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# Synthesis and characterization of the cluster compounds containing double $C_2M_2$ (M=Co, Mo) cores. The single-crystal X-ray structures of $[O(CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6]_2$ and $[O(CH_2C_2H\text{-}\mu)_2][Mo_2(C_5H_5)_2(CO)_4]_2$

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## Abstract

The treatment of dipropargyl ether with $Co_2(CO)_8$ in hexane at room temperature gave a new cluster $[O(CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6]_2$ **1**, which reacts with the cyclopentadienyl tricarbonyl molybdenum anion $[Mo(C_5H_5)(CO)_3]^-$ to form the hetero-tetranuclear clusters $[O(CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6][CoMo(C_5H_5)(CO)_5]$ **2** and $[O(CH_2C_2H\text{-}\mu)_2][CoMo(C_5H_5)(CO)_5]_2$ **3**, respectively. The reaction of $Mo_2(C_5H_4R)_2(CO)_4$ (R=H, $COOCH_2CH_3$) with dipropargyl ether gave the homo-dinuclear clusters $[HC_2CH_2OCH_2C_2H\text{-}\mu][Mo_2(C_5H_4R)_2(CO)_4]$ (R=H **4**, $COOCH_2CH_3$ **5**) and homo-tetranuclear clusters $[O(CH_2C_2H\text{-}\mu)_2][Mo_2(C_5H_4R)_2(CO)_4]_2$ (R=H **6**, $COOCH_2CH_3$ **7**), respectively. The clusters **4** and **5** reacted with $Co_2(CO)_8$ to produce the novel tetranuclear clusters $[O(CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6][Mo_2(C_5H_4R)_2(CO)_4]$ (R=H **8**, $COOCH_2CH_3$ **9**). All clusters were characterized by C/H analyses and IR and $^1$H-NMR spectroscopy and the crystal structures of **1** and $\mathbf{6 \cdot 1/2CH_2Cl_2}$ were determined. Crystals of cluster **1** are monoclinic with space group $P2_1/c$, $a = 18.149(2)$, $b = 7.0111(7)$, $c = 20.807(2)$ Å, $\beta = 115.318(7)°$, $V = 2403.7(5)$ Å$^3$, $Z = 4$ and $R = 0.030$, $R_w = 0.031$. Crystals of cluster $\mathbf{6 \cdot 1/2CH_2Cl_2}$ are triclinic with space group $P\bar{1}$, $a = 7.92(3)$, $b = 13.360(3)$, $c = 17.208(4)$ Å, $\alpha = 109.15(1)$, $\beta = 92.07(2)$, $\gamma = 93.34(2)°$, $V = 1714.3(9)$ Å$^3$, $Z = 2$ and $R = 0.040$, $R_w = 0.049$. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Carbonyl; Cluster; Cyclopentadienyl; Transition metal; Crystal structure

## 1. Introduction

Intense interest in the chemistry of dinuclear transition metal complexes bridged by unsaturated hydrocarbons continues 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 will serve as models for the understanding of the chemistry of reactive intermediates obtained during catalytic reactions like Fischer–Tropsch in heterogeneous systems. Further it is well known that the coordination of an organic molecule to metal centre 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≡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 investigated the interrelations of two C≡C groups during the capping reactions and the interrelations of two $C_2M_2$ groups during

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the exchange reactions. In this paper, we wish to report the results of a capping reaction of dipropargyl ether with dinuclear species and exchange reactions of the tetranuclear clusters with the metal exchange reagent $Na[Mo(C_5H_5)(CO)_3]$ and the crystal structures of the clusters **1** and **$6 \cdot 1/2CH_2Cl_2$**.

