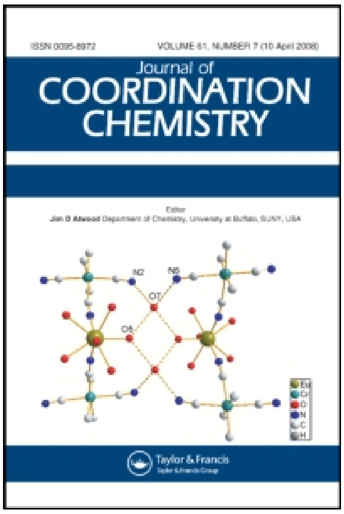

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SYNTHESIS AND CHARACTERIZATION OF BIS(η^5-SUBSTITUTED OR UNSUBSTITUTED CYCLOPENTADIENYL) HEXACARBONYLDIMOLYBDENUM-(TUNGSTEN) COMPLEXES

Xue-Nian Chen[a]; Jie Zhang[a]; Yuan-Qi Yin[a]; Jie Sun[b]
[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China [b] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China

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SYNTHESIS AND CHARACTERIZATION OF BIS(η^5-SUBSTITUTED OR UNSUBSTITUTED CYCLOPENTADIENYL) HEXACARBONYLDIMOLYBDENUM-(TUNGSTEN) COMPLEXES

XUE-NIAN CHEN[a], JIE ZHANG[a],
YUAN-QI YIN[a,]* and JIE SUN[b]

[a]*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China;* [b]*Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

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Through the reaction of $Fe_2(SO_4)_3$/HOAc aqueous solution with sodium η^5-substituted or unsubstituted cyclopentadienyltricarbonylmolybdenate(tungstate) salts $Na[M(\eta^5\text{-}C_5H_4R)(CO)_3]$, eight bis($\eta^5$-substituted or unsubstituted cyclopentadienyl) hexacarbonyldimolybdenum (tungsten) complexes $[(\eta^5\text{-}C_5H_4R)(CO)_3M]_2$ (M = Mo, R = H (**1**), COH (**2**), COC_6H_5 (**3**), $COC_6H_4COOCH_3$ (**4**); M = W, R = H (**5**), COH (**6**), COC_6H_5 (**7**), $COC_6H_4COOCH_3$ (**8**)) were prepared and characterized by analysis, IR and ^1H NMR spectra. The molecular structure of complex (**3**) was determined by single-crystal X-ray methods.

Keywords: Oxidative coupling; substituted cyclopentadiene; molybdenum; tungsten; crystal structure

INTRODUCTION

The dimer of η^5-cyclopentadienyl and substituted cyclopentadienyl tricarbonyl derivatives of chromium, molybdenum and tungsten are important carbonyl transition metal compounds. A large number of carbonyl metal

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* Corresponding author.

complexes have been derived from them and the chemical properties of these derivatives are affected by the substituents.[1] However, their syntheses are remarkably tedious. It is only for molybdenum that the direct reaction of the hexacarbonyl with dicyclopentadiene presents a feasible route to the desired compound, but it is fraught with difficulties.[2] The oxidation of salts of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ ($M = Cr, Mo, W$) has been used successfully, but the $M(CO)_6$ is required at an excess of twelve times compared to the stoichiometric equation.[3] In this paper, we report the preparation of $[(\eta^5\text{-}C_5H_4R)(CO)_3M]_2$ complexes ($M = Mo, W$; $R = H, COH, COC_6H_5, COC_6H_4COOCH_3$) by an improved oxidative coupling of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ anions. The complexes were characterized by analysis, IR and ^1H NMR spectra. The molecular structure of complex (**3**) was determined by single-crystal X-ray methods.

EXPERIMENTAL

Reactions were carried out in dried and deoxygenated solvents under nitrogen. Ferric sulfate ($x \cdot H_2O$ containing Fe 21–23%) and glacial acetic acid were of analytical grade and used without purification. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Aldrich Chem. Co. $Na(C_5H_4R)$ ($R = COH, COC_6H_5, COC_6H_4COOCH_3$),[4] $Na(C_5H_5) \cdot DME$ complexes[5] were synthesized as before. IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer and ^1H NMR on a Bruker AM 300 MHz spectrometer; C/H determinations were performed using a Carlo-Erba 1160 microanalyzer.

