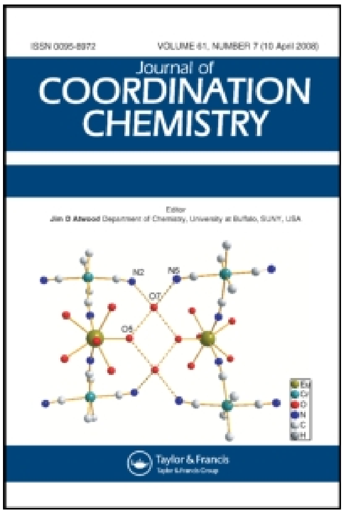


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# PREPARATION AND CHARACTERIZATION OF CLUSTER COMPLEXES CONTAINING ONE OR TWO $C_2M_2$ (M = Co, Mo) CORES

Xue-Nian Chen[a]; Jie Zhang[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, China [b] State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, China

**To cite this Article** Chen, Xue-Nian , Zhang, Jie , Yin, Yuan-Qi and Huang, Xiao-Ying(1999) 'PREPARATION AND CHARACTERIZATION OF CLUSTER COMPLEXES CONTAINING ONE OR TWO $C_2M_2$ (M = Co, Mo) CORES', Journal of Coordination Chemistry, 48: 4, 487 — 494

**To link to this Article: DOI:** 10.1080/00958979908023588

**URL:** http://dx.doi.org/10.1080/00958979908023588

*J. Coord. Chem.*, 1999, Vol. 48, pp. 487–494
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

# PREPARATION AND CHARACTERIZATION OF CLUSTER COMPLEXES CONTAINING ONE OR TWO $C_2M_2$ (M = Co, Mo) CORES

XUE-NIAN CHEN[a], JIE ZHANG[a], YUAN-QI YIN[a,*]
and 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, China;* [b]*State Key Laboratory of Structure Chemistry,*
*Fujian Institute of Research on the Structure of Matter,*
*Chinese Academy of Sciences, Fuzhou 350002, China*

*(Received 24 November 1998)*

The reaction of dipropargylether with $Mo_2(C_5H_4R)_2(CO)_4$ (R = H, $COOCH_2CH_3$), prepared by refluxing a toluene solution of $Mo_2(C_5H_4R)_2(CO)_6$ (R = H, $COOCH_2CH_3$), gave dinuclear cluster complexes $(HC_2CH_2OCH_2C_2H\text{-}\mu)[Mo_2(C_5H_4R)_2(CO)_4]$ [(**1**): R = H, (**2**): R = $COOCH_2CH_3$] and tetranuclear cluster complexes $[Mo_2(C_5H_4R)_2(CO)_4](\mu\text{-}HC_2CH_2OCH_2C_2H\text{-}\mu)[Mo_2(C_5H_4R)_2(CO)_4]$ [(**3**): R = H, (**4**): R = $COOCH_2CH_3$], respectively. When (**1**) or (**2**) was treated with an equimolar amount of octacarbonyldicobalt, the new novel tetranuclear cluster complexes $[Co_2(CO)_6](\mu\text{-}HC_2CH_2OCH_2C_2H\text{-}\mu)[Mo_2(C_5H_4R)_2(CO)_4]$ [(**5**): R = H, (**6**): R = $COOCH_2CH_3$] were obtained. These complexes were characterized by elemental analysis, IR and $^1H$ NMR spectra. The molecular structure of complex ($3 \cdot 1/2CH_2Cl_2$) was determined by single-crystal X-ray diffraction methods.

*Keywords:* Dipropargylether; octacarbonyldicobalt; cluster complexes; crystal structure

## INTRODUCTION

Interest in alkyne-cluster chemistry is due to two main reasons. The first one is the desire to gain a better knowledge of the interactions of small molecules with metal clusters, the alkyne complexes being considered as useful models for the chemisorption of small molecules on metal surfaces[1]

---

* Corresponding author.

and for carbon–carbon triple-bond activation and reduction.[2] Also, considerable analogies can be found between the coordination modes of alkynes and of carbon monoxide to several metal centres; in particular, the alkynes show a greater variety of interactions resulting from the possibility of varying substituents, and hence the polarity of the triple bond. The other main reason of interest in alkyne-cluster chemistry is the importance of acetylene as a feedstock for industrial organic chemistry. The coordination chemistry of alkyne substituents and acetylene has been studied extensively.[3] However, little information on the reaction between diynes and dinuclear species has been available.[4] We report here the interaction of a diyne with dinuclear species and the relations of two C≡CH groups during the reaction. It is found that di- or tetranuclear cluster complexes would be formed when the diyne reacted with $Mo_2(C_5H_4R)_2(CO)_4$ (R = H, $COOCH_2CH_3$) and the free radical group C≡CH in the dinuclear cluster complexes could react continuously with octacarbonyldicobalt to give novel tetranuclear cluster complexes.

