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Reaction of dipropargyl phthalate with $Co_2(CO)_8$ and $Mo_2Cp_2(CO)_4$ gives the di or tetranuclear clusters. The crystal structure of $[C_6H_4-1,2-(CO_2CH_2C_2H-\mu)_2][Co_2(CO)_6]_2$ and $[o-(HC_2CH_2OCO)C_6H_4(CO_2CH_2C_2H-\mu)][Mo_2Cp_2(CO)_4]-CH_2Cl_2$

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Abstract

The reaction of dipropargyl phthalate with $Co_2(CO)_8$ in benzene at room temperature gave a new cluster $[C_6H_4-1,2-(CO_2CH_2C_2H_{\mu})_2][Co_2(CO)_6]_2$ **1**, which reacts with the cyclopentadienyl tricarbonyl molybdenum anion $[Mo(CO)_3Cp]^-$ to form the tetranuclear clusters $[C_6H_4-1,2-(CO_2CH_2C_2H_{\mu})_2][Co_2(CO)_6][CoMoCp(CO)_5]$ **2** and $[C_6H_4-1,2-(CO_2CH_2C_2H_{\mu})_2]$ $[CoMoCp(CO)_5]_2$ **3**, respectively. The reaction of $Mo_2Cp_2(CO)_4$ with dipropargyl phthalate gave rise to the formation of the dinuclear cluster $[o-(HC_2CH_2OCO)C_6H_4(CO_2CH_2C_2H_{\mu})][Mo_2Cp_2(CO)_4]$ **4** and tetranuclear cluster $[C_6H_4-1,2-(CO_2CH_2C_2H_{\mu})_2]$ $[Mo_2Cp_2(CO)_4]_2$ **5**, respectively. The cluster **4** reacted with $Co_2(CO)_8$ to produce the tetranuclear cluster $[C_6H_4-1,2-(CO_2CH_2C_2H_{\mu})_2][Co_2(CO)_6]_2$ **1** and $[o-(HC_2CH_2OCO)C_6H_4(CO_2CH_2C_2H_{\mu})][Mo_2CP_2(CO)_4]-CH_2Cl_2$ **4**·CH₂Cl₂ were determined by single crystal X-ray diffraction methods. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal structure; Cobalt; Molybdenum; Cluster compounds

1. Introduction

Alkyne and alkynyl species bearing a C=C functional group belong to a class of surface species which may play a pivotal role in various catalytic reactions such as CO hydrogenation, and the coordination chemistry of the corresponding ligands has been studied extensively. [1,2] The interaction of alkynyl compounds with dinuclear species leading to adducts with a tetrahedral C_2M_2 core has been recognized as one of the classical reactions in the field of organometallic chemistry [3]. In recent years diyne clusters have been receiving considerable attention because of their unusual structures and reactions [4–8]. As an extension, we examined the interaction of diynes with dinuclear species and investigated the interrelations of two C=CH or C_2M_2 during the capping and exchange re-

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actions. Herein we wish to report the capping reactions of diyne ligands with dinuclear species and the exchange reactions of the tetranuclear clusters with the metal exchange reagent Na[MoCp(CO)₃]. The crystal structures of the clusters $[C_6H_4-1,2-(CO_2CH_2C_2H-\mu)_2][Co_2(CO)_6]_2$ and $[o-(HC_2CH_2OCO)C_6H_4(CO_2CH_2C_2H-\mu)][Mo_2C-p_2(CO)_4]\cdot CH_2Cl_2$ were determined by single crystal X-ray diffraction methods.

2. Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. The solvents were treated using the usual method for preparing anhydrous and deoxygenated solvents. Column chromatography was carried out using 160-200 mesh silica gel. Mo(CO)₆ were purchased from Aldrich Chem. Co. Co₂(CO)₈ was prepared according to the literature [28]. The dipropargyl phthalate was obtained by esterifica-

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tion of phthalic anhydride with propargyl alcohol and characterized by C/H analyses, IR and ¹H NMR. The IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer. The ¹H NMR spectra were measured on Bruker Am 300 MHz spectrometer. The C/H analyses were performed on a Carlo Erba 1106 type analyzer.

