单取代环戊二烯基羰基钼化合物的合成、晶体结构及热稳定性

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摘要: 单取代环戊二烯(C_5H_5R)(R=n-Butyl (**1**),Benzyl (**2**),n-Propyl (**3**),Allyl (**4**))分别和 $Mo(CO)_6$ 反应,生成 4 个新的环戊二烯基钼双核羰基配合物($C_5H_4R)_2Mo_2(CO)_6$(R=n-Butyl (**5**),Benzyl (**6**),n-Propyl (**7**),Allyl (**8**))。配合物 **5~8** 通过元素分析,IR,¹H NMR,热重进行了表征,并用 X-ray 单晶衍射法测定了配合物 **5** 和 **6** 的晶体结构。晶体结构显示配合物 **5** 属于单斜晶系,$P2_1/c$ 空间群,配合物 **6** 属于三斜晶系,$P\bar{1}$ 空间群;热重分析表明配合物 **5** 和 **6** 分别处于 107 和 162 ℃以下温度时很稳定。

关键词: 羰基钼;单取代环戊二烯基;晶体结构;X-射线衍射

Synthesis, Crystal Structures and Thermal Stability of Monsubstituted Cyclopentadienyl Dimolybdenum Carbonyl Complexes

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Abstract: Monsubstituted cyclopentadienes (C_5H_5R) (R =n-Butyl (**1**), Benzyl (**2**), n-Propyl (**3**), Allyl (**4**)) reacted with $Mo(CO)_6$ to give four new dinuclear cyclopentadienyl molybdenum carbonyl complexes ($C_5H_4R)_2Mo_2(CO)_6$ (R= n-Butyl (**5**), Benzyl (**6**), n-Propyl (**7**), Allyl (**8**)), respectively. The complexes **5~8** were characterized by elemental analysis, IR, ¹H NMR spectrum, and TG. The crystal structures of **5** and **6** were determined by X-ray single crystal diffraction. The structures show that complex **5** crystallizes in monoclinic system with space group $P2_1/c$ and complex **6** is triclinic crystal system with space group $P\bar{1}$. The TG analysis shows that the complexes **5** and **6** are stable below 107 and 162 ℃, respectively. CCDC: 883603, **5**; 881472, **6**.

Key words: molybdenum carbonyl; monsubstituted cyclopentadienyl; crystal structure; X-ray diffraction

0　Introduction

　　Cyclopentadienyl metal complexes have been extensively investigated since ferrocene has been discovered. Replacement of the hydrogen atoms by other substituents alters both the steric and electronic influences of the η^5-cyclopentadienyl ring, resulting in differing reactivity and stability of the substituted cyclopentadienyl metal complexes[1-3]. Especially for metallocene polymerization catalysts, the steric and electronic effects of cyclopentadienyl ring substituents have great influence on catalytic activity[4]. Our team has been focusing on the synthesis of a series of cyclopentad-ienyl metal carbonyl complexes[5-8]. The

goal of the research described in this and subsequent papers is to investigate the reactivity of substituted cyclopenta-dienyl with molybdenum carbonyl and to obtain sufficient structural data by single-crystal X-ray diffraction in order to understand and hopefully to predict the steric and electronic influences of cyclopentadienyl substituents on the molecular struc-tures and reactions of the corresponding biscyclopen-tadienyl dinuclear metal carbonyl complexes.

1 Experimental

1.1 General procedures

Argon atmosphere protects all operations involving air-or moisture-sensitive compounds, using standard Schlenk techniques.

Diethyl ether, xylene, and n-hexane were freshly distilled from sodium/benzophenone ketyl under nitrogen prior to use. Methylene chloride was distilled over P_2O_5 under nitrogen. The ligands (C_5H_5R) (R =n-butyl (**1**), benzyl (**2**), n-propyl (**3**), allyl (**4**)) were synthesized according to the literature[9]. Column chro-matography was carried out on alumina column using dichloromethane and petroleum ether as eluent.

^{1}H NMR spectrum was recorded on a Bruker AV 500 instrument, while IR spectrum was recorded as KBr pellets on a FT IR-8900 spectrometer. Elemental analysis was performed on a Vario EL Ⅲ analyzer. The structures of crystals were determined by Bruker Smart APEX diffractometer with graphite monochro-mated Mo $K\alpha$ (λ=0.071 073 nm) radiation. The TG-DTG measurements were carried out on a SDT Q600 V20.9 Build 20 thermogravimetric analyzer.

