographed on alumina using pentane as an eluant. A single yellow band was observed which was collected. Evaporation of the solvent gave 0.235 g of the known vinylcymantrene as a yellow oil, yield: 73%. IR (CH_2Cl_2): 2021, 1937 and 1634 cm^{-1}. ^{1}H NMR ($CDCl_3$): 6.25 (dd, 1H, J_{AX} = 17.6,

J_{BX} = 10.7 Hz, H_X); 5.47 (dd, 1H, J_{AX} = 17.6, J_{AB} = 1.0 Hz, H_A); 5.18 (dd, 1 H, J_{BX} = 10.7, J_{AB} = 1.0 Hz, H_B); 4.91 (A_2B_2 t, 2H); 4.70 (A_2B_2 t, 2H). ^{13}C NMR ($CDCl_3$): 224.8 (Mn – CO); 129.1 (vinyl); 115.6 (vinyl); 100.8 (*ipso*-Cp); 82.1 (Cp); 81.1 (Cp). MS (CI): 230 (M^+), 202 ($M^+ - CO$), 174 ($M^+ - 2$ CO), 146 ($M^+ - 3$ CO).

All Wittig reactions were carried out using the procedure described above.

(2-Propenylcyclopentadienyl)manganesetricarbonyl $[\eta^5\text{-}C_5H_4C(CH_3)=CH_2]Mn(CO)_3$

Yellow oil. Yield: 73%. IR (CH_2Cl_2): 2021, 1937 and 1637 cm^{-1}. ^1H NMR ($CDCl_3$): 5.24 (d, 1H, vinyl); 4.94 (m, 3H, vinyl and Cp); 4.69 (A_2B_2 t, 2H, Cp); 1.92 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 224.3 (Mn–CO); 135.9 (vinyl); 112.5 (vinyl, $=CH_2$); 103.7 (*ipso*-Cp); 81.9 (Cp); 80.7 (*C*p); 20.9 (CH_3). MS (CI): 244 (M^+), 216 ($M^+ - CO$), 188 ($M^+ - 2$ CO), 160 ($M^+ - 3$ CO). Anal. Found: C, 54.09; H, 3.68. $C_{11}H_9MnO_3$ calc.: C, 53.68; H, 3.98%.

(Vinylcyclopentadienyl)rheniumtricarbonyl $(\eta^5\text{-}C_5H_4C_2H_3)Re(CO)_3$

White solid, m.p. 42–43°C. Yield: 70.5%. IR (CH_2Cl_2): 2023, 1927 and 1635 cm^{-1}. ^1H NMR ($CDCl_3$): 6.30 (dd, 1 H, J_{AX} = 17.5, J_{BX} = 10.8 Hz, H_X); 5.50 (A_2B_2 t, 2H, Cp); 5.47 (d, 1H, J_{AX} = 17.5 Hz, H_A); 5.30 (A_2B_2 t, 2H, Cp); 5.14 (d, 1H, J_{BX} = 10.8 Hz, H_B). ^{13}C NMR ($CDCl_3$): 193.4 (Re–CO); 127.7 (vinyl); 116.1 (vinyl, $=CH_2$); 105.2 (*ipso*-Cp); 84.1 (Cp); 81.8 (Cp). MS (CI) (^{187}Re): 362 (M^+), 334 ($M^+ - CO$), 306 ($M^+ - 2$ CO), 278 ($M^+ - 3$ CO). Anal. Found: C, 33.30, H, 1.83. $C_{10}H_7ReO_3$ calc.: C, 33.24; H, 1.94%.

(2-Propenylcyclopentadienyl)rheniumtricarbonyl $[\eta^5\text{-}C_5H_4C(CH_3)=CH_2]Re(CO)_3$

White solid, m.p. 44–45°C. Yield: 68%. IR (CH_2Cl_2): 2022, 1924 and 1637 cm^{-1}. ^1H NMR ($CDCl_3$): 5.53 (A_2B_2 t, 2H, Cp); 5.30 (m, 3H, vinyl and Cp); 4.95 (s, 1H, vinyl); 1.92 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 194.0 (Re–CO); 135.0 (vinyl); 112.9 (vinyl, CH_2); 108.4 (*ipso*-Cp); 83.7 (Cp); 81.6 (Cp); 21.2 (CH_3). MS (CI) (^{187}Re): 376 (M^+), 348 ($M^+ - CO$), 320 ($M^+ - 2$ CO), 292 ($M^+ - 3$ CO). Anal. Found: C, 35.31, H, 2.36. $C_{11}H_9ReO_3$ calc.: C, 35.20; H, 2.40%.

