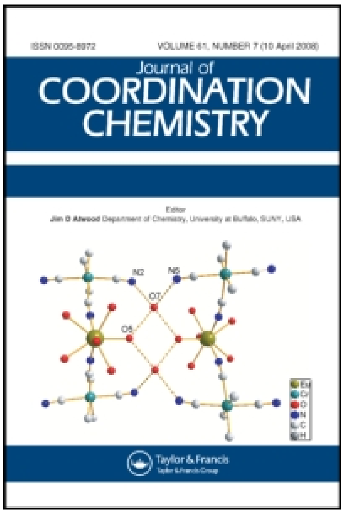


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS OF ORGANOTRANSITION METAL COMPLEXES CONTAINING *p*-METHOXYCARBONYLBENZOYLCYCLO-PENTADIENYL AND *p*-METHOXYCARBONYLPHENYL (HYDROXYMETHYL)CYCLOPENTADIENYL LIGANDS FROM SODIUM *p*-METHOXYCARBONYLBENZOYLCYCLO-PENTADIENIDE. X-RAY STRUCTURE OF η^5-*p*-$MeO_2CC_6H_4COC_5H_4Mo(CO)_3I$

Li-Cheng Song[a]; Xiang-Yang Wu[a]; Qing-Mei Hu[a]; Guang-Huai Zeng[a]; Jie Sun[b]
[a] Department of Chemistry, Nankai University, Tianjin, China [b] Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai, China

To cite this Article Song, Li-Cheng , Wu, Xiang-Yang , Hu, Qing-Mei , Zeng, Guang-Huai and Sun, Jie(1998) 'SYNTHESIS OF ORGANOTRANSITION METAL COMPLEXES CONTAINING *p*-METHOXYCARBONYLBENZOYLCYCLO-PENTADIENYL AND *p*-METHOXYCARBONYLPHENYL (HYDROXYMETHYL)CYCLOPENTADIENYL LIGANDS FROM SODIUM *p*-METHOXYCARBONYLBENZOYLCYCLO-PENTADIENIDE. X-RAY STRUCTURE OF η^5-*p*-$MeO_2CC_6H_4COC_5H_4Mo(CO)_3I$', Journal of Coordination Chemistry, 44: 1, 9 — 21

To link to this Article: DOI: 10.1080/00958979808022875

URL: http://dx.doi.org/10.1080/00958979808022875

J. Coord. Chem., 1998, Vol. 44, pp. 9–21
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF ORGANOTRANSITION METAL COMPLEXES CONTAINING *p*-METHOXYCARBONYLBENZOYLCYCLOPENTADIENYL AND *p*-METHOXYCARBONYLPHENYL (HYDROXYMETHYL)CYCLOPENTADIENYL LIGANDS FROM SODIUM *p*-METHOXYCARBONYLBENZOYLCYCLOPENTADIENIDE. X-RAY STRUCTURE OF η^5-*p*-$MeO_2CC_6H_4COC_5H_4Mo(CO)_3I$

LI-CHENG SONG[a]*, XIANG-YANG WU[a], QING-MEI HU[a], GUANG-HUAI ZENG[a] and JIE SUN[b]

[a]*Department of Chemistry, Nankai University Tianjin, 300071, China;* [b]*Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

(Received 5 May 1997; In final form 9 July 1997)

A new functionally substituted cyclopentadienyl salt *p*-$MeO_2CC_6H_4COC_5H_4Na$ (**1**) was prepared from cyclopentadienylsodium and dimethyl terephthalate in THF, and which might be utilized to synthesize a series of novel transition metal complexes containing difunctional group-substituted cyclopentadienyl ligands; **1** reacted with $M(CO)_6$(M = Mo, W) followed by treatment with PBr_3 or I_2 to give mononuclear organomolybdenum (or tungsten) halides η^5-*p*-$MeO_2CC_6H_4COC_5H_4M(CO)_3X$(**2**, M = Mo, X = Br; **3**, M = W, X = Br; **4**, M = Mo, X = I; **5**, M = W, X = I), whereas reaction of **1** with $W(CO)_6$ and successive treatment with selenium powder and MeI or $PhCH_2Cl$ afforded mononuclear organotungsten selenolate complexes η^5-*p*-$MeO_2CC_6H_4COC_5H_4W$ $(CO)_3SeMe$ (**6**) and η^5-*p*-$MeO_2CC_6H_4COC_5H_4W(CO)_3SeCH_2Ph$ (**7**). In addition, **1** reacted with $M(CO)_6$(M = Mo, W) followed by treatment with $FeCo_2(CO)_9(\mu_3\text{-}S)$ to produce the corresponding polynuclear complexes η^5-*p*-$MeO_2CC_6H_4COC_5H_4MFeCo(CO)_8(\mu_3\text{-}S)$ (**8**, M = Mo; **9**, M = W), which could be converted with $NaBH_4$ into hydroxyl derivatives η^5-*p*-$MeO_2CC_6H_4CH(OH)C_5H_4MFeCo(CO)_8(\mu_3\text{-}S)$ (**10**, M = Mo; **11**, M = W). All the new

---

*Author for correspondence.

transition metal complexes **2-11** have been fully characterized by elemental analysis, IR and ^1H NMR spectroscopy, as well as for **4** by an X-ray diffraction analysis.

