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Synthesis and properties of 1,3- and 1,4-$\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}_2\text{-}C_5H_4$: molecular structure of $[(\mu\text{-}\eta^5:\eta^5:\eta^5\text{-}C_{17}H_{15})(CH_3)Mn_2W(CO)_9]$

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Abstract

$(exo\text{-}C_5H_5\text{-}\eta^5\text{-}C_6H_6)Mn(CO)_3$ (2) reacts with $(C_6H_6)Mn(CO)_3^+$ to yield 1,3- and 1,4-$\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}_2\text{-}C_5H_4)]$ (3). 3 reacts with $Fe_2(CO)_9$ to yield $[(\mu\text{-}\eta^5:\eta^5:\eta^5\text{-}C_{17}H_{15})Mn_2Fe(CO)_8]_2$. 3 reacts with ^nBuLi to produce a lithiated compound, which reacts with $M(CO)_5Br$ (M = Mn, Re), $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W), and $FeCl_3$ to yield the corresponding organometallic compounds. The molecular structure of $[(\mu\text{-}\eta^5:\eta^5:\eta^5\text{-}C_{17}H_{15})(CH_3)Mn_2W(CO)_9]$ (6(W)) (space group $P2_1/c$; unit cell parameters $a = 11.208(6)$, $b = 19.431(3)$, $c = 12.562(2)$ Å, $\beta = 91.69\ (3)°$; $R = 0.052\%$, $R_W = 0.067\%$) has been determined.

Keywords: Tungsten; Manganese; Cyclopentadienyl; Cyclohexadienyl; Polymetallic; Crystal structure

1. Introduction

Chemical processes involving two or more organometallic units in combination are of increasing importance. Transition metal complexes which resist fragmentation are particularly attractive for studies. A common synthetic strategy for dinuclear transition metal complexes involves the use of difunctional ligands, which are capable of coordinating to two metal centres [1]. However, the scope for its application to synthesis of polymetallic compounds is limited because general approaches have not been elaborated. Recently we reported [2] that the cyclopentadiene moiety of tricarbonyl(exo-cyclopentadienyl-η^5-cyclohexadienyl)manganese could be used as a π-coordinating ligand for other organometallic compounds. In connection with this we have found that 1,3- and 1,4-$\{(\eta^5\text{-}C_6H_6)\text{-}Mn(CO)_3\}_2\text{-}C_5H_4$ (3) can be used as a π-coordinating ligand for other organometallic compounds. In this paper, the utility of **3** in the formation of several new polymetallic complexes is demonstrated (Scheme 1) and the molecular structure of **6** (W) is also reported.

2. Experimental section

All reactions were conducted under nitrogen using standard Schlenk type flask and cannula techniques. Work-up procedures were done in air.

Elemental analyses were done at the Korea Basic Science Center. ^1H NMR spectra were obtained with a Varian XL-200 or a Bruker Arx 300 instrument. Infrared spectra were recorded on a Perkin-Elmer 782 spectrophotometer (spectra measured as films on NaCl by evaporation of solvent).

$[(Benzene)Mn(CO)_3]PF_6$ (1), $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, and W), and $(exo\text{-}C_5H_5\text{-}\eta^5\text{-}C_6H_6)Mn(CO)_3$ (2) were synthesized according to published procedures [2–4].

2.1. Synthesis of 3

Compound **2** (0.34 g, 1.2 mmol) and 10 ml of THF were placed in a Schlenk flask. ^nBuLi (1.5 mmol, 0.6 ml of a 2.5 M solution in hexane) was added dropwise to the reaction flask at 0°C. While it was stirred for 1 h,

