



双核 Ru 配合物(C₅Me₄ⁱBu)₂Ru₂(CO)₄ 的合成与晶体结构

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关键词: 羰基钌; 二聚物; 结构; 环戊二烯基

中图分类号: O614.82[†]

文献标识码: A

文章编号: 1001-4861(2009)02-0377-04

Synthesis and Crystal Structure of Isobutyl-Substituted Tetramethylcyclopentadienyl Diruthenium Metal Carbonyl Complex

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Abstract: The complex (C₅Me₄ⁱBu)₂Ru₂(CO)₄ has been synthesized by the reaction of C₅Me₄ⁱBuH with Ru₃(CO)₁₂ in refluxing xylene and its molecular structure was characterized by elemental analysis, IR spectra, ¹H NMR and X-ray crystal structure determination. Crystal data for this compound: Triclinic, space group $P\bar{1}$, $M_r=668.78$, $a=0.865\ 96(17)$ nm, $b=0.892\ 90(18)$ nm, $c=0.975\ 7(2)$ nm, $\alpha=88.39(3)^\circ$, $\beta=71.64(3)^\circ$, $\gamma=84.99(3)^\circ$, $V=0.713\ 3(2)$ nm³, $Z=1$, $D_c=1.557$ g·cm⁻³, $\mu(\text{Mo } K\alpha)=1.091$ mm⁻¹, $F(000)=342$, $R_1=0.025\ 3$, $wR_2=0.067\ 6$ (observed reflections with $I>2\sigma(I)$) and $R_1=0.026\ 9$, $wR_2=0.068\ 2$ (all reflections). The structure of the dimer confirms the structure with bridging and terminal CO groups, and the Ru-Ru bond distance is 0.275 19(8) nm. CCDC: 693389.

Key words: ruthenium carbonyl; dimer; structure; cyclopentadienyl

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]. Especially for metallocene polymerization catalysts, the steric and electronic effects of cyclopentadienyl ring substituents greatly influence catalytic activity^[2]. In this study, the

reaction of isobutyl-substituted tetramethylcyclopentadiene with Ru₃(CO)₁₂ was reported. The aim is to obtain a deeper insight into the steric influences of substituents on the molecular structures and reactions of the corresponding biscyclopentadienyl dinuclear metal carbonyl complexes.

1 Experimental

1.1 General procedures

All operations involving air- or moisture-sensitive

收稿日期: 2008-09-16。收修改稿日期: 2008-11-24。

河北省自然科学基金资助项目(No.B2008000150)和河北师范大学博士启动基金资助项目(No.L2005B18)。

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compounds were carried out under an argon atmosphere using standard Schlenk techniques. Diethyl ether, xylene, and *n*-hexane were freshly distilled from sodium/benzophenone ketyl under argon prior to use. Methylene chloride was distilled over P₂O₅ under argon. 2,3,4,5-tetramethylcyclopentenone was purchased from Aldrich. Column chromatography was carried out on alumina column using dichloromethane and petroleum ether as eluent.

¹H NMR spectra was recorded on a Bruker AV 300 instrument, while IR spectrum was recorded as KBr pellet on FT IR-8900 spectrometer. Elemental analysis was performed on a VarioEL III analyzer. The ligand C₅Me₄BuH was synthesized according to the literature^[3].

1.2 Synthesis of [η^5 -(C₅Me₄Bu)₂Ru₂(CO)₄]

A solution of C₅Me₄BuH (0.25 g, 1.41 mmol) and Ru₃(CO)₁₂ (0.3 g, 0.47 mmol) in 30 mL of xylene was refluxed for 12 h. After removal of solvent, the residue was chromatographed on an alumina column using petroleum ether/CH₂Cl₂ as eluent. The orange band afforded complex as red crystals (0.358 g, 76%). m.p. 193~195 °C. Anal. Calc. for C₃₀H₄₂O₄Ru₂ (%): C, 53.87; H, 6.28. Found (%): C, 53.68; H, 6.35. ¹H NMR (300 MHz, CDCl₃): 2.15 (4H, d, C₅Me₄CH₂CH(CH₃)₂, ³J_{HH}=7.5 Hz), 0.82 (12H, d, CH(CH₃)₂, ³J_{HH}=6.9 Hz), 1.723 (12H,

s, C₅(CH₃)₂), 1.780 (12H, s, C₅(CH₃)₂), 1.57~1.62 (2H, m, CH(CH₃)₂), IR (KBr, ν_{CO} , cm⁻¹): 1 938 (s), 1 744 (s).