Keywords: molybdenum; tungsten; iron, cobalt; *p*-methoxycarbonylbenzoylcyclopentadienyl; crystal structure

INTRODUCTION

The η^5-cyclopentadienyl and η^5-substituted cyclopentadienyl ligands are most common and important and have played a major role in the development of organometallic chemistry[1-8]. Among such ligands, the η^5-functionally substituted ones have received considerable attention[9-12]. This is because the functionality on a cyclopentadienyl ring can lead to different structures and special reactivities relative to the parent cyclopentadienyl- and non-functionally substituted cyclopentadienyl organometallics. In this article, we report the synthesis and characterization of organotransition metal complexes containing difunctional group-substituted cyclopentadienyl, *i.e.*, *p*-methoxycarbonylbenzoyl- and *p*-methoxycarbonylphenyl(hydroxymethyl)cyclopentadienyl ligands, as well as the X-ray molecular structure of η^5-*p*-$MeO_2CC_6H_4COC_5H_4(CO)_3MoI$.

EXPERIMENTAL

All reactions were carried out under purified nitrogen using standard Schlenk techniques. THF and diglyme were distilled from sodium-benzophenone ketyl under nitrogen. Column chromatography and TLC were carried out by using silica gel of 300-400 mesh and silica gel G(10-40μm), respectively. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Strem Chemicals Inc. PBr_3, I_2, $NaBH_4$, MeI and $PhCH_2Cl$ were all pure reagents. $FeCo_2(CO)_9(\mu_3\text{-}S)$ was prepared according to the literature[13]. IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer, and ^1H NMR spectra on a Jeol FX 90 Q NMR spectrometer. C/H analyses were performed on a 240 C analyzer and melting points were determined on a Yanaco micromelting point apparatus (MP-500).

p-$MeO_2CC_6H_4COC_5H_4Na$ *(1)*

Into a 100 cm^3 three-necked flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube were added 0.575 g (25 mmol) of sodium sand and 40 cm^3 of THF. The mixture was stirred and cooled in an ice-bath. To this suspension was added dropwise 3 cm^3 (36 mmol) of freshly cracked cyclopentadiene and the mixture was stirred at room temperature for 3 h. To the resulting pink solution of sodium cyclopentadienide was added 4.85 g (25 mmol) of dimethylterephthalate and the mixture was stirred under reflux for 10 h. Solvent was removed under reduced pressure. The residue was thoroughly washed under nitrogen with 3 × 50 cm^3 of absolute ethyl ether and dried under vacuum to give 5.396 g (72%) of THF solvated sodium salt $C_{14}H_{11}O_3Na{\cdot}2/3C_4H_8O$ (**1**), as a yellow, slightly air-sensitive and moisture-sensitive solid. M. p. 180°C (dec.). IR(KBr, disc): $\nu_{C=O}$ 1626(m), 1710(s) cm^{-1}. ^{1}H NMR (D_2O, δ): 1.81(t, J = 6.5 Hz, 2/3 × $4H^{\beta}$ of THF), 3.68(t, J = 6.5 Hz, 2/3 × $4H^{\alpha}$ of THF), 3.88(s, 3H, CH_3), 6.16(s, 2H, H^3, H^4), 6.29(s, 2H, H^2, H^5), 7.84, 7.90, 7.94, 8.04(AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-p-$MeO_2CC_6H_4COC_5H_4Mo(CO)_3Br$ (2)

To the flask described above were added 500 mg (1.68 mmol) of sodium salt **1**, 528 mg (2 mmol) of $Mo(CO)_6$ and 30 cm^3 of THF. The mixture was stirred under reflux for 12 h. Upon cooling to room temperature, 0.21 cm^3 (2 mmol) of PBr_3 was added dropwise to the flask, and the reaction mixture was stirred for 3 h. Solvent was removed under reduced pressure and the residue extracted by CH_2Cl_2. The extracts were filtered through a short silica gel column and subsequently subjected to TLC on silica gel G plates using 1:2:1 petroleum ether/CH_2Cl_2/Et_2O as eluent. Three bands developed on the TLC plates and from the second band was obtained 123 mg (15%) of **2** as a red solid. M.p. 122-124°C; *anal.*, calcd. for $C_{17}H_{11}O_6MoBr$(%): C, 41.92; H, 2.28; found: C, 42.01; H, 2.41. IR(KBr disc): $\nu_{C=O}$ 1655(m), 1713(s); $\nu_{C\equiv O}$ 1959(vs), 2049(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 4.08(s, 3H, CH_3), 6.00(br.s, 2H, H^3, H^4), 6.20(br.s, 2H, H^2, H^5), 7.97, 8.10, 8.28, 8.41(AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-p-$MeO_2CC_6H_4COC_5H_4W(CO)_3Br$ (3)

To the flask described above were added 250 mg (0.84 mmol) of sodium salt **1**, 352 mg (1 mmol) of $W(CO)_6$ and 20 cm^3 of diglyme. The mixture was refluxed for 6 h. After diglyme was removed under reduced pressure, 30 cm^3 of THF and 0.15 cm^3 (1 mmol) of PBr_3 was added. The reaction mixture was stirred for 3 h at room temperature. After the same workup as for **2** was obtained 165 mg (34%) of **3** as a red solid. M.p. 111-113°C (dec.); *anal.*, calcd. for $C_{17}H_{11}O_6WBr$(%): C, 35.51; H, 1.93; found: C, 35.23; H, 1.66. IR(KBr disc): $\nu_{C=O}$ 1655(s), 1713(s); $\nu_{C\equiv O}$ 1942(vs), 2049(vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 4.00(s, 3H, CH_3), 5.98 (AA'BB' triplet, 2H, H^3, H^4), 6.16(AA'BB' triplet, 2H, H^2, H^5), 7.87, 7.96, 8.19, 8.28 (AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-p-MeO$_2$CC$_6$H$_4$COC$_5$H$_4$Mo(CO)$_3$I (4)