2.1. Preparation of 1

The dipropargyl phthalate (242 mg, 1 mmol) was treated with $Co_2(CO)_8$ (684 mg, 2 mmol) in benzene (40 cm³) 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 benzene as an eluent. Recrystallization from hexane–benzene gave red prismatic crystals (648 mg, 79.6%). Anal. calcd. for $C_{26}H_{10}O_{16}Co_4$: C, 38.36; H, 1.24. Found: C, 38.38; H, 1.20. IR (KBr): ν (C=O) 1737 m, 1715 m; ν (CO) 2098 s, 2055 vs, 2022 vs, 2016 vs, 2002 vs (terminal CO) cm⁻¹. ¹H NMR (CDCl₃): δ 7.81–7.57 (m, 4H, C_6H_4), 6.14 (s, 2H, 2CH) and 5.52 (s, 4H, 2CH₂) ppm.

2.2. Preparation of 2 and 3

The Mo(CO)₆ (132 mg, 0.5 mmol) was added to a solution of 89 mg (0.5 mmol) NaCp-DME in THF (30 cm³). The mixtures were heated under reflux for 20 h and cooled to room temperature. Then 200 mg (0.25 mmol) cluster 1 was added and the mixture was stirred for 60 h at room temperature. The solvent was removed under vacuum. The residue was chromatographed on silica gel using benzene $-CH_2Cl_2$ (1:1) as an eluent to give two red fractions clusters 2 and 3. Cluster 2 was recrystallized from hexane- CH_2Cl_2 at $-20^{\circ}C$ to give red crystals (70 mg, 32%). Anal. Calcd. for C₃₀H₁₅O₁₅MoCo₃: C, 40.57; H, 1.70. Found: C, 40.61; H, 1.66. IR (KBr): v (C=O) 1736 m, 1720 m; v (CO) 2098 s, 2056 vs, 2028 vs, 1944 s, 1890 m (terminal CO) cm⁻¹. ¹H NMR (CDCl₃): δ 7.80–7.54 $(m, 4H, C_6H_4), 6.06 (s, 1H, CH), 5.70 (s, 1H, CH), 5.42 (s, 1H$ 4H, 2CH₂), 5.33 (s, 5H, Cp) ppm.

The cluster **3** was recrystallized from hexane–CH₂Cl₂ at –20°C to give a red solid (52 mg, 22%). Anal. Calcd. for $C_{34}H_{20}O_{14}Mo_2Co_2$: C, 42.44; H, 2.10. Found: C, 42.38; H, 2.15. IR (KBr): ν (C=O) 1738 m, 1724 m; ν (CO) 2097 s, 2058 vs, 2000 vs, 1945 s, 1892 m (terminal CO) cm⁻¹. ¹H NMR (CDCl₃): δ 7.80–7.52 (m, 4H, C₆H₄), 5.70 (s, 2H, 2CH), 5.42 (s, 4H, 2CH₂), 5.32 (s, 10H, 2Cp) ppm.

2.3. Preparation of 4 and 5

A solution of $[Mo_2Cp_2(CO)_6]$ (490 mg, 1 mmol) in toluene (30 cm³) was refluxed for 14 h. Upon cooling to room temperature, the dipropargyl phthalate (242 mg, 1 mmol) was added and the mixtures were stirred for another 3 h at room temperature. The solvent was removed under vacuum. The residue was chromatographed on silica gel using benzene-CH₂Cl₂ as eluent to give two red fractions clusters **4** and **5**. Cluster **4** was recrystallized from hexane– CH₂Cl₂ at -20°C to give red crystals **4**·CH₂Cl₂ (280 mg, 37%). Anal. Calcd. for C₂₉H₂₂O₈Mo₂Cl₂: C, 45.75; H, 2.91. Found: C, 45.72; H, 2.90. IR (KBr): ν (C=O) 1745 m, 1725 m; ν (CO) 1993 vs, 1909 vs, (terminal CO) and 1828 vs (semi-bridge CO) cm⁻¹. ¹H NMR (CDCl₃): δ 7.78–7.54 (m, 4H, C₆H₄), 5.91 (s, 1H, CH), 5.37 (s, 2H, CH₂), 5.32 (s, 10H, 2Cp), 4.93 (d, 2H, CH₂, *J*=2.5 Hz) and 2.54 (t, 1H, =CH, *J*=2.5 Hz) ppm.