## 2. Results and discussion

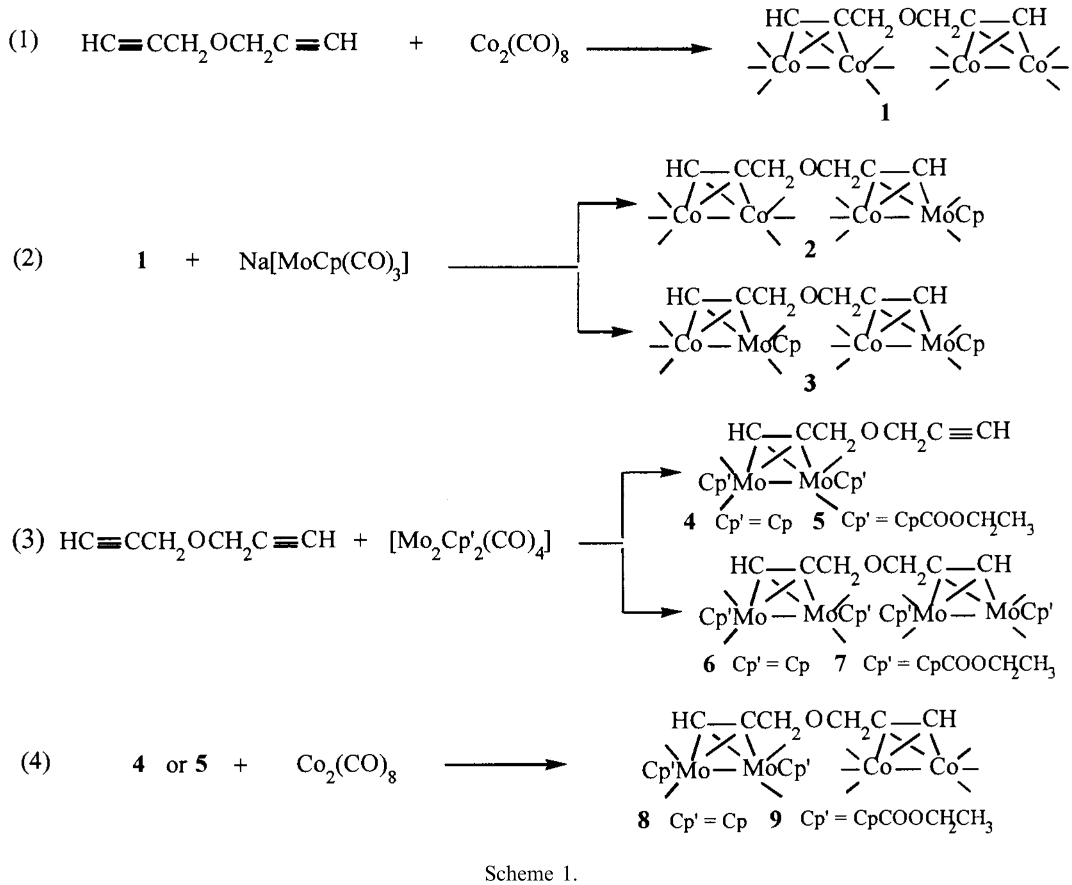
### 2.1. Preparation of *1–9*

The reactions described in this work are summarized in Scheme 1. Treatment of $Co_2(CO)_8$ in hexane with dipropargyl ether in 1:2 molar ratio at room temperature affords the cluster $[O(CH_2C_2H-\mu)_2][Co_2(CO)_6]_2$ **1** as the major product. Subsequently, the exchange regent $Na[Mo(C_5H_5)(CO)_3]$, prepared by refluxing a THF solution of $Na(C_5H_5)$ and $Mo(CO)_6$ [5], is reacted in situ with the cluster **1** at room temperature for 60 h to give two hetero-tetranuclear clusters $[O(CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6][CoMo(C_5H_5)(CO)_5]$ **2** and $[O(CH_2C_2H\text{-}\mu)_2]$ $[CoMo(C_5H_5)(CO)_5]_2$ **3**, respectively. Through in situ reactions of the dipropargyl ether with the 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 $[Mo_2(C_5H_4R)_2(CO)_6]$ (R=H, $COOCH_2CH_3$) [6], the homo-dinuclear clusters $[HC_2CH_2OCH_2C_2H\text{-}\mu][Mo_2(C_5H_4R)_2(CO)_4]$ (R=H **4**, $COOCH_2CH_3$ **5**) and homo-tetranuclear clusters $[O(CH_2C_2H\text{-}\mu)_2][Mo_2(C_5H_4R)_2(CO)_4]_2$ (R=H **6**, $COOCH_2CH_3$ **7**) were obtained. Further reactions of **4** and **5** with $Co_2(CO)_8$ in THF at room temperature produce the novel tetranuclear clusters $[O(CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6][Mo_2(C_5H_4R)_2(CO)_4]$ (R=H **8**, $COOCH_2CH_3$ **9**).

High yields are obtained in capping reactions (1), (3) and (4) and a low yield in exchange reaction (2). The reaction (2) requires a long time at room temperature, but at high temperature (refluxing THF) the reactant decomposes and the expected products are not obtained. This contrasts with the exchange reaction of the $RCCo_3(CO)_9$ clusters [7].

### 2.2. Characterization of *1–9*

All clusters show a large number of strong terminal carbonyl absorption bands located at 2102–1886 $cm^{-1}$ in their IR spectra. The absorption of carbonyl ligands coordinated to Co atoms occurs at higher wavenumbers than those coordinated to Mo atoms [8]. The IR spectra of **5**, **7** and **9** also show corresponding C=O absorption bands at 1716–1718 $cm^{-1}$, and the absorption



Scheme 1.

bands of the C≡C–H group of **4** and **5** appear at around 3300–2115 cm$^{-1}$. In the IR spectra of **4**–**9**, besides the terminal carbonyl absorption bands, there are absorption bands at around 1830 (**4, 6** and **8**) and 1850 (**5, 7,** and **9**) cm$^{-1}$ characteristic of semi-bridging carbonyls, whereas the IR spectra of **1**, **2** and **3** show only the terminal carbonyls absorption bands. Comparing the IR spectra of **4** and **6** with that of **5** and **7**, it can be seen that the carbonyl absorption bands shift to higher frequencies with substituted cyclopentadienyl instead of unsubstituted cyclopentadienyl ligands.