1.2 Synthesis of complexes 5~8

1.2.1 Synthesis of complex $[(\eta^5\text{-}C_5H_4{}^n\text{Bu})\text{Mo(CO)}_3]_2$ (**5**)

A solution of ligand **1** (0.244 g, 2.0 mmol) and $Mo(CO)_6$ (0.528 g, 2.0 mmol) in 30 mL of xylene was refluxed for 12 h. After removal of solvent xylene, the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The red band afforded complex **5** as red crystals (0.249 g, 81.1% yield), m.p. 103~105 ℃. Anal. Calcd. for $C_{24}H_{26}Mo_2O_6$ (%): C, 47.86; H, 4.35. Found (%): C, 47.83; H, 4.31. ^{1}H NMR (500 MHz, CDCl$_3$): δ: 5.26~5.28 (m, 4H,

C_5H_4), 5.47~5.61 (m, 4H, C_5H_4), 2.31 (t, J=8.0 Hz, 4H, $C_5H_4CH_2$), 1.42~1.58 (m, 8H, $(CH_2)_2$), 0.97 (t, J=7.5 Hz, 6H, CH_3), IR (KBr, ν_{CO}, cm^{-1}): 1 939(s), 1 913 (s), 1 888(s).

1.2.2 Synthesis of complexes 6, 7, 8

Using a procedure similar to that described above, the reactions of ligands **2~4** with $Mo(CO)_6$ in xylene refluxing 12 h afforded complexes **6~8** as red crystals in 72.6%, 74.6%, 69.2% yields, respectively. The complex **6**: m.p. 164 ~166 ℃. Anal. Calcd. for $C_{30}H_{22}Mo_2O_6$(%): C, 53.75; H, 3.31. Found(%): C, 53.71; H, 3.29. ^{1}H NMR (500 MHz, CDCl$_3$): δ: 5.15~5.26 (m, 4H, C_5H_4), 5.41~5.56 (m, 4H, C_5H_4), 3.72 (s, 4H, $C_6H_5CH_2$), 7.37~7.45 (m, 10H, C_6H_5), IR (KBr, ν_{CO}, cm^{-1}): 1 944(s), 1 908(s), 1 888(s). The complex **7**: m.p. 113~114 ℃. Anal. Calcd. for $C_{22}H_{22}Mo_2O_6$ (%): C, 46.01; H, 3.86. Found (%): C, 45.98; H, 3.85. ^{1}H NMR (500 MHz, CDCl$_3$): δ: 5.27~5.33 (m, 4H, C_5H_4), 5.60~5.69 (m, 4H, C_5H_4), 2.31 (t, J=7.5 Hz, 4H, CH_2), 1.57~1.63 (m, 4H, CH_2), 1.03 (t, J=7.5 Hz, 6H, CH_3), IR (KBr, ν_{CO}, cm^{-1}): 1 951(s), 1 915(s), 1 892(s). The complex **8**: m.p. 149~150 ℃. Anal. Calcd. for $C_{22}H_{18}Mo_2O_6$(%): C, 46.34; H, 3.18; Found(%): C, 46.31; H, 3.17. ^{1}H NMR (500 MHz, CDCl$_3$): δ: 5.28~5.37 (m, 4H, C_5H_4), 5.60~5.71 (m, 4H, C_5H_4), 2.31 (d, J=8.0 Hz, 4H, CH_2), 2.02 (d, J=6.0 Hz, 4H, CH_2), 5.56~5.59 (m, 2H, CH), IR (KBr, ν_{CO}, cm^{-1}): 1 952(s), 1 910(s), 1 888(s).

1.3 Crystal structure determinations for complexes 5 and 6

Crystals suitable for X-ray analysis of complexes **5** (crystal size: 0.45 mm×0.15 mm×0.11 mm)and **6** (crystal size: 0.48 mm ×0.42 mm ×0.05 mm) were grown from a CHCl$_2$/hexane (2∶1, $V∶V$) solution at room temperature. The Bruker Smart APEX diffractometer equipped with a Mo $K\alpha$ (λ=0.071 073 nm) collect the data of the crystals. The structure was solved by direct method and refined by full-matrix least squares. All calculations were performed using the SHELX-97 program system. The crystal data and summary of X-ray data collection are presented in Table 1.

CCDC: 883603, **5**; 881472, **6**.

