

对苯二甲酸二丙炔醇酯与 $\text{Co}_2(\text{CO})_8$ 、 $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ 和 $\text{RuCo}_2(\text{CO})_{11}$ 的反应

张玉华 祝馨怡 殷元骥*

(中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室, 兰州 730000)

周忠远 陈新滋

(香港理工大学应用生物及化学科技学系, 香港)

室温下, 对苯二甲酸二丙炔醇酯分别与 $\text{Co}_2(\text{CO})_8$, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ 和 $\text{RuCo}_2(\text{CO})_{11}$ 反应, 得到三个有机金属化合物 $[\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H}-\mu)_2][\text{Co}_2(\text{CO})_6]_2$ (**1**)、 $[\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H})_2][\text{RuCo}_2(\text{CO})_9]_2$ (**2**) 和 $(\text{HC}_2\text{CH}_2\text{OCO})\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H}-\mu)[\text{Mo}_2\text{Cp}_2(\text{CO})_4]$ (**3**)。研究发现三种金属核对端炔氢的屏蔽作用依次为 $\text{RuCo}_2(\text{CO})_9 > \text{Co}_2(\text{CO})_6 > \text{Mo}_2(\text{CO})_4\text{Cp}_2$ 。化合物 **1** 的晶体衍射发现, 属三斜晶系, 空间群 $P\bar{1}$, $a = 8.139(2)\text{\AA}$, $b = 8.808(3)\text{\AA}$, $c = 11.343(3)\text{\AA}$, $\beta = 96.260(6)^\circ$, $V = 773.4(4)\text{\AA}^3$, $Z = 1$, $D_c = 1.748\text{g}\cdot\text{cm}^{-3}$, $R = 0.0513$, $wR = 0.1266$ 。

关键词: 晶体结构 钴 钼 钌 有机金属化合物

分类号: O614.81

Reactions of Terephthalate with $\text{Co}_2(\text{CO})_8$, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ and $\text{RuCo}_2(\text{CO})_{11}$ and the Crystal Structure of $[\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H}-\mu)_2][\text{Co}_2(\text{CO})_6]_2$

ZHANG Yu-Hua ZHU Xin-Yi YIN Yuan-Qi*

(State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, Lanzhou 730000)

ZHOU Zhong-Yuan Albert S. C. Chan

(Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University,
Hung Hom, Kowloon, Hong Kong)

Three organometallic complexes $[\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H}-\mu)_2][\text{Co}_2(\text{CO})_6]_2$ (**1**), $[\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H})_2][\text{RuCo}_2(\text{CO})_9]_2$ (**2**) and $(\text{HC}_2\text{CH}_2\text{OCO})\text{C}_6\text{H}_4-p-(\text{CO}_2\text{CH}_2\text{C}_2\text{H}-\mu)[\text{Mo}_2\text{Cp}_2(\text{CO})_4]$ (**3**) have been prepared from the reactions of dipropargyl terephthalate with $\text{Co}_2(\text{CO})_8$, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ and $\text{RuCo}_2(\text{CO})_{11}$. From their ^1H NMR spectra, it is found that the deshielding effect of metal species on terminal alkyne follows $\text{RuCo}_2(\text{CO})_9 > \text{Co}_2(\text{CO})_6 > \text{Mo}_2(\text{CO})_4\text{Cp}_2$. The single-crystal diffraction of compound **1** was undertaken with the data: triclinic, $P\bar{1}$, $a = 8.139(2)\text{\AA}$, $b = 8.808(3)\text{\AA}$, $c = 11.343(3)\text{\AA}$, $\beta = 96.260(6)^\circ$, $V = 773.4(4)\text{\AA}^3$, $Z = 1$, $D_c = 1.748\text{g}\cdot\text{cm}^{-3}$,

收稿日期 2001-03-22。收修改稿日期: 2001-06-05。

国家自然科学基金资助项目 (No. 29871061)。

* 通讯联系人。

第一作者 张玉华, 男, 28 岁, 博士研究生, 研究方向: 新型金属有机化合物的合成。

$R = 0.0513$, $wR = 0.1266$.

