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Preparation and characterization of Mo_2C_2, $Co_2Mo_2C_2$ clusters containing functionally substituted cyclopentadienyl ligands. The crystal structures of $[Mo_2(\mu\text{-}C_2HPh)(CO)_4(\eta^5\text{-}C_5H_4C(O)Me)_2]$ and $[Co_2Mo_2(\mu_4\text{-}C_2HPh)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4C(O)Me)_2]$

Jie Zhang [a], Xue-Nian Chen [a], Yuan-Qi Yin [a,*], Xiao-Ying Huang [b]

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China*

[b] *State Key Laboratory of Structure Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China*

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Abstract

Through reactions of phenylacetylene with in situ generated metal–metal triply bonded complexes $[Mo(CO)_2(\eta^5\text{-}C_5H_4C(O)R)]_2$ (R=Me, OEt, Ph), three new μ-alkyne bridged molybdenum compounds containing functionally substituted cyclopentadienyl ligands $[Mo_2(\mu\text{-}C_2HPh)(CO)_4(\eta^5\text{-}C_5H_4C(O)R)_2]$ (R=Me, **1a**; R=OEt, **1b**; R=Ph, **1c**) were prepared. Further reaction of **1a**, **1b** or **1c** with $Co_2(CO)_8$ in refluxing toluene gave another three new butterfly compounds $[Co_2Mo_2(\mu_4\text{-}C_2HPh)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4C(O)R)_2]$ (R=Me, **2a**; R=OEt, **2b**; R=Ph, **2c**). All of these compounds were characterized fully by elemental analysis, IR and ^1H-NMR. The crystal structures of **1a** and **2a** were determined by X-ray diffraction techniques. Both **1a** and **2a** crystallized in monoclinic, with space group $P2_1(\#4)$, $a = 7.671(2)$, $b = 8.365(2)$, $c = 18.308(3)$ Å, $\beta = 98.34(1)°$, $V = 1162.3(5)$ Å^3, $Z = 2$ for **1a** and space group $P2_1/a(\#14)$, $a = 14.165(5)$, $b = 12.498(2)$, $c = 16.204(2)$ Å, $\beta = 96.50(2)°$, $V = 2850(1)$ Å^3, $Z = 4$ for **2a.** © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Preparation; Crystal structure; Molybdenum complex; Cobalt complex; Alkyne-bridged complex

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1. Introduction

The chemistry of dinuclear transition metal complexes bridged by unsaturated hydrocarbons developed rapidly and extensively in recent years [1]. As an active subject in this field, the reactivity of dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**I**) has been investigated by Morris since the late 1980s [2–6].

Complex **I** can react with $Co_2(CO)_8$ [6]. The product is a cluster expansion one with butterfly configuration in which the alkyne ligand is retained. The formation of the butterfly product approximates to the simple insertion of a dicobalt unit into the Mo–Mo bond. If it is so, the existence of a functional group on the cyclopentadienyl ring ought to have an influence on the reactivity of the dimolybdenum alkyne complex to some extent. For the electron-withdrawing effects of the functional group will affect the Mo–Mo bond strength, and the bulky functional group on the cyclopentadienyl ring will also hinder the dicobalt unit from approaching the molybdenum atoms. Additionally, it should be noted that both alkyne–Mo_2 and alkyne–Co_2Mo_2 complexes bear an intact bridging alkyne ligand. However, no report concerning the configuration differences of the same bridging alkyne ligand in these two types of complex, which is important especially when these com-

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* Corresponding author. Fax: + 86-0931-8417088.
E-mail address: hcom@ns.lzb.ac.cn (Y.-Q. Yin)

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plexes are associated with the chemistry of metal–catalyst surfaces, is available.

In this paper, we present the reactions of dimolybdenum alkyne complexes containing functionally substituted cyclopentadienyl ligands $[Mo_2(\mu\text{-}C_2HPh)(CO)_4(\eta^5\text{-}C_5H_4C(O)R)_2]$ (R=Me, OEt, Ph) **1** with $Co_2(CO)_8$ and the crystal structures of $[Mo_2(\mu\text{-}C_2HPh)(CO)_4(\eta^5\text{-}C_5H_4C(O)Me)_2]$ and $[Co_2Mo_2(\mu_4\text{-}C_2HPh)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}C_5H_4C(O)Me)_2]$. The results indicate that the existence of a functional group on the cyclopentadienyl ligand reduces the reactivity of the dimolybdenum alkyne complex and the configurations of the HCCPh ligand in alkyne–Mo_2 and alkyne–Co_2Mo_2 complexes are remarkably different.

2. Experimental

All reactions and manipulations were performed under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. The solvents were treated by the usual method for preparing anhydrous and deoxygenated solvents. Column chromatography was carried out by using silica gel of 160–200 mesh. $Co_2(CO)_8$ was from our laboratory. Phenylacetylene was purchased from Fluka. $[Mo(CO)_3(\eta^5\text{-}C_5H_4C(O)R)]_2$ (R=Me, OEt, Ph) were prepared by literature methods or slight modifications thereof [7]. Infrared spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer; ^1H-NMR spectra were recorded on a Bruker AM-300 MHz spectrometer and elemental analyses were performed on a Carlo Erba 1106-type analyzer.

2.1. Preparation of **1a**, **1b** and **1c**

Into a 100 cm^3 two-necked flask with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet were added 574 mg (1 mmol) of $[Mo(CO)_3(\eta^5\text{-}C_5H_4C(O)Me)]_2$ and 50 cm^3 of toluene. The mixture was stirred at reflux for 3 h. Upon cooling to room temperature, 5 mmol of phenylacetylene was added. After stirring the solution for an additional 2 h, solvent was removed at reduced pressure and the residue extracted by CH_2Cl_2. The extracts were concentrated and separated on silica gel column. Elution with CH_2Cl_2 developed a large brown–red band. Crystallization from CH_2Cl_2–petroleum ether solution gave 431 mg of complex **1a** as dark red solid. Yield 69.5%. Anal. Found: C, 49.99; H, 2.96. Calc. for $C_{26}H_{20}Mo_2O_6$: C, 50.32; H, 3.23%. IR (KBr disc, cm^{-1}), $\nu(C\equiv O)$: 2005s, 1957s, 1946s, 1919vs, 1838s; $\nu(C=O)$: 1680s, 1670s. ^1H-NMR ($CDCl_3$, δ, ppm): 2.20(s, 6H, $2CH_3$), 5.33–5.80(m, 8H, $2C_5H_4$), 5.82(s, 1H, CH), 7.12–7.25(m, 5H, C_6H_5).