The same procedure as that for **2** was followed, but 254 mg (1 mmol) of I_2 was used instead of PBr_3 to give 210 mg (23%) of **4** as a black solid. M.p. 106-108°C; *anal.*, calcd. for $C_{17}H_{11}O_6MoI$(%): C, 38.23; H, 2.08; found: C, 38.16; H, 2.05. IR (KBr disc): $\nu_{C=O}$ 1647(s), 1721(s); $\nu_{C\equiv O}$ 1950(vs), 1975(vs), 2041(s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 4.17(s, 3H, CH_3), 6.02(br.s, 2H, H^3, H^4), 6.22(br.s, 2H, H^2, H^5), 7.95, 8.09, 8.30, 8.42(AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-p-MeO$_2$CC$_6$H$_4$COC$_5$H$_4$W(CO)$_3$I (5)

The same procedure as that for **3** was followed, but 127 mg of I_2 was used instead of PBr_3 to give 243 mg (47%) of **5** as a black solid. M.p. 137-138°C; *anal.*, calcd. for $C_{17}H_{11}O_6WI$(%): C, 32.83; H, 1.78; found: C, 32.81; H, 1.68. IR(KBr disc): $\nu_{C=O}$ 1655(s), 1721(s); $\nu_{C\equiv O}$ 1934(vs), 1966(vs), 2022(vs) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 4.00(s, 3H, CH_3), 5.96(AA'BB' triplet, 2H, H^3, H^4), 6.16(AA'BB' triplet, 2H, H^2, H^5), 7.84, 7.94, 8.18, 8.28(AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-p-MeO$_2$CC$_6$H$_4$COC$_5$H$_4$W(CO)$_3$SeMe (6)

To the flask described above were added 250 mg (0.84 mmol) of sodium salt **1**, 352 mg (1 mmol) of $W(CO)_6$ and 20 cm^3 of diglyme. The mixture was refluxed for 6 h. After diglyme was removed under reduced pressure, 20 cm^3 of THF and 79 mg (1 mmol) of Se powder were added. The reaction mixture was stirred for 1 h at room temperature and then 0.06 cm^3 (1 mmol) of MeI was added. The reaction mixture was stirred overnight at room temperature. Solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were filtered through a short silica gel column and then subjected to TLC using 2:1 CH_2Cl_2/petroleum ether as eluent. Three bands developed on TLC plates and from the first band was obtained 62 mg (13%) of **6** as a red solid. M.p. 115-116°C; *anal.*, calcd. for $C_{18}H_{14}O_6SeW$ (%): C, 36.70; H, 2.40; found: C, 36.67; H, 2.26. IR(KBr disc): $\nu_{C=O}$ 1655(s), 1713(vs); $\nu_{C\equiv O}$ 1918(vs), 1943(s), 2016(vs), 2031(s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.84(s, 3H, $SeCH_3$), 4.02(s, 3H, OCH_3), 5.88(br.s, 2H, H^3, H^4), 6.16(br.s, 2H, H^2, H^5), 7.92, 8.02, 8.27, 8.36(AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-p-MeO$_2$CC$_6$H$_4$COC$_5$H$_4$W(CO)$_3$SeCH$_2$Ph (7)

The same procedure as for **6** was followed, but 0.12 cm^3 (1 mmol) of $PhCH_2Cl$ was used instead of MeI to give 65 mg (12%) of **7** as a red solid. M.p. 104-105°C; *anal.*, calcd. for $C_{24}H_{18}O_6SeW$(%): C, 43.33; H, 2.73; found: C, 43.22; H, 2.87. IR (KBr disc): $\nu_{C=O}$ 1647(m), 1721(s); $\nu_{C\equiv O}$ 1918(vs), 1959(s), 2024(vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 3.70(s, 2H, CH$_2$), 4.05(s, 3H, CH$_3$), 5.48(s, 2H, H^3, H^4), 5.76(s, 2H, H^2, H^5), 7.35(s, 5H, C$_6$H$_5$), 7.83, 7.92, 8.26, 8.36(AA'BB' quartet, 4H, C$_6$H$_4$) ppm.

η^5-*p*-$MeO_2CC_6H_4COC_5H_4MoFeCo(CO)_8(\mu_3\text{-}S)$ *(8)*

To the flask described above were added 250 mg (0.84 mmol) of sodium salt **1**, 264 mg (1 mmol) of Mo(CO)$_6$ and 30 cm^3 of THF. The mixture was refluxed for 12 h. Upon cooling to room temperature 458 mg (1 mmol) of FeCo$_2$(CO)$_9$(μ_3-S) was added and the reaction mixture was refluxed for 40 min. TLC showed that no starting material was left. Solvent was removed under reduced pressure. The residue was extracted with CH$_2$Cl$_2$ and the extracts were subjected to column chromatography. Petroleum ether was first used as eluent and then CH$_2$Cl$_2$ to develop two bands. The second band was further subjected to TLC separation using 3:1 Et$_2$O/petroleum ether as eluent. From the fourth band was obtained 63 mg (11%) of **8** as a black solid. M.p. 114-116°C; *anal.*, calcd. for C$_{22}$H$_{11}$CoFeMoO$_{11}$S(%): C, 38.07; H, 1.60; found: C, 38.18; H, 1.60. IR(KBr disc): $\nu_{C=O}$ 1647(m), 1721(s); $\nu_{C\equiv O}$ 1860(s), 1908(m), 1934(m), 1988(s), 2008(s), 2041(vs), 2082(s) cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 4.03(s, 3H, CH$_3$), 5.74(br.s, 2H, H^3, H^4), 6.12(br.s, 2H, H^2, H^5), 7.84, 7.97, 8.18, 8.33(AA'BB' quartet, 4H, C$_6$H$_4$) ppm.