Keywords: crystal structure cobalt molybdenum ruthenium
organometallic complexes

0 Introduction

The chemistry of di- or trinuclear transition metal complexes bridged by the unsaturated hydrocarbons has been attracting great attention because of the relevance to the chemistry of metal-catalyst surfaces^[1]. It is hoped that carbon-rich fragments bridging a dinuclear frame in homogeneous system serve as models for the understanding of the chemistry of reactive intermediates obtained during catalytic reactions. Further it is well known that the coordination of an organic molecule to metal center increases the stability of the whole system and makes the coordinated substrate active toward specific reactions that may not be possible through classical organic procedures^[2]. The coordination chemistry of the alkyne and alkynyl species bearing a $C \equiv C$ functional group has been studied extensively^[3]. Recently, diyne clusters have been receiving considerable attention because of their unusual structures and reactions^[4]. As an extension, we have investigated the interrelation of two $C \equiv C$ groups during the capping reaction and the interrelations of two C_2M_2 groups during the exchange reactions^[5]. Here the results of capping reactions of dipropargyl terephthalate with dinuclear complexes $Co_2(CO)_8$, $Mo_2Cp_2(CO)_4$ and trinuclear species $RuCo_2(CO)_{11}$ and the crystal structure of the compound **1** are reported.

1 Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenk and vacuum line techniques. The solvents were treated using the usual method for preparing anhydrous and deoxygenated solvents. Column separation was carried out using 160 ~ 200 mesh silica gel. $Co_2(CO)_8$ ^[6], $Mo_2Cp_2(CO)_6$ ^[7] and $RuCo_2(CO)_{11}$ ^[8] were prepared according to the literature. The dipropargyl terephthalate was obtained by esterification of terephthalic acid with propargyl alcohol, and characterized by C/H analysis, IR and ¹H NMR. The IR spectra were recorded on a Nicolet FT-IR 10DX spectrophotometer. The ¹H NMR spectra were recorded on a Bruker AM 400MHz spectrometer. The elemental analyses were performed on a Carlo Erba 1106 type analyzer.

The dipropargyl terephthalate (242mg, 1mmol) was treated with $Co_2(CO)_8$ (684mg, 2mmol) in THF (25cm³) at room temperature. The mixture was stirred for 2.5h, the solvent was removed and the residue was separated on 2.5cm × 30cm silica gel chromatography. Elution with hexane/CH₂Cl₂ (2:1) gave the main red band, condensing the solvent and crystallization from hexane/CH₂Cl₂ at -20°C gave red crystals [C_6H_4 -*p*-(CO₂CH₂C₂H)₂][Co₂(CO)₆]₂ (**1**) (644mg, 79%). Anal. Calcd. for C₂₆H₁₀O₁₆Co₄: C, 38.36; H, 1.24. Found: C, 38.37; H, 1.24%. IR (KBr): $\nu(C \equiv O)$ 2100vs, 2060vs, 2029vs, 1979vs, $\nu(C = O)$ 1718cm⁻¹. ¹H NMR(CDCl₃): δ 8.18 (s, 4H, C₆H₄), 6.14 (s, 2H, 2CH), 5.55 (s, 4H, 2CH₂)ppm.

The preparation of complex [C_6H_4 -*p*-(CO₂CH₂C₂H)₂][RuCo₂(CO)₉]₂ (**2**) is similar to that

