

三核钌簇合物 $[\text{PyCH}=\text{C}(\text{Ph})\text{O}]_2\text{Ru}_3(\text{CO})_8$ 的合成、结构及反应性

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摘要: 配体 PyCH_2COPh 与 $\text{Ru}_3(\text{CO})_{12}$ 在甲苯中加热回流, 得到了标题簇合物 $[\text{PyCH}=\text{C}(\text{Ph})\text{O}]_2\text{Ru}_3(\text{CO})_8$ (**1**)。通过红外光谱、核磁共振氢谱和碳谱对 **1** 的结构进行了表征, 用 X 射线单晶衍射法测定了 **1** 的结构。结果表明: 3 个钌原子呈等腰三角形分布, 其中 $\text{Ru}(2)-\text{Ru}(1)$ 和 $\text{Ru}(2)-\text{Ru}(1)'$ 的键长均为 0.280 nm, $\text{Ru}(1)-\text{Ru}(1)''$ 的键长为 0.307 nm。同时研究了簇合物 **1** 与环戊二烯及茚的反应, 分别得到双核钌羰基配合物 $[(\eta^5-\text{C}_5\text{H}_5)\text{Ru}(\text{CO})]_2(\mu-\text{CO})_2$ (**2**) 和 $[(\eta^5-\text{C}_9\text{H}_7)\text{Ru}(\text{CO})]_2(\mu-\text{CO})_2$ (**3**)。

关键词: 合成; 表征; 金属羰基簇合物; 反应性

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Synthesis, Structure and Reactivity of a Trinuclear Ruthenium Cluster Compound $[\text{PyCH}=\text{C}(\text{Ph})\text{O}]_2\text{Ru}_3(\text{CO})_8$

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Abstract: The title compound, $[\text{PyCH}=\text{C}(\text{Ph})\text{O}]_2\text{Ru}_3(\text{CO})_8$ (**1**), was obtained from the reaction of PyCH_2COPh with $\text{Ru}_3(\text{CO})_{12}$ in refluxing toluene. Compound **1** was characterized by IR, ¹H NMR, and ¹³C NMR spectroscopy as well as by single-crystal X-ray diffraction analysis. X-ray study of the cluster compound **1** shows that the three ruthenium atoms define an isosceles triangle with two distances of 0.280 nm and one of 0.307 nm. When **1** was treated with cyclopentadiene in refluxing toluene, dinuclear metal carbonyl complexes $[(\eta^5-\text{C}_5\text{H}_5)\text{Ru}(\text{CO})]_2(\mu-\text{CO})_2$ (**2**) was obtained. Similar treatment of **1** with indene gave the product $[(\eta^5-\text{C}_9\text{H}_7)\text{Ru}(\text{CO})]_2(\mu-\text{CO})_2$ (**3**). CCDC: 1437152.

Keywords: synthesis; characterization; metal carbonyl cluster compound; reactivity

0 Introduction

Transition metal carbonyl compounds are useful intermediates in the synthesis of important coordination compounds and have applications in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation^[1]. The coordination

chemistry of numerous nitrogen donor ligands has been extensively studied and their metal compounds played an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical^[2] and biochemically relevant studies of metal complexes^[3-6] and found wide range of

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applications. Furthermore, metal carbonyl derivatives of nitrogen donor ligands are important routes to prepare interesting metal carbonyl complexes^[7-8].

Many metal carbonyl cluster compounds have been prepared and their structures have been determined. Triosmium cluster containing phenoxy^[9] and triruthenium cluster containing methoxy^[10] have been studied in detail. These clusters maintain a structure based on an equilateral triangle of metals and only rarely is an isosceles triangle formed. Our interest in investigation of the reactions of metal carbonyls with pyridine derivatives has prompted us to investigate the reaction of $\text{Ru}_3(\text{CO})_{12}$ with PyCH_2COPh . In order to develop a deeper understanding of the structure and reactivity of pyridine-containing alcohol compound, here we report the synthesis, structure and reaction activity of a new pyridine-alkoxide cluster compound.