Preparation of Complexes (1)–(4)

To a solution of $Na(C_5H_5) \cdot DME$ (3.5 g, 20 mmol) in THF (90 cm^3) was added $Mo(CO)_6$ (5.2 g, 20 mmol). The mixture was heated under reflux for 20 h and cooled to 0°C. To it was added a solution of deoxygenated hydrated ferric sulfate (10.6 g, 20 mmol) in water (70 cm^3) and glacial acetic acid (20 cm^3) over a period of *ca* 15 min and the mixture was stirred for 1 h. The colour changed from yellow to purple and fine purple crystals of $[(\eta^5\text{-}C_5H_5)(CO)_3M]_2$ precipitated. These were filtered off, washed with water (40–50°C), then with petroleum ether and dried to obtain (**1**).

Complexes (**2**)–(**4**) were prepared using the same procedure as that for (**1**), $Na(C_5H_4R)$ ($R = COH, COC_6H_5, COC_6H_4COOCH_3$) being used instead of $Na(C_5H_5) \cdot DME$, respectively.

Preparation of Complexes (5)–(8)

To a solution of $Na(C_5H_5) \cdot DME$ (3.5 g, 20 mmol) in diglyme (90 cm^3) was added $W(CO)_6$ (7.0 g, 20 mmol). The mixture was heated under reflux for 6 h and cooled to 0°C. The workup was similar to that for (**1**). Complex (**5**) was obtained as a red solid.

Complexes (**6**)–(**8**) were prepared using the same procedure as that for (**5**), $Na(C_5H_4R)$ ($R = COH, COC_6H_5, COC_6H_4COOCH_3$) being used instead of $Na(C_5H_5) \cdot DME$, respectively. Elemental analyses and some physical properties of the complexes are summarized in Table I.

Crystallography of Complex (3)

A red primatic crystal of complex (**3**) suitable for X-ray diffraction was obtained from a CH_2Cl_2 solution at −20°C. A crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm was mounted on a glass fibre. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromatised MoKα ($\lambda = 0.71069$ Å) radiation and a 12 kW rotating anode generator. A total of 3356 reflections was collected; 3147 were unique ($R_{int} = 0.018$). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 19 carefully centred reflections in the range $18.54° < 2\theta < 26.73°$ corresponded to a primitive monoclinic cell. The data were collected at a temperature of 20 ± 1°C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2644 observed reflection ($I > 3.00\sigma(I)$) and 218

TABLE I Elemental analysis and some physical properties of complexes

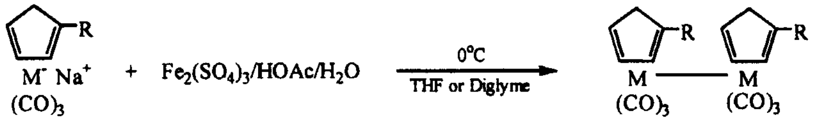
	Complexes		*Colour*	*Yield* (%)	*m.p.* (°C)	*Found* (*calcd.*) %	
	M	*R*				*C*	*H*
(**1**)	Mo	H	Red	81.2			
(**2**)	Mo	COH	Red	86.8	140(dec)	36.80 (36.87)	1.93 (2.00)
(**3**)	Mo	COC_6H_5	Red	92.4	168–170	55.21 (55.15)	2.90 (2.98)
(**4**)	Mo	$COC_6H_4COOCH_3$	Red	82.6	148(dec)	47.34 (47.26)	3.12 (3.23)
(**5**)	W	H	Red	83.8			
(**6**)	W	COH	Red	84.4	168(dec)	27.53 (27.65)	1.44 (1.38)
(**7**)	W	COC_6H_5	Red	88.7	184–186	35.93 (36.00)	2.26 (2.28)
(**8**)	W	$COC_6H_4COOCH_3$	Red	92.6	134(dec)	37.94 (37.88)	2.50 (2.56)

variable parameters and converged with unweighted and weighted agreement factors of $R = (\sum||F_o| - |F_c||)/\sum|F_o| = 0.023$, $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.032$. All calculation was performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

RESULTS AND DISCUSSION

In many methods of preparation of $[(\eta^5\text{-}C_5H_4R)(CO)_3M]_2$;[2–10] it is only for molybdenum that the direct reaction of $Mo(CO)_6$ with dicyclopentadiene provides the expected complex. Unfortunately, conditions for this preparation appear to be rather critical and not readily reproduced.[2] Birdwhistell's reported method,[3] using the oxidation of salts of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$, is undoubtedly successful for $[\eta^5\text{-}C_5H_4R)(CO)_3M]_2$, but the large excess of $M(CO)_6$ required could cause much inconvenience in the procedure. In other preparations, either the yield is low[7–10] or the reactants are difficult to obtain.[6] We report here an improved oxidation method. It is simple and appears to be widely applicable. The reaction described in this work is presented in Scheme 1.