2.1.1. Preparation of **1b** and **1c**

Procedures were similar to that for the preparation of **1a**.

1b. (317 mg, 46.6%) Anal. Found: C, 49.27; H, 3.40. Calc. for $C_{28}H_{24}Mo_2O_8$: C, 49.41; H, 3.53%. IR (KBr disc, cm^{-1}), $\nu(C\equiv O)$: 2001s, 1928s, 1853s; $\nu(C=O)$: 1716s. ^1H-NMR ($CDCl_3$, δ, ppm): 1.22–1.27 (t, 6H, $2CH_3$), 4.13–4.20 (q, 4H, $2CH_2$), 5.28–5.88 (m, 8H, $2C_5H_4$), 5.85 (s, 1H, CH), 7.12–7.25 (m, 5H, C_6H_5).

1c. (305 mg, 41.0%) Anal. Found: C, 57.83; H, 3.14. Calc. for $C_{36}H_{24}Mo_2O_6$: C, 58.06; H, 3.23%. IR (KBr disc, cm^{-1}), $\nu(C\equiv O)$: 1999s, 1947s, 1926vs, 1850s; $\nu(C=O)$: 1650m, 1633m. ^1H-NMR ($CDCl_3$, δ, ppm): 5.30–5.89(m, 8H, $2C_5H_4$), 5.83(s, 1H, CH), 7.08–7.15(m, 5H, C_6H_5), 7.37–7.66(m, 10H, $2C(O)C_6H_5$).

2.2. Preparation of **2a**, **2b** and **2c**

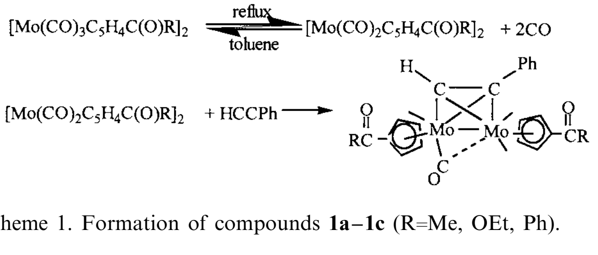
To the flask described above were added 137 mg (0.4 mmol) of $Co_2(CO)_8$, 248 mg (0.4 mmol) of **1a** and 30

Table 1
Crystal and refinement data for **1a** and **2a**

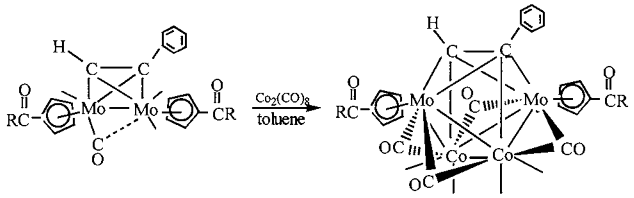
Compounds	**1a**	**2a**
Empirical formula	$C_{26}H_{20}Mo_2O_6$	$C_{30}H_{20}Co_2Mo_2O_{10}$
Formula weight	620.32	850.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (#4)	$P2_1/a$ (#14)
$F(000)$	616	1672
Lattice parameters		
a (Å)	7.671(2)	14.165(5)
b (Å)	8.365(2)	12.498(2)
c (Å)	18.308(3)	16.204(2)
β (°)	98.34(1)	96.50(2)
V (Å^3)	1162.3(5)	2850(1)
Z	2	4
D_c (g cm^{-3})	1.772	1.981
Absorptive coefficient (cm^{-1})	10.92	20.41
Temperature (°C)	23	23
$2\theta_{max}$ (°)	52.0	52.0
No. observations ($I > 2.00\sigma(I)$)	2240	4831
No. variables	306	397
R^a	0.041	0.030
wR^b	0.045	0.039
Goodness of fit indicator	1.11	1.10
Max. shift in final cycle	0.0007	0.001
Largest difference peak and hole (e Å^{-3})	1.06, −0.85	0.52, −0.73

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

[b] $wR = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2]^{1/2}$



Scheme 1. Formation of compounds **1a**–**1c** (R=Me, OEt, Ph).



Scheme 2. Formation of compounds **2a**–**2c** (R=Me, OEt, Ph).