The $^1$H-NMR spectra of all clusters **1**–**9** show the presence of hydrogen atoms in their corresponding organic groups. The singlets at about $\delta$ 4.85–4.47 are caused by the protons of the methylene ($CH_2$) connected to $C_2H$ coordinated to M–M, and these protons appear at higher field if the $C_2H$ is coordinated to $Mo_2$ rather than $Co_2$. For the substituted cyclopentadienyl rings, the $^1$H-NMR spectra of **5**, **7** and **9** exhibit two sets of bands in the range $\delta$ 5.90–5.40, comprising an upfield singlet ca. $\delta$ 5.40 assignable to the two protons at 3,4-positions of the substituted cyclopentadienyl rings and two downfield singlets between $\delta$ 5.90 and 5.76 assignable to the 2,5-protons, resulting from the different deshielding effects of electron-withdrawing groups $COOCH_2CH_3$ on these nuclei. 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 coordinated terminal alkyne (C–CH) are influenced by the metal coordinated to the C–CH group. These protons appear at about $\delta$ 6.07 when the $C_2H$ groups coordinated to Co–Co in the clusters **1, 2, 8** and **9** and appear at about $\delta$ 5.70 when the $C_2H$ groups coordinated to Co–Mo in **2** and **3**. However, they appear at about $\delta$ 5.80 when the $C_2H$ groups coordinated to Mo–Mo bonded with unsubstituted cyclopentadienyl in **4, 6** and **8** and appear at about $\delta$ 6.00 when the $C_2H$ groups coordinated to Mo–Mo bonded with substituted cyclopentadienyl in **5, 7** and **9**. This fact, together with the chemical shift of protons of methylene and the IR spectra, led us to conclude that the two exchange reactions of a $Mo(C_5H_5)(CO)_2$ group with the $C_2Co_2$ cores do not occur on the same $C_2Co_2$ unit in cluster **1**; thus, product **3** contains two $C_2CoMo$ cores and not one $C_2Co_2$ core and one $C_2Mo_2$ core in contrast to clusters **8** and **9**. In the $^1$H-NMR spectra of clusters **4** and **5** besides the above information, a doublet at $\delta$ 4.13 and triplet at $\delta$ 2.43 are assignable to the protons of the methylene ($CH_2$) connected C≡CH group and the proton of uncoordinated terminal alkyne (C≡CH), respectively. Two signals of $CH_3$ and $CH_2$ in the $CH_3CH_2$ group of **5, 7** and **9** are observed at $\delta$ 1.29 and $\delta$ 4.22.

From the IR and $^1$H-NMR spectra, the configurations of the isomeric clusters **3** and **8** could be distinguished. The IR spectra of the cluster **3** do not indicate semi-bridging carbonyls but the IR spectra of the cluster **8** suggest a semi-bridging carbonyl at 1830 cm$^{-1}$. Because of the semi-bridging carbonyl occurs in the $C_2Mo_2(C_5H_5)_2(CO)_4$, $C_2W_2(C_5H_5)_2(CO)_4$ and $C_2MoW(C_5H_5)_2(CO)_4$ cores and do not occur in the $C_2CoMo(C_5H_5)(CO)_5$ core [5b, 9]. It could be considered that cluster **3** possesses two $C_2CoMo(C_5H_5)(CO)_5$ cores and cluster **8** possesses one of $C_2Co_2(CO)_6$ core and one of $C_2Mo_2(C_5H_5)_2(CO)_4$ core. In $^1$H-NMR spectra, the two protons of two $C_2H$ groups of cluster **3** appear at the same chemical shift at $\delta$ 5.70. This illustrates that two protons occur in the same chemical environment. However the two protons of two $C_2H$ groups of cluster **8** appear as two singlets at $\delta$ 6.06 and 5.85, respectively. Compared to the $^1$H-NMR spectra of cluster **1** ($C_2H$ coordinated to Co–Co, δ 6.07) and clusters **4** and **6** ($C_2H$ coordinated to Mo–Mo, $\delta$ 5.81 and 5.80), the singlet at $\delta$ 6.06 is assignable to the proton of $C_2H$ group coordinated to Co–Co and at $\delta$ 5.85 to the proton of $C_2H$ group coordinated Mo–Mo. Similarly, four protons of two $CH_2$ groups appear also as a singlet at $\delta$ 4.75 in cluster **3** and two singlets at $\delta$ 4.67 and 4.66 in cluster **8**. Evidently the effects of M–M on the chemical shift of protons of $CH_2$ group is smaller than that of the $C_2H$ group because of remote distances. All these are consistent with the configurations of isomer clusters **3** and **8**.

### 2.3. Structure of 1 and $6 \cdot 1/2CH_2Cl_2$

The crystal structures of **1** and $\mathbf{6 \cdot 1/2CH_2Cl_2}$ were determined by X-ray structural analyses. Crystal data are collected in Table 1. Tables 2 and 3 give the atomic coordinates and selected bond lengths and angles are listed in Tables 4 and 5. Figs. 1 and 2 show the molecular structures of **1** and $\mathbf{6 \cdot 1/2CH_2Cl_2}$, respectively.