The cluster **5** was recrystallized from hexane– CH_2Cl_2 at $-20^{\circ}C$ to give a red oil (208 mg, 19%). Anal. Calcd. for $C_{42}H_{30}O_{12}Mo_4$: C, 45.42; H, 2.72. Found: C, 45.51; H, 2.65. IR (KBr): ν (C=O) 1742 m, 1728 m; ν (CO) 1990 vs, 1905 vs (terminal CO) and 1830 vs (semi-bridge CO) cm⁻¹. ¹H NMR (CDCl₃): δ 7.80–7.56 (m, 4H, C₆H₄), 5.80 (s, 2H, 2CH), 5.38 (s, 4H, 2CH₂), 5.29 (m, 20H, 4Cp) ppm.

2.4. Preparation of 6

The cluster **4** (150 mg, 0.2 mmol) was treated with $Co_2(CO)_8$ (70 mg, 0.2 mmol) in benzene (20 cm³) 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 benzene as an eluent. Recrystallization from hexane-CH₂Cl₂ at -20°C to give a red solid cluster **6** (130 mg, 68%). Anal. Calcd. for $C_{34}H_{20}O_{14}Mo_2Co_2$: C, 42.44; H, 2.10. Found: C, 42.42; H, 2.08. IR (KBr): ν (C=O) 1734 m, 1718 m; ν (CO) 2099 vs, 2058 vs, 2025 vs, 1918 s (terminal CO) and 1839 vs (semi-bridge CO) cm⁻¹. ¹H NMR (CDCl₃): δ 7.78–7.56 (m, 4H, C₆H₄), 6.06 (s, 1H, CH), 5.85 (s, 1H, CH), 5.42 (s, 4H, 2CH₂), 5.32 (s, 10H, 2Cp) ppm.

2.5. Single crystal structure determination of 1 and $4 \cdot CH_2Cl_2$

Crystals suitable for an X-ray diffraction analysis were obtained by recrystallization from hexane–CH₂Cl₂ and mounted on glass fibers tip onto a goniometer. Diffraction measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation (λ =0.71069 Å) and a 12 kW rotating anode generator. Unit cells were determined and refined by a least-squares method using 23 reflections in the range 13.39<2 θ <21.40° for 1 and 18 reflections in the range 14.96<2 θ <21.68° for 4·CH₂Cl₂. The data were collected at a temperature of 20±1°C using the ω -2 θ scan technique.

The structure of each compound was solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

3. Results and discussion

The reaction of dipropargyl phthalate with $Co_2(CO)_8$ in benzene at room temperature gave the cluster $[C_6H_4-1,2-(CO_2CH_2C_2H-\mu)_2][Co_2(CO)_6]_2$ **1.** The exchange regent Na[MoCp(CO)_3], prepared by refluxing a THF solution of NaCp and Mo(CO)_6 [9–14], was reacted in situ with the cluster **1** at room temperature for 60 h to give two tetranuclear clusters $[C_6H_4-1,2-(CO_2CH_2C_2H-\mu)_2][Co_2(CO)_6][CoMoCp(CO)_5]$ **2** and $[C_6H_4-1,2-(CO_2CH_2C_2H-\mu)_2][CoMoCp(CO)_5]_2$ **3.** Through the in situ reaction of dipropargyl phthalate with the triply bonded complex $[Mo_2Cp_2(CO)_4]$, prepared by refluxing a toluene solution of the metal-metal single bonded dimer $[Mo_2Cp_2(CO)_6]$ [15], the dinuclear cluster $[o-(HC_2CH_2OCO)C_6H_4(CO_2CH_2C_2H-\mu)]$ $[Mo_2Cp_2(CO)_4]$ **4** and tetranuclear cluster $[C_6H_4-1,2-(CO_2CH_2C_2H-\mu)_2]$ $[Mo_2Cp_2(CO)_4]_2$ **5** are obtained. Further reaction of **4** with $Co_2(CO)_8$ in THF at room temperature produce the cluster **6**. These reactions described in this work are summarized in Scheme 1.