1 Experimental

1.1 General considerations

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker Av III-600 instrument in CDCl_3 . IR spectra were recorded as KBr disks on a Thermo Fisher 50 spectrometer. Elemental analyses were obtained on a Vario EL III analyzer. The ligand precursor PyCH_2COPh was synthesized according to the literatures^[11-12].

1.2 Reaction of ligand precursor with $\text{Ru}_3(\text{CO})_{12}$ in xylene

A solution of ligand precursor PyCH_2COPh (0.18 g, 0.938 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (0.3 g, 0.469 mmol) in 30 mL of toluene was refluxed for 6 h. After removal of solvent under reduced pressure, the residue was

chromatographed on an alumina column using petroleum ether/ ethyl acetate as eluent. The orange-red band was eluted and collected. After vacuum removal of the solvents from the above eluate, the residue was recrystallized from *n*-hexane/ CH_2Cl_2 at room temperature to give the title compound **1** as orange-red crystals (Yield: 0.148 g, 34.3%). m.p. 190.1°C. Anal. Calcd. for $\text{C}_{34}\text{H}_{20}\text{N}_2\text{O}_{10}\text{Ru}_3$ (%): C, 44.40; H, 2.19; N, 3.05. Found (%): C, 44.32; H, 2.12; N, 3.00. ^1H NMR (600 MHz, CDCl_3): 8.35 (d, 1H, $J=5.0$ Hz, Py-H), 7.81~7.82 (m, 1H, Py-H), 7.58 (s, 2H, -CH=C-), 7.42~7.51 (m, 4H, Py-H), 7.38 (d, 2H, $J=6.0$ Hz, Ph-H), 7.35 (t, 3H, $J=11.5$ Hz, Ph-H), 7.20~7.32 (m, 3H, Ph-H), 7.27 (s, 2H, Ph-H), 7.25 (s, 2H, Py-H), ^{13}C NMR (CDCl_3 , 150 MHz): δ 49.8, 50.8, 100.4, 101.3, 117.5, 117.8, 121.5, 124.1, 124.4, 124.6, 124.9, 125.8, 126.9, 127.3, 127.5, 127.7, 128.4, 135.3, 136.5, 139.9, 140.1, 146.1, 152.7, 152.9, 153.4, 153.7, 153.8, 160.2, 164.3, 166.0, 192.5, 193.0, 203.4, 203.5. IR (cm^{-1}): 2 047(s), 1 967(s), 1 923(s).

1.3 Crystal structure determination

Crystal of the title compound suitable for X-ray diffraction was isolated from the slow evaporation of hexane-dichloromethane solution. Data collection were performed on a Bruker SMART 1000 CCD detector with graphite monochromated $\text{Mo } K\alpha$ ($\lambda=0.071\ 073$ nm) radiation using the φ - ω scan technique. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using the SHELXL-97 program system^[13]. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions riding on the parent atoms and refined with fixed thermal parameters. Crystallographic data and experimental details of the structure determinations are given in Table 1.

CCDC: 1437152.

Table 1 Crystal data and structure refinement parameters for title compound

Empirical formula	$\text{C}_{34}\text{H}_{20}\text{N}_2\text{O}_{10}\text{Ru}_3$
Formula weight	919.73
Temperature / K	298(2)
Crystal system	Monoclinic
Space group	$C2/c$

Continued Table 1

a / nm	2.240 15(19)
b / nm	1.185 06(11)
c / nm	1.422 75(13)
$\beta / (^\circ)$	116.903(2)
V / nm^3	3.368 2(5)
Z	4
$F(000)$	1 800
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.814
μ / mm^{-1}	1.388
Crystal dimension / mm	0.49×0.45×0.40
θ Range / (°)	2.84~25.02
Reflection collected	8 182
Independent reflection	2 948
R_{int}	0.025 5
Parameter	222
Goodness of fit on F^2	1.114
$R_1, wR_2 [I > 2\sigma(I)]$	0.025 3, 0.055 0
R_1, wR_2 (all data)	0.039 3, 0.062 6
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	1 194, -470

