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Convergent synthetic routes to heterobimetallic compounds: crystal and molecular structure of 1-(η^5-cyclopentadienyl manganese tricarbonyl) - 1-(η^6-phenyl chromium tricarbonyl) ethanol [1]

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Abstract

13 heterobimetallic compounds have been prepared by a convergent synthetic strategy employing reactions of a lithiocyclopentadienyl or lithioarene metal complex with formyl, acetyl or carbomethoxy functionalized derivatives of a second metal. The resulting lithium alkoxide products were converted to the corresponding alcohols by dilute acid work-up. Two methanol derivatives were successfully converted to their corresponding methane derivatives by reaction with trifluoroacetic acid followed by reaction of the resultant carbocation with sodium tetrahydroborate. Reaction of 1-[η^6-$C_6H_5Cr(CO)_3$]-1-[η^5-$C_5H_4Mn(CO)_3$]C_2H_3OH with trifluoroacetic acid results in dehydration to yield the corresponding ethene derivative. The molecular structure of 1-[η^6-$C_6H_5Cr(CO)_3$]-1-[η^5-$C_5H_4Mn(CO)_3$]C_2H_3OH was determined: monoclinic, $P2_1/c$, $a = 7.936(2)$, $b = 19.844(8)$, $c = 11.774(4)$ Å, $\beta = 91.58(2)°$, $V = 1853(1)$ Å^3, $Z = 4$, $R(F) = 4.52\%$.

Keywords: Half-sandwich; Heterobimetallic; Cyclopentadienyl; Carbonyl; Group 6; Group 7

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1. Introduction

Heterobimetallic compounds in which two metal atoms have the potential to bind to, or interact with, a substrate have been a target of research by this group and others for some time [1]. In particular we have been concerned with the synthesis of compounds in which two cyclopentadienyl metal (or arene/cyclopentadienyl) moieties are coupled through the rings [2]. Variation of the ring linkage allows flexibility in the relative positions of the metals. Linear routes to these compounds have been reported in which a second cyclopentadienyl ring is introduced onto one cyclopentadienyl metal group followed by metallation with a second metal [3]. In a few cases it has been possible to monometallate bis(cyclopentadienyl) ligands, leaving the second, unsubstituted ring free for subsequent chemistry [4]. In one remarkable case, the simultaneous introduction of two different metals was achieved without significant complications from homobimetallic substitution [5]. We have recently reported the facile synthesis of heterobimetallic compounds using 'twisted' ruthenium derivatives of the form $Ru(CO)_2(\eta^5,\eta^1\text{-}C_5H_4\text{–}CH_2\text{–}C_5H_4)$, in which the η^1-cyclopentadienyl ring is readily metallated [6]. Similar 'twisted' titanocene and zirconocene compounds have been shown to be heterobimetallic precursors by Green and coworkers [7].

The reaction of lithiocyclopentadienyl metal carbonyl intermediates with carbonyl groups to form carbinol derivatives is well known [8–10]. The availability of a number of formyl-, acetyl-, and carbomethoxyarene and cyclopentadienyl metal carbonyl derivatives [11] prompted us to examine a convergent route to heterobimetallic compounds. In this strategy, lithiocyclopentadienyl, or lithioarenemetal, intermediates are reacted with formyl-, acetyl-, and carboalkoxy derivatives of different metals as shown in Scheme 1 for the synthesis of a chromium/manganese heterobimetallic compound. This strategy has previously been employed by Kolobova et al. [9] for the synthesis of a pair of

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[1] Dedicated to our friend and colleague, Professor Dr. Max Herberhold, on the joyous occasion of his 60th birthday. Fröhlich Geburtstag!

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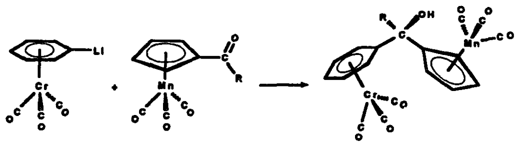


Scheme 1. Convergent synthetic strategy.

manganese homobimetallic compounds and a manganese/rhenium heterobimetallic compound. Reduction of the carbinol products has proved possible in a few cases.

2. Results and discussion

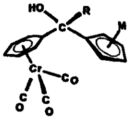
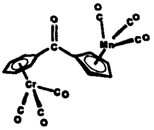
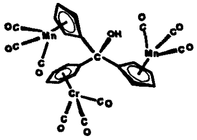
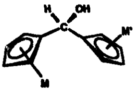
Formyl-, acetyl-, and carbomethoxy compounds were prepared by literature procedures [8–10]. Lithiation of cyclopentadienyl manganese tricarbonyl, cyclopentadienyl rhenium tricarbonyl, and benzene chromium tricarbonyl was carried out at −78 °C in THF using *n*-butyl lithium/TMEDA [12]. Lithiation of (η^5-C_5H_5)$W(CO)_3CH_3$, (η^5-C_5H_5)$Fe(CO)_2CH_3$ and (η^5-C_5H_5)$Fe(CO)_2CH_2C_6H_5$ was also carried out at −78 °C, but required *sec*-butyl lithium [10,13]. Addition of the organic carbonyl compound to the lithium reagent results in immediate reaction and formation of a lithium alkoxide precipitate. Dilute acid work-up of the reaction mixtures gave the product carbinol derivatives that were subsequently purified by column chromatography on alumina. Compounds prepared by this procedure are presented in Table 1.