Table 1　Crystal structure parameters of complexes 5 and 6

Complex	5	6
Formula	$C_{24}H_{26}Mo_2O_6$	$C_{30}H_{22}Mo_2O_6$
Formula weigh	602.33	670.36
Temperature / K	298(2)	298(2)
Crystal size / mm	0.45×0.15×0.11	0.48×0.42×0.05
λ / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	0.779 11(12)	0.725 4(3)
b / nm	1.180 57(18)	0.976 6(3)
c / nm	1.341 9(2)	1.026 4(4)
α / (°)		95.704(4)
β / (°)	99.024(2)	102.335(4)
γ / (°)		104.302(4)
V / nm³	1.219 0(3)	0.679 4(4)
Z	2	1
D_c / (g·cm⁻³)	1.641	1.638
μ / mm⁻¹	1.064	0.965
$F(000)$	604	334
θ range / (°)	2.31~25.50	2.06~25.50
Reflections collected / unique	6 280 / 2 262 (R_{int}=0.021 6)	3 504 / 2 471 (R_{int}=0.027 8)
Max. / Min. transmission	0.891 9 / 0.645 9	0.953 4 / 0.654 6
Goodness of fit on F^2	1.066	1.057
R_1, wR_2 ($I>2\sigma(I)$)	R_1=0.025 2, wR_2=0.059 8	R_1=0.035 5, wR_2=0.096 1
R_1, wR_2 (all data)	R_1=0.028 6, wR_2=0.061 4	R_1=0.037 4, wR_2=0.098 2
ρ_{min}, ρ_{max} / (e·nm⁻³)	−510, 254	−760, 773

2　Results and discussion

2.1　Synthesis of complexes 5~8

The reactions of the ligands ($C_5H_5{}^nBu$, $C_5H_5CH_2C_6H_5$, $C_5H_5{}^nPropyl$, C_5H_5Allyl) with Mo(CO)₆, refluxing in xylene for 12 h produced the corresponding Mo-Mo bonded dinuclear complexes (complex **5**: 81.1%, complex **6**: 72.6%, complex **7**: 74.6%, complex **8**: 69.2%) (Scheme 1). The solvent hexane/CH_2Cl_2 (1∶2, $V∶V$) evaporated slowly and produced the suitable single crystal.
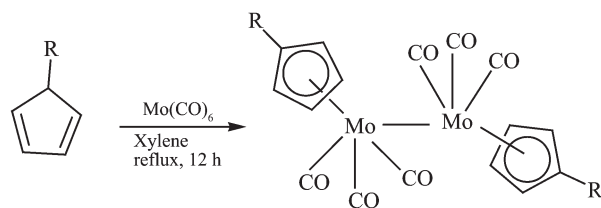
R=n-butyl (**5**), benzyl (**6**), n-propyl (**7**), allyl (**8**)

Scheme 1　Synthesis of complexes **5**~**8**

The IR spectra of dimolybdenum complexes all showed strong CO absorption peaks (complex **5** at 1 939(s), 1 913(s), 1 888(s) cm⁻¹; complex **6** at 1 944 (s), 1 908 (s), 1 888 (s) cm⁻¹; complex **7** at 1 951(s), 1 915(s), 1 892(s) cm⁻¹, complex **8** at 1 952(s), 1 910 (s), 1 888 (s) cm⁻¹) in the terminal ν_{CO} region, which consist with the facts that the complexes are similar structures. The ¹H NMR spectra of complexes **5**~**8** all showed two groups of peaks for the cyclopentadienyl (complex **5** at 5.26~5.28, 5.47~5.61; complex **6** at 5.15~5.26, 5.41~5.56; complex **7** at 5.27~5.33, 5.60~5.69; complex **8** at 5.28~5.37, 5.60~5.71). Meanwhile, the ¹H NMR spectrum of complex **5** showed four groups of peaks for n-butyl (CH₃ at 0.97, (CH₂)₂ at 1.42~1.58, $C_5H_4CH_2$ at 2.31), the ¹H NMR spectrum of complex **6** showed two groups of peaks for benzyl (phenyl at 7.37~7.45 and PhCH₂ at 3.72), the ¹H

NMR spectrum of complex **7** showed three groups of peaks for *n*-propyl (CH$_3$ at 1.03, CH$_2$ at 1.57~1.63, C$_5$H$_4$CH$_2$ at 2.31) and the ^{1}H NMR spectrum of complex **8** showed three groups of peaks for allyl (CH at 5.56~5.59, C$_5$H$_4$CH$_2$ at 2.31, CH$_2$ 2.02).

The results above agree with the single crystal X-ray diffraction analysis results.

## 2.2　Crystal structures of the complexes 5 and 6

The structures of complexes **5** and **6** were presented in Fig.1 and 2, respectively. The selected bond lengths and angles are listed in Table 2.