The various substituted cyclopentadiene salts are obtained in solid form in THF by refluxing $Na(C_5H_5)$ with the corresponding ester.[4] In order to obtain the solid form of unsubstituted cyclopentadienide salts, DME is selected as solvent to give $Na(C_5H_5)\cdot DME$ as white acicular crystals.[5] These substituted or unsubstituted cyclopentadienide salts react in refluxing THF with an equimolar amount of $Mo(CO)_6$ for 20 h or in refluxing diglyme with an equimolar amount of $W(CO)_6$ for 6 h to give $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ salts. Finally, the $[(\eta^5\text{-}C_5H_4R)(CO)_3M]_2$ dimers are obtained in high yield by oxidation of the carbonyl anion using a mild oxidizing agent – an aqueous solution of ferric sulfate containing a small amount of acetic acid. The purity of the products is generally high. Further purification may be effected by recrystallization, but often this is not necessary. The yield of products is routinely greater than 80%.



SCHEME 1

IR Spectra

Important IR data for the complexes are shown in Table II. Several absorption bonds in the region 1972–1866 cm^{-1} are characteristic of carbonyl and the absorption bands in the region 1725–1644 cm^{-1} are characteristic of ester or ketonic carbonyls. In addition to the bands given in Table II, bands due to the ferrocenyl groups of complex (**1**) appear at 3115, 1428, 1419 and 1823 cm^{-1}. Other complexes give similar bands.

^{1}H NMR Spectra

As seen in Table II, the ^{1}H NMR spectra of all complexes show the presence of their corresponding organic groups. The singlet at about δ 9.70 is caused by aldehyde protons in complexes (**2**) and (**6**). The multiplets at δ 8.16–7.46 are due to the protons of phenyl groups in complexes (**3**), (**4**), (**7**) and (**8**). For the substituted cyclopentadienyl rings, ^{1}H NMR spectra exhibit two sets of bands at around δ 5.90–5.40, an upfield singlet at about δ 5.40 (two protons) is assigned to two *m*-H atoms of the substituted cyclopentadienyl and a downfield singlet at about δ 5.90 to *o*-H resulting from the different deshielding effects of electron-withdrawing groups COR ($R = H, C_6H_5, C_6H_4COOCH_3$) to *o*-H and *m*-H.[12] In complexes (**1**) and (**5**), the protons of unsubstituted cyclopentadienyl appear as a singlet in the range δ

TABLE II Some characteristic IR and ^{1}H NMR data for the complexes

	IR (cm^{-1})		^{1}*H NMR* (δ, ppm, $CDCl_3$)
	$\nu(C{\equiv}O)$	$\nu(C{=}O)$	
(**1**)	1951vs, 1922vs, 1866vs		5.30 (s, 10H, $2C_5H_5$)[a]
(**2**)	2018m, 1963vs, 1904vs	1695s	9.70 (s, 2H, 2COH); 5.83 (s, 4H, $2C_5H_4$)[b]; 5.41 (s, 4H, $2C_5H_4$)[c]
(**3**)	2018m, 1972vs, 1929vs, 1893vs	1649s	7.80–7.46 (m, 10H, $2C_6H_5$); 5.89 (s, 4H, $2C_5H_4$)[b]; 5.34 (s, 4H, $2C_5H_4$)[c]
(**4**)	2020m, 1957vs, 1930vs, 1901vs	1725s, 1656s	8.16–7.81 (m, 8H, $2C_6H_4$); 5.87 (s, 4H, $2C_5H_4$)[b]; 5.39 (s, 4H, $2C_5H_4$)[c]; 3.96 (s, 6H, $2CH_3$)
(**5**)	1948vs, 1914vs, 1876vs		5.39 (s, 10H, $2C_5H_5$)[a]
(**6**)	2011m, 1959vs, 1893vs	1697s	9.66 (s, 2H, 2COH); 5.86 (s, 4H, $2C_5H_4$)[b]; 5.52 (s, 4H, $2C_5H_4$)[c]
(**7**)	2014m, 1970vs, 1921vs, 1902vs	1644s	7.80–7.46 (m, 10H, $2C_6H_5$); 5.93 (s, 4H, $2C_5H_4$)[b]; 5.50 (s, 4H, $2C_5H_4$)[c]
(**8**)	2013m, 1960vs, 1905vs	1724s, 1658s	8.16–7.80 (m, 8H, $2C_6H_4$); 5.90 (s, 4H, $2C_5H_4$)[b]; 5.52 (s, 4H, $2C_5H_4$)[c]; 3.96 (s, 6H, $2CH_3$)