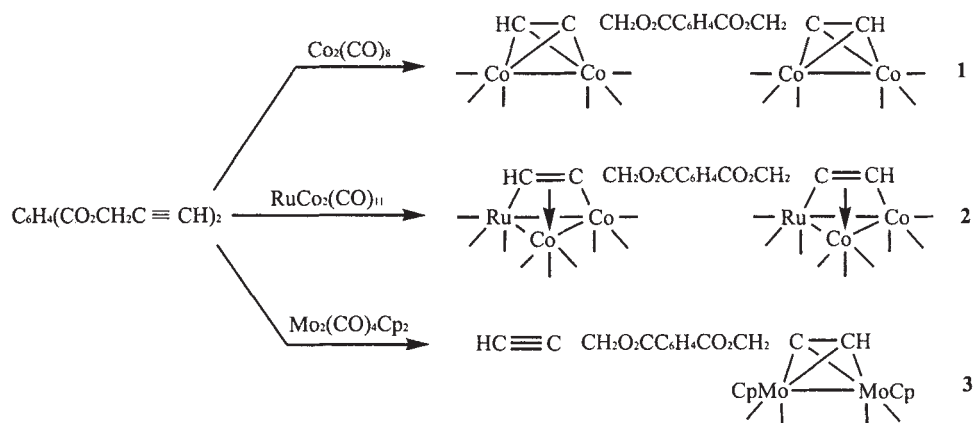
described above. Yield 68%. Anal. Calcd. for $\text{C}_{32}\text{H}_{10}\text{O}_{22}\text{Co}_4\text{Ru}_2$: C, 32.45; H, 0.85. Found: C, 32.48; H, 0.86%. IR (KBr): $\nu(\text{C}\equiv\text{O})$ 2104vs, 2058vs, 2039vs, 2011vs, 1892m, $\nu(\text{C}=\text{O})$ 1720 cm^{-1} . ^1H NMR(CDCl_3): δ 9.44 ~ 8.12(d, 6H, 2CH and C_6H_4), 5.14(s, 4H, 2 CH_2), 5.30 ~ 5.14(d, 2H, CH_2)ppm.

Compound $[(\text{HC}_2\text{CH}_2\text{OCO})\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2\text{CH}_2\text{C}_2\text{H-}\mu)][\text{Mo}_2\text{Cp}_2(\text{CO})_4]$ (**3**) was prepared as follows: A solution of $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ (490mg, 1mmol) in toluene (25cm^3) was refluxed for 15h. After cooling to room temperature, the dipropargyl terephthalate (121mg, 0.5mmol) was added and the mixture was stirred at room temperature for another 2h. The solvent was removed and the residue was chromatographed on silica gel column using $\text{CH}_2\text{Cl}_2/\text{ether}(10:1)$ as eluent to give the main red band. Removal of the solvent and crystallization from hexane/ CH_2Cl_2 at -20°C gave red solids (264mg, 48%). Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{O}_8\text{Mo}_2$: C, 50.12; H, 2.98. Found: C, 50.10; H, 2.31%. IR(KBr): $\nu(\equiv\text{CH})$ 3283w, $\nu(\text{C}\equiv\text{C})$ 2129, $\nu(\text{C}\equiv\text{O})$ 1989vs, 906vs, 1827vs, $\nu(\text{C}=\text{O})$ 1724m, 1688 cm^{-1} . ^1H NMR(CDCl_3): δ 8.19(s, 4H, C_6H_4), 5.82(s, H, CH), 5.41(s, 2H, CH_2), 5.34 ~ 5.33(d, 10H, 2Cp, $J=4.25\text{Hz}$), 4.98 ~ 4.96(q, 2H, CH_2 , $J=2.6\text{Hz}$), 2.57 ~ 2.56(t, 1H, $\equiv\text{CH}$, $J=2.3\text{Hz}$)ppm.

2 Results and Discussion

All the reactions described in this work are summarized in Scheme 1. Treatment of $\text{Co}_2(\text{CO})_8$ and $\text{RuCo}_2(\text{CO})_{11}$ respectively with dipropargyl ester $\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2\text{CH}_2\text{C}_2\text{H})_2$ in 2:1 molar rate at room temperature affords the compound $[\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2\text{CH}_2\text{C}_2\text{H})_2][\text{Co}_2(\text{CO})_6]_2$ (**1**) and $[\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2\text{CH}_2\text{C}_2\text{H})_2][\text{RuCo}_2(\text{CO})_9]_2$ (**2**). However, using the same procedure the expected linked compound $[\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2\text{CH}_2\text{C}_2\text{H})_2][\text{Mo}_2(\text{CO})_4\text{Cp}_2]_2$ can not be separated from the reaction, only the mono-capping product $[(\text{HC}_2\text{CH}_2\text{OCO})\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2\text{CH}_2\text{C}_2\text{H-}\mu)][\text{Mo}_2\text{Cp}_2(\text{CO})_4]$ (**3**) can be obtained. Compounds **1** and **2** are more stable than **3** both in air and in solvent.