The reaction (2) required a long time at room temperature, but at high temperature (refluxing THF) the reactant decomposes and the expected product could not be ob-



Scheme 1.

tained. These are inconsistent with the exchange reaction of the $RCCo_3(CO)_9$ clusters [16–19].

In the IR spectra of clusters **4**, **5** and **6**, besides the terminal carbonyls absorption bands exhibited in the range 2099–1905 cm⁻¹, there are absorption bands at around 1830 cm⁻¹ characteristic of bridging carbonyls. The IR spectra of clusters **1**, **2** and **3** show only the terminal carbonyls in the range 2098–1890 cm⁻¹. In clusters **1–6**, there are two absorption bands in the range 1745–1715 cm⁻¹ characteristic of carbonyls of the ester group of the ligands.

In the ¹H NMR spectra of all clusters 1-6, a singlet at about $\delta = 5.32$ arises from the protons of the cyclopentadienyl ring (C₅H₅) and singlets at δ =5.52–5.32 arise from the two or four protons of the methylene (CH_2) connected C-CH group. The protons of the coordinated terminal alkyne (C-CH) appear in the region $\delta = 6.14$ -5.70, as expected [4,14,15]; because of the reduction in the $C \equiv C$ triple-bond character there is a downfield shift in the position of these terminal protons with respect to the free ligand (δ =2.50). It is important to note that the chemical shift of coordinated terminal alkyne (C-CH) is affected by the nature of the metal coordinated to C-CH group. These protons appear in the range $\delta = 6.14 - 6.06$ when the C-CH group is coordinated to Co-Co in clusters 1, 2 and 6 and appear in the range $\delta = 5.91 - 5.80$ when the C–CH group is coordinated to Mo-Mo in clusters 4, 5 and 6. However, they appear at $\delta = 5.70$ when the C–CH group is coordinated to Co–Mo in clusters 2 and 3. The ¹H NMR spectra of cluster 4, besides the above signals, exhibited a doublet at $\delta = 4.93$ and a triplet at 2.54 assigned to the protons of

Table	1
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Crystallographic	parameters	for 1	and	$4 \cdot CH_2$	Cl
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the methylene (CH₂) connected to the C=CH group and the proton of uncoordinated terminal alkyne (C=CH). These data are consistent with the structure of **4**, which is produced by the coordination of a Mo₂Cp₂(CO)₄ group to one of the two C=C bonds and does not affect coordination to the other C=C bond. It is worth pointing out that the chemical shift of the proton attached to the C₂Co₂ cores appeared at lower fields than that of the proton connected to the C₂Mo₂ cores. This is consistent with the literature [20,21].

The configurations of isomer clusters 3 and 6 could be deduced from their IR and ¹H NMR spectra. The IR spectrum of cluster 3 did not exhibit a signal due to a semi-bridging carbonyl but the IR spectrum of the cluster 6 shows a semi-bridging carbonyl at 1830 cm⁻¹. Because 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 does not occur in the $C_2CoMo(C_5H_5)(CO)_5$ core [14,22-26], it could be considered that cluster **3** possesses two $C_2CoMo(C_5H_5)(CO)_5$ cores and cluster 6 possesses one $C_2Co_2(CO)_6$ core and one $C_2Mo_2(C_5H_5)_2(CO)_4$ core. In the ¹H NMR spectra, the two protons of two C₂H groups of cluster 3 appear with the same chemical shift at $\delta = 5.70$. This illustrates that two protons occur in the same chemical environment. However, the two protons of the two C₂H groups of cluster **6** appear as two singlets at $\delta = 6.06$ and 5.85, respectively. Comparing with the ¹H NMR spectra of cluster 1 (C_2 H coordinated to Co–Co, δ =6.14) and clusters **4** and **6** (C₂H coordinated to Mo–Mo, δ =5.91 and 5.85), the singlet at δ =6.06 is assignable to the protons of the C₂H group