## EXPERIMENTAL

All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk techniques. All solvents were thoroughly dried according to standard procedures[5] and distilled immediately before use. Chromatographic separations and purifications were performed on 160–200 mesh silical gel. $Mo(CO)_6$ was obtained from Aldrich Chemical Company; $Co_2(CO)_8$,[6] $HC_2CH_2OCH_2C_2H$,[7] $Mo_2(C_5H_4COOCH_2CH_3)_2$-$(CO)_6$[8] were prepared according to the literature. IR spectra were recorded on a Nicokel FT-IR 10DX spectrophotometer. $^1H$ NMR spectra were measured on a Brucker AM-300 MHz spectrometer. Elemental analyses were performed on a Carlo Erba 1106 analyzer.

### Preparation of Clusters (1)–(4)

A solution of $Mo_2(C_2H_5)_2(CO)_6$ (490 mg, 1 mmol) in toluene (30 $cm^3$) was refluxed for 14 h. Upon cooling to room temperature, dipropargylether (94 mg, 1 mmol) was added and the mixtures were stirred for another 3 h at room temperature. The solvent was removed under vacuum and the products were chromatographed on a 2.5 × 20 cm silica gel column using $CH_2Cl_2$/petroleum ether (2 : 1) as eluent to give two red fractions of clusters (**1**) and (**3**). Cluster (**1**) was recrystallized from hexane/$CH_2Cl_2$ at −20°C to give red, air-stable crystals, 170 mg 32.2% yield. m.p. 98°C (dec.). Calcd. for $C_{20}H_{16}O_5Mo_2$ (%): C, 45.47; H, 3.05. Found: C, 45.51; H, 3.08. IR (KBr, disc) 3308s (≡C–H), 2114w (C≡C), 1979vs, 1888vs (terminal CO), 1829s (semi-bridging CO) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 5.81 (s, 1H, C–CH coordinated to Mo–Mo); 5.33 (s, 10H, $2C_5H_5$); 4.58 (s, 2H, $CH_2$–C–C); 4.13 (d, 2H, $CH_2$–C≡C, $J = 2.4$ Hz); 2.42 (t, 1H, C≡C–H, $J = 2.4$ Hz).

Cluster (**3**) was recrystallized from hexane/$CH_2Cl_2$ at −20°C to give red crystals **3**·1/2$CH_2Cl_2$, 160 mg, 33.3% yield. m.p. 82°C (dec.). Calcd. for $C_{34}H_{26}O_9Mo_4 \cdot 1/2CH_2Cl_2$ (%): C, 41.24; H, 2.71. Found: C, 41.26; H, 2.72. IR (KBr, disc) 1988vs, 1901vs (terminal CO), 1827s (semi-bridging CO) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 5.80 (s, 2H, 2C–CH); 5.32 (s, 20H, $4C_5H_5$); 4.52(s, 4H, $2CH_2$).

Procedures for the preparation of (**2**) and (**4**) were similar to that for the preparation of (**1**) and (**3**). Cluster (**2**), 240 mg, 35.7% yield. Calcd. for $C_{26}H_{24}O_9Mo_2$ (%): C, 46.44; H, 3.60. Found: C, 46.41; H, 3.58. IR (KBr, disc) 3300s (≡C–H), 2115w (C≡C), 2003vs, 1924vs (terminal CO), 1851s (semi-bridging CO), 1716vs (C=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 6.00 (s, 1H, C–CH coordinated to Mo–Mo); 5.90, 5.76, 5.40 (t, 8H, $2C_5H_4$); 4.55 (s, 2H, $CH_2$–C–C); 4.22 (q, 4H, $2CH_2$, $J = 7.1$ Hz); 4.13 (d, 2H, $CH_2$–C≡C, $J = 2.4$ Hz); 2.42 (t, 1H, C≡C–H, $J = 2.4$ Hz); 1.29 (t, 6H, $2CH_3$, $J = 7.0$ Hz).