Table 2
Positional parameters and B_{eq} for compound **1a**

Atom	x	y	z	B_{eq} [a]
Mo(1)	0.42279(9)	0.1947	0.66495(4)	1.96(3)
Mo(2)	0.49024(9)	0.28407(12)	0.82282(4)	2.10(3)
O(1)	0.7022(10)	0.2184(14)	0.5570(4)	5.6(5)
O(2)	0.3647(16)	0.5584(11)	0.6353(7)	7.2(6)
O(3)	0.0951(8)	0.3449(10)	0.7675(4)	4.1(3)
O(4)	0.4238(11)	−0.0666(10)	0.8652(5)	4.6(4)
O(5)	0.3091(13)	0.1257(15)	0.4511(5)	6.9(6)
O(6)	0.1651(11)	0.5182(12)	0.9474(5)	5.2(4)
C(1)	0.6032(12)	0.2116(16)	0.5981(5)	3.2(4)
C(2)	0.3862(14)	0.4287(12)	0.6473(7)	3.0(4)
C(3)	0.2442(12)	0.3125(12)	0.7822(5)	2.9(4)
C(4)	0.4434(13)	0.0650(14)	0.8471(6)	2.8(4)
C(5)	0.6517(10)	0.2829(15)	0.7381(5)	2.4(3)
C(6)	0.6319(11)	0.1263(13)	0.7532(5)	2.3(3)
C(7)	0.7536(11)	−0.0082(12)	0.7659(5)	2.5(3)
C(8)	0.8701(12)	−0.0180(13)	0.8318(5)	2.9(4)
C(9)	0.9886(12)	−0.1413(15)	0.8456(5)	3.3(4)
C(10)	0.9961(11)	−0.2602(13)	0.7949(6)	3.5(5)
C(11)	0.8814(14)	−0.2545(12)	0.7286(6)	3.5(4)
C(12)	0.7625(13)	−0.1278(13)	0.7150(5)	3.0(4)
C(13)	0.2287(12)	0.1018(14)	0.5678(5)	3.0(4)
C(14)	0.1309(12)	0.1437(13)	0.6257(6)	3.0(4)
C(15)	0.1769(11)	0.0362(13)	0.6843(5)	2.8(4)
C(16)	0.3065(13)	−0.0676(12)	0.6655(5)	2.9(4)
C(17)	0.3406(14)	−0.0282(13)	0.5944(6)	3.3(4)
C(18)	0.2200(14)	0.1753(18)	0.4950(6)	4.2(6)
C(19)	0.0980(17)	0.310(2)	0.4776(7)	5.9(7)
C(20)	0.4390(11)	0.4273(12)	0.9239(5)	2.6(4)
C(21)	0.5994(14)	0.3395(13)	0.9456(6)	3.6(4)
C(22)	0.7226(13)	0.4024(18)	0.9037(7)	4.4(5)
C(23)	0.6429(18)	0.5265(15)	0.8585(7)	4.6(6)
C(24)	0.4728(15)	0.5413(12)	0.8722(6)	3.0(4)
C(25)	0.2705(13)	0.4100(13)	0.9550(5)	2.9(4)
C(26)	0.2354(15)	0.2619(18)	0.9917(6)	4.7(6)

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

cm^3 of toluene. The mixture was stirred at reflux for 40 min, a colour change from red to deep green was observed. After addition of 5 g of silica gel the solvent was removed and the residue chromatographed. Elution with CH_2Cl_2–ether (3:1) produced a small red band of unreacted **1a** and a large blue band of product **2a** (dark blue solid, 81 mg, 23.8%). Anal. Found: C, 42.13; H, 2.20. Calc. for $C_{30}H_{20}Co_2Mo_2O_{10}$: C, 42.35; H, 2.35%. IR (KBr disc, cm^{-1}), ν(C≡O): 2050s, 2021vs, 2000s, 1981s, 1855s, 1833vs, 1809vs; ν(C=O): 1681s. ^{1}H-NMR ($CDCl_3$, δ, ppm): 2.34(s, 6H, $2CH_3$), 4.84–5.52(m, 8H, $2C_5H_4$), 6.77–7.05(m, 5H, C_6H_5), 8.28(s, 1H, CH).

2.2.1. *Preparation of* ***2b*** *and* ***2c***

Procedures were similar to that for the preparation of **2a**.

2b. (54 mg, 19.8%) Anal. Found: C, 42.09; H, 2.55. Calc. for $C_{32}H_{24}Co_2Mo_2O_{12}$: C, 42.20; H, 2.64%. IR (KBr disc, cm^{-1}), ν(C≡O): 2058s, 2028vs, 1844s, 1808s;

Table 3
Positional parameters and B_{eq} for compound **2a**

Atom	x	y	z	B_{eq} [a]
Mo(1)	0.72774(2)	0.05487(2)	0.633111(17)	1.83(1)
Mo(2)	0.84042(2)	0.09541(3)	0.873111(18)	2.08(1)
Co(1)	0.73894(3)	−0.05082(4)	0.77863(3)	2.22(2)
Co(2)	0.89162(3)	0.01962(4)	0.73003(3)	2.07(2)
O(1)	0.5775(2)	−0.1213(3)	0.64933(19)	4.2(1)
O(2)	0.8586(2)	−0.1214(3)	0.5755(2)	5.0(2)
O(3)	0.8440(2)	−0.1364(3)	0.9408(2)	4.8(2)
O(4)	1.0571(2)	0.0770(3)	0.8603(2)	4.0(1)
O(5)	0.5747(3)	−0.0945(3)	0.8672(2)	5.6(2)
O(6)	0.7722(3)	−0.2784(3)	0.7560(3)	7.7(2)
O(7)	1.0389(2)	0.0986(3)	0.6335(2)	4.5(2)
O(8)	0.9920(3)	−0.1821(3)	0.7658(3)	6.8(2)
O(9)	0.8628(2)	0.2963(3)	0.53310(19)	4.0(1)
O(10)	0.5923(2)	0.1592(3)	0.9327(2)	5.4(2)
C(1)	0.6409(3)	−0.0617(3)	0.6581(2)	2.9(2)
C(2)	0.8220(3)	−0.0555(3)	0.6109(2)	3.0(2)
C(3)	0.8340(3)	−0.0578(3)	0.9030(2)	3.1(2)
C(4)	0.9749(3)	0.0754(3)	0.8519(2)	2.9(2)
C(5)	0.6367(3)	−0.0756(3)	0.8335(3)	3.2(2)
C(6)	0.7631(3)	−0.1895(3)	0.7649(3)	3.8(2)
C(7)	0.9817(3)	0.0715(3)	0.6723(2)	2.7(2)
C(8)	0.9510(3)	−0.1058(4)	0.7511(3)	3.5(2)
C(9)	0.8113(2)	0.1468(3)	0.7395(2)	1.9(1)
C(10)	0.7248(2)	0.1031(3)	0.7667(2)	1.9(1)
C(11)	0.8303(2)	0.2632(3)	0.7311(2)	2.0(1)
C(12)	0.9232(3)	0.3018(3)	0.7293(2)	2.8(1)
C(13)	0.9412(3)	0.4097(3)	0.7258(3)	3.3(2)
C(14)	0.8675(3)	0.4825(3)	0.7239(3)	3.6(2)
C(15)	0.7765(3)	0.4465(3)	0.7278(3)	3.2(2)
C(16)	0.7581(3)	0.3381(3)	0.7311(2)	2.5(1)
C(21)	0.7507(3)	0.1589(3)	0.5176(2)	2.4(1)
C(22)	0.6792(2)	0.2073(3)	0.5593(2)	2.4(1)
C(23)	0.6007(3)	0.1382(4)	0.5557(2)	3.1(2)
C(24)	0.6232(3)	0.0455(4)	0.5106(3)	3.3(2)
C(25)	0.7138(3)	0.0585(3)	0.4871(2)	2.9(2)
C(26)	0.8424(3)	0.2087(3)	0.5047(2)	2.9(2)
C(27)	0.9060(3)	0.1484(4)	0.4529(3)	4.6(2)
C(31)	0.7546(3)	0.1600(3)	0.9766(2)	2.7(1)
C(32)	0.7813(3)	0.2474(3)	0.9291(2)	3.0(2)
C(33)	0.8799(3)	0.2562(4)	0.9389(3)	4.0(2)
C(34)	0.9160(3)	0.1753(5)	0.9935(3)	4.6(2)
C(35)	0.8395(3)	0.1167(4)	1.0177(2)	3.7(2)
C(36)	0.6552(3)	0.1252(4)	0.9815(3)	3.5(2)
C(37)	0.6389(5)	0.0499(6)	1.0497(4)	7.3(4)