1.4 Reactivity of **1** with cyclopentadiene in toluene

A solution of **1** (0.299 g, 0.325 mmol) and cyclopentadiene (0.043 g, 0.650 mmol) in 30 mL of toluene was refluxed for 24 h. After removal of solvent under reduced pressure, the residue was chromatographed on an alumina column using petroleum ether/ethyl acetate as eluent. The orange-red band was eluted and collected. After vacuum removal of the solvents from the above eluate, the residue was recrystallized from *n*-hexane/CH₂Cl₂ at room temperature to give compound **2** as orange-red crystals (Yield: 0.06 g, 41.7%). ¹H NMR (600 MHz, CDCl₃): δ 5.28 (s, 8H, C₅H₅), 3.49 (s, 2H, C₅H₅); ¹³C NMR (150 MHz, CDCl₃): δ 89.3, 217.4.

1.5 Reactivity of **1** with indene in toluene

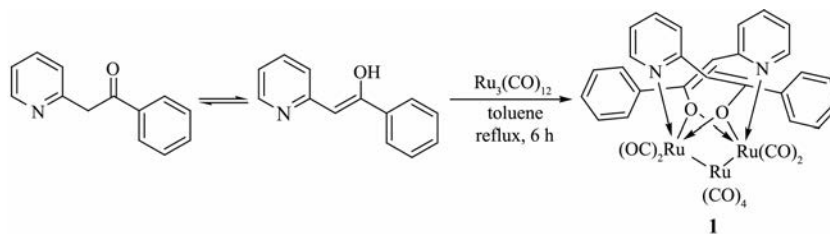
Using a procedure similar to that described above, reaction of **1** with indene gave **3** in 32.4% yield. ¹H NMR (600 MHz, CDCl₃): 7.22~7.24 (m, 4H, C₉H₇), 7.13~7.15 (m, 4H, C₉H₇), 5.56 (d, 4H, $J=2.4$ Hz, C₉H₇), 5.50 (t, 2H, $J=2.4$ Hz, C₉H₇); ¹³C NMR (150 MHz, CDCl₃): 78.6, 96.7, 109.9, 120.0, 125.8.

2 Results and discussion

2.1 Synthesis and characterization of compound **1**

Refluxing a mixture of Ru₃(CO)₁₂ and PyCH₂COPh in toluene for 6 h resulted in formation of the title cluster compound **1**. The equation of the reaction is followed (Scheme 1).

The IR spectrum of the title compound shows



Scheme 1 Synthesis of title compound

only three terminal carbonyl absorptions at 2 047, 1 967 and 1 946 cm^{-1} , indicating the presence of several types of terminal carbonyl ligands.