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the solution turned to a deep yellow-brown. The resulting solution was transferred via syringe to another flask containing **1** (0.54 g, 1.5 mmol) in 10 ml of THF at 0°C. After stirring for 0.5 h at 0°C, the reaction mixture was allowed to warm to room temperature. To the reaction mixture several drops of saturated aqueous NH_4Cl solution were added. The resulting solution was extracted with 30 ml of diethyl ether and distilled water, and then the organic layer was collected, dried ($MgSO_4$), and evaporated to yield a yellow residue. The yellow residue was chromatographed on neutral alumina with diethylether/hexane (v/v, 1:10). After evaporation of the solvent, **3** was obtained in 59% yield (0.35 g). The isomer ratio 2:1 was determined by integration of the characteristic signals of each isomer in the ^1H NMR spectrum. IR (NaCl) ν (CO) 2011, 1918 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.72 (t, 5.1 Hz, H^3), [5.63 (s), 5.59 (s), 5.45 (s); two of them belong to major isomer and one belongs to minor isomer], 4.83 (t, 6.1 Hz, $H^{2,4}$), 3.40 (t, 6.1 Hz, H^6, major isomer), 3.37 (t, 6.10 Hz, H^6, minor isomer), 3.24 (t, 6.10 Hz, $H^{1,5}$), 2.49 (s, 2H on Cp sp^3 carbon, major isomer), 2.33 (s, 2H on Cp sp^3 carbon, minor isomer) ppm; Anal. Found: C, 55.09; H, 3.02. $C_{23}H_{16}Mn_2O_6$ calc.: C, 55.44; H, 3.24%.

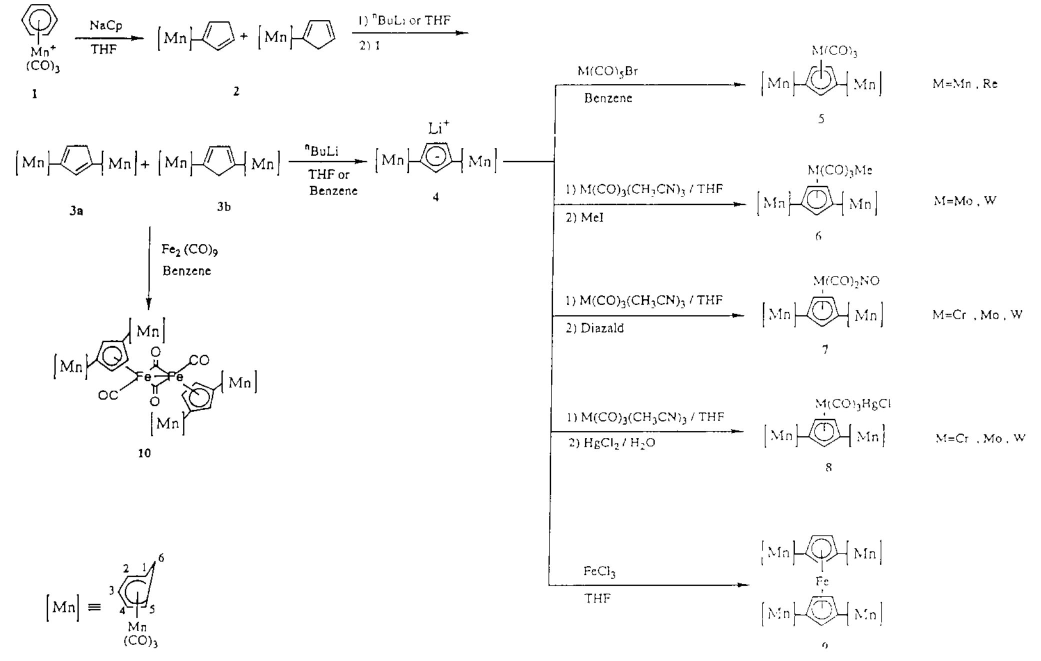
2.2. Synthesis of *5* (Mn)