lusters 1		$4 \cdot CH_2Cl_2$
Formula	$C_{26}H_{10}O_{16}CO_{4}$	$C_{28}H_{20}O_8MO_2-CH_2Cl_2^{a}$
Formula weight	814.06	761.27
Crystal system	Monoclinic	Triclinic
Space	$P2_1/a$	P-1
a (Å)	8.521(2)	10.964(3)
<i>b</i> (Å)	29.143(6)	12.941(3)
<i>c</i> (Å)	12.918(7)	10.859(2)
α (°)		93.29(2)
$oldsymbol{eta}$ (°)	100.12(3)	92.81(2)
γ (°)		107.67(2)
$V(\text{\AA}^3)$	3158(2)	1462.1(6)
Ζ	4	2
$D_{\rm cal} ~({\rm g~cm}^{-3})$	1.712	1.729
F(000)	1608.00	756.00
μ (Mo-K α) (cm ⁻¹)	21.37	10.88
Temp. (°C)	20.0	20.0
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
$2\theta_{\max}$ (°)	51.0	49.9
No. of reflections	Total: 5610	Total: 4204
Measured	Unique: 5194 ($R_{int} = 0.028$)	Unique: 3912 ($R_{int} = 0.017$)
No. observations	3151 (I>2.00 <i>\sigma</i> (I))	3234 (<i>I</i> >2.50σ (<i>I</i>))
No. variables	455	370
Residuals: $R^{\rm b}$; $R^{\rm b}_{\rm w}$	0.044; 0.048	0.029; 0.037

^a A unit cell contained the two **4** and two CH_2Cl_2 .

^b $R = (\Sigma ||F_{\circ}||F_{\circ}||) / \Sigma |F_{\circ}|, R_{w} = [\Sigma w (F_{\circ}|-|F_{\circ}|)^{2} / \Sigma w F_{\circ}^{2}]^{1/2}.$



Fig. 1. Molecular structure of cluster 1.

coordinated to Co–Co and at δ =5.85 to the protons of the C₂H group coordinated to Mo–Mo. All these are consistent with the configurations of isomers of clusters **3** and **6**.

In order to further establish the structures of 1-6, single crystal structure determinations of 1 and $4 \cdot CH_2Cl_2$ were

Table 2								
Selected	bond	lengths	(Å)	and	angles	(°)	for	1

	•
Co(1)-Co(2) 2.472(1)	Co(3)-Co(4) 2.475(1)
Co(1)-C(7) 1.951(6)	Co(3)-C(19) 1.956(6)
Co(1)-C(8) 1.955(6)	Co(3)-C(20) 1.937(7)
Co(2)-C(7) 1.937(6)	Co(4)-C(19) 1.937(7)
Co(2)-C(8) 1.942(6)	Co(4)-C(20) 1.926(7)
C(7)-C(8) 1.319(8)	C(19)-C(20) 1.317(9)
C(14)-C(15) 1.36(1)	C(11)-C(12) 1.403(8)
Co(2)-Co(1)-C(7) 50.3(2)	Co(4)-Co(3)-C(19) 50.2(2)
Co(2)-Co(1)-C(8) 50.4(2)	Co(4)-Co(3)-C(20) 50.0(2)
C(7)-Co(1)-C(8) 39.5(2)	C(19)-Co(3)-C(20) 39.6(3)
Co(1)-Co(2)-C(7) 50.8(2)	Co(3)-Co(4)-C(19) 50.9(2)
Co(1)-Co(2)-C(8) 50.8(2)	Co(3)-Co(4)-C(20) 50.3(2)
C(7)-Co(2)-C(8) 39.8(2)	C(19)-Co(4)-C(20) 39.9(3)
C(7)-C(8)-C(9) 140.9(6)	C(18)-C(19)-C(20) 143.3(6)
C(8)-C(7)-H(1) 141(4)	C(19)-C(20)-H(10) 140(3)

Table 3

Selected bond lengths (Å) and angles (°) for $4 \cdot CH_2Cl_2$

(1)-C(15) 2.194(4)
(2)-C(15) 2.126(4)
5)-C(16) 1.348(6)
9)-C(24) 1.391(6)
(2)-C(4) 1.965(5)
(2)-Mo(1)-C(16) 47.5(1)
(1)-Mo(2)-C(15) 47.3(1)
5)-Mo(2)-C(16) 36.2(2)
(2)-C(16)-C(15) 68.8(3)
6)–C(27)–C(28) 179.2(6)
7)-C(28)-H(20) 168.6

undertaken using X-ray diffraction methods. Table 1 lists their crystallographic data. The selected bond lengths and angles are given in Table 2 for 1 and Table 3 for 4· CH_2Cl_2 , respectively. Fig. 1 and Fig. 2 show the molecular structures of the 1 and 4 clusters, respectively.