As seen in Fig. 1, a $Co_2(CO)_6$ unit coordinates to each of the two alkynyl groups of dipropargyl ether. The $C_2Co_2$ core adopts a pseudo-tetrahedral geometry and the overall conformations of the two $(CH_2C_2H)Co_2(CO)_6$ moieties in **1** resemble each other. The two Co–Co bond distances are 2.468(9) and 2.4866(9) Å, the Co–C bond distances in the $C_2Co_2$ cores are in the range 1.938(6)–1.961(4) Å comparable with those of related dicobalt complexes [4c, 10]. The C(13)–C(14) and C(17)–C(18) distances lie also in the normal region of μ-alkyne-hexacarbonyldicobalt compounds.

As seen in Fig. 2, 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 described previously for $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2$ ($\mu$-$C_2H_2$) [9c]. The $C_2Mo_2$ core adopts a pseudo-tetrahedral geometry. The two Mo–Mo bond lengths are 2.9706(9) and 2.9739(9) Å. The Mo–C bond lengths in $C_2Mo_2$ cores are in the

Table 1
Crystal and refinement data for the clusters **1** and **$6\cdot 1/2CH_2Cl_2$**

| Clusters | **1** | **$6\cdot 1/2CH_2Cl_2$** |
|---|---|---|
| Formula | $C_{18}H_6O_{13}Co_4$ | $C_{34}H_{26}O_9Mo_4\cdot 1/2\ CH_2Cl_2$ |
| $M_r$ | 665.97 | 1004.80 |
| System | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| $F(000)$ | 1304.00 | 982.00 |
| $a$ (Å) | 18.149(2) | 7.921(3) |
| $b$ (Å) | 7.0111(7) | 13.360(3) |
| $c$ (Å) | 20.897(2) | 17.208(4) |
| $\alpha$ (°) | | 109.15(1) |
| $\beta$ (°) | 115.318(7) | 92.0(7) |
| $\gamma$ (°) | | 93.34(2) |
| $V$ (Å$^3$) | 2403.7(5) | 1714.3(9) |
| $Z$ | 4 | 2 |
| $D_{calc}$ (g cm$^{-1}$) | 1.840 | 1.946 |
| $\mu$ (Mo–K$_\alpha$) (cm$^{-1}$) | 27.76 | 15.28 |
| Temperature (°C) | 20.0 | 23.0 |
| Scan type | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| $2\theta_{max}$ (°) | 50.0 | 51.9 |
| No. observations | 2372 ($I>2.50\ \sigma(I)$) | 5564 ($I>2.00\ \sigma(I)$) |
| No. variables | 316 | 442 |
| $R$[a] | 0.030 | 0.040 |
| $R_w$[b] | 0.031 | 0.049 |
| Goodness-of-fit indicator | 1.20 | 1.35 |
| Max peak in final diff. map (e Å$^{-3}$) | 0.25 | 0.96 |
| Min peak in final diff. map (e Å$^{-3}$) | −0.25 | −1.32 |

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

range 1.937(6)–2.212(5) Å. These are comparable to the corresponding values in $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2$ $(\mu\text{-}C_2H_2)$ [9c].

It should be noted that the C(3)–O(3) carbonyl bound to Mo(2) atom and the C(5)–O(5) carbonyl bound to Mo(3) are semi-bridging and the other carbonyls are terminal. This is confirmed by the asymmetry parameters α(0.49) of C(3)–O(3) and α(0.46) of C(5)–O(5) which are well within the range (0.1–0.6) for semi-bridging carbonyls, whereas that of the other carbonyls falls out of the range [9c–e]. The coexistence of both terminal and semi-bridging carbonyls are in good agreement with the IR spectra of the cluster **4**–**9** showing several strong absorption bands from 2095 to 1829 cm$^{-1}$.

Finally, the crystal structure analyses of **$6\cdot 1/2CH_2Cl_2$** also shows that two molecule of **6** and one molecules of $CH_2Cl_2$ are present in one unit cell, but with long intermolecular distances between these molecules.

## 3. Experimental

All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk techniques. All solvents were dried thoroughly and distilled immediately before use. IR spectra were recorded on a Nicolet FT-IR 10DX spectrophotometer. $^1$H-NMR spectra were measured on a Bruker AM-300 MHz spectrometer. Elemental analyses were performed on a Carlo Erba 1106 type analyzer. The $Mo(CO)_6$ was bought from Aldrich Chemical Company; and the $Co_2(CO)_8$ [11], $HC_2CH_2OCH_2C_2H$ [12], $CH_3CH_2CO\text{-}COC_5H_4Na$ [13], $Mo_2(C_5H_4COOCH_2CH_3)_2(CO)_6$ [14] were prepared according to literature.