Cluster (**4**), 170 mg, 27.2% yield. m.p. 74–76°C. Calcd. for $C_{46}H_{42}O_{17}Mo_4$ (%): C, 44.18; H, 3.39. Found: C, 44.22; H, 3.41. IR (KBr, disc) 2001vs, 1934vs (terminal CO), 1851s (semi-bridging CO), 1718s (C=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 5.99 (s, 2H, 2C–CH); 5.90, 5.74, 5.40 (t, 16H, $4C_5H_4$); 4.47 (s, 4H, $2CH_2$–C–C); 4.22 (q, 8H, $4CH_2$, $J = 7.1$ Hz); 1.28 (t, 12H, $4CH_3$, $J = 7.0$ Hz).

### Preparation of (5) and (6)

The cluster (**1**) (105 mg, 0.2 mmol) was treated with $Co_2(CO)_8$ (70 mg, 0.2 mmol) in THF (20 $cm^3$) at room temperature. After stirred for 2 h, the solvent was removed in reduced pressure and the residue purified by chromatography on silica gel using $CH_2Cl_2$/petroleum ether (2 : 1) as an eluent. Recrystallization from hexane/$CH_2Cl_2$ at −20°C gave red solid cluster (**5**), 100 mg, 61.4% yield. m.p. 98°C (dec.). Calcd. for $C_{26}H_{16}O_{11}Co_2Mo_2$ (%): C, 38.36; H, 1.98. Found: C, 38.34; H, 1.96. IR (KBr, disc) 2097s, 2060vs, 2043vs, 2028vs, 2015vs, 2002vs, 1982vs, 1914vs (terminal CO), 1830vs (semi-bridging CO) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 6.06 (s, 1H, C–CH coordinated to Co–Co); 5.85 (s, 1H, C–CH coordinated to Mo–Mo); 5.32 (s, 10H, $2C_5H_5$); 4.67, 4.66 (d, 4H, $2CH_2$).

Cluster (**6**) was prepared using the same procedure as that for (**5**). The cluster (**2**) was used instead of the cluster (**1**). Some of (**6**) was obtained as red oil, 113 mg, 59.0% yield. Calcd. for $C_{32}H_{24}O_{15}Co_2Mo_2$ (%): C, 40.11; H, 2.52. Found: C, 40.06; H, 2.51. IR (KBr, disc) 2095s, 2054vs, 2023vs, 1925vs (terminal CO), 1853s (semi-bridging CO), 1716s (C=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 6.07 (s, 1H, C–CH coordinated to Co–Co); 6.02 (s, 1H, C–CH coordinated to Mo–Mo); 5.90, 5.76, 5.41 (t, 8H, $2C_5H_4$); 4.67 (s, 4H, $2CH_2$); 4.23 (s, 4H, $2CH_2$); 1.29 (s, 6H, $2CH_3$).

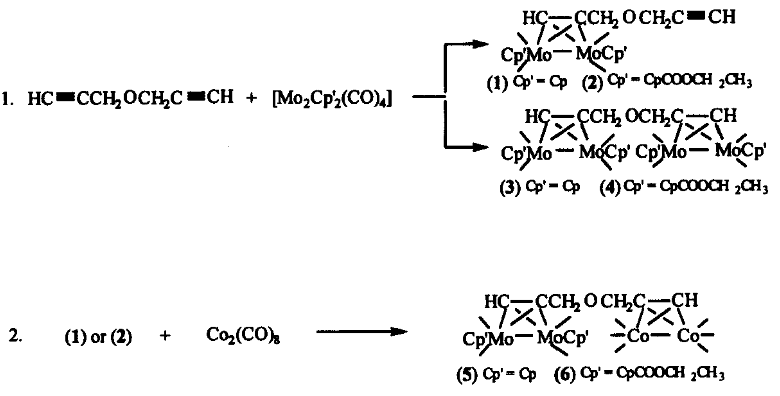
### Crystallography of Cluster (3 · 1/2CH$_2$Cl$_2$)