1.3 Crystal structure determination

A suitable orange-red block crystal with dimensions of 0.14 mm × 0.12 mm × 0.08 mm was selected for structure analysis. The data collection was performed on a Bruker Smart 1000 CCD diffractometer equipped with a Mo *K*α radiation ($\lambda=0.071\ 073\ \text{nm}$). A total of 4 050 reflections were collected in the range of $2.75^\circ \leq \theta \leq 25.02^\circ$ using SMART program, of which 2 483 were unique ($R_{\text{int}}=0.033\ 8$) and 2 295 with ($I > 2\sigma(I)$) were considered as observed. Semiempirical absorption corrections were applied using the SADABS program^[4]. The structure was solved by direct method and refined by full-matrix least squares. All calculations were performed using the SHELXTL program system. The final full-matrix least-squares refinement gave $R=0.025\ 3$, $wR=0.067\ 6$ ($w=1/[\sigma^2(F_o^2)+(0.030\ 6P)^2+0.008\ 3P]$, where $P=(F_o^2+2F_c^2)/3$) based on 2 295 observed reflections with $I > 2\sigma(I)$. $S=1.069$, $(\Delta/\sigma)_{\text{max}}=0.000$, $(\Delta\rho)_{\text{max}}=515\ \text{e}\cdot\text{nm}^{-3}$ and $(\Delta\rho)_{\text{min}}=-520\ \text{e}\cdot\text{nm}^{-3}$. The crystal data and summary of X-ray data collection are presented in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC: 693389.

Table 1 Crystal data and structure refinement for the title complex

Empirical formula	C ₃₀ H ₄₂ O ₄ Ru ₂	μ / mm^{-1}	1.091
Formula weight	668.78	$F(000)$	342
Temperature / K	113(2)	Crystal size / mm	0.14×0.12×0.08
Wavelength / nm	0.071 073	θ range for data collection / (°)	2.75 to 25.02
Crystal system	Triclinic	Limiting indices	$-10 \leq h \leq 9, -10 \leq k \leq 10, -10 \leq l \leq 11$
Space group	$P\bar{1}$	Reflections collected / unique (R_{int})	4 050 / 2 483 (0.033 8)
a / nm	0.865 96(17)	Completeness to $\theta=25.02^\circ / \%$	98.2
b / nm	0.892 90(18)	Absorption correction	Semi-empirical from equivalents
c / nm	0.975 7(2)	Max. and min. transmission	0.917 8 and 0.862 3
$\alpha / (^\circ)$	88.39(3)	Refinement method	Full-matrix least-squares on F^2
$\beta / (^\circ)$	71.64(3)	Data / restraints / parameters	2 483 / 6 / 169
$\gamma / (^\circ)$	84.99(3)	Goodness of fit on F^2	1.070
V / nm^3	0.713 3(2)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.025\ 3, wR_2=0.067\ 6$
Z	1	R indices (all data)	$R_1=0.026\ 9, wR_2=0.06\ 8$
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.557	Largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	515 and -520

Table 2 Selected bond distances (nm) and angles ($^\circ$) for the title complex

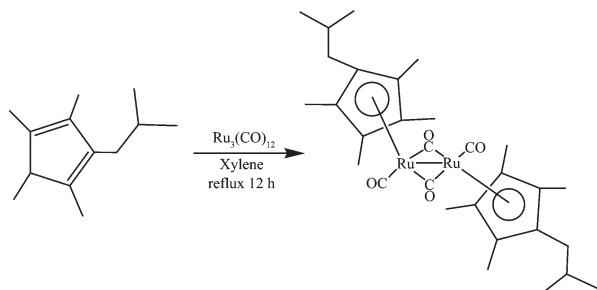
Ru1-C6	0.229 4(3)	C4-C5	0.142 3(4)	O2-C2	0.118 7(3)
Ru1-C7	0.227 1(2)	C5-C6	0.143 4(4)	Ru-Cp(CEN)	0.191 16
C2-Ru1(A)	0.204 6(3)	C6-C7	0.143 6(3)		
C3-C4	0.143 8(4)	O1-C1	0.114 6(3)		
Ru1-C2-Ru1(A)	84.81(10)	C1-Ru1-C3	94.69(10)	C2(A)-Ru1-C4	95.81(10)
C1-Ru1-C2	92.95(11)	C2-Ru1-C3	132.78(10)	C1-Ru1-Ru1(A)	94.46(8)
C1-Ru1-C2(A)	93.06(11)	C1-Ru1-C4	113.29(10)	C2-Ru1-Ru1(A)	47.77(7)
C2-Ru1-C2(A)	95.19(10)	C2-Ru1-C4	150.85(10)	C2(A)-Ru1-Ru1(A)	47.42(7)