Table 2
Non-hydrogen atomic coordinates and isotropic thermal parameters for **1**[a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Co(1) | 0.90129(4) | 0.2465(1) | 0.36212(3) | 3.98(2) |
| Co(2) | 0.82448(4) | 0.1733(1) | 0.23502(3) | 3.85(2) |
| Co(3) | 0.70271(4) | −0.2287(1) | 0.49138(3) | 3.81(2) |
| Co(4) | 0.55614(4) | −0.24778(9) | 0.40734(3) | 3.68(1) |
| O(1) | 0.9016(3) | 0.4498(7) | 0.4838(2) | 8.4(1) |
| O(2) | 0.9554(3) | −0.1390(6) | 0.4190(2) | 7.5(1) |
| O(3) | 1.0431(3) | 0.4308(7) | 0.3545(2) | 8.8(2) |
| O(4) | 0.8755(3) | −0.2285(6) | 0.2456(2) | 7.4(1) |
| O(5) | 0.9180(3) | 0.3911(7) | 0.1741(2) | 8.8(2) |
| O(6) | 0.6651(3) | 0.1434(9) | 0.1168(2) | 10.7(2) |
| O(7) | 0.8612(2) | −0.0629(7) | 0.5178(2) | 8.2(1) |
| O(8) | 0.7390(3) | −0.6365(6) | 0.4958(2) | 7.7(1) |
| O(9) | 0.6927(3) | −0.1321(8) | 0.6244(2) | 9.1(2) |
| O(10) | 0.5363(3) | −0.6298(6) | 0.3442(2) | 7.3(1) |
| O(11) | 0.4982(3) | −0.2500(6) | 0.5190(2) | 7.5(1) |
| O(12) | 0.4205(2) | −0.0446(6) | 0.2985(2) | 7.6(1) |
| O(13) | 0.7384(2) | −0.0904(5) | 0.3336(2) | 4.34(8) |
| C(1) | 0.9031(3) | 0.3684(9) | 0.4375(3) | 5.5(2) |
| C(2) | 0.9357(3) | 0.0092(9) | 0.3975(3) | 5.1(1) |
| C(3) | 0.9891(3) | 0.3597(8) | 0.3579(3) | 5.6(2) |
| C(4) | 0.8559(3) | −0.0736(8) | 0.2410(3) | 4.8(1) |
| C(5) | 0.8832(3) | 0.3032(8) | 0.1970(3) | 5.2(1) |
| C(6) | 0.7281(4) | 0.156(1) | 0.1617(3) | 6.5(2) |
| C(7) | 0.8010(3) | −0.1309(8) | 0.5088(3) | 5.3(1) |
| C(8) | 0.7257(3) | −0.4797(8) | 0.4948(3) | 4.9(1) |
| C(9) | 0.6974(3) | −0.1713(8) | 0.5739(3) | 5.6(1) |
| C(10) | 0.5445(3) | −0.4854(8) | 0.3708(3) | 4.7(1) |
| C(11) | 0.5194(3) | −0.2508(8) | 0.4751(3) | 5.1(1) |
| C(12) | 0.4723(3) | −0.1257(7) | 0.3407(3) | 4.8(1) |
| C(13) | 0.8045(3) | 0.3692(7) | 0.2912(3) | 4.3(1) |
| C(14) | 0.7854(3) | 0.2032(6) | 0.3084(2) | 3.7(1) |
| C(15) | 0.7208(3) | 0.1065(7) | 0.3216(3) | 4.3(1) |
| C(16) | 0.6706(3) | −0.1998(7) | 0.3298(2) | 4.5(1) |
| C(17) | 0.6491(3) | −0.1670(7) | 0.3903(2) | 3.6(1) |
| C(18) | 0.6333(3) | −0.0357(6) | 0.4277(3) | 4.0(1) |