η^5-*p*-$MeO_2CC_6H_4COC_5H_4WFeCo(CO)_8(\mu_3\text{-}S)$ *(9)*

To the flask described above were added 250 mg (0.84 mmol) of sodium salt **1**, 352 mg (1 mmol) of W(CO)$_6$ and 20 cm^3 of diglyme. The mixture was refluxed for 6 h. After diglyme was removed under reduced pressure, 458 mg (1 mmol) of FeCo$_2$(CO)$_9$(μ_3-S) and 30 cm^3 of THF were added and the mixture was refluxed for 40 min. The same workup as for **8** gave 300 mg (46%) of **9** as a black solid. M.p. 128-130°C; *anal.*, calcd. for C$_{22}$H$_{11}$CoFeWO$_{11}$S (%): C, 33.79; H, 1.42; found: C, 33.95; H, 1.23. IR (KBr disc): $\nu_{C=O}$ 1647(s), 1721(s); $\nu_{C\equiv O}$ 1852(s), 1926(s), 1975(vs), 2007(vs), 2041(vs), 2082(s) cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 4.00(s, 3H, CH$_3$), 5.60-5.96(m, 2H, H^3, H^4), 6.00-6.26(m, 2H, H^2, H^5), 7.88, 7.98, 8.22, 8.32(AA'BB' quartet, 4H, C$_6$H$_4$) ppm.

η^5-*p*-$MeO_2CC_6H_4CH(OH)C_5H_4MoFeCo(CO)_8(\mu_3\text{-}S)$ *(10)*

To the flask described above were added 70 mg (0.1 mmol) of **8**, 7.63 mg (0.2 mmol) of NaBH$_4$ and 5 cm^3 of MeOH. The mixture was stirred for 20 mins at room temperature. Solvent was removed under reduced pressure and the mixture was extracted with CH_2Cl_2. The extracts were subjected to TLC separation using CH_2Cl_2 as eluent and six bands developed. From the fourth band was obtained 30 mg (43%) of **10** as a black solid. M.p. 183-185°C(dec.); *anal.*, calcd. for $C_{22}H_{13}CoFeMoO_{11}S$(%): C, 37.96; H, 1.88; found: C, 37.70; H, 1.90. IR(KBr disc): $\nu_{C=O}$ 1704(s); $\nu_{C\equiv O}$ 1918(m), 1948(s), 1968(s), 1983(s), 2024(vs), 2065(s); ν_{OH} 3411(br.) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.66(br.s, 1H, OH), 3.97(s, 3H, CH_3), 5.22-5.92 (m, 5H, CH, C_5H_4), 7.54, 7.62, 8.08, 8.16(AA'BB' quartet, 4H, C_6H_4) ppm.

η^5-*p*-$MeO_2CC_6H_4CH(OH)C_5H_4WFeCo(CO)_8(\mu_3\text{-}S)$ (*11*)

The same procedure as that for **10** was followed, but 80 mg (0.1 mmol) of **9** was used instead of **8** to give 42 mg (54%) of **11** as a black solid. M.p. 111-112°C; *anal.*, calcd. for $C_{22}H_{13}CoFeWO_{11}S$(%): C, 33.70; H, 1.67; found: C, 33.69; H, 1.61. IR(KBr disc): $\nu_{C=O}$ 1704(s); $\nu_{C\equiv O}$ 1877(s), 1958(s), 1983(vs), 2024(vs), 2073(s); ν_{OH} 3419(br.) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.80(br.s, 1H, OH), 3.96(s, 3H, CH_3), 5.24-5.88 (m, 5H, CH, C_5H_4), 7.50, 7.60, 8.08, 8.18 (AA'BB' quartet, 4H, C_6H_4) ppm.

Single-crystal structure determination of 4

Single-crystals of **4** suitable for X-ray diffraction were obtained by slow evaporation of CH_2Cl_2/petroleum ether solution. A single-crystal measuring 0.20 × 0.20 × 0.30 mm was mounted on a glass fibre and placed on a Rigaku AFC7R diffractometer with graphite monochromated MoKα radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. A total of 3613 independent reflections was collected at 20°C by ω-2θ scan mode, of which 3033 independent reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in subsequent refinement. The data were corrected for Lp factors. Crystal data are listed in Table I.

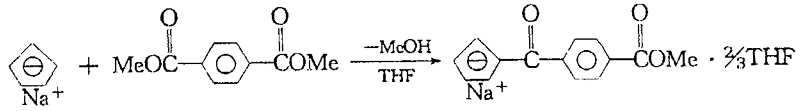
The structure was solved by direct methods and Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Final refinement by full-matrix least-squares methods for non-hydrogen atoms converged to give the unweighted and weighted agreement factors 0.034 (R) and 0.053 (R_w). All calculations were performed using the TEXSAN program system crystallographic software package of the Molecular Structure Corporation.

TABLE I Crystallographic data for **4**.