In principle, all of the parent compounds in the present series undergo ring lithiation and ring carbonyl functionalized examples of each are known. The choice of which metal reactant would be lithiated and which would be ring functionalized was made on the basis of ease of preparation of the ring functionalized compounds. Thus all ethanol derivatives were prepared from acetophenone chromium tricarbonyl, and all but one (**6**) of the methanol derivatives were prepared from either formylcyclopentadienyl manganese tricarbonyl or formylcyclopentadienyl rhenium tricarbonyl.

In the case of the reaction of lithiocyclopentadienyl manganese tricarbonyl with methylbenzoate chromium tricarbonyl, two products were isolated. These were shown to be the known (η^5-cyclopentadienyl manganese tricarbonyl)(η^6-phenyl chromium tricarbonyl) ketone (**7**) resulting from simple substitution of the methoxy group by the lithio intermediate, and the trimetallic compound bis(η^5-cyclopentadienyl manganese tricarbonyl)(η^6-phenyl chromium tricarbonyl)carbinol (**8**) resulting from attack of excess lithio intermediate on **7**.

All compounds were characterized by IR, ^1H and ^{13}C NMR, mass spectrometry and elemental analysis. Alcohol resonances were confirmed by proton exchange with D_2O in deuterochloroform. In all cases, the IR spectra in the metal-carbonyl region of the bi- and trimetallic compounds are the simple addition of the carbonyl stretching bands of the starting materials. NMR spectra of the compounds were consistent with the expected

Table 1

Compound No.	M	R
		
1	$Mn(CO)_3$	H
2	$Mn(CO)_3$	CH_3
3	$Re(CO)_3$	H
4	$Re(CO)_3$	CH_3
5	$Fe(CO)_2CH_3$	CH_3
6	$Fe(CO)_2CH_2C_6H_5$	H
 **7**	 **8**	
		
	M	M′
9	$Fe(CO)_2CH_3$	$Mn(CO)_3$
10	$Fe(CO)_2CH_2C_6H_5$	$Mn(CO)_3$
11	$Fe(CO)_2CH_3$	$Re(CO)_3$
12	$W(CO)_3CH_3$	$Mn(CO)_3$
13	$W(CO)_3CH_3$	$Re(CO)_3$

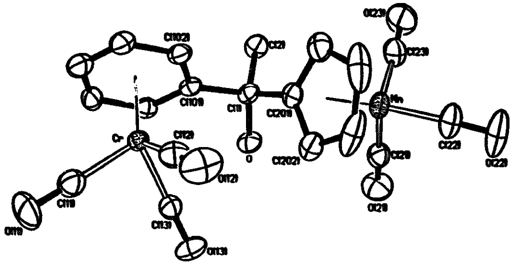


Fig. 1. Molecular structure of **2**.

Table 2
Crystallographic data for $C_{19}H_{13}CrMnO_7$

(a) Crystal parameters			
formula	$C_{19}H_{13}CrMnO_7$	V (Å^3)	1853(1)
formula weight	444.2	Z	4
crystal system	monoclinic	crystal dimensions (mm^3)	0.20 × 0.28 × 0.32
space group	$P2_1/c$	crystal color	yellow
a (Å)	7.936(2)	D_{calc} (g cm^3)	1.605
b (Å)	19.844(8)	(Mo Kα) (cm^{-1})	13.10
c (Å)	11.774(4)	temperature (K)	247
β (°)	91.58(2)	T(max)/T(min)	1.33
(b) Data collection			
diffractometer	Siemens P4	data collected (h,k,l)	±11, +23, +14
monochromator	graphite	reflections collected	3895
radiation	Mo Kα (λ = 0.71073 Å)	independent reflections	3727
2θ scan range (°)	4.0–50.0	independent observed reflections $F_o \geq 4\sigma(F_o)$	2560
(c) Refinement [a]			
$R(F)$ (%)	5.42	$\Delta(\rho)$ (e Å^{-3})	0.39
$R(wF)$ (%)	5.69	N_o/N_v	10.1
Δ/σ (max)	0.02	GOF	1.18

[a] Quantity minimized $\Sigma w\Delta^2$; $R = \Sigma\Delta/\Sigma(F_o)$; $R(w) = \Sigma\Delta w^{1/2}/\Sigma(F_o \cdot w^{1/2})$, $\Delta = |(F_o - F_c)|$.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Cr–C(11)	1.844(6)	C(11)–O(11)	1.148(7)
Cr–C(12)	1.836(5)	C(12)–O(12)	1.154(6)
Cr–C(13)	1.844(6)	C(13)–O(13)	1.154(5)
Mn–C(21)	1.779(5)	C(21)–O(21)	1.154(6)
Mn–C(22)	1.787(6)	C(22)–O(22)	1.153(8)
Mn–C(23)	1.783(6)	C(23)–O(23)	1.161(7)
C(1)–O	1.436(5)	C(1)–C(2)	1.515(6)
C(1)–C(101)	1.537(6)	C(1)–C(201)	1.514(6)
Cr–C(11)–O(11)	177.6(5)	Mn–C(21)–O(21)	178.2(5)
Cr–C(12)–O(12)	178.0(4)	Mn–C(22)–O(22)	177.2(5)
Cr–C(13)–O(13)	179.2(4)	Mn–C(23)–O(23)	176.2(5)
C(2)–C(1)–O	109.3(3)	C(101)–C(1)–C(201)	109.8(3)

structures. Ring and metal-carbonyl resonances could be assigned by comparison to the parent species.