2.2 X-ray crystal structure

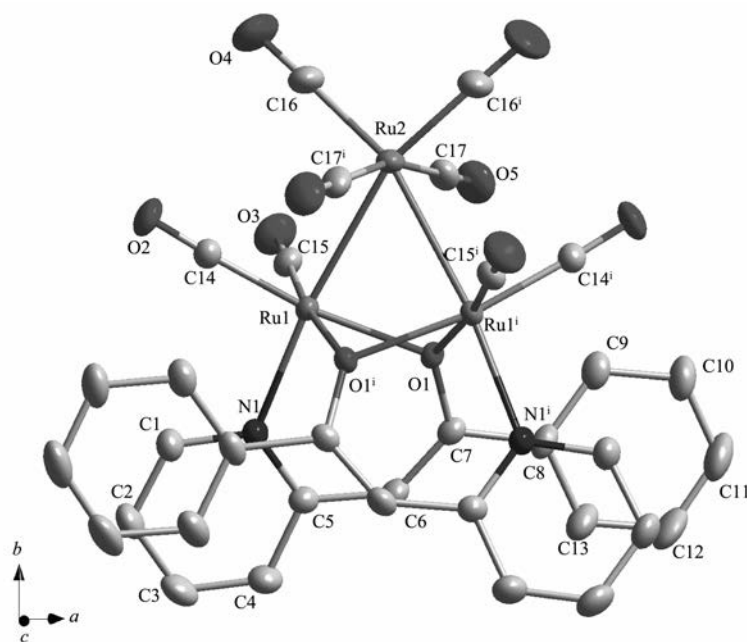
The molecular structure of **1** was confirmed by X-ray diffraction analysis. The ORTEP is shown in Fig.1. The selected bond lengths and bond angles are given in Table 2. The title compound crystallizes in monoclinic space group $C2/c$ with four molecules in the unit cell. As shown in Fig.1, the molecular structure is a triruthenium cluster, two ligands are

simultaneously coordinated to two ruthenium atoms with a $\mu_2\text{-O}$ atom behaving as a three-electron donor. The data show that the three ruthenium atoms form an isosceles triangle with two Ru-Ru distances of 0.280 nm and one of 0.307 nm. This symmetric bonding indicates that the oxygens act as three-electron donors, which in terms of the noble gas formalism means that there will be no Ru(1)-Ru(1)ⁱ bond, as shown in Fig.1. The elongated Ru(1)-Ru(1)ⁱ bond distance of 0.307 nm may well be a result of this. The structure found is very similar to that of $\text{Ru}_3(\text{CO})_8$

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

Ru(2)-Ru(1)	0.280 01(5)	Ru(2)-C(16)	0.193 3(5)	Ru(2)-Ru(1) ⁱ	0.280 01(5)
Ru(2)-C(16) ⁱ	0.193 3(5)	Ru(1)-Ru(1) ⁱ	0.306 93(6)	Ru(2)-C(17)	0.194 0(5)
Ru(1)-O(1)	0.212 2(2)	Ru(2)-C(17) ⁱ	0.194 0(5)	Ru(1)-N(1)	0.2175(3)
C(5)-C(6)	0.144 8(5)	Ru(1)-O(1) ⁱ	0.218 9(2)	C(6)-C(7)	0.134 6(5)
O(1)-Ru(1) ⁱ	0.218 9(2)	C(7)-C(8)	0.150 1(5)		
C(15)-Ru(1)-O(1)	98.32(12)	O(1)-Ru(1)-O(1) ⁱ	75.82(9)	C(14)-Ru(1)-O(1)	169.23(13)
N(1)-Ru(1)-O(1) ⁱ	89.08(9)	C(15)-Ru(1)-N(1)	94.45(13)	O(1)-Ru(1)-Ru(2)	84.53(6)
C(14)-Ru(1)-N(1)	99.65(13)	O(1) ⁱ -Ru(1)-Ru(2)	83.35(5)	C(14)-Ru(1)-O(1)	99.01(13)
Ru(2)-Ru(1)-Ru(1) ⁱ	56.766(7)	C(15)-Ru(1)-O(1) ⁱ	173.17(12)	Ru(1)-O(1)-Ru(1) ⁱ	90.78(8)

Symmetry codes: ⁱ 1-x, y, 1/2-z



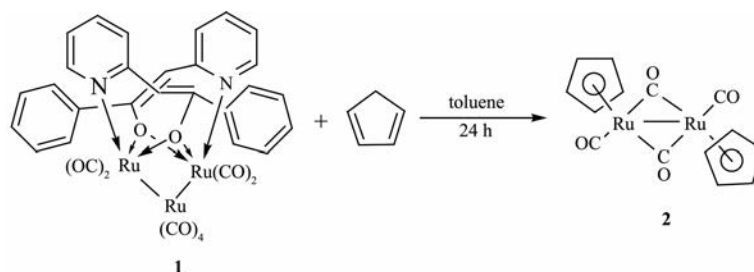
Symmetry codes: ⁱ 1-x, y, 1/2-z; Ru1...Ru2 0.280 0 nm