[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 3
Non-hydrogen atomic coordinates and isotropic thermal parameters for **6 · 1/2CH$_2$Cl$_2$**[a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Mo(1) | 0.53909(6) | 0.48108(3) | 0.19807(3) | 2.65(2) |
| Mo(2) | 0.49692(5) | 0.59645(3) | 0.37515(3) | 2.24(2) |
| Mo(3) | 0.98551(6) | 0.86857(3) | 0.16186(3) | 2.60(2) |
| Mo(4) | 1.05698(5) | 1.04845(3) | 0.31853(3) | 2.43(2) |
| O(1) | 0.5660(7) | 0.6007(4) | 0.0707(3) | 6.1(2) |
| O(2) | 0.1528(6) | 0.4924(5) | 0.1697(4) | 6.6(3) |
| O(3) | 0.3097(6) | 0.3738(4) | 0.3311(3) | 5.5(2) |
| O(4) | 0.8407(6) | 0.5226(4) | 0.4161(4) | 5.9(2) |
| O(5) | 0.9770(7) | 1.0814(4) | 0.1268(3) | 5.9(2) |
| O(6) | 0.6048(5) | 0.8650(4) | 0.1942(3) | 5.3(2) |
| O(7) | 1.3945(6) | 1.0940(4) | 0.2442(4) | 6.3(2) |
| O(8) | 1.2939(7) | 1.0166(4) | 0.4553(3) | 5.8(2) |
| O(9) | 0.9059(5) | 0.7488(3) | 0.3574(2) | 3.5(1) |
| C(1) | 0.5570(8) | 0.5580(5) | 0.1179(4) | 3.8(2) |
| C(2) | 0.2921(8) | 0.4891(5) | 0.1812(4) | 3.8(2) |
| C(3) | 0.3870(7) | 0.4532(5) | 0.3403(4) | 3.5(2) |
| C(4) | 0.7111(7) | 0.5480(5) | 0.4008(4) | 3.5(2) |
| C(5) | 0.9782(8) | 1.0071(5) | 0.1485(4) | 4.0(2) |
| C(6) | 0.7459(7) | 0.8675(4) | 0.1810(4) | 3.4(2) |
| C(7) | 1.2727(7) | 1.0761(4) | 0.2698(4) | 3.4(2) |
| C(8) | 1.2073(8) | 1.0287(4) | 0.4051(4) | 3.6(2) |
| C(9) | 0.5273(6) | 0.6480(4) | 0.2736(3) | 2.6(2) |
| C(10) | 0.6784(6) | 0.6165(4) | 0.2874(3) | 2.5(2) |
| C(11) | 0.8596(7) | 0.6555(4) | 0.2889(4) | 3.2(2) |
| C(12) | 0.8533(7) | 0.8442(4) | 0.3488(3) | 3.2(2) |
| C(13) | 0.9572(6) | 0.8853(4) | 0.2929(3) | 2.6(2) |
| C(14) | 1.1200(6) | 0.8826(4) | 0.2736(3) | 2.7(2) |
| C(15) | 0.7317(10) | 0.3766(5) | 0.1194(5) | 5.3(3) |
| C(16) | 0.7733(8) | 0.3806(5) | 0.2001(5) | 4.6(3) |
| C(17) | 0.6365(9) | 0.3322(5) | 0.2264(5) | 4.5(3) |
| C(18) | 0.5097(9) | 0.2985(5) | 0.1633(5) | 4.6(3) |
| C(19) | 0.5666(10) | 0.3247(5) | 0.0956(5) | 5.0(3) |
| C(20) | 0.3954(10) | 0.6479(6) | 0.5047(4) | 5.0(3) |
| C(21) | 0.2567(9) | 0.6396(5) | 0.4515(5) | 5.0(3) |
| C(22) | 0.2834(8) | 0.7153(6) | 0.4143(4) | 4.5(3) |
| C(23) | 0.4364(8) | 0.7722(5) | 0.4453(4) | 4.2(2) |
| C(24) | 0.5043(8) | 0.7304(5) | 0.5007(4) | 4.5(3) |
| C(25) | 1.2101(10) | 0.8064(8) | 0.0798(5) | 6.3(3) |
| C(26) | 1.1603(15) | 0.7300(8) | 0.1091(5) | 6.9(4) |
| C(27) | 1.0027(16) | 0.6914(6) | 0.0794(7) | 7.2(5) |
| C(28) | 0.9482(11) | 0.7458(9) | 0.0306(5) | 6.9(4) |
| C(29) | 1.0824(16) | 0.8169(6) | 0.0286(5) | 6.7(4) |
| C(30) | 0.7902(8) | 1.0996(5) | 0.3664(5) | 4.8(3) |
| C(31) | 0.9158(10) | 1.1506(6) | 0.4273(5) | 5.4(3) |
| C(32) | 1.0172(9) | 1.2187(5) | 0.3983(5) | 5.3(3) |
| C(33) | 0.9552(8) | 1.2079(5) | 0.3194(5) | 4.9(3) |
| C(34) | 0.8162(7) | 1.1350(5) | 0.3000(5) | 4.3(2) |
| Cl | 0.3539(4) | 0.0595(2) | 0.0092(2) | 11.3(2) |
| C(35) | 0.446(2) | −0.0304(13) | −0.0497(10) | 6.5(7) |

[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 angles (°) for **1**

| | | | |
|---|---|---|---|
| Co(1)–Co(2) | 2.4686(9) | Co(3)–Co(4) | 2.4866(9) |
| C(13)–C(14) | 1.308(6) | C(17)–C(18) | 1.316(6) |
| Co(1)–C(13) | 1.948(5) | Co(3)–C(17) | 1.959(4) |
| Co(1)–C(14) | 1.939(4) | Co(3)–C(18) | 1.938(5) |
| Co(2)–C(13) | 1.939(5) | Co(4)–C(17) | 1.952(4) |
| Co(2)–C(14) | 1.958(5) | Co(4)–C(18) | 1.961(4) |
| Co(2)–Co(1)–C(13) | 50.4(1) | Co(4)–Co(3)–C(17) | 50.4(1) |
| Co(2)–Co(1)–C(14) | 51.0(1) | Co(4)–Co(3)–C(18) | 50.8(1) |
| C(13)–Co(1)–C(14) | 39.3(2) | C(17)–Co(3)–C(18) | 39.5(2) |
| Co(1)–Co(2)–C(13) | 50.7(1) | Co(3)–Co(4)–C(17) | 50.6(1) |
| Co(1)–Co(2)–C(14) | 50.3(1) | Co(3)–Co(4)–C(18) | 50.0(1) |
| C(13)–Co(2)–C(14) | 39.2(2) | C(17)–Co(4)–C(18) | 39.3(2) |
| Co(1)–C(13)–C(14) | 69.9(3) | Co(3)–C(17)–C(18) | 69.4(3) |
| Co(2)–C(14)–C(13) | 69.6(3) | Co(4)–C(18)–C(17) | 70.0(3) |