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

Table 4
Selected bond lengths (Å) and bond angles (°) for compound **1a**

Mo(1)–Mo(2)	2.957(1)	Mo(1)–C(5)	2.176(9)	Mo(1)–C(14)	2.290(9)	Mo(1)–C(16)	2.37(1)
Mo(1)–C(1)	1.98(1)	Mo(1)–C(6)	2.182(9)	Mo(1)–C(17)	2.30(1)	Mo(1)–C(15)	2.374(9)
Mo(1)–C(2)	2.00(1)	Mo(1)–C(13)	2.28(1)	Mo(2)–C(4)	1.93(1)	Mo(2)–C(3)	1.94(1)
Mo(2)–C(5)	2.120(9)	Mo(2)–C(6)	2.22(1)	Mo(2)–C(20)	2.29(1)	Mo(2)–C(21)	2.33(1)
Mo(2)–C(24)	2.34(1)	Mo(2)–C(22)	2.36(1)	Mo(2)–C(23)	2.38(1)	O(1)–C(1)	1.15(1)
O(3)–C(3)	1.17(1)	O(5)–C(18)	1.20(1)	O(6)–C(25)	1.21(1)	C(5)–C(6)	1.35(1)
C(6)–C(7)	1.46(1)	C(7)–C(12)	1.38(1)	C(7)–C(8)	1.40(1)	C(8)–C(9)	1.37(1)
C(9)–C(10)	1.37(2)	C(10)–C(11)	1.39(1)	C(11)–C(12)	1.40(1)	C(13)–C(17)	1.43(1)
C(13)–C(14)	1.43(1)	C(13)–C(18)	1.46(1)	C(14)–C(15)	1.41(1)	C(15)–C(16)	1.40(1)
C(16)–C(17)	1.40(1)	C(18)–C(19)	1.47(2)	C(20)–C(24)	1.39(1)	C(20)–C(21)	1.44(1)
C(20)–C(25)	1.49(1)	C(21)–C(22)	1.40(2)	C(22)–C(23)	1.41(2)	C(23)–C(24)	1.37(1)
C(25)–C(26)	1.45(2)	Mo(1)–C(3)	2.88(1)				
C(1)–Mo(1)–C(2)	85.7(5)	C(1)–Mo(1)–C(5)	77.5(4)	C(1)–Mo(1)–C(6)	88.4(4)		
C(1)–Mo(1)–C(13)	88.7(4)	C(1)–Mo(1)–C(14)	123.9(4)	C(1)–Mo(1)–C(17)	82.5(5)		
C(1)–Mo(1)–C(16)	111.5(5)	C(1)–Mo(1)–C(15)	140.7(4)	C(1)–Mo(1)–Mo(2)	123.2(3)		
C(5)–Mo(1)–C(6)	36.1(4)	C(5)–Mo(1)–C(13)	166.2(3)	C(5)–Mo(1)–C(14)	157.0(4)		
C(5)–Mo(1)–C(17)	138.6(4)	C(5)–Mo(1)–C(16)	125.5(4)	C(5)–Mo(1)–C(15)	133.2(3)		
C(5)–Mo(1)–Mo(2)	45.7(2)	C(6)–Mo(1)–C(13)	144.4(4)	C(6)–Mo(1)–C(14)	139.8(4)		
C(6)–Mo(1)–C(17)	108.3(4)	C(6)–Mo(1)–C(16)	89.4(4)	C(6)–Mo(1)–C(15)	104.9(3)		
C(6)–Mo(1)–Mo(2)	48.5(3)	C(13)–Mo(1)–C(14)	36.4(3)	C(13)–Mo(1)–C(17)	36.3(4)		
C(13)–Mo(1)–C(16)	59.0(4)	C(13)–Mo(1)–C(15)	59.0(3)	C(13)–Mo(1)–Mo(2)	148.1(2)		
C(4)–Mo(2)–C(3)	90.1(4)	C(4)–Mo(2)–C(5)	108.2(5)	C(4)–Mo(2)–C(6)	72.0(4)		
C(4)–Mo(2)–C(20)	104.5(4)	C(4)–Mo(2)–Mo(1)	88.5(3)	C(3)–Mo(2)–C(5)	111.0(4)		
C(3)–Mo(2)–C(6)	112.5(4)	C(3)–Mo(2)–C(20)	88.5(3)	C(3)–Mo(2)–C(21)	122.6(4)		
C(3)–Mo(2)–C(24)	85.9(4)	C(3)–Mo(2)–C(22)	142.4(4)	C(3)–Mo(2)–C(23)	114.3(5)		
C(3)–Mo(2)–Mo(1)	68.5(3)	C(5)–Mo(2)–C(6)	36.2(4)	C(5)–Mo(2)–C(20)	141.4(4)		
C(5)–Mo(2)–Mo(1)	47.3(2)	C(6)–Mo(2)–C(20)	158.5(3)	C(6)–Mo(2)–Mo(1)	47.3(2)		
C(20)–Mo(2)–Mo(1)	153.8(2)	O(1)–C(1)–Mo(1)	177(1)	O(2)–C(2)–Mo(1)	178(1)		
O(3)–C(3)–Mo(2)	169.1(8)	O(4)–C(4)–Mo(2)	175.8(9)	C(6)–C(5)–Mo(2)	76.1(6)		
C(6)–C(5)–Mo(1)	72.2(6)	Mo(2)–C(5)–Mo(1)	87.0(3)	C(5)–C(6)–C(7)	133.8(9)		
C(5)–C(6)–Mo(1)	71.7(6)	C(5)–C(6)–Mo(2)	67.7(6)	C(7)–C(6)–Mo(1)	134.9(7)		
C(7)–C(6)–Mo(2)	136.1(7)	Mo(1)–C(6)–Mo(2)	84.3(3)	C(12)–C(7)–C(8)	117.0(9)		
C(12)–C(7)–C(6)	123.1(8)	C(17)–C(13)–C(18)	125(1)	O(6)–C(25)–C(20)	119(1)		
O(3)–C(3)–Mo(1)	117.6(7)						