[a] 5.20 and 5.30 in the literature.[5]
[b] *o*-H in substituted cyclopentadienyl.
[c] *m*-H in substituted cyclopentadienyl.

5.39–5.30 (δ 5.33–5.20 in the literature[5]). In the ^{1}H NMR spectra of complexes (**4**) and (**8**), besides the above, a singlet at 3.96 is due to methyl proton.

Structure of Complex (3)

The molecular structure of complex (**3**) is shown in Figure 1, crystal data are collected in Tables III and IV gives selected bond lengths and angles. Final atomic coordinates are listed in Table V. As seen in Figure 1, the molecule exhibits a centre of symmetry and the Mo–Mo distance is 3.2347(6) Å. Each Mo atom is coordinated by three carbonyls and one phenylcarbonylcyclopentadienyl ligand. Two phenylcarbonylcyclopentadienyl rings are found to lie on opposite sides of the molecule. The perpendicular distance from

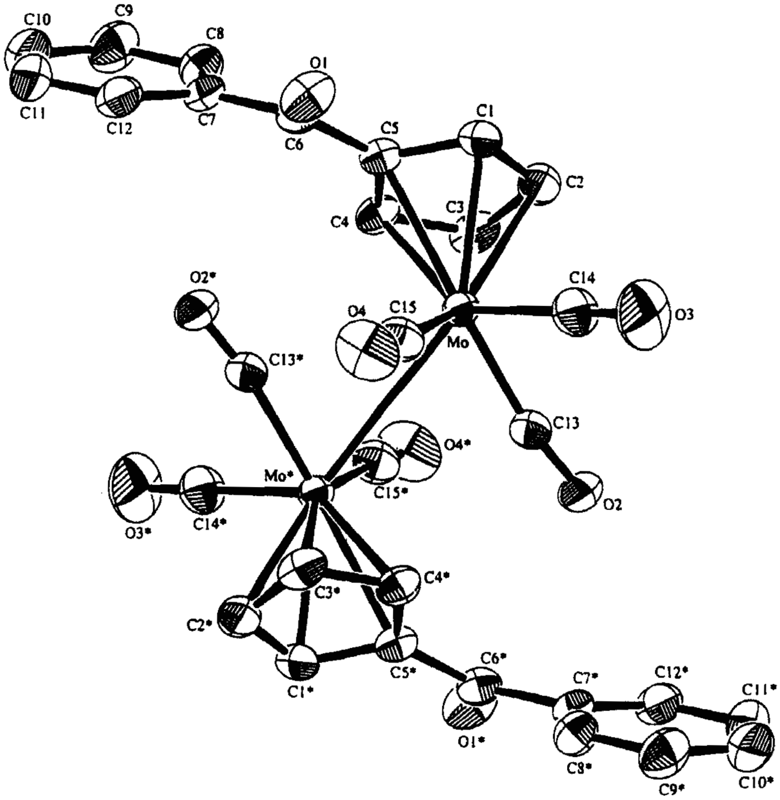


FIGURE 1 Molecular structure of complex (3).

TABLE III Summary of crystal and intensity data for complex (3)

Formula	$C_{30}H_{18}O_{18}Mo_2$
F.W.	698.35
Crystal system	Monoclinic
Space group	$P2_1/c$
$F(000)$	692.00
a (Å)	8.260(4)
b (Å)	14.313(2)
c (Å)	11.093(3)
β (°)	91.97(3)
V (Å^3)	1310.7(7)
Z	2
$D_{calc.}$ $(g \cdot cm^{-1})$	1.769
μ (MoKα) (cm^{-1})	10.08
Temperature (°C)	20.0
Scan type	ω–2θ
$2\theta_{max}$ (°)	55.0
No. observations	2644 ($I > 3.00\,\sigma(I)$)
No. variables	218
R^a, $R_w{}^b$	0.023, 0.032

$^aR = (\sum||F_o| - |F_c||)/\sum|F_o|$.
$^bR_w = [\sum_\omega(|F_o| - |F_c|)^2/\sum_\omega F_o^2]^{1/2}$.