X-ray quality single crystals of **2** were obtained from petroleum ether/dichloromethane. The molecular structure (Fig. 1) reveals that the two metal moieties assume a conformation between a *syn*- and *anti*-orientation. Analysis of the alcohol unit revealed no close contacts that might suggest hydrogen bonding between the alcohol and metals. All bond lengths and angles are within normal ranges for these classes of compounds. X-ray crystallographic data are summarized in Table 2. Selected bond lengths and angles are presented in Table 3.

Reaction of compounds **1** and **3** with trifluoroacetic acid followed by sodium tetrahydroborate yielded the corresponding methylene bridged products **14** and **15** respectively. Upon addition of trifluoroacetic acid the solutions turn deep blue, indicating the formation of an intermediate carbocation. Attempted use of a similar reduction technique on the ethanol derivative **2** resulted in dehydration to yield the ethylene derivative **16**. Again, all new compounds have been fully characterized.

Attempts to reduce the iron and tungsten derivatives **9** and **12** were unsuccessful. It was noted that deep colors indicative of carbocation formation did appear on acid addition, but that these colors faded rapidly prior to addition of sodium tetrahydroborate. We are unaware of any literature describing exocyclic carbocations of the $CpFe(CO)_2R$ or $CpW(CO)_3Me$ series, and are now initiating studies on these materials.

3. Experimental

All solvents were dried and distilled under nitrogen. Preparative chromatography was conducted using nitrogen flushed solvents and neutral (CAMAG) alumina. Infrared spectra were recorded on a Bio-Rad Qualimatic FTIR spectrometer operating at 2 cm^{-1} resolution. ^{1}H and ^{13}C NMR spectra were recorded on an IBM NR-300 MHz NMR spectrometer and were referenced to appropriate solvent resonances. Mass spectrometry was carried out by Dr. Gary Knerr of the University of Idaho on a VG 7070-HS GC/MS using direct insertion. Elemental analyses were carried out by Desert Analytics of Tuscon, AZ.

4. Experimental procedure for synthesis of carbinol compounds

The procedure listed below for the synthesis of **1** was used with slight modifications in the preparation of all new carbinol compounds. For compounds involving iron or tungsten moieties, *sec*-butyl lithium was substituted for *n*-butyl lithium/TMEDA in the lithiation step.

4.1. (η^6-Phenylchromium tricarbonyl)(η^5-cyclopentadienyl manganese tricarbonyl) methanol (1)

A 300 ml Schlenk flask containing benzene chromium tricarbonyl (250 mg, 1.2 mmol) was evacuated and backfilled with nitrogen. Approximately 100 ml of air-free THF was added under nitrogen and the solution cooled to −78 °C in a dry ice/isopropanol bath. Tetramethylethylenediamine (TMEDA) (1.0 ml) was added by pipette, followed by dropwise addition of *n*-butyllithium (1.0 M in hexanes, 3.0 ml) over 10 min. The solution was maintained at −78 °C and stirred for 90 min, during which time the solution color changed from light to dark yellow. Formylcyclopentadienyl manganese tricarbonyl (278 mg, 1.2 mmol) in THF (10 ml) was added and the solution allowed to warm to room temperature. After 4 h dilute (6 M) hydrochloric acid (5 ml) was added. The solution was dried with magnesium sulfate, filtered through Celite, and the solvent removed by rotary evaporator. The resulting yellow-brown oil was chromatographed on alumina. Initial elution with petroleum ether removed unreacted starting material. Continued elution with dichloromethane gave a yellow band which produced **1** as a bright yellow solid after removal of the solvent: 273 mg, 52% yield. M.p. 145–146 °C. Recrystallization was achieved by vapor diffusion of petroleum ether into a dichloromethane solution of the compound. This methodology yielded an analytically pure sample. IR (cm^{-1}, CH_2Cl_2): 2024 (s), 1972 (s), 1928 (s), 1898 (s). ^{1}H NMR (δ, $CDCl_3$): 5.65 (d, 1H, $J = 5$ Hz, Ph-C*H*OH-Cp), 5.36 (m, 4H, Ph), 5.10 (s, 1H, Ph), 4.90 (s, 2H, Cp), 4.68 (s, 2H, Cp), 2.34 (d, 1H, $J = 5$ Hz, -O*H*). ^{13}C NMR (δ, $CDCl_3$): 232.4 (Cr-*C*O), 224.1 (Mn-*C*O), 113.1 (*ipso* Ph), 105.9 (*ipso* Cp), 92.2 (Ph), 91.4 (Ph), 90.2 (Ph), 82.9 (Cp), 81.8 (Cp), 80.8 (Cp), 68.5 (Ph-*C*HOH-Cp). MS: 446 (M^+, 14%), 362 (M^+ − 3CO, 23%), 278 (M^+ − 6CO, 100%), 210 (100%), 208 (M^+ − 6CO, −Cr, −H_2O, 62%). Anal. Found: C, 48.18; H, 2.52. $C_{18}H_{11}CrMnO_7$ Calc.: C, 48.48; H, 2.49%.