Styrenechromiumtricarbonyl $(\eta^6\text{-}C_6H_5C_2H_3)Cr(CO)_3$

Yellow solid, m.p. 78–79°C (lit 80–81°C [5]). Yield: 73%. IR (CH_2Cl_2): 1969, 1895 and 1630 cm^{-1}. ^1H NMR ($CDCl_3$): 6.30 (dd, 1H, J_{AX} = 17.4, J_{BX} = 10.8 Hz, H_X); 5.65 (d, 1H, J_{AX} = 17.4, H_A); 5.44–5.2 (m, 6H, phenyl, H_B). ^{13}C NMR ($CDCl_3$): 232.8 (Cr–CO); 133.6 (vinyl); 116.5 (vinyl, $=CH_2$); 105.5 (*ipso*-Ph); 92.6 (Ph); 91.3 (Ph); 90.6 (Ph). MS (CI): 240 (M^+), 212 ($M^+ - CO$), 184 ($M^+ - 2$ CO), 156 ($M^+ - 3$ CO).

(2-Propenyl)benzenechromiumtricarbonyl $[\eta^6\text{-}C_6H_5C(CH_3)=CH_2]Cr(CO)_3$

Yellow solid, m.p. 80–81°C. Yield: 68%. IR (CH_2Cl_2): 1968, 1892 and 1630 cm^{-1}. ^1H NMR ($CDCl_3$): 5.54–5.49 (m, 2H); 5.41–5.30 (m, 4H); 5.13 (s, 1H); 2.03 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 232.8 (Cr–CO); 139.5 (vinyl); 114.7 (vinyl, $=CH_2$); 109.5 (*ipso*-Ph); 92.0 (Ph); 91.9 (Ph); 90.6 (Ph); 20.7 (CH_3). MS (CI): 254 (M^+), 226 ($M^+ - CO$), 198 ($M^+ - 2$ CO), 170 ($M^+ - 3$ CO). Anal. Found: C, 56.69; H, 3.94. $C_{12}H_{10}CrO_3$ calc.: C, 56.44; H, 3.79%.

Synthesis of ethyl 3-(cyclopentadienylmanganesetricarbonyl)-3-hydroxypropionate $(CO)_3Mn[\eta^5\text{-}C_5H_4CH(OH)CH_2CO_2C_2H_5]$

An oven-dried 100 mL three-necked flask with spin bar, addition funnel and reflux condenser was charged with activated zinc dust (0.29 g, 4.5 mmol), and anhydrous bis(methoxy)ethane (5 mL). A mixture of ethyl bromoacetate (0.75 g, 4.5 mmol) and bis(methoxy)ethane (10 mL) was added dropwise and the solution stirred for 2 h at 40–50°C. At the end of this time, **2a** (0.35 g, 1.5 mmol) in bis(methoxy)ethane (10 mL) was added dropwise and the mixture stirred under reflux overnight. The reaction mixture was cooled in an ice bath and stirred vigorously while 10% sulfuric acid (10 mL) was added to destroy the zinc complex. The aqueous layer was removed by dropper and the organic phase was washed with water until neutral and then dried over magnesium sulfate. The mixture was filtered and the solvent removed by rotary evaporator. The resulting residue was chromatographed on an alumina column. Elution with a 57:40:3 petroleum ether/dichloromethane/methanol (57:40:3) solution eluted a single yellow band. After evaporation of the solvent, this gave 0.31 g of ethyl 3-(cyclopentadienylmanganesetricarbonyl)-3-hydroxypropionate as a yellow oil, yield: 64.5%. IR (CH_2Cl_2): 3600–3400 (broad), 2024s, 1942s, 1722m. ^{1}H NMR ($CDCl_3$): 4.88 (s, 1H, C(OH)*H*); 4.79 (A_2B_2 t, 2H, Cp); 4.63 (A_2B_2 t, 2H, Cp); 4.17 (q, 2H, J = 6.8 Hz, C*H*$_2$CH$_3$); 3.23 (s, 1H, O*H*); 2.66 (d, 2H, CH(OH)–C*H*$_2$); 1.27 (t, 3H, J = 6.8 Hz, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$): 224.5 (Mn–CO); 171.6 (*C*O$_2$); 106.7 (*ipso*-Cp); 82.0 (Cp); 81.6 (Cp); 81.5 (Cp); 80.8 (Cp); 64.3 (*C*H(OH)CH$_2$); 61.0 (CH(OH)*C*H$_2$); 42.6 (*C*H$_2$CH$_3$); 13.8 (CH$_2$*C*H$_3$). MS (FAB): 319 ($M^+ - 1$); (CI) 302 ($M^+ - H_2O$), 292 ($M^+ -$ CO), 264 ($M^+ -$ 2 CO), 236 ($M^+ -$ 3 CO). Anal. Found: C, 48.89; H, 4.25. $C_{13}H_{13}MnO_6$ calc.: C, 48.75; H, 4.06%.