Compound **3** (0.50 g, 1.0 mmol) and 20 ml of benzene were placed in a Schlenk flask. ^nBuLi (1.2 mmol, 0.17 ml of 7 M solution in hexane) was added dropwise at room temperature. After being stirred for 1 h, $Mn(CO)_5Br$ (0.36 g, 1.3 mmol) was added while being vigorously flushed with nitrogen gas. The reaction mixture was refluxed for a day, cooled to room temperature, and filtered through anhydrous $MgSO_4$ in a fritted glass filter. Removal of solvent gave yellow crude solids. The yellow solid was column-chromatographed on silica gel with diethyl ether/hexane (v/v, 1:10). After evaporation of solvent, a 40% yield of compound **5** (Mn) was obtained: Mp. 149°C. IR (NaCl) ν (CO) 2005, 1910 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.77 (t, 5.1 Hz, $H^{3,3'}$), 4.91 (t, 5.6 Hz, $H^{2,4,2',4'}$), 4.23 (s, 2H, Cp), 4.18 (s, 1H, Cp), 3.28 (t, 6.1 Hz, $H^{1,5,1',5'}$), 3.10 (t, 5.6 Hz, $H^{6,6'}$) ppm. Anal. Found: C, 49.11; H, 2.72. $C_{26}H_{15}Mn_3O_9$ calc.: C, 49.09; H, 2.38%.

5 (Re): Mp. 144°C. IR ν (CO) 2016, 1914 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.77 (t, $J = 5.1$ Hz, 2H), 4.90 (t, $J = 5.3$ Hz, 4H), 4.81 (s, 2H), 4.77 (s, 1H), 3.30–3.12 (m, 6H) ppm. Anal. Calc. $C_{26}H_{15}Mn_2O_9Re$ Found: C, 41.02; H, 2.23: C, 40.69; H, 1.97%.

2.3. Synthesis of *6* (W)

Compound **3** (0.255 g, 0.5 mmol) and 10 ml of THF were placed in a Schlenk flask. ^tBuLi (0.56 mmol, 0.33 ml of a 1.7 M solution in hexane) was added dropwise to the reaction flask at 0°C. After stirring for 30 min, the resulting solution was transferred via cannula to another flask containing $W(CO)_3(CH_3CN)_3$ (generated in situ from $W(CO)_6$ (1.5 mmol) and used without isolation) in 10 ml of THF. The reaction mixture was refluxed for 12 h and then cooled to room temperature. MeI (2.5 mmol) was added to the resulting solution. The solution was stirred for 5 h, and the solvent was removed on a rotary evaporator. The resulting residue was extracted with diethyl ether. The ether



Scheme 1.

extracts were evaporated to dryness. The yellow residue was column-chromatographed on silica gel with diethyl ether/hexane (v/v, 1:5). The yield of **6** (W) was 69%: Mp. 132°C. IR (NaCl) ν (CO) 2020, 1910 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.77 (tt, 5.3, 1.3 Hz, $H^{3,3'}$), 4.93–4.90 (t + t, 5.4, 5.5 Hz, $H^{2,4,2',4'}$), 4.73 (d, 1.9 Hz, 2H, Cp), 4.51 (t, 1.9 Hz, 1H, Cp), 3.12–3.32 (m, 6H, $H^{1,5,6,1',5',6'}$), 0.32 (s, Me) ppm; Anal. Found: C, 41.89; H, 2.24. $C_{27}H_{18}Mn_2O_9W$ calc.: C, 41.57; H, 2.33%.

6 (Mo). Yield: 63%. Mp. 129°C. IR (NaCl) ν (CO) 2001, 1914 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.76 (t, 5.3 Hz, $H^{3,3'}$), 4.92–4.89 (t + t, 6.1, 6.2 Hz, $H^{2,4,2',4'}$), 4.66 (d, 1.9 Hz, 2H, Cp), 4.48 (t, 1.9 Hz, 1H, Cp), 3.20–3.33 (m, $H^{1,5,1',5'}$), 3.10 (t, 5.7 Hz, $H^{6,6'}$), 0.27 (s, Me) ppm; Anal. Found: C, 46.92; H, 2.72. $C_{27}H_{18}Mn_2MoO_9$ calc.: C, 46.85; H, 2.62%.