v(C=O): 1718s. ^{1}H-NMR (CDCl$_3$, δ, ppm): 1.33(s, 6H, 2CH$_3$), 4.28(s, 4H, 2CH$_2$), 4.90–5.57(m, 8H, 2C$_5$H$_4$), 6.70–7.03(m, 5H, C$_6$H$_5$), 8.34(s, 1H, CH).

2c. (120 mg, 41.1%) Anal. Found: C, 49.21; H, 2.38. Calc. for $C_{40}H_{24}Co_2Mo_2O_{10}$: C, 49.28; H, 2.46%. IR (KBr disc, cm^{-1}), *v*(C≡O): 2061s, 2034vs, 1839s, 1797s; *v*(C=O): 1652m. ^{1}H-NMR (CDCl$_3$, δ, ppm): 4.92–5.67(m, 8H, 2C$_5$H$_4$), 6.58–6.98(m, 5H, C$_6$H$_5$), 7.42–7.81(m, 10H, 2C(O)C$_6$H$_5$), 8.45(s, 1H, CH).

2.3. Crystallography of **1a** and **2a**

Crystals of **1a** suitable for diffraction analysis were grown from CH$_2$Cl$_2$ solution and those of **2a** were grown from petroleum ether/CH$_2$Cl$_2$ solution at −20°C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator.

The structures were solved by the Patterson method and refined by the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms. All calculations were performed on a MICRO VAX 3100 computer using the TEXSAN program system. Crystal data and experimental details are collected in Table 1.

3. Results and discussion

The formations of compounds **1a**–**1c** is shown in Scheme 1.

The first step is a reversible reaction. According to the literature procedure [5,8], 10–24 h is necessary. In our attempt to shorten the reaction time, we reduced the concentration of the reaction system (1 mmol/50 cm^3). This favored the decarbonylation process greatly. In most cases, 3–5 h was sufficient for this step. The second step could be achieved instantly, for there was no difference in yields to let the second step react for 1 h or for 10 h. Compounds **1a**–**1c** are air-stable red solids. They are soluble in polar solvent like CH$_2$Cl$_2$ and THF.

Heating a toluene solution of **1a**, **1b** or **1c** with 1 equivalent of Co$_2$(CO)$_8$ to reflux can cause a reaction

(Scheme 2). The products (**2a**–**2c**) are cluster expansion ones with butterfly configuration that can be readily isolated by column chromatography as air-stable dark green or dark blue solids. Compared with their analogous complex with unsubstituted cyclopentagienyl ligands [$Mo_2(\mu\text{-}HC \equiv CPh)(CO)_4(\eta^5\text{-}C_5H_5)_2$] [6], complex **1a**, **1b** or **1c** requires a longer time to react with $Co_2(CO)_8$ under the same reaction condition. For the reaction of [$Mo_2(\mu\text{-}HC \equiv CPh)(CO)_4(\eta^5\text{-}C_5H_5)_2$] with $Co_2(CO)_8$, the reactants are completely consumed within 30 min, while for the reaction of **1a**, **1b** or **1c** with $Co_2(CO)_8$, although 40 min is employed, a quantity of unreacted dimolybdenum alkyne complex can always be isolated. This indicates that the existence of an