The crystal structures (Fig.1 and Fig.2) indicate that the complex **5** is monoclinic crystal system and the complex **6** is triclinic crystal system. Besides, the crystals have *trans* conformation with six terminal carbonyl ligands and Cp ring planes are parallel, respectively. Similar to the cyclopentadienyl analogue *trans*-[CpMo(CO)$_3$]$_2$, the complex **6** is C_i symmetry, while the complex **5** is C_{2h}^5 symmetry. And the X-ray diffraction analyses also show that in complexes **5** and
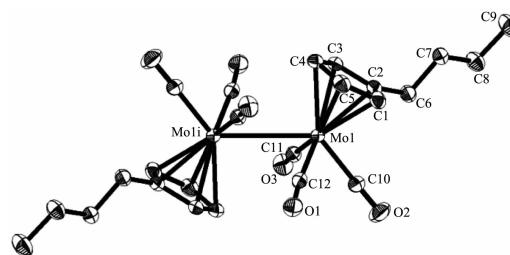
Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: i: −*x*, −*y*, −*z*

Fig.1　Structure of complex **5** with the atomic numbering scheme
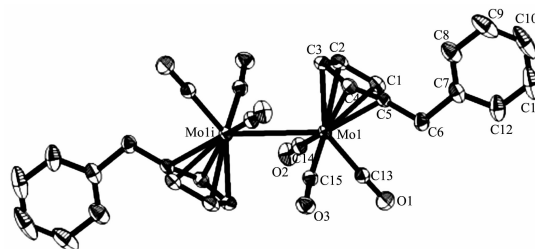
Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: i: −*x*+1, −*y*, −*z*+1

Fig.2　Structure of complex **6** with the atomic numbering scheme

Table 2　Selected bond distances (nm) and angles (°) for complexes 5 and 6

5					
Mo(1)-Mo(1i)	0.322 9	C(5)-Mo(1)	0.234 6(3)	C(12)-O(1)	0.114 3(3)
C(1)-Mo(1)	0.322 9	C(10)-Mo(1)	0.195 9(3)	C(10)-O(2)	0.146(3)
C(2)-Mo(1)	0.233 2(2)	C(11)-Mo(1)	0.198 4(3)	C(11)-O(3)	0.114 4(3)
C(3)-Mo(1)	0.235 4(2)	C(12)-Mo(1)	0.198 5(3)		
C(4)-Mo(1)	0.237 4(3)	C(6)-C(7)	0.152 1(4)		
C(10)-Mo(1)-C(1)	87.79(11)	C(10)-Mo(1)-C(11)	79.06(11)	C(11)-Mo(1)-C(3)	97.06(10)
C(10)-Mo(1)-C(2)	88.94(10)	C(10)-Mo(1)-C(12)	77.81(11)	C(11)-Mo(1)-C(12)	105.68(11)
C(10)-Mo(1)-C(3)	121.07(10)	C(11)-Mo(1)-C(1)	140.15(10)		
C(10)-Mo(1)-C(4)	144.49(10)	C(11)-Mo(1)-C(2)	105.84(10)		
6					
Mo(1)-Mo(1i)	0.323 1	C(5)-Mo(1)	0.232 9(3)	C(13)-O(1)	0.115 0(5)
C(1)-Mo(1)	0.232 4(3)	C(13)-Mo(1)	0.195 6(4)	C(14)-O(2)	0.114 4(4)
C(2)-Mo(1)	0.234 4(4)	C(14)-Mo(1)	0.114 4(4)	C(15)-O(3)	0.114 8(4)
C(3)-Mo(1)	0.237 0(4)	C(15)-Mo(1)	0.198 4(4)		
C(4)-Mo(1)	0.235 6(3)	C(6)-C(7)	0.151 7(5)		
C(13)-Mo(1)-C(1)	88.14(15)	C(13)-Mo(1)-C(5)	87.06(14)	C(14)-Mo(1)-C(3)	120.46(14)
C(13)-Mo(1)-C(2)	120.13(15)	C(13)-Mo(1)-C(14)	78.89(16)	C(14)-Mo(1)-C(5)	140.97(13)
C(13)-Mo(1)-C(3)	144.00(14)	C(13)-Mo(1)-C(15)	78.59(15)		
C(13)-Mo(1)-C(4)	118.08(15)	C(14)-Mo(1)-C(1)	106.89(14)		

Symmetry code: **5**: i: −*x*, −*y*, −*z*; **6**: i: −*x*+1, −*y*, −*z*+1.