2.4. Synthesis of **7**

The typical procedure was almost the same as in the synthesis of **6** (W), except that Diazald is used instead of MeI. **7** (W): Yield: 66%. Mp. 172°C. IR (NaCl) ν (CO) 2002, 1929 cm^{-1}, ν (NO) 1648 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.78 (t, 5.1 Hz, $H^{3,3'}$), 5.10 (t, 1.9 Hz, 1H, Cp), 5.07 (d, 1.9 Hz, 2H, Cp), 4.91 (t, 5.3 Hz, $H^{2,4,2',4'}$), 3.20–3.28 (m, $H^{1,5,6,1',5',6'}$) ppm; Anal. Found: C, 39.26; H, 1.96; N, 1.73. $C_{25}H_{15}Mn_2NO_9W$ calc.: C, 39.14; H, 1.97; N, 1.83%.

7 (Cr): Yield: 43%. Mp. 146°C. IR (NaCl) ν (CO) 2002, 1929 cm^{-1}; ν (NO) 1692 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.77 (t, 5.1 Hz, $H^{3,3'}$), 4.90 (t, 6.2 Hz, $H^{2,4,2',4'}$), 4.53 (s, 3H, Cp), 3.21–3.30 (m, $H^{1,5,1',5'}$), 3.10 (t, 5.8 Hz, $H^{6,6'}$) ppm; Anal. Found: C, 47.62; H, 2.50; N, 2.17. $C_{25}H_{15}CrMn_2NO_9$ calc.: C, 47.27; H, 2.38; N, 2.20%.

7 (Mo): Yield: 72%. Mp. 155°C. IR (NaCl) ν (CO) 2000, 1926 cm^{-1}, ν (NO) 1657 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.77 (t, 5.1 Hz, $H^{3,3'}$), 5.04 (t, 1.5 Hz, 1H, Cp), 5.00 (d, 1.5 Hz, 2H, Cp), 4.90 (t, 5.9 Hz, $H^{2,4,2',4'}$), 3.10–3.32 (m, $H^{1,5,6,1',5',6'}$) ppm; Anal. Found: C, 44.68; H, 2.18; N, 1.81. $C_{25}H_{15}Mn_2MoNO_9$ calc.: C, 44.21; H, 2.23; N, 2.06%.

2.5. Synthesis of **8**

A typical procedure is almost the same as the synthesis of **6** (W), except $HgCl_2$ is used instead of MeI. **8** (W): Yield: 43%. Mp. 153°C dec. IR (NaCl) ν (CO) 2001, 1930 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.80 (tt, 5.3, 1.2 Hz, $H^{3,3'}$), 5.07 (d, 1.7 Hz, 2H, Cp), 5.03 (t, 2.0 Hz, 1H, Cp), 4.96 (t, 5.9 Hz, $H^{2,4,2',4'}$), 3.07–3.30 (m, $H^{1,5,6,1',5',6'}$) ppm; Anal. Found: C, 31.82; H, 1.65. $C_{26}H_{15}ClHgMn_2O_9W$ calc.: C, 31.19; H, 1.51%.

8 (Cr): Yield: 48%. Mp. 183°C dec. IR (NaCl) ν (CO) 2009, 1921 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.78 (tt, 5.3, 1.2 Hz, $H^{3,3'}$), 4.93–4.90 (t + t, 5.8, 6.1 Hz, $H^{2,4,2',4'}$), 4.47 (d, 1.9 Hz, 2H), 4.37 (t, 1.9 Hz, 1H), 3.20–3.37 (m, $H^{1,5,1',5'}$), 3.01 (t, 5.8 Hz, $H^{6,6'}$) ppm. Due to the instability of **8** (Cr), we failed to obtain analytical data.

8 (Mo): Yield: 57%. Mp. 120°C dec. IR (NaCl) ν (CO) 2022, 1925 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.80 (t, 5.2 Hz, $H^{3,3'}$), 4.87–5.04 (m, 7H, Cp + $H^{2,4,2',4'}$), 3.15–3.30 (m, $H^{1,5,1',5'}$), 3.04 (t, 5.6 Hz, $2H^{6,6'}$) ppm; Anal. Found: C, 33.37; H, 1.66. $C_{26}H_{15}ClHgMn_2MoO_9$ calc.: C, 34.20; H, 1.67%.