Crystals of **3** · $1/2CH_2Cl_2$ suitable for diffraction analysis were grown from hexane/$CH_2Cl_2$ solution at −20°C. The crystals were mounted on a glass fibre. Preliminary examination and data collection were performed with MoK$\alpha$ radiation ($\lambda = 0.71069$ Å) on an Enraf-nonius CAD4 diffractometer equipped with graphite monochromators. The structure of **3** · $1/2CH_2Cl_2$ was solved by the Patterson method. The molybdenum atoms and cobalt atoms were located and coordinates of the remaining non-hydrogen atoms were found from a difference map. The structure was refined by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a MICRO VAX3100 computer using the TEXSAN program system.

## RESULTS AND DISCUSSION

The reactions described in this work are summarized in Scheme 1. Through *in situ* reaction of the dipropargylether with a triply bonded complex $[Mo_2(C_5H_4R)_2(CO)_4]$ (R = H, $COOCH_2CH_3$), prepared by refluxing a toluene solution of metal–metal single bonded dimer $[Mo_2(C_5H_4)_2(CO)_6]$ (R=H, $COOCH_2CH_3$), the homo-dinuclear clusters $[HC_2CH_2OCH_2C_2H\text{-}\mu]$-$[Mo_2(C_5H_4R)_2(CO)_4]$ [(**1**): R = H; (**2**): R = $COOCH_2CH_3$] and homo-tetranuclear clusters $[Mo_2(C_5H_4R)_2(CO)_4](\mu\text{-}HC_2CH_2OCH_2C_2H\text{-}\mu)$ $[Mo_2\text{-}(C_5H_4R)_2(CO)_4]$ [(**5**): R = H; (**6**): R = $COOCH_2CH_3$].

All clusters show a large number of stronger terminal carbonyl absorption bands located at 2097–1886 $cm^{-1}$ and the bridging carbonyl absorption bands was at 1830 $cm^{-1}$ for (**1**), (**3**) and (**5**) and 1850 $cm^{-1}$ for (**2**), (**4**) and (**6**) in the IR spectra. The IR spectra of (**2**), (**4**) and (**6**) also show corresponding C=O absorption bands at 1716–1718 $cm^{-1}$, and the absorption bands of the C≡C–H group of (**1**) and (**2**) appear at around 3300 and 2115 $cm^{-1}$.



SCHEME 1

Comparing the IR spectra (**2**) and (**4**) with that of (**1**) and (**3**), the carbonyl absorption bands shift upfield with substituted cyclopentadienyl instead of unsubstituted cyclopentadienyl. $^1H$ NMR spectra of all clusters show their presence of their corresponding organic groups. Singlets at about $\delta$ 4.67–4.47 are caused by the methylene protons connected with C–CH coordinated to M–M. For the substituted cyclopentadienyl rings, $^1H$ NMR spectra of (**2**), (**4**) and (**6**) exhibit two sets of bands at around $\delta$ 5.90–5.40; upfield, one singlet at about $\delta$ 5.40 (two proton) is assigned to two *m*-H atoms of the substituted cyclopentadienyl and downfield two singlets between $\delta$ 5.90–5.76 to *o*-H resulting from the different desheilding effects of electron-withdrawing groups $COOCH_2CH_3$ to *o*-H and *m*-H. In the other clusters, the protons of unsubstituted cyclopentadienyl appear as a singlet in the range $\delta$ 5.30–5.40. It is interesting that the chemical shifts of protons of the coordinated terminal alkyne (C–CH) are influenced by different metals coordinated to the C–CH group in the range $\delta$ 6.07–5.80. In the $^1H$ NMR spectra of clusters (**1**) and (**2**), a doublet at $\delta$ 4.13 and triplets $\delta$ 2.43 are assigned to the protons of the methylene connected to the C≡CH group and the proton of the uncoordinated terminal alkyne (C≡CH). Two signals, $CH_3$ and $CH_2$ in the $CH_3CH_2$ group of (**2**), (**4**) and (**6**), are observed at $\delta$ 1.29 and $\delta$ 4.22.