Formula	$C_{34}H_{22}O_{12}Mo_2I_2$
Formula weight	1068.23
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	13.040(4)
b (Å)	20.671(7)
c (Å)	7.157(2)
α (deg)	98.96(3)
β (deg)	103.62(3)
γ (deg)	105.56(2)
Z	2
V (Å^3)	1756(1)
Dc (g cm^{-3})	2.020
F(000)	1024.00
λ (MoKα) (Å)	0.71069
μ (cm^{-1})	25.34
R	0.034
R_w	0.053
Goodness of fit indicator	1.76
Largest peak in final diff map (e Å^{-3})	0.75

RESULTS AND DISCUSSION

It has been reported that reactions of sodium cyclopentadienide with esters RCOOR′ give sodium carbonyl functionally-substituted cyclopentadienide.9 We recently found that the analogous reaction of an equivalent of sodium cyclopentadienide with dimethyl terephthalate afforded sodium *p*-methoxycarbonylbenzoylcyclopentadienide, **1**, as a slightly air-sensitive and moisture-sensitive solid (*1*).

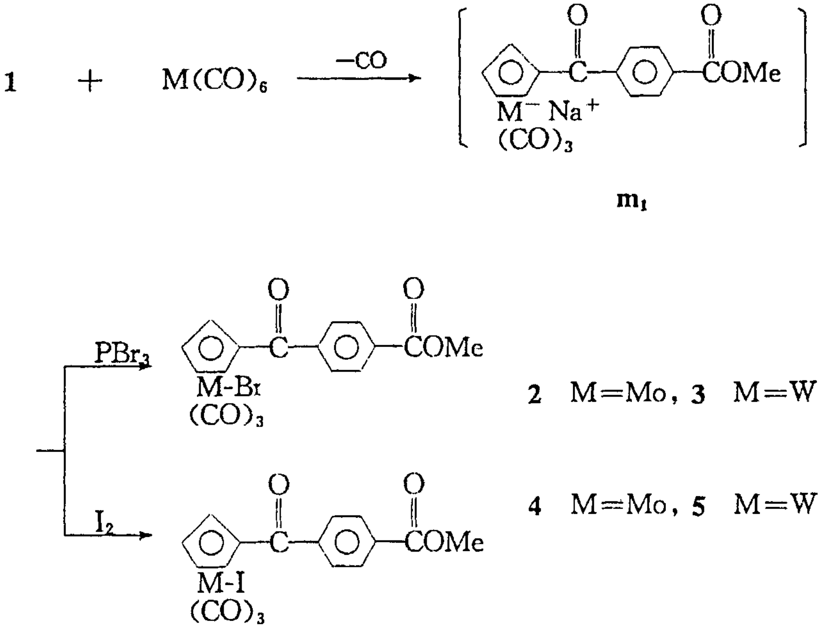


(*1*)

The IR spectrum of **1** shows one absorption band at 1626 cm^{-1} for its ketonic carbonyl and one absorption band at 1710 cm^{-1} for its ester carbonyl. The ^{1}H NMR spectrum of **1** exhibits respective resonance peaks for Me, C_6H_4 and C_5H_4 groups, as well as two triplets assigned to α- and β-protons of THF. The sodium salt **1** is solvated by THF and it would be reasonably formulated as $C_{14}H_{11}O_3Na{\cdot}2/3C_4H_8O$ according to the integration of corresponding signals in its ^{1}H NMR spectrum.

Sodium salt **1** can be used to synthesize a series of mono- and polynuclear organotransition metal complexes. For example, treatment of salt **1** with group 6 metal carbonyls $M(CO)_6$ (M = Mo, W) and subsequent reaction of the intermediate $\mathbf{m_1}$ with PBr_3 or I_2 gave organomolybdenum and organotungsten halides **2-5** (*2*), whereas salt **1** reacted with $M(CO)_6$ (M = W), followed by successive treatment of $\mathbf{m_1}$ (M = W) with elemental selenium and $PhCH_2Cl$ or MeI, to yield organotungsten selenolate complexes **6** and **7** (*3*). However, attempts to prepare molybdenum analogues of **6** and **7** through similar reactions as in (*3*) were unsuccessful, possibly due to the intermediate $\mathbf{m_2}$ (M = Mo) being hardly formed by selenium insertion into the Mo-Na bond, even though selenium insertion into the Mo-Li bond had been reported to be quite facile[14].

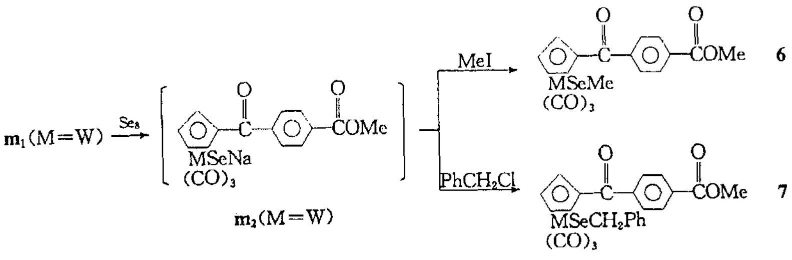
We further found that polynuclear compounds **8** and **9** could be prepared from an isolobal displacement reaction[15,16] of a d^9ML_3 $Co(CO)_3$ fragment in $FeCo_2(CO)_9(\mu_3\text{-}S)$ by a d^5ML_5 fragment η^5-*p*-$MeO_2CC_6H_4COC_5H_4M(CO)_2$,



2 M=Mo, **3** M=W

4 M=Mo, **5** M=W

(*2*)

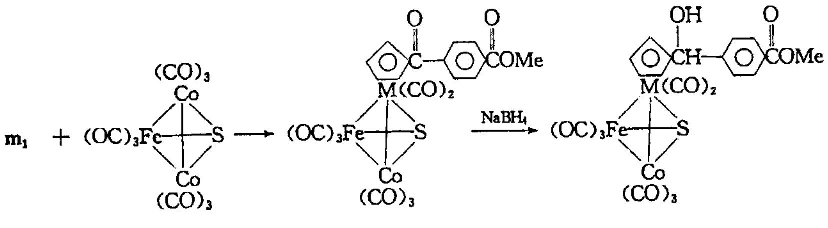


6

7

(3)

derived from the intermediate **m$_1$**; these were in turn converted to products **10** and **11** when treated with excess $NaBH_4$ (*4*).