2.6. Synthesis of **9**

Compound **3** (0.325 g, 0.65 mmol) and 10 ml of THF were placed in a Schlenk flask. ^{n}BuLi (0.85 mmol, 0.53 ml of a 1.6 M solution in hexane) was added dropwise to the reaction flask at 0°C. After stirring for 1 h, the lithium salt solution was added to excess $FeCl_3$ in 10 ml of THF. The resulting solution was refluxed for 24 h, cooled to room temperature, and filtered over anhydrous $MgSO_4$ in a fritted glass filter. The THF solution was treated with excess diethyl ether and water. The ether extracts were collected, dried over anhydrous $MgSO_4$, and concentrated. The ether solution was purified by column-chromatography on silica gel eluting with diethyl ether/hexane (v/v, 1:3). The yield was 23%: Mp. 137°C. IR (NaCl) ν (CO) 2020, 1920 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.78 (t, 5.1 Hz, 4H), 4.88 (t, 5.4 Hz, 4H), 4.84 (t, 6.3 Hz, 4H), 3.51 (d, 1.2 Hz, 4H), 3.21–3.36 (m, 14H) ppm; Anal. Found: C, 53.60; H, 3.32. $C_{46}H_{30}FeMn_4O_{12}$ calc.: C, 52.60; H, 2.88%. Satisfactory analysis could not be obtained. Attempts at further purification resulted in partial decomposition of the material.

2.7. Synthesis of **10**

Excess $Fe_2(CO)_9$ was added to the benzene solution (20 ml) of compound **3** (0.249 g, 0.50 mmol) at room temperature. The reaction mixture was refluxed for 12 h. After the solution was cooled, solids were filtered off. The filtrate was evaporated and the residue was redissolved in THF. Compound **10** was obtained in 67% yield by treating a THF solution with excess n-hexane: Mp. 246°C. IR (NaCl) ν (CO) 2001, 1921 cm^{-1}, ν (C=O) 1765 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.74 (t, 4.8 Hz, 4H), 4.90–4.87 (t + t, 5.9, 6.4 Hz, 8H), 4.26 (t, 1.8 Hz, 2H), 3.26 -3.49 (m, 16H) ppm; Anal. Found: C, 48.74; H, 2.75. $C_{50}H_{30}Fe_2Mn_4O_{16}$ calc.: C, 49.30; H, 2.48%.

2.8. X-ray data collection, structure determination, and refinement for **6** *(W)*

A brown crystal of **6** (W), shaped as a block of approximate dimensions 0.33 × 0.24 × 0.24 mm, was mounted on an Enraf-Noinus CAD4 automated diffractometer equipped with a Mo X-ray tube and a

Table 1
Crystal data and data collection parameters for **6** (W)

Formula	$C_{27}H_{18}O_9Mn_2W$
Fw	780.16
System	Monoclinic
Space group	$P2_1/c$
a, Å	11.208(6)
b, Å	19.431(3)
c, Å	12.562(2)
β, deg	91.69(3)
V, Å^3	2734
Z	4
$F(000)$	1504
ρ (calcd), gcm^{-3}	1.89
Crystal dimensions	0.33 × 0.24 × 0.24
2θ limits, deg	$3 < 2\theta < 50$
No. of total reflns.	3175
No. of reflns. used	3034
Variables	172
R	0.052
Rw	0.067

graphite crystal monochromator. The orientation matrix and unit cell parameters were determined from 25 machine-centred reflections with $15° < 2\theta < 30°$. Data were corrected for Lorentz and polarization effects. Intensity data were empirically corrected with Ψ-scan data. The structure was solved by conventional heavy atom methods. All calculations were carried out on a VAX computer with use of the SHELXS 86 and SHELX 76 programs. For the W and Mn atoms thermal parameters were anisotropic. The positional parameters of all hydrogen atoms were generated in ideal positions with fixed isotropic thermal parameters. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Complete lists of thermal parameters and structural factors are available from the authors.