The IR spectra of **1** and **2** showed intense absorption bands in the range of 2104 ~ 1892 cm^{-1} assigned to the carbonyls bound to Cobalt and Ruthenium atoms. And the three strong vibrational frequencies at 1989, 1906 and 1827 cm^{-1} in IR spectrum of **3** are characteristic of carbonyls attached



Scheme 1

to Molybdenum atom, the weak absorption bands at 3283 and 2129 cm^{-1} mean that terminal alkyne exist in molecule. The ^1H NMR spectra of these compounds are very characteristic. Because of the introduction of metal species, the chemical shift of terminal alkyne proton was strongly influenced with respect to that free ligand (2.57 ~ 2.56ppm). The proton resonance in ($\mu\text{-C}=\text{CH}$) $\text{RuCo}_2(\text{CO})_9$ appeared at 9.44 and 8.12ppm as two singlets, and that in ($\mu\text{-C}\equiv\text{CH}$) $\text{Co}_2(\text{CO})_6$ was observed at 6.14ppm and that in ($\mu\text{-C}\equiv\text{CH}$) $\text{Mo}_2(\text{CO})_4\text{Cp}_2$ was at 5.82ppm. So we could draw the conclusion that the deshielding effects of three cluster species on the proton of terminal alkyne follow the series $\text{RuCo}_2(\text{CO})_9 > \text{Co}_2(\text{CO})_6 > \text{Mo}_2\text{Cp}_2(\text{CO})_4$. As for the resonance of methylene connected to coordinated alkyne, they are less influenced appeared in the range of 5.55 ~ 5.14ppm.

Table 1 Crystal Data and Structure Refinement for Compound 1

empirical formula	$\text{C}_{26}\text{H}_{10}\text{O}_{16}\text{Co}_4$
formula weight	814.06
crystal system	triclinic
space group	$P\bar{1}$
$F(000)$	402
$a/\text{\AA}$	8.139(2)
$b/\text{\AA}$	8.808(3)
$c/\text{\AA}$	11.343(3)
$\beta/^\circ$	96.260(6)
$V/\text{\AA}^3$	773.4(4)
Z	1
$D_c/(\text{g}\cdot\text{cm}^{-3})$	1.748
$\mu(\text{Mo } K\alpha)/\text{mm}^{-1}$	2.181
crystal dimensions/mm	0.22 × 0.20 × 0.16
temperature/K	294(2)
$\theta_{\text{max}}/^\circ$	27.55
No. of reflections independent	3510
No. observations [$I > 2\sigma(I)$]	2017
No. Variables	209
$^a R$, $^b wR$ [$I > 2\sigma(I)$]	0.0513, 0.1266
largest diff. peak and hole/ $(\text{e}\cdot\text{\AA}^{-3})$	0.602, -0.288

$$^a R = \sum |F_0| - |F_c| / \sum |F_0|, \quad ^b wR = [\sum \omega(|F_0| - |F_c|)^2 / \sum \omega F_0^2]^{1/2}$$

Table 2 Selected Bond Lengths(\AA) and Angles($^\circ$) for Compound 1

Co(1)-C(2)	1.802(3)	Co(2)-C(4)	1.811(3)	Co(1)-C(1)	1.813(3)
Co(2)-C(6)	1.814(3)	Co(1)-C(3)	1.817(3)	Co(2)-C(8)	1.942(2)
Co(1)-C(8)	1.937(2)	Co(2)-C(7)	1.948(2)	Co(1)-C(7)	1.941(2)
C(7)-C(8)	1.332(3)	Co(1)-Co(2)	2.4834(7)	C(8)-C(9)	1.473(3)
Co(2)-C(5)	1.792(3)	C(10)-C(11)	1.483(3)		
C(8)-Co(1)-C(7)	40.16(9)	C(7)-C(8)-C(9)	139.2(2)	C(8)-Co(1)-Co(2)	50.28(7)
C(7)-C(8)-Co(1)	70.10(13)	C(7)-Co(1)-Co(2)	50.44(7)	C(9)-C(8)-Co(1)	135.79(16)
C(8)-Co(2)-C(7)	40.03(9)	C(7)-C(8)-Co(2)	70.23(15)	C(8)-Co(2)-Co(1)	50.10(6)
C(9)-C(8)-Co(2)	134.20(16)	C(7)-Co(2)-Co(1)	50.20(6)	Co(1)-C(8)-Co(2)	79.61(9)
C(8)-C(7)-Co(1)	69.74(12)	C(8)-C(7)-Co(2)	69.74(14)	Co(1)-C(7)-Co(2)	79.36(8)