Fig.1 ORTEP view of the title compound **1** with 30% probability level ellipsoids

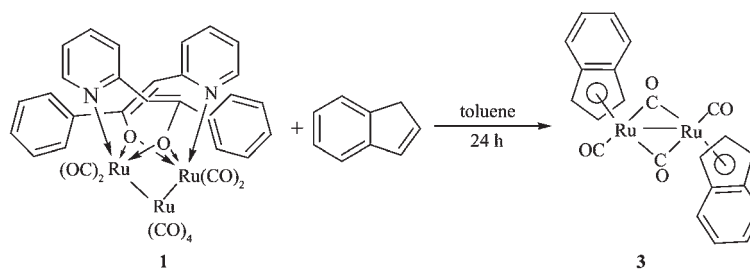
$[\text{C}_9\text{H}_6\text{NO}]_2$ ^[14] or $\text{Ru}_3(\text{CO})_8(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2$ ^[9]. The Ru-Ru distances are slightly longer than $\text{Ru}_3(\text{CO})_8[\text{C}_9\text{H}_6\text{NO}]_2$ (0.277 and 0.304 nm) and $\text{Ru}_3(\text{CO})_8(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2$ (0.273, 0.274 and 0.301 nm). Each pyridyl group is coordinated to one ruthenium atom, and the distance between the pyridyl nitrogen and the ruthenium atom is 0.217 5(3) nm (Ru(1)-N(1)). The bond distance of the C(6)-C(7) is close to the bond distance of standard C=C (0.133 7 nm). Obviously, C(6)-C(7) is a double bond. The Ru(1)-O-Ru(1)ⁱ bond angle is 90.8°, slightly bigger than the Ru-O-Ru bond angles in $\text{Ru}_3(\text{CO})_8[\text{C}_9\text{H}_6\text{NO}]_2$ (89.6° and 89.9°) and $\text{Ru}_3(\text{CO})_8(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2$ (89.9° and 90.7°).

2.3 Reactions of compound 1 with cyclopentadiene or indene in toluene

When the compound **1** reacted with cyclopentadiene or indene, dinuclear metal carbonyl



Scheme 2 Reactivity of compound **1** with cyclopentadiene



Scheme 3 Reactivity of compound **1** with indene

3 Conclusions

Reaction of PyCH_2COPh with $\text{Ru}_3(\text{CO})_{12}$ in refluxing toluene was investigated. A new trinuclear cluster compound was obtained and determined by single-crystal X-ray diffraction. The reactivity of the title compound reacted with cyclopentadiene or indene was also studied, and the results clearly reveal that the coordination properties of cyclopentadiene and

complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})]_2(\mu\text{-CO})_2$ (**2**) or $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{CO})]_2(\mu\text{-CO})_2$ (**3**) were obtained (Schemes 2 and 3). Complexes **2** and **3** are known products^[15-16]. Complexes **2** and **3** were also characterized by single-crystal X-ray diffraction analyses (Supporting Information). A plausible mechanism for the **2** was proposed. First, the reaction of compound **1** and cyclopentadiene produce the coordinatively unsaturated (η^4 -cyclopentadiene) dicarbonylruthenium. Then the ruthenium hydride $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{H}]$ is formed by activation of the C-H bond of cyclopentadiene. Finally, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{H}]$ dimerized to form the ruthenium dimer **2** by eliminating H_2 . The generation mechanism of **3** is same as that of **2**. The results show that the coordination properties of cyclopentadiene and indene are higher than that of pyridine alcohol.

indene are higher than that of pyridine alcohol.

Supporting information is available at <http://www.wjhxsb.cn>

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