4.2. 1-(η^6-Phenyl chromium tricarbonyl)-1-(η^5-cyclopentadienyl manganese tricarbonyl) ethanol (2)

Yellow crystals, m.p. 145–146 °C. Yield 38%. IR (cm^{-1}, CH_2Cl_2): 2023 (s), 1969 (s), 1939 (s), 1892 (s). ^{1}H NMR (δ, $CDCl_3$): 5.70–5.23 (br, complex multiplet, 5H, Ph), 4.93 (s, 2H, Cp), 4.62 (s, 2H, Cp), 2.09 (s, 1H, -O*H*), 1.79 (s, 3H, Ph-COHCH_3-Cp). ^{13}C NMR (δ, $CDCl_3$): 233.0 (Cr-*C*O), 224.4 (Mn-*C*O), 111.9 (*ipso* Ph), 109.4 (*ipso* Cp), 94.3 (Ph), 92.2 (Ph), 89.8 (Ph), 84.4 (Cp), 81.2 (Cp), 79.9 (Cp), 70.9 (Ph-*C*OHCH_3-Cp). MS: 460 (M^+, 9.12%), 442 (M^+ − H_2O, 5%), 404 (M^+ − 2CO, 2%), 376 (M^+ − 3CO, 20%), 290 (M^+ − 5CO, −CH_2O, 100%), 274 (M^+ −

6CO, $-\mathrm{H_2O}$, 14%), 222 ($\mathrm{M^+}-$6CO, $-\mathrm{H_2O}$, −Cr, 71%), 167 ($\mathrm{M^+}-$6CO, $-\mathrm{H_2O}$, −Cr, −Mn, 23%). Anal. Found: C, 49.50; H, 2.70. $\mathrm{C_{19}H_{13}CrMnO_7}$ Calc.: C, 49.59; H, 2.85%.

4.3. (η^6-Phenyl chromium tricarbonyl)(η^5-cyclopentadienyl rhenium tricarbonyl) methanol (3)

Yellow crystals, m.p. 72–74°C. Yield 18%. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): 2025 (s), 1972 (s), 1929 (s), 1900 (s). ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 5.61–5.06 (br, m, 10H, phenyl, Cp, PhC*H*OHCp), 2.31 (s, 1H, -O*H*). ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 232.7 (Cr–*C*O), 193.2 (Re–*C*O), 112.8 (*ipso* Ph), 109.1 (*ipso* Cp), 92.8 (Ph), 92.0 (Ph), 91.5 (Ph), 90.0 (Ph), 85.1 (Cp), 83.5 (Cp), 82.9 (Cp), 68.4 (Ph*C*HOHCp). MS: 578 ($\mathrm{M^+}$, 4%), 494 ($\mathrm{M^+}-$3CO, 13%), 476 ($\mathrm{M^+}-$3CO, $-\mathrm{H_2O}$, 30%), 410 ($\mathrm{M^+}-$6CO, 25%), 356 ($\mathrm{M^+}-$6CO, −Cr, 100%). Anal. Found: C, 37.50; H, 2.02. $\mathrm{C_{18}H_{11}CrO_7Re}$ Calc.: C, 37.44; H, 1.92%.

4.4. 1-(η^6-Phenyl chromium tricarbonyl)-1-(η^5-cyclopentadienyl rhenium tricarbonyl) ethanol (4)

Yellow crystals, m.p. 185–187°C. Yield 43%. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): 2025 (s), 1971 (s), 1929 (s), 1897 (s). ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 5.67–5.25 (complex multiplet, 9H, Ph/Cp), 2.05 (s, 1H, -O*H*), 1.81 (s, 3H, -CH_3). ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 232.5 (Cr–*C*O), 193.8 (Re–*C*O), 117.1 (*ipso* Ph), 106.9 (*ipso* Cp), 94.3 (Ph), 92.2 (Ph), 92.1 (Ph), 89.9 (Ph), 89.6 (Ph), 85.3 (Cp), 83.1 (Cp), 82.5 (Cp), 70.95 (Ph-*C*($\mathrm{CH_3}$)OH–Cp), 32.3 (–*C*$\mathrm{H_3}$). MS: 592 ($\mathrm{M^+}$, 1%), 508 ($\mathrm{M^+}-$3CO, 5%), 490 ($\mathrm{M^+}-$3CO, $-\mathrm{H_2O}$, 12%), 462 ($\mathrm{M^+}-$4CO, $-\mathrm{H_2O}$, 6%), 410 ($\mathrm{M^+}-$4CO, $-\mathrm{H_2O}$, −Cr, 18%), 354 ($\mathrm{M^+}-$6CO, $-\mathrm{H_2O}$, −Cr, 100%). Anal. Found: C, 38.25; H, 2.29. $\mathrm{C_{19}H_{13}CrO_7Re}$ Calc.: C, 38.58; H, 2.22%.