TABLE IV Selected bond lengths (Å) and angles (°) for complex (3)

Mo–Mo*	3.2347(6)	Mo–C(13)	1.976(2)
Mo–C(14)	1.959(3)	Mo–C(15)	1.995(3)
C(5)–C(6)	1.493(3)	C(6)–C(7)	1.497(3)
C(1)–C(5)	1.425(3)	C(4)–C(5)	1.424(3)
C(7)–C(8)	1.392(3)	C(7)–C(12)	1.385(3)
C–C (av., phenyl ring)	1.383	C–C (av., Cp ring)	1.419
Mo*–C(13)	3.072	Mo*–C(15)	3.304
Mo–Cp (av.)	2.017		
Mo–C(13)–O(2)	171.0(2)	Mo–C(14)–O(3)	178.1(3)
Mo–C(15)–O(4)	175.2(2)		

Mo to the plane of the ring is 2.017 Å; The C–C distance in the phenylcarbonylcyclopentadienyl rings is in the range 1.410(4)–1.425(3) Å with an average of 1.419(5) Å, comparable to those of related complexes.[13] The average Mo–CO distance is 1.977 Å and the average of Mo–C–O angles is 174.76°. These also are normal.[13]

It is noted that since the π-system of the group CO–C_6H_5 would be quite well conjugated with that of the cyclopentadienyl ring, the bond lengths C(5)–C(6) (1.493 Å) and C(6)–C(7) (1.497 Å) become much shorter than a normal C–C single bond (1.54 Å), but longer than a C=C double bond (1.34 Å). Bond lengths C(1)–C(5) (1.425 Å) and C(4)–C(5) (1.424 Å) in the

TABLE V Final atomic coordinates and equivalent thermal parameters (Å^2) for the heavy atoms

Atom	*x/a*	*y/b*	*z/c*	*B (eq)*
Mo	0.58481(2)	0.46133(1)	0.12377(2)	2.007(5)
O(1)	0.5186(2)	0.1948(1)	0.1273(2)	3.62(4)
O(2)	0.6533(3)	0.6739(1)	0.0990(2)	3.86(4)
O(3)	0.9491(3)	0.4822(2)	0.1968(3)	5.79(6)
O(4)	0.7533(3)	0.3491(2)	−0.0794(2)	4.90(5)
C(1)	0.5555(3)	0.3606(2)	0.2851(2)	2.81(5)
C(2)	0.5315(3)	0.4531(2)	0.3267(2)	3.25(5)
C(3)	0.3899(3)	0.4888(2)	0.2688(2)	2.99(5)
C(4)	0.3232(3)	0.4178(2)	0.1927(2)	2.51(4)
C(5)	0.4257(2)	0.3379(1)	0.2024(2)	2.35(4)
C(6)	0.4022(3)	0.2441(1)	0.1457(2)	2.53(4)
C(7)	0.2336(3)	0.2116(1)	0.1145(2)	2.41(4)
C(8)	0.1009(3)	0.2394(2)	0.1796(2)	3.00(5)
C(9)	−0.0523(3)	0.2066(2)	0.1475(3)	3.92(6)
C(10)	−0.0737(4)	0.1470(2)	0.0509(3)	4.31(7)
C(11)	0.0571(4)	0.1181(2)	−0.0123(3)	4.19(6)
C(12)	0.2113(3)	0.1497(2)	0.0194(2)	3.25(5)
C(13)	0.6251(3)	0.5959(2)	0.0980(2)	2.63(4)
C(14)	0.8152(3)	0.4731(2)	0.1689(3)	3.43(6)
C(15)	0.6893(3)	0.3926(2)	−0.0093(2)	3.10(5)

cyclopentadienyl ring and C(7)–C(8) (1.392 Å) and C(7)–C(12) (1.385 Å) in the phenyl ring become longer slightly than average (1.4195 and 1.383 Å, respectively).

Finally, attention is drawn to the carbonyls coordinated to molybdenum. The C(13)–O(2) distances correspond to semi-bridging carbonyls and the others C(14)–O(3) and C(15)–O(4) are terminal. This is because the asymmetry parameter α (0.55) of C(13)–O(2) is well within the range (0.1–0.6) for semi-bridging carbonyls, whereas that of the other carbonyls falls outside the range.[14–16]

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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