### 3.1. Preparation of **1–9**

**1**. The dipropargyl ether (94 mg, 1 mmol) was reacted with Co$_2$(CO)$_8$ (684 mg, 2 mmol) in hexane (30 cm$^3$) at room temperature. After being stirred for 2 h, the solvent was removed under reduced pressure and the residue purified by chromatography on silica gel using petroleum ether (60–90°) as an eluent. Recrystallization from hexane/CH$_2$Cl$_2$ gave red prismatic crystals (410 mg, 61.6%). m.p. 52–54°C. Anal. Calc. for C$_{18}$H$_6$O$_{13}$Co$_4$: C, 32.46; H, 0.91. Found: C, 32.42; H, 0.98. IR (KBr, disc) 2102s, 2095s, 2060vs, 2039vs, 2022vs, 2010vs (terminal CO) cm$^{-1}$. $^1$H-NMR (CDCl$_3$) $\delta$ 6.07 (s, 2H, 2C–CH); 4.85 (s, 4H, 2CH$_2$).

**2** and **3**. The Mo(CO)$_6$ (132 mg, 0.5 mmol) was added to a solution of 89 mg (0.5 mmol) NaC$_5$H$_5$·DME in THF (30 cm$^3$). The mixture was heated under reflux for 20 h and cooled to room temperature. Then 165 mg (0.25 mmol) of cluster **1** was added and the mixture was stirred at room temperature for 60 h. The solvent was

Table 5
Selected bond lengths (Å) and angles (°) for **6 · 1/2CH$_2$Cl$_2$**

| | | | |
|---|---|---|---|
| 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–CO (t co, av) | 178.43 | | |

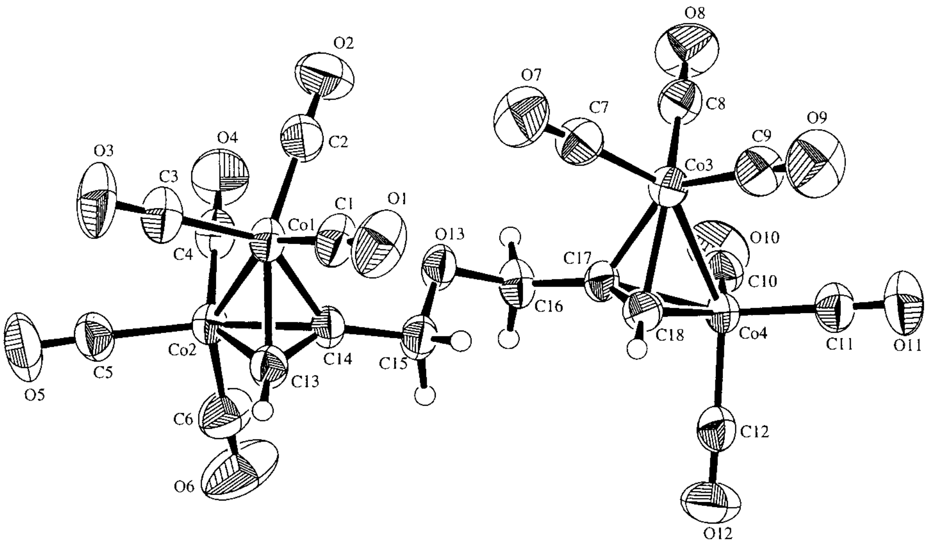


Fig. 1. Molecular structure of **1**.

removed under vacuum, the residue was extracted by minimum amount of $CH_2Cl_2$ and the products were chromatographed on a 2.5 × 20 cm silica gel column using $CH_2Cl_2$/petroleum ether (1:1) as eluent to give two red fractions of clusters **2** and **3**. Cluster **2** was recrystallized from hexane/$CH_2Cl_2$ at $-20$°C to give red crystals (70 mg, 37.8%). m.p. 152°C (dec.). Anal. Calc. for $C_{22}H_{11}O_{12}Co_3Mo$: C, 35.70; H, 1.50. Found: C, 35.65; H, 1.47. IR (KBr, disc) 2097s, 2055vs, 2025vs, 2000vs, 1943s, 1890m (terminal CO) $cm^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$ 6.06 (s, 1H, C–CH coordinated to Co–Co); 5.70 (s, 1H, C–CH coordinated to Co–Mo); 5.44 (s, 5H, $C_5H_5$); 4.83 (s, 2H, $CH_2$ connected with $C_2H$(Co–Co)); 4.78 (s, 2H, $CH_2$ connected with $C_2H$(Co–Mo)).

The cluster **3** was recrystallized from hexane/$CH_2Cl_2$ at $-20$°C to give a red oil (30 mg, 29.5%). Anal. Calc. for $C_{26}H_{16}O_{11}Co_2Mo_2$: C, 38.36; H, 1.98. Found: C, 38.30; H, 2.02. IR (KBr, disc) 2051vs, 1981vs, 1940vs, 1886m (terminal CO) $cm^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$ 5.70 (s, 2H, 2C–CH); 5.43 (s, 10H, $2C_5H_5$); 4.75 (s, 4H, $2CH_2$).