6, every molybdenum atom is coordinated with a η^5-cyclopentadienyl and three carbony ligands, respectively. The Mo-Mo single bond distance (complex **5**: 0.322 9 nm; complex **6**: 0.323 1 nm) is comparable to that in *trans*-[(η^5-C_5H_4)CH(CH_3)(C_2H_5)Mo(CO)$_3$]$_2$ (0.322 3 nm)[8] and *trans*-[(η^5-C_5H_4)CH(C_2H_5)(C_2H_5)Mo(CO)$_3$]$_2$ (0.322 8 nm)[8], and is slightly shorter than *trans*-[(η^5-C_5Me_4)benzylMo(CO)$_3$]$_2$ (0.326 6 nm)[10] and *trans*-[(η^5-C_5Me_4)(CH_2)$_3CH_3$Mo(CO)$_3$]$_2$(0.328 6 nm)[11]. The distances between Mo and Cp ring are 0.2012 nm (complex **5**) and 0.2011 nm (complex 6), respectively. The two distances are both shorter than that in [(η^5-C_5Me_4)(CH_2)$_3CH_3$Mo(CO)$_3$]$_2$ (0.2027 nm)[11]. The comparisons made above indicate that the number of cyclopentadienyl substituent have some effect on the metal-metal bond length.

2.3　Thermal property

Thermal stability studies were performed for the title complexes. The TG-DTG curves of complex **5** at heating rate of 1 ℃·min^{-1}. The thermal decomposition process of complex **5** completes in four steps as is shown by the DTG curve. The TG curve indicates that the mass loss are 1.81% (0.316 3 mg), 11.39% (1.996 mg), 45.46% (7.965 mg), 13.43% (2.353 mg), respectively. The first and second steps are considered to be the removal of 3 mmol of CO (theoretical loss is 13.946%). The third step is considered to be the removal of 1 mmol of $C_{18}H_{26}O_2$ (theoretical loss is 45.49%). And the fourth step is considered to be the removal of 3 mmol of CO (theoretical loss is 13.95%). It can also be seen from the IR spectrum of the intermediate for the last stage that the absorption valence band of the C=O group disappear.

The DSC curve clearly illustrates that there are four exothermic peaks with an enthalpy value of 53.43 J·g^{-1} between 98.39~107.87 ℃, 65.75 J·g^{-1} between 170.60 ~202.51 ℃, 11.17 J·g^{-1} between 276.64 ~ 288.55 ℃ and 41.82 J·g^{-1} between 590.26~643.81 ℃ and two endothermic peaks with an enthalpy value of 65.75 J·g^{-1} between 107.87~170.60 ℃, 11.17 J·g^{-1} between 202.51~276.64 ℃.

The TG-DTG curves of complex **6** at heating rate of 1 ℃·min^{-1}. And the thermal decomposition process

of complex **6** also completes in four steps as is shown by the DTG curve. The TG curve indicates that the mass loss are 9.601% (1.012 mg), 20.36% (2.146 mg), 11.74% (1.238 mg), 8.303% (0.8753 mg), respectively. The first step is considered to be the removal of 1 mmol of C_5H_4 (theoretical loss is 9.547%). The second and third steps are considered to be the removal of 2 mmol of C_7H_7O (theoretical loss is 31.92%). And the fourth step is considered to be the removal of 2 mmol of CO (theoretical loss is 8.354%). According to the theory, there are four C=O groups in the intermediate for the last stage. But the IR spectrum of the intermediate for the last stage that the absorption valence band of the C =O group disappear, indicating that the complex **6** has been completely decomposed.

The DSC curve clearly illustrates that there are three exothermic peaks with an enthalpy value of 256.9 J·g^{-1} between 162.21~176.11 ℃, 111.8 J·g^{-1} between 282.27 ~309.17 ℃, 6.488 Jg^{-1} between 382.28~391.10 ℃ and two endothermic peaks with an enthalpy value of 111.8 J·g^{-1} between 176.11~282.27 ℃, 6.488 J·g^{-1} between 309.17~382.28 ℃.

3　Conclusions

In summary, four new dinuclear molybdenum carbonyl complexes have been synthesized by the reactions of cyclopentadiene derivatives with Mo(CO)$_6$ in refluxing xylene. The structures of complexes **5** and **6** have been characterized by the X-ray single crystal diffractometer. Comparing the structure of the type Cp$^*_2$Mo$_2$(CO)$_6$ (where Cp*=substituted cyclopentadienyl ligand), we see that the ligands coordinate to the Mo center by η^5 mode and changing the substituents has some effect on the cyclopentadienyl coordination ability and the Mo-Mo bond length. Thermal decomposition of complexes **5** and **6** occurs in four steps, performing endothermic and exothermic processes. The complexes **5** and **6** can be completely decomposed in the last stage.

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