In order to further established the structures of these complexes, single crystal structure determination of **1** was undertaken using X-ray diffraction method. The crystallographic data and the se-

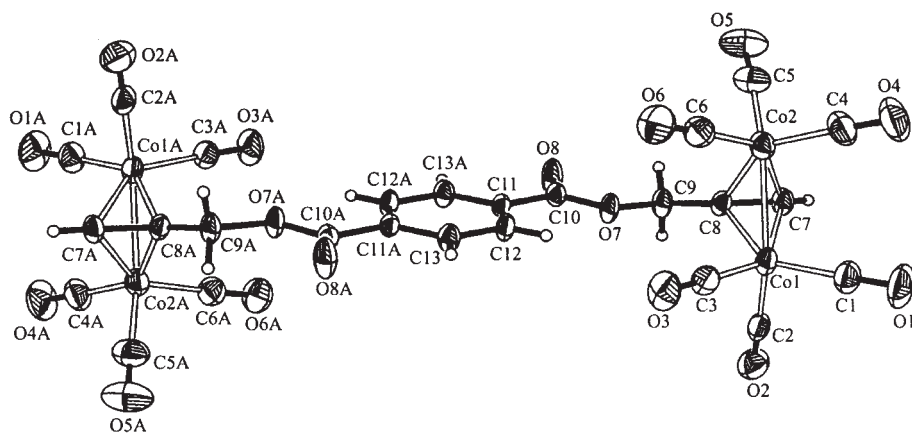


Fig. 1 Molecular structure of compound 1

lected bond lengths and angles are given in Tables 1 and 2. The molecular structure and the packing diagram are shown in Figs. 1 and 2.

As seen in Fig. 1, a $\text{Co}_2(\text{CO})_6$ unit is coordinated to one of the two alkynyl groups of dipropargyl terephthalate, each cobalt atom is coordinated by three terminal carbonyls. The C_2Co_2 core adopts a pseudo-tetrahedral geometry. The Co-Co bond length is $2.4834(7)\text{ \AA}$, and the two Co-C bond distances in the C_2Co_2 cores are $1.948(2)$ and $1.937(2)\text{ \AA}$ respectively, comparable with those of related dicobalt complexes^[4a, 9] and our previous reports^[5b, 5d, 10]. The C(7)-C(8) bond length is $1.332(3)\text{ \AA}$, which is much longer than the normal $\text{C}\equiv\text{C}$ bond lengths but in the normal region of μ -alkyne-hexanecarbonyldicobalt compounds. The bond distance of C(10)-C(11) is $1.483(3)\text{ \AA}$, shorter than normal C-C single bond length, and the torsion angle of C(13)-C(12)-C(11)-C(10) is $-179.5(2)^\circ$, so the two $\pi(\text{C}=\text{O})$ systems are conjugated together with the $\pi(\text{C}_6\text{H}_4)$ system.

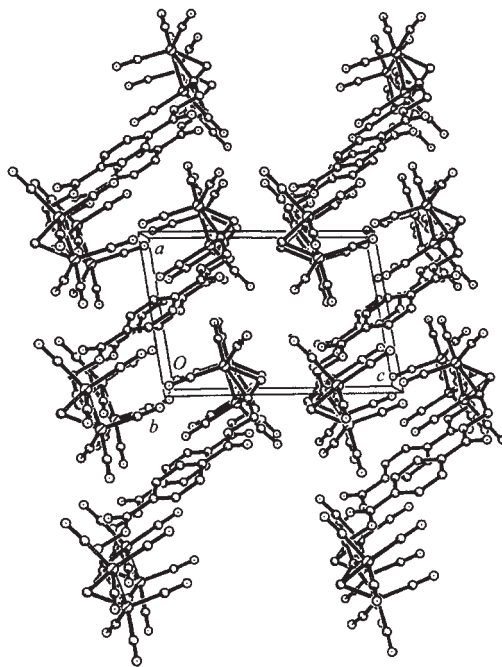


Fig. 2 Packing diagram of compound 1

References

- [1] (a) Muetterties E. L., Rhodin T. N., Brucker C. F., Band E., Pretzer W. R. *Chem. Rev.*, **1979**, **79**, 91;
- (b) Brady R. C., Pettit R. *J. Am. Chem. Soc.*, **1980**, **102**, 6181;
- (c) Muetterties E. L. *J. Organomet. Chem.*, **1980**, **200**, 177;
- (d) Gibson V. C., Parkin G., Bercaw J. E. *Organometallics*, **1991**, **10**, 220;