As seen in Fig. 1, a $\text{Co}_2(\text{CO})_6$ unit coordinates to each of the two alkynyl groups of dipropargyl phthalate. The C_2Co_2 core adopts a pseudo-tetrahedral geometry. The overall conformations of the two $(\text{CH}_2\text{CCH})\text{Co}_2(\text{CO})_6$ moieties in **1** resemble each other. The two Co–Co bond



Fig. 2. Molecular structure of cluster 4·CH₂Cl₂.

lengths are 2.472(1) and 2.475(1) Å, the Co–C bond distances in the C_2Co_2 cores are in the range 1.926(7)–1.956(6) Å comparable with those of related dicobalt complexes [4,27]. The C(7)–C(8) and C(19)–C(20) distances are 1.319(8) and 1.317(9) Å, respectively, in the normal region of μ -alkyne–hexacarbonyldicobalt compounds. The bond angles C(7)–C(8)–C(9), H(1)–C(7)–C(8), C(18)–C(19)–C(20) and H(10)–C(20)–C(19) are 140.9(6), 141(4), 143.3(6) and 140(3)°, respectively. These data also lie in the normal range [4,27].

As seen in Fig. 2, the overall conformations of the $(C \equiv CH)Mo_2Cp_2(CO)_4$ moieties are quite similar to those previously described for $[\eta^5 - C_5H_5Mo(CO)_2]_2(\mu - C_2H_2)$ [24]. The C_2Mo_2 core adopts a pseudo-tetrahedral geometry. The Mo(1)–Mo(2) bond length is 2.9811(5) Å and the C(15)–C(16) bond length is 1.348(6) Å, respectively. The Mo–C bond lengths in the C_2Mo_2 cores are in the range 2.202(4)–2.126(4) Å. These data are comparable to the corresponding values in $[\eta^5 - C_5H_5Mo(CO)_2]_2(\mu - C_2H_2)$ [24].

The C(15)–C(16) distance of 1.348(6) Å is longer than the C(27)–C(28) distance of 1.134(7) Å. The bond angles C(15)–C(16)–C(17) and C(16)–C(15)–H are 135.3(4) and 138.6°, in contrast with the C(26)–C(27)–C(28) angle of 179.2(6)° and the C(27)–C(28)–H angle of 168.6°. These differences in bond distances and angles between the two alkynyl groups are due to the coordination of the $Mo_2Cp_2(CO)_4$ group.

The conformations of the phenyl groups showed a contradiction between **1** and **4**. The C(21)–C(22) distance of 1.365(8) Å is very close to that of the C(19)–C(14) distance of 1.391(6) Å in cluster **4**; however, the C(11)–C(12) distance of 1.403(8) Å is longer than the C(14)–C(15) distance of 1.36(1) Å in cluster **1**. The differences in the bond lengths are likely to depend on the effect of the two large coordinated $CO_2CH_2C_2CO_2(CO)_6$ groups.

Finally, it was found, through structural analysis of the carbonyls attached to the metal atoms, that the carbonyl C(4)–O(4) bonded to Mo(2) is a linear semi-bridging carbonyl. The values for judging the type of carbonyl C(4)–O(4) fall in the range typical for linear semi-bridging carbonyls [24–26], i.e. O(4)–C(4)–Mo(2)=169.7(4)°, C(4)–Mo(2)–Mo(1)=68.6(1)°, α =0.48 [calculated from Mo(2)–C(4)=1.965(6) Å, Mo(1)...C(4)=2.911(5) Å]. Thus, the structural analysis of **4** provides a reasonable explanation for its IR spectrum having one band at a frequency as low as 1830 cm⁻¹.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request (CCDC deposition numbers 105636 and 105638).

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