Table 5
Selected bond lengths (Å) and bond angles (°) for compound **2a**

Mo(1)–Co(2)	2.687(1)	Mo(1)–Co(1)	2.6912(7)	Mo(2)–Co(2)	2.6792(7)	Mo(2)–Co(1)	2.6947(8)
Co(2)–Co(1)	2.542(1)	Mo(1)–C(1)	1.979(4)	Mo(1)–C(2)	1.980(4)	Mo(1)–C(10)	2.252(3)
Mo(1)–C(9)	2.288(3)	Mo(1)–C(22)	2.311(4)	Mo(1)–C(23)	2.319(4)	Mo(1)–C(21)	2.332(3)
Mo(1)–C(24)	2.341(4)	Mo(1)–C(25)	2.352(4)	Mo(2)–C(3)	1.980(4)	Mo(2)–C(4)	1.988(4)
Mo(2)–C(10)	2.241(3)	Mo(2)–C(9)	2.251(3)	Mo(2)–C(32)	2.303(4)	Co(1)–C(6)	1.785(4)
Co(1)–C(5)	1.811(4)	Co(1)–C(10)	1.941(3)	Co(1)–C(1)	2.269(4)	Co(1)–C(3)	2.295(4)
Co(2)–C(7)	1.788(4)	Co(2)–C(8)	1.792(4)	Co(2)–C(9)	1.969(3)	Co(2)–C(2)	2.270(4)
Co(2)–C(4)	2.293(4)	O(1)–C(1)	1.165(5)	O(2)–C(2)	1.158(5)	O(3)–C(3)	1.158(5)
O(4)–C(4)	1.157(5)	O(5)–C(5)	1.111(5)	O(6)–C(6)	1.130(5)	O(7)–C(7)	1.132(5)
O(8)–C(8)	1.126(5)	O(9)–C(26)	1.210(5)	O(10)–C(36)	1.199(5)	C(9)–C(10)	1.456(5)
C(9)–C(11)	1.489(5)	C(11)–C(16)	1.385(5)	C(11)–C(12)	1.405(5)	C(12)–C(13)	1.376(5)
C(13)–C(14)	1.382(6)	C(14)–C(15)	1.374(6)	C(15)–C(16)	1.382(5)	C(21)–C(22)	1.416(5)
C(21)–C(25)	1.426(5)	C(21)–C(26)	1.478(5)	C(22)–C(23)	1.404(5)	C(23)–C(24)	1.425(6)
C(24)–C(25)	1.390(6)	C(26)–C(27)	1.502(6)				
C(1)–Mo(1)–C(2)	88.4(2)	C(1)–Mo(1)–C(10)	85.5(1)	C(1)–Mo(1)–C(9)	119.8(1)		
C(1)–Mo(1)–C(22)	123.9(1)	C(1)–Mo(1)–C(23)	88.8(2)	C(1)–Mo(1)–C(21)	136.1(1)		
C(1)–Mo(1)–C(24)	77.7(2)	C(1)–Mo(1)–C(25)	103.7(2)	C(1)–Mo(1)–Co(1)	55.6(1)		
C(1)–Mo(1)–Co(2)	106.0(1)	C(2)–Mo(1)–C(10)	116.6(1)	C(2)–Mo(1)–C(9)	100.7(1)		
C(2)–Mo(1)–C(22)	130.3(2)	C(2)–Mo(1)–C(23)	135.3(2)	C(2)–Mo(1)–C(21)	94.8(2)		
C(2)–Mo(1)–C(24)	100.7(2)	C(2)–Mo(1)–C(25)	79.1(2)	C(2)–Mo(1)–Co(2)	55.8(1)		
C(2)–Mo(1)–Co(1)	81.0(1)	C(10)–Mo(1)–C(9)	37.4(1)	C(10)–Mo(1)–C(22)	103.9(1)		
C(10)–Mo(1)–C(23)	107.6(1)	C(10)–Mo(1)–C(21)	129.9(1)	C(10)–Mo(1)–C(24)	138.6(1)		
C(10)–Mo(1)–C(25)	162.4(1)	C(10)–Mo(1)–Co(2)	65.82(8)	C(25)–Mo(1)–Co(2)	124.0(1)		
C(25)–Mo(1)–Co(1)	151.7(1)	Co(2)–Mo(1)–Co(1)	56.42(2)	C(10)–Mo(1)–Co(1)	45.17(9)		
C(9)–Mo(1)–C(22)	94.2(1)	C(9)–Mo(1)–Co(2)	45.77(8)	C(9)–Mo(1)–Co(1)	67.21(8)		
C(22)–Mo(1)–C(23)	35.3(1)	C(22)–Mo(1)–Co(2)	128.6(1)	C(22)–Mo(1)–Co(1	147.34(9)		
C(10)–Mo(2)–C(34)	148.1(2)	C(10)–Mo(2)–Co(2)	66.10(9)	C(3)–Mo(2)–C(4)	89.6(2)		
C(3)–Mo(2)–C(10)	100.3(1)	C(3)–Mo(2)–C(9)	120.1(1)	C(3)–Mo(2)–Co(2)	83.9(1)		
C(3)–Mo(2)–Co(1)	56.3(1)	C(4)–Mo(2)–C(10)	120.2(1)	C(4)–Mo(2)–C(9)	86.8(1)		
C(4)–Mo(2)–Co(2)	56.5(1)	C(4)–Mo(2)–Co(1)	106.1(1)	C(10)–Mo(2)–C(9)	37.8(1)		
C(10)–Mo(2)–C(32)	90.1(1)	C(10)–Mo(2)–Co(1)	45.1(7)	C(9)–Mo(2)–C(32)	96.2(1)		
C(9)–Mo(2)–Co(2)	46.08(8)	C(9)–Mo(2)–Co(1)	67.61(9)	Co(2)–Mo(2)–Co(1)	56.47(2)		
C(6)–Co(1)–C(5)	94.0(2)	C(6)–Co(1)–C(10)	165.6(2)	C(6)–Co(1)–C(1)	86.6(2)		
C(6)–Co(1)–C(3)	88.4(2)	C(5)–Co(1)–C(10)	98.1(2)	C(5)–Co(1)–Co(2)	165.5(1)		
C(5)–Co(1)–Mo(1)	122.9(1)	C(10)–Co(1)–Co(2)	72.9(1)	C(10)–Co(1)–Mo(1)	55.4(1)		
C(10)–Co(1)–Mo(2)	55.0(1)	C(1)–Co(1)–C(3)	174.1(1)	C(1)–Co(1)–Co(2)	102.3(1)		
C(1)–Co(1)–Mo(1)	46.0(1)	C(3)–Co(1)–Mo(2)	45.9(1)	Co(2)–Co(1)–Mo(1)	61.71(2)		
Co(2)–Co(1)–Mo(2)	61.46(2)	Mo(1)–Co(1)–Mo(2)	98.01(2)	C(7)–Co(2)–C(8)	94.0(2)		
C(7)–Co(2)–C(9)	101.6(2)	C(7)–Co(2)–Co(1)	166.2(1)	C(8)–Co(2)–C(9)	162.3(2)		
C(9)–Co(2)–Co(1)	74.8(1)	C(9)–Co(2)–Mo(2)	55.4(1)	C(9)–Co(2)–Mo(1)	56.4(1)		
C(10)–C(9)–C(11)	124.3(3)	C(10)–C(9)–Co(2)	103.5(2)	C(10)–C(9)–Mo(2)	70.7(2)		
C(10)–C(9)–Mo(1)	70.0(2)	C(11)–C(9)–Co(2)	132.0(2)	C(11)–C(9)–Mo(2)	110.6(2)		
Co(2)–C(9)–Mo(2)	78.5(1)	Co(2)–C(9)–Mo(1)	77.9(1)	Mo(2)–C(9)–Mo(1)	127.2(2)		
C(9)–C(10)–Co(1)	108.8(2)	C(9)–C(10)–Mo(2)	71.5(2)	C(9)–C(10)–Mo(1)	72.6(2)		
Co(1)–C(10)–Mo(2)	79.9(1)	Co(1)–C(10)–Mo(1)	79.5(1)	Mo(2)–C(10)–Mo(1)	129.6(1)		
C(16)–C(11)–C(12)	117.4(3)	C(16)–C(11)–C(9)	121.2(3)	C(22)–C(21)–C(26)	125.1(3)		
O(1)–C(1)–Co(1)	122.2(3)	O(1)–C(1)–Mo(1)	159.5(3)	Mo(1)–C(1)–Co(1)	78.3(1)		
O(2)–C(2)–Co(2)	122.6(3)	O(2)–C(2)–Mo(1)	159.0(3)	Mo(1)–C(2)–Co(2)	78.1(1)		
O(3)–C(3)–Mo(2)	160.6(4)	O(3)–C(3)–Co(1)	121.4(3)	Mo(2)–C(3)–Co(1)	77.8(1)		
O(4)–C(4)–Mo(2)	161.5(3)	O(4)–C(4)–Co(2)	121.3(3)	Mo(2)–C(4)–Co(2)	77.1(1)		
O(5)–C(5)–Co(1)	177.6(4)	O(6)–C(6)–Co(1)	175.5(5)	O(7)–C(7)–Co(2)	175.9(4)		
O(8)–C(8)–Co(2)	176.8(5)						