(*4*)

8 M=Mo
9 M=W

10 M=Mo
11 M=W

Compounds **2-11** are new and have been fully characterized by elemental analysis, IR and ^{1}H NMR spectroscopy. For mononuclear compounds **2-7** the IR spectra show one absorption band at 1646-1656 cm^{-1}, one band at 1712-1721 cm^{-1} and two or three bands at 1917-2049 cm^{-1}, characteristic of ketonic, ester and terminal carbonyl groups, respectively. For polynuclear compounds **8** and **9**, IR spectra show one ketonic carbonyl band at 1647 cm^{-1}, one ester carbonyl band at 1721 cm^{-1} and six or seven terminal carbonyl bands at 1851-2081 cm^{-1}, whereas those for **10** and **11** exhibit one ester carbonyl band at 1704 cm^{-1}, one hydroxyl band at about 3415 cm^{-1} and five or six terminal carbonyl bands at 1877-2074 cm^{-1}. The ^{1}H NMR spectra of **2-11** all indicate the existence of their respective organic groups. For example, in their ^{1}H NMR spectra there is one singlet at about 4 ppm and one quartet in the range 7.5-8.1 ppm, characteristic of the methoxy and *para*-disubstituted C_6H_4 group, respectively. In addition, in the ^{1}H NMR spectra of **2-11** the signals between about 5-6 ppm are assigned to substituted cyclopentadienyls and in those of **10** and **11** signals at about 2.7 ppm are assigned to their hydroxyl groups. D/H exchange between **10** (or **11**) and D_2O may occur, since the hydroxyl signals disappeared when determining their ^{1}H NMR spectra in the presence of D_2O.

In order to unambiguously confirm the structure of **4** and to establish the general structural features of the functionally substituted cyclopentadieny ligand in compounds **2-11** as well as in sodium salt **1**, an X-ray single-crystal diffraction analysis for **4** was undertaken. The results showed that for **4** there are two structures with similar geometric parameters in each asymmetric unit. Figure 1 shows the two structures. The nearest interatomic distance between the two structures is 3.13 Å [O(5)-O(8)], which is beyond the sum of normal van der Waals radii. Atomic coordinates and thermal parameters are given in Table II. Selected bond lengths and angles are listed in Tables III and Table IV, respectively. From Figure 1 it is seen that both structures of **4** are very similar to those of η^5-$Ph_5C_5Mo(CO)_3I$[17] and η^5-$Bz_5C_5Mo(CO)_3I$,[18] which have a four-

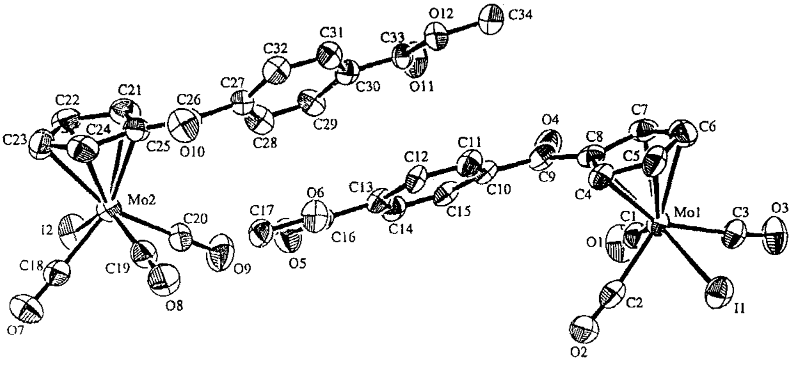


FIGURE 1 Structure of **4** showing the atom numbering scheme.

legged piano stool arrangement, if observed by ignoring the substituents on the cyclopentadienyl ring. The Mo-I bond lengths in **4** are 2.837 [Mo(1)-I(1)] and 2.841 Å [Mo(2)-I(2)], very close to those in $Ph_5C_5Mo(CO)_3I$(2.866 Å)[17] and $Bz_5C_5Mo(CO)_3I$(2.850 Å)[18]. The cyclopentadienyl centroid to Mo(1) and Mo(2) distances for **4** are 1.982 and 1.994 Å, also very close to those in $Ph_5C_5Mo(CO)_3I$(2.042 Å)[17] and $Bz_5C_5Mo(CO)_3I$(2.002 Å)[18]. From the least-squares planes it can be seen that for one structure of **4**, C_9 and O_4 are basically located in the C_4-through-C_8 cyclopentadienyl plane, and C_{16} and O_5 are located in the C_{10}-through-C_{15} benzene ring plane. Similarly, for the other structure of **4**, C_{26} and O_{10} are basically situated in the C_{21}-through-C_{25} cyclopentadienyl plane, and C_{33} and O_{11} in the C_{27}-through-C_{32} benzene ring plane. That is, in both structures the ketonic and ester carbonyls are conjugated quite well with the cyclopentadienyl and benzene ring, respectively. In addition, the bond lengths of ketonic carbonyls C_9-O_4 and C_{26}-O_{10} are 1.242(9) and 1.225(9) Å, whereas those of ester carbonyls C_{16}-O_5 and C_{33}-O_{11} are 1.191(10) and 1.178(10) Å. The shorter ester carbonyls are consistent with the IR data of **4**. In addition, the two ring planes, namely the C_4-through-C_8 cyclopentadienyl and C_{10}-through-C_{15} benzene ring planes, the C_{21}-through-C_{25} and C_{27}-through-C_{32} planes are not coplanar; dihedral angles are 33.3° and 43.9°, respectively.