Note: All β-hydroxy complexes were prepared by a similar route.

Ethyl 3-(Cyclopentadienylmanganesetricarbonyl)-3-hydroxybutyrate $(CO)_3Mn[\eta^5\text{-}C_5H_4C(CH_3)(OH)CH_2CO_2C_2H_5]$

Yellow oil, yield: 62%. IR (CH_2Cl_2): 3600–3400 (broad), 2022s, 1932s, 1715m. ^{1}H NMR ($CDCl_3$): 4.93–4.83 (m, 2H, Cp), 4.62–4.54 (m, 2H, Cp); 4.18 (q, 2H, C*H*$_2$CH$_3$); 4.00 (s, 1H, O*H*); 2.67 (s, 2H, C(CH$_3$)(OH)C*H*$_2$); 1.51 (s, 3H, C(C*H*$_3$)(OH)); 1.26 (t, 3H, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$): 224.7 (Mn–CO); 171.8 (CO$_2$); 112.3 (*ipso*-Cp); 83.9 (Cp); 82.8 (Cp); 80.7 (Cp); 79.9 (Cp); 68.7 (*C*H(OH)CH$_2$); 6.10 (CH(OH)*C*H$_2$); 47.6 (*C*H$_2$CH$_3$); 30.0 (C(*C*H$_3$)(OH)); 14.1 (CH$_2$*C*H$_3$). MS (FAB): 333 ($M^+ - 1$), 306 ($M^+ -$ CO), 278 ($M^+ -$ 2 CO), 250 ($M^+ -$ 3 CO); (CI) 317 ($M^+ -$ OH), 250 ($M^+ -$ 3 CO). Anal. Found: C, 50.39; H, 4.51. $C_{14}H_{15}MnO_6$ calc.: C, 50.29; H, 4.49%.

Ethyl 3-(cyclopentadienylrheniumtricarbonyl)-3-hydroxypropionate $(CO)_3Re[\eta^5\text{-}C_5H_4CH(OH)CH_2CO_2C_2H_5]$

Yellow oil, yield: 60%. IR (CH_2Cl_2): 3600–3450 (broad); 2026s, 1935s, 1723m. ^{1}H NMR ($CDCl_3$): 5.45 (A_2B_2 t, 2H, Cp); 5.27 (A_2B_2 t, 2H, Cp); 4.91–4.77 (dd, 1H, J_{AX} = 8.6, J_{BX} = 4.0 Hz, C*H*$_X$(OH)CH$_2$); 4.18 (q, 2H, J = 7.3 Hz, C*H*$_2$CH$_3$); 3.29 (s, 1H, O*H*); 2.67 (d, 1H, J_{BX} = 4.0 Hz, CH(OH)C*H*$_2$); 2.64 (d, 1H, J_{AX} = 8.6 Hz, CH(OH)C*H*$_2$); 1.27 (t, 3H, J = 7.3 Hz, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$): 193.7 (Re–CO); 171.7 (*C*O$_2$); 111.1 (*ipso*-Cp); 83.6 (Cp); 83.2 (Cp); 83.1 (2 carbons, Cp); 64.1 (*C*H(OH)CH$_2$); 61.2 (CH(OH)*C*H$_2$); 43.1 (*C*H$_2$CH$_3$); 14.1 (CH$_2$*C*H$_3$). MS