4.5. 1-(η^6-Phenyl chromium tricarbonyl)-1-(η^5-cyclopentadienyl iron dicarbonyl methyl) ethanol (5)

Brown–red oil. Yield 18%. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): 2008 (s), 1969 (s), 1949 (s), 1893 (s). ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 5.70–4.62 (br, m, 9H, Ph, Cp), 2.13 (s, 1H, -O*H*), 1.81 (s, 3H, –CH_3), 0.16 (s, 3H, Fe–CH_3). ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 232.7 (Cr–*C*O), 216.9 (Fe–*C*O), 118.2 (*ipso* Ph), 111.1 (*ipso* Cp), 94.2 (Ph), 92.3 (Ph), 92.0 (Ph), 90.0 (Ph), 89.8 (Ph), 85.1 (Cp), 84.4 (Cp), 83.8 (Cp), 70.9 (Ph*C*MeOHCp), 31.3 (PhCOH*C*$\mathrm{H_3}$), 7.59 (Fe–*C*$\mathrm{H_3}$). MS: 448 ($\mathrm{M^+}$, 8%), 431 ($\mathrm{M^+}-$OH, 14%), 420 ($\mathrm{M^+}-$CO, 13%), 392 ($\mathrm{M^+}-$2CO, 10%), 364 ($\mathrm{M^+}-$3CO, 43%), 336 ($\mathrm{M^+}-$4CO, 14%), 308 ($\mathrm{M^+}-$5CO, 39%), 291 ($\mathrm{M^+}-$5CO, −OH, 100%). Anal. Found: C, 50.87; H, 3.80. $\mathrm{C_{19}H_{16}CrFeO_6}$ Calc.: C, 50.92; H, 3.59%.

4.6. (η^6-Phenyl chromium tricarbonyl)(η^5-cyclopentadienyl iron dicarbonyl benzyl) methanol (6)

Brown–red oil. Yield 15%. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): 2007 (s), 1971 (s), 1953 (s), 1894 (s). ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 7.12 (m, 5H, $\mathrm{CH_2}$*Ph*), 5.53–4.19 (br, m, 10H, phenyl, Cp, PhC*H*OHCp), 2.70 (s, 2H, -CH_2Ph), 2.11 (s, 1H, O*H*). ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 232.4 (Cr–*C*O), 216.5 (Fe–*C*O), 152.8 (*ipso* $\mathrm{CH_2Ph}$), 128.4 (Ph), 127.4 (Ph), 123.6 (Ph), 113.2 (*ipso* Ph), 104.2 (*ipso* Cp), 92.9 (Ph), 91.7 (Ph), 91.4 (Ph), 90.6 (Ph), 89.9 (Ph), 85.2 (Cp), 84.7 (Cp), 83.2 (Cp), 68.0 (Ph*C*HOHCp), 5.94 (Fe–*C*$\mathrm{H_2}$Ph). MS: 510 ($\mathrm{M^+}$, 2%), 482 ($\mathrm{M^+}-$CO, 4%), 454 ($\mathrm{M^+}-$2CO, 45%), 370 ($\mathrm{M^+}-$5CO, 19%), 279 ($\mathrm{M^+}-$5CO, −Bz, 77%), 227 ($\mathrm{M^+}-$5CO, −Bz, −Cr, 100%). Anal. Found: C, 56.84; H, 3.55. $\mathrm{C_{24}H_{18}CrFeO_6}$ Calc.: C, 56.50; H, 3.56%.

4.7. Bis-(η^5-cyclopentadienyl manganese tricarbonyl)(η^6-phenyl chromium tricarbonyl) methanol (7)

Compounds **7** and **8** were separated by elution on alumina using 20% dichloromethane in petroleum ether. **8** is eluted as an orange band trailed by **7**. Yellow crystals, m.p. 216–218°C (decomp.). Yield 18%. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): 2024 (s), 1973 (m), 1943 (s), 1901 (m). ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 5.67 (d, 2H, *o*-Ph), 5.55 (t, 1H, *p*-Ph), 5.19 (d, 2H, *m*-Ph), 5.00 (m, 2H, Cp), 4.91 (m, 2H, Cp), 4.68 (m, 4H, Cp), 2.55 (s, 1H, –O*H*). ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 232.3 (Cr–*C*O), 224.0 (Mn–*C*O), 115.5 (*ipso* Cp), 109.0 (*ipso* Ph), 96.0, 93.8, 88.3 (Ph), 86.4, 85.3, 80.7, 80.2 (Cp), 73.0 (*C*–OH). Ms: 648 ($\mathrm{M^+}$, 29%), 631 ($\mathrm{M^+}-$OH, 19%), 564 ($\mathrm{M^+}-$3CO, 100%), 547 ($\mathrm{M^+}-$3CO, −OH, 47%), 512 ($\mathrm{M^+}-\mathrm{Cr(CO)_3}$, 13%), 495 ($\mathrm{M^+}-\mathrm{Cr(CO)_3}$, −OH, 13%), 480 ($\mathrm{M^+}-$6CO, 35%), 452 ($\mathrm{M^+}-$7CO, 14%, 428 ($\mathrm{M^+}-\mathrm{C_5H_4Mn(CO)_3}$, −OH, 50%), 411 ($\mathrm{M^+}-\mathrm{Cr(CO)_3}$, $-\mathrm{Mn(CO)_3}$, 15%), 396 ($\mathrm{M^+}-$9CO, 38%). Anal. Found: C, 48.23; H, 1.93. $\mathrm{C_{26}H_{14}CrMn_2O_{10}}$ Calc.: C, 48.16; H, 2.16%.