3. Results and discussion

3.1. Synthesis of 3

Treatment of (exo-C_5H_5-η^5-C_6H_6)$Mn(CO)_3$ (**2**) with ^nBuLi and then with (C_6H_6)$Mn(CO)_3^+$ (**1**) in THF at 0°C led to a light yellow dimanganese complex, [{(η^5-C_6H_6)$Mn(CO)_3$}$_2$(μ-C_5H_4)] (**3**), in 60% yield. According to the ^1H NMR spectrum, compound **3** is a mixture of two isomers **3a** and **3b** (2:1) having different positions of the double bonds on the cyclopentadiene ring (Scheme 1) [5]. Compound **3** is air-stable and highly soluble in organic solvents.

3.2. Reaction of 3 with organometallic compounds

Compound **3** can be easily lithiated in high efficiency by treating with ^tBuLi or ^nBuLi. The lithiated compound, presumably **4**, was used without isolation. Refluxing **4** with $Mn(CO)_5Br$ in benzene produces the yellow compound **5** (Mn) in 40% yield. Treatment of **4** with $Re(CO)_5Br$ in refluxing benzene produced compound **5** (Re) in 30% yield. Treatment of **4** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then MeI led to the isolation of compounds **6** (Mo) and **6** (W), respectively. Compound **6** (Cr) is highly unstable and could not be characterized completely. However, compounds **6** (Mo) and **6** (W) are moderately stable under nitrogen. The ^1H NMR spectra for the methyl group of **6** (Mo) and **6** (W) display singlet peaks at 0.27 and 0.32 ppm, respectively. Single crystals of **6** (W) suitable for X-ray studies were grown in hexane solution and the structure of **6** (W) was verified by an X-ray crystallographic analysis (see below). Treatment of **4** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then with Diazald led to the isolation of compounds **7** (Cr), **7** (Mo), and **7** (W), respectively. Compounds **7** in the solid state are quite stable under N_2. The IR spectra of nitrosyl ligands in compounds **7** (Cr), **7** (Mo), and **7** (W) display absorption frequencies 1692, 1657 and 1648 cm^{-1}, respectively. As previously described [6], the stretching frequencies of nitrosyl ligands decrease as the central metal becomes heavier.

Treatment of **4** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then with $HgCl_2$ led to the isolation of compounds **8** (Cr), **8** (Mo), and **8** (W), respectively. Due to the the instability of compounds **8**, we failed to obtain complete combustion data. Treatment of **4** with $FeCl_3$ led to the isolation of compound **9** in 23% yield, a heterometallic derivative of ferrocene. Satisfactory combustion analysis could not be obtained. Attempts at further purification resulted in partial decomposition of **9**.

Treatment of **3** with $Fe_2(CO)_9$ led to the isolation of compound **10** in 67% yield. The IR spectrum of **10** displays a bridging carbonyl frequency at 1765 cm^{-1}.

3.3. X-ray crystal structure of 6 (W)

Crystals of **6** (W) were grown in hexane solution. The molecular structure of **6** (W) is obtained by X-ray crystallographic study. Final fractional atomic coordinates with equivalent isotropic parameters are given in Table 2. The geometry of **6** (W) along with the atomic numbering scheme used is depicted in Fig. 1, and selected bond distances and angles are given in Table 3. The geometric parameters of (cyclohexadienyl)$Mn(CO)_3$ portion in **6** (W) are in agreement with those found in other compounds such as [$(EtCO_2)_2CH$-η^5-C_6H_6]$Mn(CO)_3$ [7], [$(OC)_5Re$-η^5-C_6H_6]$Mn(CO)_3$ [8], (Ph-η^5-C_6H_6)$Mn(CO)_3$ [9], [η^5-3-($N(CH_2CH_2O)_3Si$)-6-($Me_3CCO_2CH_2$)-C_6H_5]$Mn(CO)_3$ [10], [η^5-1-$N(CH_2CH_2O)_3Si$-6-Ph-C_6H_5]$Mn(CO)_3$ [11], [{exo-$(MeO)_2P(O)$-η^5-CH}$Mn(CO)_3$] [12], and [{endo-$(EtO)_2P(O)$-η^5-