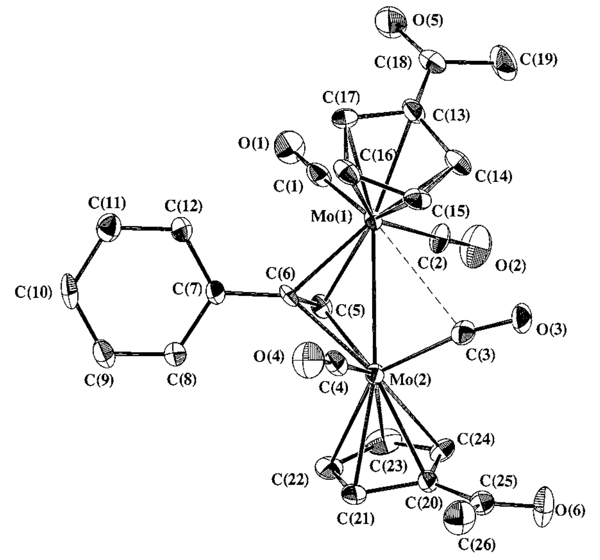


Fig. 1. The molecular structure of compound **1a**.

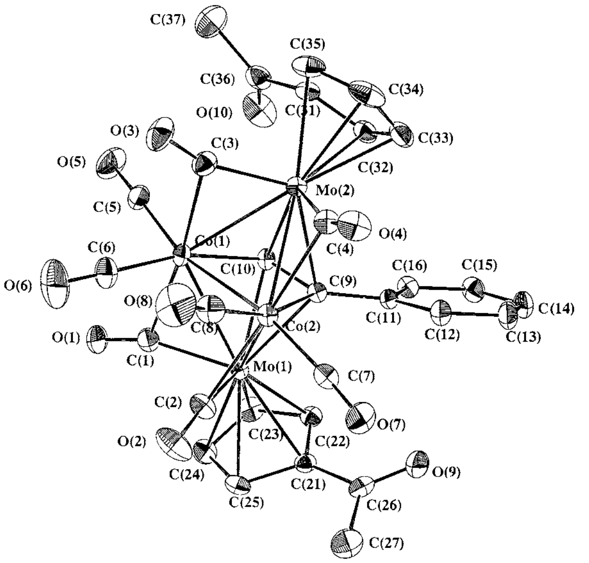


Fig. 2. The molecular structure of compound **2a**.

electron-withdrawing group on the cyclopentadienyl ligand makes the dimolybdenum alkyne complex more difficult to react with $Co_2(CO)_8$.

All the compounds were well characterized by elemental analysis, IR and ^{1}H-NMR. The molecular formulae of the clusters were readily apparent from their elemental analyses. In the IR spectra of **1a**–**1c**, besides 2–4 absorption bands caused by terminal carbonyls in the range 1919–2005 cm^{-1} and one band caused by semi-bridging carbonyl in the range 1838–1853 cm^{-1}, there are 1–2 absorption bands in the range 1633–1716 cm^{-1}, exhibited by the carbonyls (C=O) on the substituted cyclopentadienyl rings. The IR spectra of **2a**–**2c** contain peaks attributable to terminal carbonyls in the range 1981–2061 cm^{-1} and bridging carbonyls in the range 1808–1855 cm^{-1}, and one peak corresponding to the carbonyls (C=O) on the substituted cyclopentadienyl rings in the range 1652–1718 cm^{-1}. For the C–H and C–Ph units in the intact alkyne ligand, **1a**, **1b**, **1c** show one singlet around 5.83 ppm (CH) and one multiplet in the range 7.08–7.25 ppm (CPh) while **2a**, **2b**, **2c** show one singlet around 8.35 ppm (CH) and one multiplet in the range 6.58–7.05 ppm (CPh) in their ^{1}H-NMR spectra. For the eight protons on the two substituted cyclopentadienyl rings (C_5H_4), all the compounds show a multiplet in the range 5.28–5.89 ppm (for **1a**, **1b**, **1c)** or 4.90–5.67 ppm (for **2a**, **2b**, **2c**). In most cases, this multiplet consists of four asymmetric singlets in the same ratio that should be contributed to differences of the chemical small environment of the four protons on each cyclopentadienyl ring [9]. It should be mentioned that the IR spectra of **1a** and **1c** show two C=O absorption bands rather than one. This indicates that the two substituted cyclopentadienyl rings in compounds **1a**–**1c** are not equivalent. This may be explained by the existence of the semi-bridging carbonyl between the two molybdenum atoms and/or the unsymmetrical alkyne ligand coordinated to them.