**4** and **6**. A solution of $Mo_2(C_5H_5)_2(CO)_6$ (490 mg, 1 mmol) in toluene (30 $cm^3$) was refluxed for 14 h. Upon cooling to room temperature, the dipropargyl ether (94 mg, 1 mmol) was added and the mixtures were stirred for another 3 h at room temperature. The solvent was removed under vacuum, 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 **4** and **6**. Cluster **4** was recrystallized from hexane/$CH_2Cl_2$ at $-20$°C to give red crystals (170 mg, 32.2%). m.p. 98°C (dec.). Anal. Calc. 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) $cm^{-1}$. $^1$H-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).

The cluster **6** was recrystallized from hexane/$CH_2Cl_2$ at $-20$°C to give red crystals **6 · 1/2 $CH_2Cl_2$** (160 mg, 33.3%). m.p. 82°C (dec.). Anal. Calc. 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) $cm^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$ 5.80 (s, 2H, 2C–CH); 5.32 (s, 20H, $4C_5H_5$); 4.52 (s, 4H, $2CH_2$).

**5** and **7**. Procedures for the preparation of **5** and **7** were similar to that for the preparation of **4** and **6**.

**5** (240 mg, 35.7%). Anal. Calc. 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) $cm^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$ 6.00 (s, 1H, C–CH coordinated to Mo–Mo); 5.90–5.40 (m, 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).

**7** (170 mg, 27.2%). m.p. 74–76°C. Anal. Calc. 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) $cm^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$ 5.99 (s, 2H, 2C–CH); 5.90–5.40 (m, 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).

**8**. The cluster **4** (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 stirring 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 a red solid cluster **8** (100 mg,

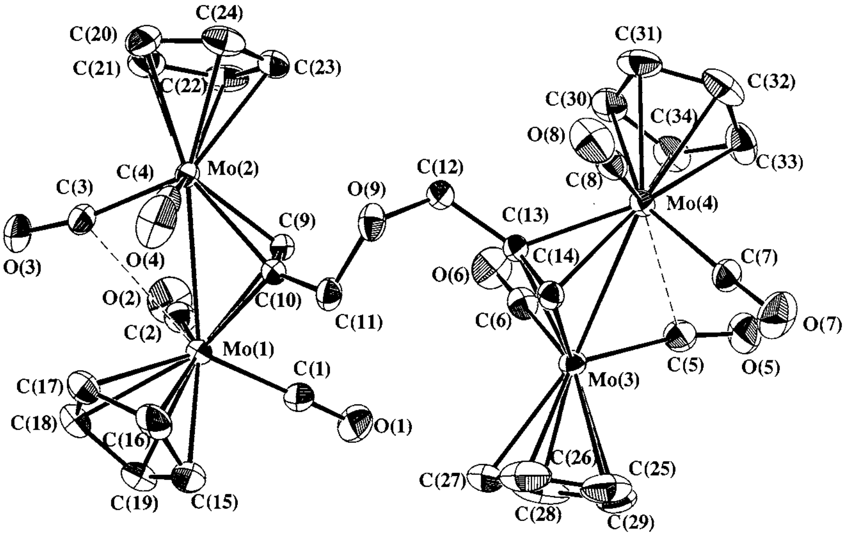


Fig. 2. Molecular structure of **6·1/2CH$_2$Cl$_2$**.

61.4%). m.p. 98°C (dec.). Anal. Calc. 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$^{-1}$. $^1$H-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$_5$H$_5$); 4.67, (s, 2H, CH$_2$), 4.66, (s, 2H, CH$_2$).

**9**. Procedures for the preparation of **9** were similar to that for the preparation of **8**. (113 mg, 59.0%). Anal. Calc. 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$^{-1}$. $^1$H-NMR (CDCl$_3$) $\delta$ 6.07 (s, 1H, C–CH coordinated to Co–Co); 6.02 (s, 1H, C–CH coordinated to Mo–Mo); 5.90–5.41 (m, 8H, 2C$_5$H$_4$); 4.67 (s, 4H, 2CH$_2$); 4.23 (s, 4H,2CH$_2$); 1.29 (s, 6H, 2CH$_3$).

### *3.2. X-ray structure characterization of **1** and **6·1/2 CH$_2$Cl$_2$***

Crystals of **1** and **6·1/2CH$_2$Cl$_2$** suitable for diffraction analysis were grown from hexane/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 Rigaku AFC7R and Enraf–Nonius CAD4 diffractometer equipped with graphite monochromators for cluster **1** and **6·1/2CH$_2$Cl$_2$**, respectively.

The structure of the cluster **1** was solved by direct methods [15] and expanded using Fourier techniques [16]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Full-matrix least-squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o)]^{-1} = 4F_o^2[\sigma^2(F_o^2)]^{-1}$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2][Lp]^{-2}$. Neutral atom scattering factors were taken from Cromer and Waber [17]. All calculations were performed using the TEXSAN [18] crystallographic software package of Molecular Structure Corporation.

The structure of **6·1/2 CH$_2$Cl$_2$** was solved by the Patterson method. The Molybdenum atoms and Cobalt atoms were located by the heavy-atom method. The coordinates of the remaining non-hydrogen atoms were found from a difference map. The structure was refined by the Full-matrix Least-Squares method with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a MICRO VAX3100 computer using the TEXSAN program system.

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