Table 2
Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) of compound **6** (W)

atom	x	y	z	U_{eq} [a]
W	7294(0)	5928(0)	3137(0)	37(0)
Mn1	7114(2)	5917(1)	−1678(1)	42(1)
Mn2	7485(1)	2966(1)	4409(1)	45(1)
O1	8990(9)	5727(5)	5407(8)	79(3)
O2	9111(10)	7220(6)	2211(9)	92(3)
O3	9733(9)	5981(4)	−1685(7)	65(3)
O4	6784(11)	5118(7)	−3608(9)	107(4)
O5	6530(9)	7132(5)	−2983(8)	83(3)
O6	6402(11)	1584(7)	4285(9)	115(4)
O7	9610(11)	2997(7)	5924(10)	115(4)
O8	6381(10)	3384(6)	6427(9)	101(3)
O9	6593(15)	7041(8)	4429(12)	134(5)
C1	8629(11)	5807(6)	4557(10)	52(3)
C2	8668(12)	6743(7)	2617(10)	62(3)
C3	8709(13)	5970(6)	−1742(11)	55(4)
C4	6945(11)	5419(7)	−2826(11)	62(3)
C5	6780(10)	6662(6)	−2488(9)	52(3)
C6	6820(15)	2173(9)	4325(12)	83(5)
C7	8743(12)	2569(7)	4965(11)	69(4)
C8	6823(13)	3208(7)	5632(11)	78(4)
C9	7116(13)	6662(7)	3978(11)	65(3)
C10	6063(9)	5420(5)	2993(7)	38(2)
C11	6881(8)	4860(5)	3042(7)	33(2)
C12	7608(8)	4900(5)	2134(7)	34(2)
C13	7196(7)	5478(5)	1520(7)	28(2)
C14	6275(9)	5799(5)	2041(8)	38(2)
C15	7710(9)	5664(5)	405(8)	37(2)
C16	7337(9)	5144(5)	−409(8)	39(2)
C17	6226(10)	5131(6)	−853(8)	48(3)
C18	5510(11)	5737(6)	−877(9)	52(3)
C19	6065(9)	6354(5)	−438(8)	41(2)
C20	7253(9)	6310(5)	−19(7)	37(2)
C21	6917(8)	4304(5)	3921(7)	36(2)
C22	8086(11)	979(5)	9216(9)	47(3)
C23	8646(10)	1419(6)	8508(8)	45(3)
C24	7921(11)	1839(6)	7792(10)	58(3)
C25	6662(11)	1797(6)	7890(9)	56(3)
C26	6209(9)	1321(5)	8576(7)	37(2)
C27	98239 11)	5660(7)	2870(10)	60(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalalized U_{ij} tensor.

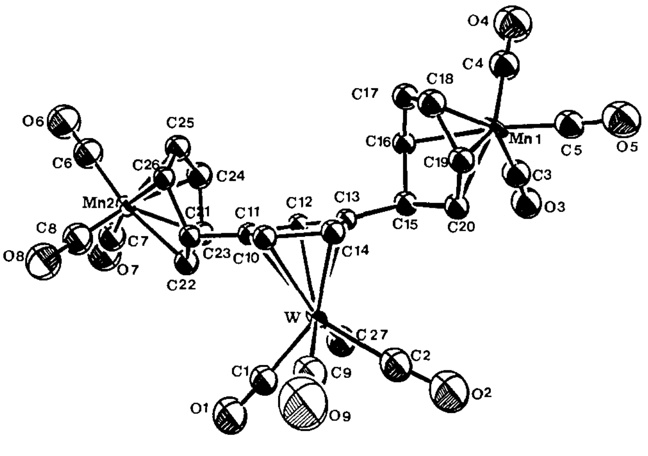


Fig. 1. Molecular structure of compound **6** (W), with the atom-labelling scheme.