89%. IR ($\mathrm{CH_2Cl_2}$): 2025s, 1940s, 1711s, 1646m cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): 7.23 (d, 1H, $J = 15.8$ Hz, vinyl); 6.09 (d, 1H, $J = 15.8$ Hz, vinyl); 5.09 ($\mathrm{A_2B_2}$ t, 2H, Cp); 4.80 ($\mathrm{A_2B_2}$ t, 2H, Cp); 4.23 (q, 2H, $J = 7.1$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$); 1.31 (t, 3H, $J = 7.1$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$): 223.8 (Mn–CO); 166.0 ($C\mathrm{O_2}$); 137.7 (vinyl); 119.1 (vinyl); 93.8 (*ipso*-Cp); 84.1 (Cp); 82.9 (Cp); 60.6 ($C\mathrm{H_2CH_3}$); 14.0 ($\mathrm{CH_2}C\mathrm{H_3}$). MS (CI): 302 ($M^+$), 274 ($M^+ -$ CO), 246 ($M^+ -$ 2 CO), 218 ($M^+ -$ 3 CO). Anal. Found: C, 51.78; H, 3.72. $\mathrm{C_{13}H_{11}MnO_5}$ calc.: C, 51.70; H, 3.64%.

Ethyl E-3-*(cyclopentadienylmanganesetricarbonyl)butenoate* $(CO)_3Mn[\eta^5\text{-}C_5H_4C(CH_3)=CHCO_2C_2H_5]$

Orange solid, m.p. 61–62°C. Yield: 91%. IR ($\mathrm{CH_2Cl_2}$): 2024s, 1940s, 1709s, 1631m cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): 6.06 (s, 1H, vinyl); 5.12 ($\mathrm{A_2B_2}$ t, 2H, Cp); 4.78 ($\mathrm{A_2B_2}$ t, 2H, Cp); 4.78 (q, 2H, $J = 6.8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$); 2.34 (s, 3H, $\mathrm{C}H_3$); 1.30 (t, 3H, $J = 6.8$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$): 224.0 (Mn–CO), 166.1 ($C\mathrm{O_2}$); 148.0 ($\mathrm{CpMn}C\mathrm{(CH_3)}$); 115.3 ($C\mathrm{HCO_2Et}$); 101.1 (*ipso*-Cp); 82.7 (Cp); 82.6 (Cp); 60.1 ($C\mathrm{H_2CH_3}$); 16.7 ($C\mathrm{H_3}$); 14.3 ($\mathrm{CH_2}C\mathrm{H_3}$). MS (CI): 316 ($M^+$), 260 ($M^+ -$ 2 CO), 232 ($M^+ -$ 3 CO). Anal. Found: C, 53.64; H, 4.42. $\mathrm{C_{14}H_{13}MnO_5}$ calc.: C, 53.16; H, 4.11%.

Ethyl E-3-*(cyclopentadienylrheniumtricarbonyl)propenoate* $(CO)_3Re[\eta^5\text{-}C_5H_4CH=CHCO_2C_2H_5]$