Finally, it is noteworthy that $MeO_2CC_6H_4COC_5H_4$ in complexes **1-11**, due to special steric and electronic effects, would have different chemical behaviour in comparison with monofunctionally substituted cyclopentadienyl ligands such as $MeCOC_5H_4$ and $MeO_2CC_5H_4$. For example, while the carbonyl group in the acetyl substituent of η^5-$MeCOC_5H_4WFeCo(CO)_8(\mu_3\text{-}S)$ was reported to react with both $NaBH_4$ and MeMgI to give the hydroxyl group of secondary and tertiary alcohol derivatives,[12] the carbonyl group in the methoxycarbonylbenzoyl

TABLE II Final atomic coordinates and B_{eq} for *4*

atom	*x/a*	*y/b*	*z/c*	B_{eq}
I(1)	−0.09291(5)	−0.43357(3)	−0.31302(9)	5.20(2)
I(2)	0.61745(5)	0.40382(4)	0.4148(1)	5.63(2)
Mo(1)	0.09918(5)	−0.34302(4)	−0.01510(9)	3.23(2)
Mo(2)	0.40468(6)	0.33847(4)	0.45378(10)	3.50(2)
O(1)	0.3396(6)	−0.2713(4)	−0.038(1)	5.9(2)
O(2)	0.0597(6)	−0.2569(4)	−0.3327(9)	5.8(2)
O(3)	0.1749(5)	−0.4709(4)	−0.135(1)	6.0(2)
O(4)	0.3196(5)	−0.1894(3)	0.3481(8)	5.1(2)
O(5)	0.1767(6)	0.1046(4)	0.2154(10)	5.8(2)
O(6)	0.0122(5)	0.0538(3)	0.2510(8)	4.6(2)
O(7)	0.3560(5)	0.4322(4)	0.1627(9)	5.9(2)
O(8)	0.1739(6)	0.2509(4)	0.1531(10)	6.1(2)
O(9)	0.4611(6)	0.2157(4)	0.227(1)	6.6(2)
O(10)	0.1675(5)	0.2237(3)	0.6663(9)	5.4(2)
O(11)	0.4861(5)	−0.0159(3)	0.7492(9)	5.3(2)
O(12)	0.3240(4)	−0.0600(3)	0.8029(8)	4.3(1)
C(1)	0.2515(8)	−0.2988(5)	−0.028(1)	4.4(2)
C(2)	0.0711(7)	−0.2897(5)	−0.229(1)	4.3(2)
C(3)	0.1455(7)	−0.4266(5)	−0.101(1)	4.4(2)
C(4)	0.0171(6)	−0.2861(4)	0.182(1)	3.5(2)
C(5)	−0.0193(7)	−0.3535(5)	0.192(1)	4.6(2)
C(6)	0.0686(8)	−0.3771(5)	0.273(1)	4.7(2)
C(7)	0.1673(7)	−0.3200(5)	0.320(1)	4.1(2)
C(8)	0.1370(7)	−0.2612(5)	0.2673(10)	3.7(2)
C(9)	0.2198(6)	−0.1935(4)	0.305(1)	3.6(2)
C(10)	0.1881(6)	−0.1300(4)	0.2930(9)	3.1(2)
C(11)	0.0922(7)	−0.1218(5)	0.327(1)	4.0(2)
C(12)	0.0675(6)	−0.0613(4)	0.310(1)	3.5(2)
C(13)	0.1394(6)	−0.0084(4)	0.2677(10)	3.2(2)
C(14)	0.2374(7)	−0.0148(5)	0.239(1)	4.0(2)
C(15)	0.2624(6)	−0.0746(5)	0.254(1)	3.6(2)
C(16)	0.1130(7)	0.0560(5)	0.242(1)	3.8(2)
C(17)	−0.0173(7)	0.1147(5)	0.229(1)	4.4(2)
C(18)	0.3753(7)	0.3977(5)	0.268(1)	4.0(2)
C(19)	0.2581(8)	0.2830(5)	0.262(1)	4.4(2)
C(20)	0.4424(7)	0.2600(5)	0.307(1)	4.2(2)
C(21)	0.4617(7)	0.3246(5)	0.777(1)	4.8(2)
C(22)	0.4938(8)	0.3966(5)	0.793(1)	5.3(3)
C(23)	0.3980(9)	0.4162(5)	0.724(1)	5.4(3)
C(24)	0.3063(8)	0.3576(6)	0.672(1)	4.9(3)
C(25)	0.3415(7)	0.2982(5)	0.701(1)	3.9(2)
C(26)	0.2664(7)	0.2308(5)	0.689(1)	4.2(2)
C(27)	0.3056(6)	0.1696(4)	0.713(1)	3.3(2)
C(28)	0.3947(6)	0.1595(5)	0.650(1)	4.2(2)
C(29)	0.4222(6)	0.1002(5)	0.671(1)	4.0(2)
C(30)	0.3632(6)	0.0505(4)	0.745(1)	3.6(2)
C(31)	0.2753(6)	0.0617(4)	0.808(1)	4.0(2)
C(32)	0.2463(6)	0.1212(5)	0.792(1)	4.1(2)
C(33)	0.4001(8)	−0.0111(4)	0.764(1)	3.7(2)
C(34)	0.3537(8)	−0.1221(5)	0.824(1)	5.5(3)