In order to further confirm the structures of these complexes and compare the different configurations of the bridging HC≡CPh ligand in **1** and **2**, X-ray single-crystal structure analyses of **1a** and **2a** were undertaken. The final atomic coordinates and thermal parameters of the non-hydrogen atoms for **1a** and **2a** are given in Tables 2 and 3. Selected bond lengths and angles are listed in Tables 4 and 5. The molecular structures of **1a** and **2a** are presented in Figs. 1 and 2.

The molecule of compound **1a** consists of a quasi-tetrahedral cluster core Mo_2C_2 and two acetylcyclopentadienyl, four carbonyl ligands. In the Mo_2C_2 cluster core, the Mo–Mo bond length (2.957(1) Å), the C–C bond length (1.35(1) Å) and the average Mo–C bond length (2.175 Å) are very close to the corresponding values found in $[Mo_2(\mu\text{-}C_2H_2)(CO)_4\text{-}(\eta^5\text{-}C_5H_4C(O)O\text{-}Me)_2]$ [8]. The two acetylcyclopentadienyl ligands extend in different directions and one of them is much closer to the phenyl group than the other (see Fig. 1). The C(3)O(3) carbonyl is a linear semi-bridging one, because the values for judging the type of carbonyls of C(3)O(3) are within the range of linear semi-bridging carbonyls [10,11]. Namely, $\angle O(3)C(3)Mo(2) = 169.1(8)^\circ$, $\angle C(3)Mo(2)Mo(1) = 68.5(3)^\circ$, $Mo(1)\cdots C(3) = 2.88(1)$ Å, asymmetric parameter is 0.48.

As seen in Fig. 2, compound **2a** is a butterfly cluster with bridging alkyne ligand. The butterfly core consists of two cobalt atoms which form the hinge and two molybdenum atoms which act as the wingtips. Each molybdenum atom bears an acetylcyclopentadienyl ring and each cobalt atom has two terminal carbonyl ligands. In addition, each Co–Mo bond is spanned by an asymmetrically bridging carbonyl ligand which is more closely bonded to molybdenum than to cobalt. For these carbonyls, the Mo–C–O angles are in the range 159.0(3)–161.5(3)°, the asymmetric parameters are in the range 0.146–0.159, so they can be classed as semi-bridging carbonyls [6,12]. The alkyne ligand lies parallel to the Co–Co bond and is bonded to all four metal atoms. Under the asymmetrical environment of the alkyne ligand (HCCPh), the two acetylcyclopentadienyl ligands extend in different directions. In the butterfly core, the Co–Co bond length (2.542(1) Å), the average Co–Mo bond length (2.688 Å) and the average Co–C bond length (1.955 Å) are close to the corresponding values observed in the related cluster [6]. The Mo···Mo distance is 4.06(5) Å, well beyond the range of possible bonding. The average C–Mo bond length (2.258 Å) is much longer than the corresponding value found in compound **1a**.

In both **1a** and **2a**, the bridging alkyne ligand (HCCPh) is intact. However, its geometrical parameters are remarkably different. In **1a**, the C(5)–C(6) bond length is 1.35(1) Å, close to a C=C double bond. The C(6)–C(7) bond length is 1.46(1) Å, much shorter than a C–C single bond. $\angle$C(5)C(6)C(7) = 133.8(9)°, greatly twisted from the linear configuration for a normal alkyne complex. In **2a**, the C(9)–C(10) bond length is 1.456(5) Å, longer than a C=C double bond but shorter than a C–C single bond. The C(9)–C(11) bond length is 1.489(5) Å, slightly shorter than a C–C single bond. $\angle$C(10)C(9)C(11) = 124.3(3)°, even more greatly twisted from the linear configuration for a normal alkyne complex. In both **1a** and **2a**, the phenyl group remains unchanged. From these geometrical parameters, it can be seen that the two bridging carbon atoms (C(5) and C(6)) in complex **1a** are more like unsaturated sp^2 carbon atoms while the ones (C(9) and C(10)) in **2a** are more like saturated sp^3 carbon atoms.

4. Conclusion

The existence of a bulky electron-withdrawing functional group on the cyclopentadienyl ligand can reduce the reactivity of dimolybdenum alkyne complex. This supports the proposition that the formation of the butterfly product approximates to the simple insertion of a dicobalt unit into the Mo–Mo bond. In the Mo_2C_2 cluster core, the two bridging carbon atoms are more like unsaturated sp^2 carbon atoms while in the $Co_2Mo_2C_2$ cluster core the two bridging carbon atoms are more like saturated sp^3 carbon atoms.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 113327 for compound **1a** and No. 113328 for compound **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.uk.

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References

[1] H.E. Amouri, M. Gruselle, Chem. Rev. 96 (1996) 1077.

[2] G. Conole, K.A. Hill, M. Mcpartlin, M.J. Mays, M.J. Morris, J. Chem. Soc. Chem. Commun. (1989) 688.

[3] G. Conole, M. Mcpartlin, M.J. Mays, M.J. Morris, J. Chem. Soc. Dalton Trans. (1990) 2359.

[4] H. Adams, N.A. Bailey, S.R. Gay, T. Hamilton, M.J. Morris, J. Organomet. Chem. 493 (1995) C25.

[5] H. Adams, L.J. Gill, M.J. Morris, Organometallics 15 (1996) 4182.

[6] H. Adams, N.A. Bailey, L.J. Gill, M.J. Morris, F.A. Wildgoose, J. Chem. Soc. Dalton Trans. (1996) 1437.

[7] L.C. Song, J.Y. Shen, Chem. J. Chinese Universities 13 (1992) 1227.

[8] L.C. Song, J.Y. Shen, Q.M. Hu, X.Y. Huang, Inorg. Chim. Acta 249 (1996) 175.

[9] H.P. Wu, Y.Q. Yin, Q.C. Yang, Polyhedron 15 (1996) 43.

[10] M.D. Curtis, W.M. Butler, J. Organomet. Chem. 155 (1978) 131.

[11] R.J. Klingler, W.M. Butler, M.D. Curtis, J. Am. Chem. Soc. 100 (1978) 5034.

[12] M.D. Curtis, K.R. Han, W.M. Butler, Inorg. Chem. 19 (1980) 2096.