4.8. (η^5-Cyclopentadienyl manganese tricarbonyl)(η^6-phenyl chromium tricarbonyl) ketone (8)

Orange crystals, m.p. 125–129°C. Yield 37%. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): 2033 (s), 1984 (s), 1948 (s), 1910 (s), 1720 (w). ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 6.06 (d, 2H, *o*-Ph), 5.64 (t, 1H, *p*-Ph), 5.55 (t, 2H, AA'BB', Cp), 5.28 (t, 2H, *m*-Ph), 4.91 (t, 2H, AA'BB', Cp). ^{13}C NMR (δ, $\mathrm{CDCl_3}$): 320.3 (Cr–*C*O), 222.6 (Mn–*C*O), 187.7 (*C*=O), 96.3 (*ipso*), 94.6 (3C, Ph), 88.9 (Ph), 87.6 (Cp), 83.6 (Cp). [Note: second *ipso* carbon was not observed.] MS: (CI) 445 ($\mathrm{M^+}$+H, 10%), 388 ($\mathrm{M^+}-$2CO, 70%), 361 ($\mathrm{M^+}-$3CO, +H, 88%), 332 ($\mathrm{M^+}-$4CO, 21%), 304 ($\mathrm{M^+}-$5CO, 8%), 276 ($\mathrm{M^+}-$6CO, 50%, 253 (Ph–CO–CpMn(CO)$^+$, 18%), 224 (Ph–CO–CpMn$^+$, 85%), 221 (Cp–CO–PhCr$^+$, 38%). Anal. Found: C, 49.00; H, 1.99. $C_{18}H_9CrMnO_7$ Calc.: C, 48.66; H, 2.03%.

4.9. (η^5-Cyclopentadienyl iron dicarbonyl methyl)(η^5-cyclopentadienylmanganese tricarbonyl) methanol (**9**)

Yellow crystals, m.p. 67–70 °C. Yield 26%. IR (cm^{-1}, CH_2Cl_2): 2022 (s), 2008 (s), 1944 (s). ^{1}H NMR (δ, $CDCl_3$): 4.69 (br, m, 9H, Cp, CpC*H*OHCp), 2.09 (s, 1H, –O*H*), 0.18 (s, 3H, Fe–CH_3). ^{13}C NMR (δ, $CDCl_3$): 224.5 (Mn–*C*O), 216.8 (Fe–*C*O), 106.9 (*ipso* Ph), 106.2 (*ipso* Cp), 84.8 (Ph), 83.9 (Ph), 83.3 (Ph), 82.8 (Ph), 81.6 (Ph), 80.9 (Cp), (Cp), 64.8 (Cp–*C*HOH–Cp), –22.23 (Fe–CH_3). MS: 393 (M$^+$ – Me, –OH, 9.9%), 339 (M$^+$ – 3CO, –H, 3%), 280 (M$^+$ – 2CO, –Fe, –Me, –OH, 20%), 196 (M$^+$ – 5CO, –Me, –Fe, –OH, 92%), 141 (M$^+$ – 5CO, –Me, –Fe, –OH, –Mn, 100%). Anal. Found: C, 48.64, H, 3.58. $C_{17}H_{13}FeMnO_6$ Calc.: C, 48.15; H, 3.09%.

4.10. (η^5-Cyclopentadienyl manganese tricarbonyl)(η^5-cyclopentadienyl iron dicarbonyl benzyl) methanol (**10**)

Brown–red oil. Yield 35%. IR (cm^{-1}, CH_2Cl_2): 2022 (s), 2007 (s), 1939 (s). ^{1}H NMR (δ, $CDCl_3$): 7.24 (br, m, 5H, CH_2*Ph*), 4.85–4.52 (br, m, 9H, Cp, Cp-C*H*OHCp), 2.69 (s, 2H, –CH_2Bz), 1.88 (s, 1H, –O*H*). ^{13}C NMR (δ, $CDCl_3$): 224.7 (Mn–*C*O), 216.6 (Fe-*C*O), 152.8 (*ipso* Ph), 128.4 (Ph), 127.4 (Ph), 123.5 (Ph), 106.8 (*ipso* Cp), 105.6 (*ipso* Cp), 89.0 (Cp), 85.1 (Cp), 84.9 (Cp), 83.3 (Cp), 82.8 (Cp), 81.5 (Cp), 81.0 (Cp), 64.2 (Cp*C*HOHCp), 5.88 (Fe–CH$_2$Bz). MS: 510 (M$^+$, 1%), 476 (M$^+$ – 34, 29%), 448 (M$^+$ – 34, –CO, 11%), 392 (M$^+$ – 34, –3CO, 25%), 364 (M$^+$ – 34, –4CO, 60%), 281 (M$^+$ – 34, –5CO, –Mn, 100%). Anal. Found: C, 55.52; H, 3.63. $C_{23}H_{17}FeMnO_6$ Calc.: C, 55.23; H, 3.43%.