- (e) Bruce M. I. *Chem. Rev.*, **1991**, **91**, 197.
- [2] (a) Wojcicki A., Schuchart C. E. *Coord. Chem. Rev.*, **1990**, **29**, 97;
(b) Magnus P., Pitterna T. *J. Chem. Soc. Chem. Commun.*, **1991**, 541;
(c) Germanas J., Aubert C., Vollhardt K. P. C. *J. Am. Chem. Soc.*, **1991**, **113**, 4006;
(d) Welker M. E. *Chem. Rev.*, **1992**, **92**, 97;
(e) Caffyn A. J. M., Nicholas K. M. *In Comprehensive Organometallic Chemistry*, Pergamon: NY, **1995**.
- [3] (a) Sappa E., Tiripicchio A., Braunstein P. *Chem. Rev.*, **1983**, **83**, 203;
(b) Amouri H. E., Gruselle M. *Chem. Rev.*, **1996**, **96**, 1077;
(c) Youngs W. J., Tessier C. A., Bradshaw J. D. *Chem. Rev.*, **1999**, **99**, 3153.
- [4] (a) Housecroft C. E., Johnson B. F. G., Khan M. S., Lewis J., Raithby P. R., Robson M. E., Wilkinson D. A. *J. Chem. Soc. Dalton Trans.*, **1992**, 3171;
(b) Corrigan J. F., Doherty S., Tayler N. J. *Organometallics*, **1993**, **12**, 1365;
(c) Onitsuku K., Tao X. Q., Wang W. Q., Otsuka Y., Sonogashira K., Adachi T., Yoshida T. *J. Organomet. Chem.*, **1994**, **413**, 195;
(d) Karpov M. G., Tunik S. P., Denisov V. R., Starova G. L., Nikolskii A. B., Dolgushin F. M., Yanovsky A. I., Struchkov Y. T. *J. Organomet. Chem.*, **1995**, **485**, 219.
- [5] (a) Chen X. N., Zhang J., Yin Y. Q., Huang X. Y. *Organometallics*, **1999**, **18**, 3164;
(b) Chen X. N., Zhang J., Wu S. L., Yin Y. Q., Wang W. L., Sun J. *J. Chem. Soc. Dalton Trans.*, **1999**, 1987;
(c) Chen X. N., Zhang J., Yin Y. Q., Huang X. Y., Sun J. *J. Organomet. Chem.*, **1999**, **579**, 227;
(d) Zhang J., Chen X. N., Yin Y. Q., Wang W. L., Huang X. Y. *J. Organomet. Chem.*, **1999**, **582**, 252;
(e) Chen X. N., Zhang J., Ding E. R., Yin Y. Q. *J. Sun, Polyhedron.*, **1999**, **18**, 1555;
(f) Chen X. N., Zhang J., Yin Y. Q., Huang X. Y. *J. Coord. Chem.*, **1999**, **48**, 487.
- [6] King R. B. *Transition-Metal Compound, In: Organometallic Syntheses, Vol. 1*, Academic Press: NY, **1965**, p98.
- [7] Birdwhistell R., Hackett P., Manning A. R. *J. Organomet. Chem.*, **1978**, **157**, 239.
- [8] Roland E., Vahrenkamp H. *Angew. Chem. Int. Ed. Engl.*, **1981**, **20**, 679.
- [9] Dickson R. S., Fraser P. J. *Adv. Organomet. Chem.*, **1974**, **12**, 323.
- [10] Zhang Y. H., Chen X. N., Zhang J., Yin Y. Q., Wu J. J., Huang Z. X. *J. Chem. Res(S)*, **2000**, 378.