The structure of the cluster **3** · $1/2CH_2Cl_2$ was determined by X-ray structure analysis. Crystal data are collected in Tables I and II gives selected bond lengths and angles. Figure 1 shows the molecular structure. $Mo_2(C_5H_5)_2(CO)_4$ unit coordinates to each of the two alkynyl groups of dipropargylether. The overall conformations of the two $(CCH)Mo_2(C_5H_5)_2(CO)_4$ moieties resemble each other and are quite similar to those previously described for

TABLE I Summary of crystal and refinement data for cluster ($3 \cdot 1/2CH_2Cl_2$)

| | |
|---|---|
| Formula | $C_{34}H_{26}O_9Mo_4 \cdot 1/2CH_2Cl_2$ |
| F.W. | 1004.80 |
| Crystal system | triclinic |
| Space group | P-1 |
| $F(000)$ | 982.00 |
| $a$ (Å) | 7.921(3) |
| $b$ (Å) | 13.360(3) |
| $c$ (Å) | 17.208(4) |
| $\alpha$ (°) | 109.15(1) |
| $\beta$ (°) | 92.0(7) |
| $\gamma$ (°) | 93.34(2) |
| $V$ (Å$^3$) | 1714.3(9) |
| $Z$ | 2 |
| $D_{calc.}$ ($g \cdot cm^{-1}$) | 1.946 |
| $\mu$ (MoK$\alpha$) ($cm^{-1}$) | 15.28 |
| Temperature (°C) | 23.0 |
| Scan type | $\omega$–$2\theta$ |
| $2\theta_{max}$ (°) | 51.9 |
| No. observations | 5564 ($I > 2.00\ \sigma(I)$) |
| No. variables | 442 |
| $R^a$, $R_w{}^b$ | 0.040, 0.049 |

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w F_o^2]^{1/2}$.

TABLE II Selected bond lengths (Å) and angles (°) for ($3 \cdot 1/2CH_2Cl_2$)

| | | | |
|---|---|---|---|
| Mo(1)–Mo(2) | 2.9706(9) | Mo(3)–Mo(4) | 2.9739(9) |
| C(9)–C(10) | 1.331(7) | C(13)–C(14) | 1.343(7) |
| Mo(1)–C(10) | 2.162(5) | Mo(3)–C(13) | 2.212(5) |
| Mo(1)–C(9) | 2.192(5) | Mo(3)–C(14) | 2.112(5) |
| Mo(2)–C(10) | 2.190(5) | Mo(4)–C(13) | 2.171(5) |
| Mo(2)–C(9) | 2.095(5) | Mo(4)–C(14) | 2.188(5) |
| Mo(2)–C(3) | 1.949(6) | Mo(3)–C(5) | 1.942(6) |
| Mo(1)–C(3) | 2.888(6) | Mo(4)–C(5) | 2.833(6) |
| C(3)–O(3) | 1.154(7) | C(5)–O(5) | 1.170(7) |
| Mo(1)–Cp | 1.9876 | Mo(3)–Cp | 2.0129 |
| Mo(2)–Cp | 2.0129 | Mo(4)–Cp | 1.9957 |
| C–O(t co, av) | 1.1369 | | |
| C(9)–Mo(1)–Mo(2) | 44.8(1) | C(14)–Mo(4)–Mo(3) | 45.2(1) |
| C(10)–Mo(1)–Mo(2) | 47.3(1) | C(13)–Mo(4)–Mo(3) | 47.9(1) |
| C(10)–Mo(1)–C(9) | 35.6(2) | C(13)–Mo(4)–C(14) | 35.9(2) |
| C(9)–Mo(2)–Mo(1) | 47.5(1) | C(14)–Mo(3)–Mo(4) | 47.3(1) |
| C(10)–Mo(2)–Mo(1) | 46.6(1) | C(13)–Mo(3)–Mo(4) | 46.7(1) |
| C(9)–Mo(2)–C(10) | 36.1(2) | C(14)–Mo(3)–C(13) | 36.1(2) |
| C(10)–C(9)–Mo(1) | 71.0(3) | C(13)–C(14)–Mo(4) | 71.4(3) |
| C(9)–C(10)–Mo(2) | 68.1(3) | C(14)–C(13)–Mo(3) | 67.9(3) |
| O(3)–C(3)–Mo(2) | 169.3(5) | O(5)–C(5)–Mo(3) | 168.8(6) |
| Mo–C–O (t co, av) | 178.43 | | |