4.11. (η^5-Cyclopentadienyl iron dicarbonyl methyl)(η^5-cyclopentadienyl rhenium tricarbonyl) methanol (**11**)

Yellow crystals, m.p. 64–66 °C. Yield 59%. IR (cm^{-1}, CH_2Cl_2): 2025 (s), 2009 (s), 1948 (s), 1930 (s). ^{1}H NMR (δ, $CDCl_3$): 5.45 (s, 2H, Cp), 5.26 (s, 2H, Cp), 5.14 (s, 1H, –CHO*H*), 4.91–4.67 (br, 4H, Cp), 2.07 (s, 1H, –O*H*), 0.27 (s, 3H, Fe–CH_3). ^{13}C NMR (δ, $CDCl_3$): 216.7 (Fe–*C*O), 193.5 (Re–*C*O), 111.1 (*ipso* Cp), 105.8 (*ipso* Cp), 86.4 (Cp), 86.3 (Cp), 85.8 (Cp), 85.6 (Cp), 85.3 (Cp), 84.8 (Cp), 84.7 (Cp), 84.5 (Cp), 66.0 (Cp–*C*HOH–Cp), –20.7 (Fe–CH_3). MS: M$^+$ (not observed), 412 (M$^+$ – 2CO, –Fe, –Me, –OH, 100%), 384 (M$^+$ – CO from 412, 12%), 356 (M$^+$ – 2CO from 412, 20%), 328 (M$^+$ – 3CO from 412, 43%). Anal. Found: C, 37.11; H, 2.33. $C_{17}H_{13}FeO_6Re$ Calc.: C, 36.77; H, 2.36%.

4.12. (η^5-Cyclopentadienyl tungsten tricarbonyl methyl)(η^5-cyclopentadienylmanganese tricarbonyl) methanol (**12**)

Brown crystals, m.p. 83–86 °C. Yield 54%. IR (cm^{-1}, CH_2Cl_2): 2023 (s), 2016 (s), 1932 (br). ^{1}H NMR (δ, $CDCl_3$): 5.47 (s, 1H, Cp–C*H*OH–Cp), 5.31 (s, 2H, Cp), 5.16 (s, 1H, Cp), 4.92 (s, 1H, Cp), 4.83 (s, 1H, Cp), 4.71 (s, 1H, Cp), 4.66 (s, 1H, Cp), 2.08 (s, 1H, –O*H*), 0.41 (s, 3H, W–CH_3). ^{13}C NMR (δ, $CDCl_3$): 228.9 (W–*C*O), 215.3 (W–*C*O), 224.8 (Mn–*C*O), 114.9 (*ipso* Cp), 106.9 (*ipso C*), 91.98 (Cp), 91.3 (Cp), 89.8 (Cp), 89.2 (Cp), 82.8 (Cp), 81.9 (Cp), 81.1 (Cp), 65.04 (Cp–*C*HOH–Cp), –33.7 (W–CH_3). MS: 580 (M$^+$, 16%), 524 (M$^+$ – 2CO, 9%), 496 (M$^+$ – 3CO, 60%), 440 (M$^+$ – 5CO, 89%), 412 (M$^+$ – 6CO, 38%), 397 (M$^+$ – Me, –6CO, 33%). Anal. Found: C, 37.47; H, 2.24. $C_{18}H_{13}MnO_7W$ Calc.: C, 37.27; H, 2.26%.

4.13. (η^5-Cyclopentadienyl tungsten tricarbonyl methyl)(η^5-cyclopentadienyl rhenium tricarbonyl) methanol (**13**)

Brown crystals, m.p. 114–116 °C. Yield 30%. IR (cm^{-1}, CH_2Cl_2): 2026 (s), 2017 (s), 1928 (br). ^{1}H NMR (δ, $CDCl_3$): 5.50 (br, m, 8H, Cp), 5.20 (s, 1H, Cp–C*H*OH–Cp), 2.10 (s, 1H, –O*H*), 0.43 (s, 3H, W–CH_3). ^{13}C NMR (δ, $CDCl_3$): 228.6 (W–*C*O), 215.5 (W–*C*O), 193.3 (Re–*C*O), 114.5 (*ipso* Cp), 111.2 (*ipso C*), 92.1 (Cp), 91.4 (Cp), 89.9 (Cp), 89.2 (Cp), 84.4 (Cp), 84.2 (Cp), 83.6 (Cp), 83.2 (Cp), 64.8 (Cp–*C*HOH–Cp), –33.7 (W–CH_3). MS: 712 (M$^+$, 32%), 656 (M$^+$ – 2CO, 11%), 628 (M$^+$ – 3CO, 97%), 600 (M$^+$ – 4CO, 29%). Anal. Found: C, 30.64; H, 1.87. $C_{18}H_{13}O_7ReW$ Calc.: C, 30.40; H, 1.84%.