Light yellow solid, m.p. 90–91°C. Yield: 95%. IR ($\mathrm{CH_2Cl_2}$): 2028s, 1937s, 1710s, 1646m cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): 7.29 (d, 1H, $J = 16$ Hz, vinyl); 6.09 (d, 1H, $J = 16.1$ Hz, vinyl); 5.67 ($\mathrm{A_2B_2}$ t, 2H, Cp); 5.36 ($\mathrm{A_2B_2}$ t, 2H, Cp); 4.22 (q, 2H, $J = 7.3$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$); 1.30 (t, 3H, $J = 7.3$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$): 192.9 (Re–CO); 165.9 ($C\mathrm{O_2}$); 136.0 ($\mathrm{Cp}C\mathrm{H}$, vinyl); 119.1 ($\mathrm{H}C\mathrm{CO_2}$, vinyl); 97.7 (*ipso*-Cp); 85.2 (Cp); 84.7 (Cp); 60.8 ($C\mathrm{H_2CH_3}$); 14.2 ($\mathrm{CH_2}C\mathrm{H_3}$). MS (CI)(^{187}Re): 434 (M^+), 406 ($M^+ -$ CO), 378 ($M^+ -$ 2 CO), 350 ($M^+ -$ 3 CO). Anal. Found: C, 36.24; H, 2.57. $\mathrm{C_{13}H_{11}ReO_5}$ calc.: C, 36.02; H, 2.54%.

Ethyl E-3-*(cyclopentadienylrheniumtricarbonyl)butenoate* $(CO)_3Re[\eta^5\text{-}C_5H_4C(CH_3)=CHCO_2C_2H_5]$

Light yellow solid, m.p. 79–80°C. Yield: 94%. IR ($\mathrm{CH_2Cl_2}$): 2027s, 1939s, 1710s, 1632m cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): 6.08 (q, 1H, $J = 1.2$ Hz, vinyl); 5.68 ($\mathrm{A_2B_2}$ t, 2H, Cp); 5.35 ($\mathrm{A_2B_2}$ t, 2H, Cp); 4.18 (q, 2H, $J = 6.8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$); 2.33 (d, 3H, $J = 1.2$ Hz, $\mathrm{C}H_3$); 1.30 (t, 3H, $J = 6.8$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$): 193.0 (Re–CO); 165.9 ($C\mathrm{O_2}$); 146.3 ($\mathrm{CpRe}C\mathrm{(CH_3)}$); 115.8 ($C\mathrm{HCO_2Et}$); 105.7 (*ipso*-Cp); 84.3 (Cp); 83.7 (Cp); 60.1 ($C\mathrm{H_2CH_3}$); 17.1 ($C\mathrm{H_3}$); 14.2 ($\mathrm{CH_2}C\mathrm{H_3}$). MS (CI)(^{187}Re): 448 (M^+), 420 ($M^+ -$ CO), 392 ($M^+ -$ 2 CO), 364 ($M^+ -$ 3 CO). Anal. Found: C, 37.63; H, 2.82. $\mathrm{C_{14}H_{13}ReO_5}$ calc.: C, 37.58; H, 2.91%.

Ethyl E-3-*(phenylchromiumtricarbonyl)propenoate* $(CO)_3Cr[\eta^6\text{-}C_6H_5CH=CHCO_2C_2H_5]$

Red-orange solid, m.p. 106–107°C. Yield: 67%. IR ($\mathrm{CH_2Cl_2}$): 1976s, 1904s, 1711s, 1641m cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): 7.20 (d, 1H, $J = 15.6$ Hz, vinyl); 6.25 (d, 1H, $J = 15.6$ Hz, vinyl); 5.54 (d, 2H, *ortho*-Ph); 5.44 (t, 1H, *para*-Ph); 5.33 (t, 2H, *meta*-Ph); 4.26 (q, 2H, $J = 7.2$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$); 1.33 (t, 3H, $J = 7.2$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$): 231.6 (Cr–CO); 165.7 ($C\mathrm{O_2}$); 141.3 ($\mathrm{Cp}C\mathrm{H}$, vinyl); 119.5

89%. IR (CH_2Cl_2): 2025s, 1940s, 1711s, 1646m cm^{-1}. ^1H NMR ($CDCl_3$): 7.23 (d, 1H, J = 15.8 Hz, vinyl); 6.09 (d, 1H, J = 15.8 Hz, vinyl); 5.09 (A_2B_2 t, 2H, Cp); 4.80 (A_2B_2 t, 2H, Cp); 4.23 (q, 2H, J = 7.1 Hz, $C\mathit{H}_2CH_3$); 1.31 (t, 3H, J = 7.1 Hz, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): 223.8 (Mn–CO); 166.0 ($\mathit{C}O_2$); 137.7 (vinyl); 119.1 (vinyl); 93.8 (*ipso*-Cp); 84.1 (Cp); 82.9 (Cp); 60.6 ($\mathit{C}H_2CH_3$); 14.0 ($CH_2\mathit{C}H_3$). MS (CI): 302 (M^+), 274 (M^+ − CO), 246 (M^+ − 2 CO), 218 (M^+ − 3 CO). Anal. Found: C, 51.78; H, 3.72. $C_{13}H_{11}MnO_5$ calc.: C, 51.70; H, 3.64%.