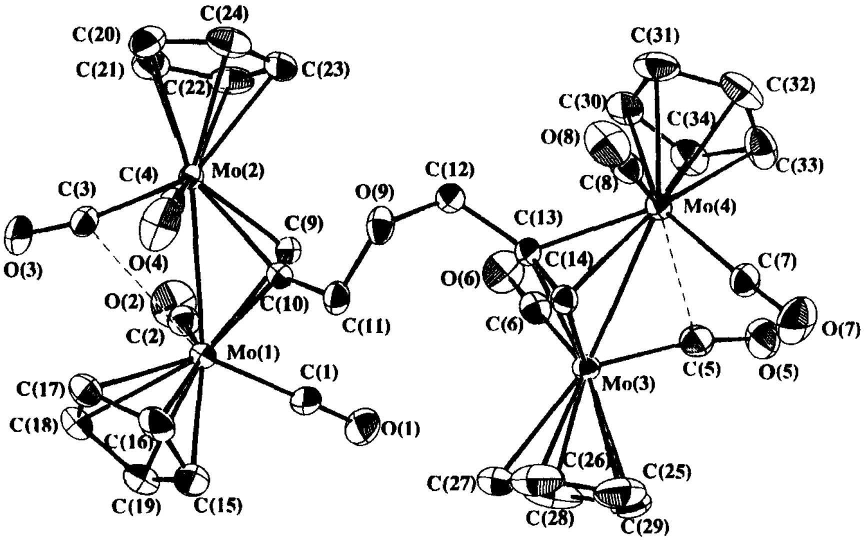


FIGURE 1 Molecular structure of cluster ($3 \cdot 1/2CH_2Cl_2$).

$[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(\mu\text{-}C_2H_2)$.[9] The $C_2Mo_2$ core adopts a *pseudo*-tetrahedral geometry; each Mo atom is coordinated to two carbonyl ligands and one cyclopentadienyl ligand. Two Mo–Mo bond lengths are 2.9706(9) and 2.9739(9) Å. Mo–C and C–C bond lengths in $C_2Mo_2$ cores are in the range 1.937(6)–2.212(5) and 1.331(7)–1.343(7) Å. These data are comparable to corresponding values in $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(\mu\text{-}C_2H_2)$.[9] Mo(2)–C(3)–O(3) and Mo(3)–C(5)–O(5) bond angles are 169.3(5)° and 168.8(6)°, respectively. The average values of other Mo–C–O bond angles is 178.4°. On the other hand, the asymmetry parameters, $\alpha$, of 0.49 for C(3)–O(3) and 0.46 for C(5)–O(5) are within the range (0.1–0.6) for semi-bridging carbonyls.[10] We thus consider the C(3)–O(3) and C(5)–O(5) carbonyls to be the semi-bridging carbonyls. The coexistence of both terminal and semi-bridging carbonyls is in good agreement with the IR spectra of all clusters, showing several strong absorption bands from 2097 to 1829 $cm^{-1}$.

## *Acknowledgements*

This work was supported by the NNSF of China, and the Foundation of the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

## *Supplementary Material*

Full lists of crystallographic data are available from the authors.

## *References*

[1] E.L. Muetteries, T.N. Rhodin, E. Band, C.F. Brucker and W.R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).

[2] E.L. Muetteries, *Bull Soc. Chim. Belg.*, **85**, 451 (1976); **84**, 953 (1975).

[3] H.El. Amouri and M. Gruselle, *Chem. Rev.*, **96**, 1007 (1996).

[4] K. Onitsuku, Xin-Qung Tao and Wen-Qing Wang, *J. Organomet. Chem.*, **413**, 195 (1994).

[5] D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals* (Pergamon, New York, 1980).

[6] R.B. King, *Organomatallic Syntheses, Vol. 1, Transition-Metal Compound* (Academic Press, New York, 1965), p. 92.

[7] L. Brandsma, *Preparative Acetylenic Chemistry* (Elsevier, The Netherlands, 1988), p. 261.

[8] Li-Cheng Song and J.-Y. Shen, *Chem. J. Univ.*, **13**, 1229 (1992).

[9] W.I. Bailey, M.H. Chisholm and F.A. Cotton, *J. Am. Chem. Soc.*, **100**, 5764 (1978).

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