C$_6$H$_6$}Mn(CO)$_3$] [12]. The cyclohexadienyl rings are nearly planar (with a maximum deviation of 0.013(10) Å for ring 1 (atoms C16–C20) and 0.033(11) Å for ring 2 (atoms C22–C26), respectively) and the dihedral angle between the two rings is 61.9°. The cyclohexadienyl rings are folded about C22–C21–C26 and C16–C15–C20 with angles of 40.6° and 38.0°, respectively. The manganese atoms are located 1.717(1) Å from ring 1 and 1.727(1) Å from ring 2. The Cp ring is nearly planar with a maximum deviation of 0.010(9) Å. The distance between W and a Cp centroid (2.002 Å) is quite similar to those found in previously investigated CpW complexes: (CH$_3$)(CO)$_3$W[η^5-C$_5$H$_4$-{(η^5-C$_6$H$_6$)-Mn(CO)$_3$}] (2.002 Å) [2]; [CpW(CO)$_3$]$_2$ (2.01(1) Å) [13]; CpW(CO)$_3$AuPh$_3$ (2.01(6) Å) [14]; CpW(CO)$_3$SC(S)N(CH$_3$)$_2$ (2.004(3) Å) [15]. The coordination spheres of all the metals (W, Mn1, and Mn2) can be viewed as pseudo octahedra, assuming that the Cp and cyclohexadienyl rings occupy three coordination sites. The bond distance of W–C (CH$_3$) (2.226(13) Å) is relatively shorter than those found in (CH$_3$)(CO)$_3$W[η^5-C$_5$H$_4$-{(η^5-C$_6$H$_6$)Mn(CO)$_3$}] of 2.309(7) Å and CpW(CO)$_3$-(C$_5$H$_9$) of 2.343(9) Å [16]. The W–C (Cp) bond distances range from 2.286(10) to 2.384(9) Å with an average of 2.339 Å, which is close to those found in (CH$_3$)(CO)$_3$W[η^5-C$_5$H$_4$-{(η^5-C$_6$H$_6$)Mn(CO)$_3$}] of 2.335 Å [2], in CpW(CO)$_3$SC(S)N(CH$_3$)$_2$ of 2.339 Å [15], and in [CpW(CO)$_3$]$_3$Ga of 2.343 Å [17]. The mean C–C distance in the Cp ring (1.419 Å) is typical of distances found in other CpW complexes.

Table 3
Selected bond distances (Å) and angles (°) for compound **6**(W)

W–C(1)	1.944(13)	W–C(2)	1.914(13)
W–C(9)	2.007(14)	W–C(10)	2.310(10)
W–C(12)	2.383(9)	W–C(14)	2.286(10)
W–C(27)	2.226(13)	Mn(1)–C(3)	1.795(15)
Mn(1)–C(4)	1.743(13)	Mn(1)–C(5)	1.802(12)
Mn(1)–C(16)	2.199(10)	Mn(1)–C(17)	2.111(11)
Mn(1)–C(18)	2.115(12)	Mn(1)–C(19)	2.153(10)
Mn(1)–C(20)	2.220(10)	C(10)–C(11)	1.423(13)
C(11)–C(12)	1.424(13)	C(12)–C(13)	1.431(13)
C(13)–C(14)	1.387(13)	C(13)–C(15)	1.571(13)
C(2)–W–C(1)	104.1(5)	C(9)–W–C(1)	77.3(5)
C(9)–W–C(2)	78.4(6)	C(1)–W–C(27)	75.3(5)
C(2)–W–C(27)	73.4(5)	C(10)–C(11)–C(12)	107.9(8)
C(11)–C(12)–C(13)	107.0(8)	C(12)–C(13)–C(14)	109.4(8)
C(11)–C(10)–C(14)	107.9(8)	C(13)–C(14)–C(10)	107.9(8)
C(3)–Mn(1)–C(4)	94.5(6)	C(3)–Mn(1)–C(5)	96.8(5)
C(4)–Mn(1)–C(5)	87.9(5)	C(15)–C(20)–C(19)	120.3(9)
C(16)–C(15)–C(20)	104.3(8)	C(16)–C(17)–C(18)	120.4(1)
C(17)–C(18)–C(19)	116.1(0)		

In conclusion, we have demonstrated that exploring the use of compound **3** or the lithiated compound **4** as a π-coordinating ligand is a synthetically valuable procedure for making poly-metallic compounds. With the appropriate organometallic reagents, polymetallic compounds with several combinations of transition metals can be easily obtained. The polymetallic compounds reported in this paper may be used to study the cooperative action of reactive metal centres toward various substrates.

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