Ethyl E-3-*(cyclopentadienylmanganesetricarbonyl)butenoate* $(CO)_3Mn[\eta^5\text{-}C_5H_4C(CH_3)=CHCO_2C_2H_5]$

Orange solid, m.p. 61–62°C. Yield: 91%. IR (CH_2Cl_2): 2024s, 1940s, 1709s, 1631m cm^{-1}. ^1H NMR ($CDCl_3$): 6.06 (s, 1H, vinyl); 5.12 (A_2B_2 t, 2H, Cp); 4.78 (A_2B_2 t, 2H, Cp); 4.78 (q, 2H, J = 6.8 Hz, $C\mathit{H}_2CH_3$); 2.34 (s, 3H, $C\mathit{H}_3$); 1.30 (t, 3H, J = 6.8 Hz, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): 224.0 (Mn–CO), 166.1 ($\mathit{C}O_2$); 148.0 ($CpMn\mathit{C}(CH_3)$); 115.3 ($\mathit{C}HCO_2Et$); 101.1 (*ipso*-Cp); 82.7 (Cp); 82.6 (Cp); 60.1 ($\mathit{C}H_2CH_3$); 16.7 ($\mathit{C}H_3$); 14.3 ($CH_2\mathit{C}H_3$). MS (CI): 316 (M^+), 260 (M^+ − 2 CO), 232 (M^+ − 3 CO). Anal. Found: C, 53.64; H, 4.42. $C_{14}H_{13}MnO_5$ calc.: C, 53.16; H, 4.11%.

Ethyl E-3-*(cyclopentadienylrheniumtricarbonyl)propenoate* $(CO)_3Re[\eta^5\text{-}C_5H_4CH=CHCO_2C_2H_5]$

Light yellow solid, m.p. 90–91°C. Yield: 95%. IR (CH_2Cl_2): 2028s, 1937s, 1710s, 1646m cm^{-1}. ^1H NMR ($CDCl_3$): 7.29 (d, 1H, J = 16 Hz, vinyl); 6.09 (d, 1H, J = 16.1 Hz, vinyl); 5.67 (A_2B_2 t, 2H, Cp); 5.36 (A_2B_2 t, 2H, Cp); 4.22 (q, 2H, J = 7.3 Hz, $C\mathit{H}_2CH_3$); 1.30 (t, 3H, J = 7.3 Hz, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): 192.9 (Re–CO); 165.9 ($\mathit{C}O_2$); 136.0 ($Cp\mathit{C}H$, vinyl); 119.1 ($H\mathit{C}CO_2$, vinyl); 97.7 (*ipso*-Cp); 85.2 (Cp); 84.7 (Cp); 60.8 ($\mathit{C}H_2CH_3$); 14.2 ($CH_2\mathit{C}H_3$). MS (CI)(^{187}Re): 434 (M^+), 406 (M^+ − CO), 378 (M^+ − 2 CO), 350 (M^+ − 3 CO). Anal. Found: C, 36.24; H, 2.57. $C_{13}H_{11}ReO_5$ calc.: C, 36.02; H, 2.54%.