4.14. (η^6-Phenyl chromium tricarbonyl)(η^5-cyclopentadienyl manganese tricarbonyl) methane (**14**)

1 (500 mg) and a spinbar were placed in a 100 ml, round-bottomed flask. After the flask was evacuated and backflushed with nitrogen, dichloromethane (30 ml) was added under nitrogen. Dropwise addition of trifluoroacetic acid (1.0 ml) caused the color of the solution to change from yellow to blue. After 15 min of stirring a slight excess of sodium tetrahydroborate was added and the mixture stirred for a further 30 min. Aqueous sodium hydroxide (20 ml) was slowly added to the flask. The solution was transferred to a separatory funnel, ethyl ether was added and the aqueous phase was removed. The organic phase was dried with magnesium sulfate, filtered, and the solvent removed. The resultant brown oil was chromatographed on alumina with a 50:50 mixture of petroleum ether/methylene chloride. A single yellow band was eluted that gave **14** as yellow-orange crystals, m.p. 93–96°C. Yield 143 mg, 54%. Recrystallization from petroleum ether/dichloromethane yielded an analytically pure sample. IR (cm^{-1}, CH_2Cl_2): 2022 (s), 1971 (s), 1934 (s), 1892 (s). ^1H NMR (δ, $CDCl_3$): 5.44–5.17 (br, m, 5H, phenyl), 4.80–4.62 (br, m, 4H, Cp), 3.32 (s, 2H, $-CH_2$). ^{13}C NMR (δ, $CDCl_3$): 232.5 (Cr–*C*O), 224.1 (Mn–*C*O), 110.9 (*ipso Ph*), 101.5 (*ipso* Cp), 92.9 (Ph), 92.5 (Ph), 91.5 (Ph), 83.7 (Cp), 82.0 (Cp), 33.4 (Ph–CH_2–Cp). MS: 430 (M^+, 18%), 346 ($M^+ - 3CO$, 100%), 318 ($M^+ - 4CO$, 22%), 290 ($M^+ - 5CO$, 44%), 262 ($M^+ - 6CO$, 10%), 210 ($M^+ - 6CO$, $-Cr$, 57%). Anal. Found: C, 50.22; H, 2.68. $C_{18}H_{11}CrMnO_6$ Calc.: C, 50.25; H, 2.58%.

4.15. *(η^6-Phenyl chromium tricarbonyl)(η^5-cyclopentadienyl rhenium tricarbonyl) methane (15)*

Yellow crystals, m.p. 82–84°C. Yield 52%. IR (cm^{-1}, CH_2Cl_2): 2024 (s), 1970 (s), 1927 (s), 1895 (s). ^1H NMR (δ, $CDCl_3$): 5.33–5.17 (br, m, 9H, phenyl, Cp), 3.43 (s, 2H, $-CH_2$). ^{13}C NMR (δ, $CDCl_3$): 232.5 (Cr–*C*O), 193.6 (Re–*C*O), 109.9 (*ipso* Ph), 105.6 (*ipso* Cp), 92.9 (Ph), 92.5 (Ph), 91.2 (Ph), 84.8 (Cp), 83.8 (Cp), 33.4 (Ph–CH_2–Cp). MS: 561 (M^+, 20%), 477 ($M^+ - 3CO$, 82%), 449 ($M^+ - 4CO$, 51%), 421 ($M^+ - 5CO$, 47%), 393 ($M^+ - 6CO$, 40%), 342 ($M^+ - 6CO$, $-Cr$, 100%). Anal. Found: C, 38.77; H, 1.87. $C_{18}H_{11}CrO_6Re$ Calc.: C, 38.55; H, 1.97%.

4.16. *1-(η^6-Phenyl chromium tricarbonyl)-1-(η^5-cyclopentadienyl manganese tricarbonyl) ethene (16)*

Yellow crystals, m.p. 93–95°C. Yield 51%. IR (cm^{-1}, CH_2Cl_2): 2023 (s), 1969 (s), 1939 (s), 1892 (s). ^1H NMR (δ, $CDCl_3$): 5.67, 5.58 (s, 2H, $C{=}CH_2$), 5.51 (br, m, 5H, Ph), 4.96 (br, 2H, Cp), 4.72 (br, 2H, Cp). ^{13}C NMR (δ, $CDCl_3$): 232.2 (Cr–*C*O), 223.9 (Mn–*C*O), 137.2 ($C{=}CH_2$), 119.3 ($C{=}CH_2$), 109.5 (*ipso* Ph), 100.9 (*ipso* Cp), 94.2 (Ph), 93.3 (Ph), 90.2 (Ph), 83.6 (Cp), 81.8 (Cp). MS: 442 (M^+, 53%), 358 ($M^+ - 3CO$, 100%), 302 ($M^+ - 5CO$, 72%), 274 ($M^+ - 6CO$, 46%), 219 ($M^+ - 6CO$, $-Mn$, 62%). Anal. Found: C, 51.51; H, 2.49. $C_{19}H_{11}CrMnO_6$ Calc.: C, 51.61; H, 2.51%.

5. Crystallographic studies

Crystal, data collection, and refinement parameters are given in Table 2. A suitable crystal was selected and mounted with epoxy cement on a glass fiber. The unit cell parameters were obtained by least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\Theta \leq 24°$).

The systematic absences in the diffraction data are uniquely consistent for the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. Semi-empirical ellipsoid absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of scattering factors are contained in the SHELXTS PLUS (4.2) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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