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha).$$

TABLE III Selected bond lengths (Å) for **4**.

atom	*atom*	*distance*	*atom*	*atom*	*distance*
I(1)	Mo(1)	2.837(1)	I(2)	Mo(2)	2.841(1)
Mo(1)	C(1)	1.98(1)	Mo(1)	C(8)	2.283(7)
Mo(2)	C(25)	2.295(8)	O(4)	C(9)	1.242(9)
O(6)	C(16)	1.321(10)	O(6)	C(17)	1.43(1)
O(10)	C(26)	1.225(9)	O(11)	C(33)	1.178(10)
O(12)	C(33)	1.329(10)	C(8)	C(9)	1.46(1)
C(13)	C(16)	1.49(1)	C(25)	C(26)	1.45(1)
C(30)	C(31)	1.39(1)	C(30)	C(33)	1.49(1)

TABLE IV Selected bond angles(°) for **4**.

atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
I(1)	Mo(1)	C(1)	130.6(2)	C(1)	Mo(1)	C(8)	88.5(3)
I(2)	Mo(2)	C(18)	76.0(2)	C(18)	Mo(2)	C(25)	139.7(3)
C(4)	C(8)	C(7)	105.6(8)	C(4)	C(8)	C(9)	132.4(7)
O(4)	C(9)	C(8)	118.4(7)	O(4)	C(9)	C(10)	119.5(7)
C(14)	C(13)	C(16)	118.1(7)	O(5)	C(16)	O(6)	123.4(8)
O(6)	C(16)	C(13)	113.3(7)	C(21)	C(25)	C(24)	105.6(8)
C(21)	C(25)	C(26)	129.3(8)	O(10)	C(26)	C(25)	118.9(8)
C(25)	C(26)	C(27)	122.6(7)	C(31)	C(30)	C(33)	123.3(7)
O(11)	C(33)	O(12)	124.0(8)	O(11)	C(33)	C(30)	124.9(8)

substituent of complex **9** can only react with NaBH$_4$ to afford the hydroxyl group of secondary alcohol derivative **11**. Furthermore, the yields of products **2-11** are generally lower than those of corresponding complexes containing monofunctionally substituted cyclopentadienyl ligands such as η^5-RC$_5$H$_4$Mo(CO)$_3$X (R = MeCO, MeCO$_2$C; X = Br, I)[19] and η^5-RC$_5$H$_4$MFeCo(CO)$_8$(μ_3-S) (M = Mo, W; R = MeCO, MeO$_2$C)[12] prepared using similar synthetic procedures.

SUPPLEMENTAL MATERIAL

Tables of fractional atomic coordinates, thermal parameters, interatomic distances, observed and calculated structure factors are available on request from the authors.

Acknowledgements

We are grateful to the National Natural Science Foundation of China, the Laboratory of Organometallic Chemistry at the Shanghai Institute of Organic Chemistry and State Key Laboratory of Elemento-Organic Chemistry for financial support of this work.

References

1. W.E. Watts, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, (Pergamon Press, Oxford, 1982), p. 1013.
2. C. Janiak and H. Schumann, *Adv. Organomet. Chem.*, **33**, 291, (1991).
3. R.B. King, *Coord. Chem. Rev.*, **20**, 155, (1976).
4. P.M. Maitlis, *Acc. Chem. Rev.*, **11**, 301, (1978).
5. H. Schumann, *Pure Appl. Chem.*, **63**, 813, (1991).
6. W.-M. Tsai, M.D. Rausch and R.D. Rogers, *Organometallics*, **15**, 2591, (1996).
7. M. Fei, S.K. Sur and D.R. Tyler, *Organometallics*, **10**, 419, (1991).
8. J.W. Chambers, A.J. Baskar, S.G. Bott, J.L. Atwood and M.D. Rausch, *Organometallics*, **5**, 1635, (1986).
9. D.W. Macomber, W.P. Hart and M.D. Rausch, *Adv. Organomet. Chem.*, **21**, 1, (1982).
10. L.-C. Song, H. Yang, Q. Dong and Q.-M. Hu, *J. Organomet. Chem.*, **414**, 137, (1991).
11. L.-C. Song, J.-Y. Shen, Q.-M. Hu, R.-J. Wang and H.-G. Wang, *Organometallics*, **12**, 408, (1993).
12. L.-C. Song, J.-Y. Shen, Q.-M. Hu and X.-Y. Huang, *Organometallics*, **14**, 98, (1995).
13. M. Cowie, R.L. Dekock, T.R. Wagenmaker, D. Seyferth, R.S. Henderson and M.K. Gallagher, *Organometallics*, **8**, 119, (1989).
14. W. Eikons, C. Kienitz, P.G. Jones and C. Thöne, *J. Chem. Soc., Dalton Trans.*, 3329, (1994).
15. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **21**, 711, (1982).
16. H. Vahrenkamp, *Comments Inorg. Chem.*, **4**, 253, (1985).
17. L.-C. Song, Q.-M. Hu, J.-S. Yang, X.-C. Cao, R.-J. Wang and T.C.W. Mak, *Inorg. Chim. Acta*, **245**, 109, (1996).
18. L.-C. Song, L.-Y. Zhang, Q.-M. Hu and X.-Y. Huang, *Inorg. Chim. Acta*, **230**, 127, (1995).
19. L.-C. Song, Q. Dong and Q.-M. Hu, *Acta Chim. Sin.*, **49**, 1129, (1991).