Ethyl E-3-*(cyclopentadienylrheniumtricarbonyl)butenoate* $(CO)_3Re[\eta^5\text{-}C_5H_4C(CH_3)=CHCO_2C_2H_5]$

Light yellow solid, m.p. 79–80°C. Yield: 94%. IR (CH_2Cl_2): 2027s, 1939s, 1710s, 1632m cm^{-1}. ^1H NMR ($CDCl_3$): 6.08 (q, 1H, J = 1.2 Hz, vinyl); 5.68 (A_2B_2 t, 2H, Cp); 5.35 (A_2B_2 t, 2H, Cp); 4.18 (q, 2H, J = 6.8 Hz, $C\mathit{H}_2CH_3$); 2.33 (d, 3H, J = 1.2 Hz, $C\mathit{H}_3$); 1.30 (t, 3H, J = 6.8 Hz, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): 193.0 (Re–CO); 165.9 ($\mathit{C}O_2$); 146.3 ($CpRe\mathit{C}(CH_3)$); 115.8 ($\mathit{C}HCO_2Et$); 105.7 (*ipso*-Cp); 84.3 (Cp); 83.7 (Cp); 60.1 ($\mathit{C}H_2CH_3$); 17.1 ($\mathit{C}H_3$); 14.2 ($CH_2\mathit{C}H_3$). MS (CI)(^{187}Re): 448 (M^+), 420 (M^+ − CO), 392 (M^+ − 2 CO), 364 (M^+ − 3 CO). Anal. Found: C, 37.63; H, 2.82. $C_{14}H_{13}ReO_5$ calc.: C, 37.58; H, 2.91%.

Ethyl E-3-*(phenylchromiumtricarbonyl)propenoate* $(CO)_3Cr[\eta^6\text{-}C_6H_5CH=CHCO_2C_2H_5]$

Red-orange solid, m.p. 106–107°C. Yield: 67%. IR (CH_2Cl_2): 1976s, 1904s, 1711s, 1641m cm^{-1}. ^1H NMR ($CDCl_3$): 7.20 (d, 1H, J = 15.6 Hz, vinyl); 6.25 (d, 1H, J = 15.6 Hz, vinyl); 5.54 (d, 2H, *ortho*-Ph); 5.44 (t, 1H, *para*-Ph); 5.33 (t, 2H, *meta*-Ph); 4.26 (q, 2H, J = 7.2 Hz, $C\mathit{H}_2CH_3$); 1.33 (t, 3H, J = 7.2 Hz, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): 231.6 (Cr–CO); 165.7 ($\mathit{C}O_2$); 141.3 ($Cp\mathit{C}H$, vinyl); 119.5

($HCCO_2$, vinyl); 98.8 (*ipso*-Ph); 92.8 (Ph); 92.6 (Ph); 90.1 (Ph); 60.9 (CH_2CH_3); 14.2 (CH_2CH_3). MS (CI): 312 (M^+), 256 ($M^+ - 2$ CO), 228 ($M^+ - 3$ CQ). Anal. Found: C, 54.26; H, 3.82. $C_{14}H_{12}CrO_5$ calc.: C, 53.85; H, 3.85%.

Ethyl E-3-*(phenylchromiumtricarbonyl)butenoate* $(CO)_3Cr[\eta^6\text{-}C_6H_5C(CH_3)=CH\text{-}CO_2C_2H_5]$

Orange solid, m.p. 74–75°C. Yield: 75%. IR (CH_2Cl_2): 1972s, 1900s, 1713s, 1630m cm^{-1}. ^1H NMR ($CDCl_3$): 6.16 (q, 1H, $J = 1.5$ Hz, vinyl); 5.57 (d, 2H, *meta*-Ph); 5.44 (t, 1H, *para*-Ph); 5.32 (t, 2H, *meta*-Ph); 4.21 (q, 2H, $J = 6.8$ Hz, CH_2CH_3); 2.44 (d, 3H, $J = 1.5$ Hz, CH_3); 1.31 (t, 3H, $J = 6.8$ Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$): 232.0 (Cr–CO); 165.8 (CO_2); 150.8 ($CpC(CH_3)$)); 118.2 ($CHCO_2Et$); 108.5 (*ipso*-Ph); 93.1 (Ph); 91.7 (Ph); 90.7 (Ph); 60.3 (CH_2CH_3); 17.0 (CH_3); 14.2 (CH_3CH_3). MS (CI): 326 (M^+), 270 ($M^+ - 2$ CO), 242 ($M^+ - 3$ CO). Anal. Found: C, 55.02; H, 4.32. $C_{15}H_{14}CrO_5$ calc.: C, 55.21; H, 4.29%.

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