Symmetry code: (A) $-x+1, -y+1, -z+1$; CEN: centroid of the cyclopentadienyl ring.

2 Results and discussion

2.1 Synthesis of $(C_5Me_4Bu)_2Ru_2(CO)_4$

When ligand C_5Me_4BuH reacted with $Ru_3(CO)_{12}$ under refluxing xylene for 12 h, the corresponding Ru-Ru bonded dinuclear complex (76%) was obtained (Scheme 1). Slow evaporation of the solvent from the complex in hexane- CH_2Cl_2 solution gave single crystal suitable for X-ray diffraction.



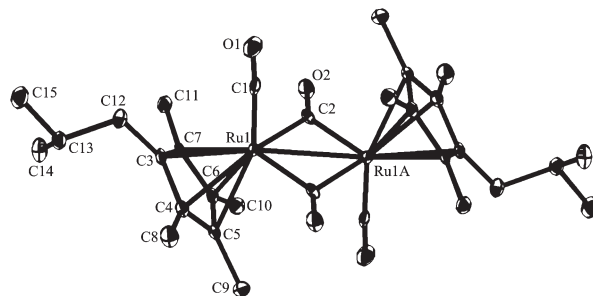
Scheme 1

The 1H NMR spectra of the diruthenium complex shows two groups of singlets for the four methyl protons. The IR spectra of diruthenium complex shows a strong terminal carbonyl absorption at 1938 cm^{-1} and a strong bridging carbonyl absorption at 1744 cm^{-1} . This result agrees with the single crystal structure.

2.2 Crystal Structure of $(C_5Me_4Bu)_2Ru_2(CO)_4$

The crystal structure of the dimer (Fig.1) reveals that the complex has a *trans* conformation with two bridging carbonyl ligands. Similar to the cyclopentadienyl analogue $trans-[η^5-CpRu(CO)(μ-CO)]_2$ ^[5] (where Cp=cyclopentadienyl ligand), both the structures are *trans* form and have C_i symmetry. The two cyclopentadienyl

ring planes are parallel. Two carbonyls are bridged and two carbonyls are terminal. The Ru-Ru bond distance is $0.275\ 19(8)\text{ nm}$ and the Ru-Cp centroid is $0.191\ 16\text{ nm}$. The Ru-Ru Bond distance is slightly longer than that in $trans-[η^5-CpRu(CO)(μ-CO)]_2$ [$0.273\ 5(2)\text{ nm}$]^[5], and $trans-[η^5-CpMe_4hexRu(CO)(μ-CO)]_2$ [$0.274\ 29(8)\text{ nm}$]^[6], is slightly shorter than that in $[(η^5-C_5Me_5)Ru(CO)(μ-CO)]_2$ [$0.275\ 2(1)\text{ nm}$]^[7], and $[(η^5-C_5Me_4Et)Ru(CO)(μ-CO)]_2$ [$0.275\ 84(5)\text{ nm}$]^[8]. This distance is comparable to those found in other substituted cyclopentadienyl ruthenium di-carbonyl dimers^[9].



Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: A: $-x+1, -y+1, -z+1$

Fig.1 Structure of the title complex with the atomic numbering scheme

In conclusion, comparing the range of structures that have been determined for complexes of the type $Cp^*Ru_2(CO)_4$ (where Cp^* =substituted cyclopentadienyl ligand), we find that the same overall structure with two bridging and two terminal CO groups is presented in all compounds. We also see that the Cp^* ligands are *trans* in the dimeric structures in the solid state. Changing the substituents has only a small effect on the Ru-Ru

bond length as well as on the Ru-CO (bridge) bond lengths.

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