

## Molybdenum and tungsten complexes containing the 1,2-di-*tert*-butylcyclopentadienyl ligand

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### Abstract

The recently reported 1,2-di-*tert*-butylcyclopentadienyl ligand has been used to prepare new Group 6 metal complexes. Lithium 1,2-di-*tert*-butylcyclopentadienide (**1**) reacts cleanly with  $M(\text{CO})_6$  ( $M = \text{Mo}, \text{W}$ ) and following acidification and oxidation gives, depending upon reaction conditions,  $[\text{M}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3]_2$  ( $M = \text{Mo}$  (**2**),  $\text{W}$  (**3**)) or  $[\text{Mo}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2)\text{O}]_2(\mu^2\text{-O})_2$  (**4**). The hexacarbonyl dimer **2** is easily oxidized by  $\text{Br}_2$  to the tricarbonyl bromide complex,  $[\text{Mo}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3\text{Br}]$  (**5**). Crystal data for **2** with Mo K  $\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation at 296 K:  $\text{Mo}_2\text{C}_{32}\text{H}_{42}\text{O}_6$ ,  $a = 7.470(3) \text{ \AA}$ ,  $b = 8.658(3) \text{ \AA}$ ,  $c = 13.319(6) \text{ \AA}$ ,  $\alpha = 84.16(3)^\circ$ ,  $\beta = 80.26(3)^\circ$ ,  $\gamma = 75.04(3)^\circ$ ; triclinic space group  $P\bar{1}$  (No. 2),  $Z = 1$ ,  $R = 3.44\%$ ,  $R_w = 3.61\%$ . Crystal data for **4** with Mo K  $\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation at 296 K:  $\text{Mo}_2\text{C}_{26}\text{H}_{42}\text{O}_4$ ,  $a = 12.886(3) \text{ \AA}$ ,  $b = 16.877(5) \text{ \AA}$ ,  $c = 12.316(3) \text{ \AA}$ , orthorhombic space group  $Pccn$  (No. 56),  $Z = 4$ ,  $R = 3.46\%$ ,  $R_w = 5.00\%$ .

**Keywords:** Molybdenum; Tungsten; Cyclopentadienyls; Carbonyl; Oxide

### 1. Introduction

We have recently reported the synthesis of the 1,2-di-*tert*-butylcyclopentadienyl anion [1] and a variety of its mononuclear complexes with Fe [1], Ru [2], Re [2], Sn [2], and Tl [2]. Here we describe its reactions with the hexacarbonyls of molybdenum and tungsten, and the characterization of a number of new Group 6 complexes of this sterically demanding ligand.

### 2. Results and discussion

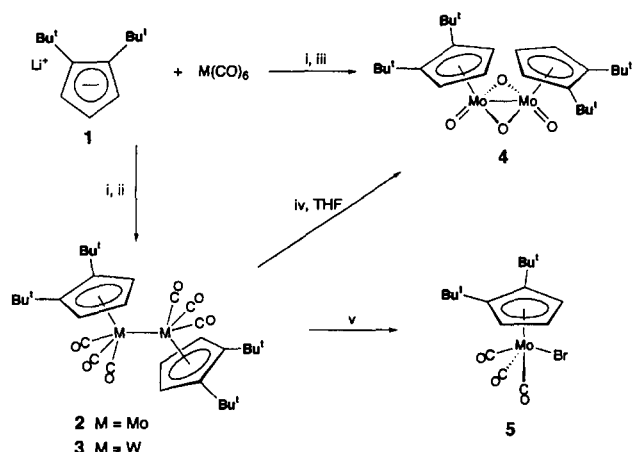
#### 2.1. Synthesis and spectroscopic properties

Using a procedure similar to that of Manning et al. [3], the reaction of lithium 1,2-di-*tert*-butylcyclopentadienide (**1**) with  $M(\text{CO})_6$  ( $M = \text{Mo}, \text{W}$ ) in refluxing diglyme, followed by acidification with glacial acetic acid and then oxidation by Fe(III), affords the purple, microcrystalline dimeric complexes  $[\text{M}(\eta^5\text{-}1,2\text{-}$

$\text{C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3]_2$  ( $M = \text{Mo}$  (**2**),  $\text{W}$  (**3**)) (Scheme 1). The infrared spectra of **2** and **3** (Table 1) are typical of other complexes of the type  $[\text{M}(\text{CH}_{(5-x)}\text{Me}_x)(\text{CO})_3]_2$  ( $M = \text{Mo}, \text{W}$ ) and exhibit two very strong stretches in the carbonyl region with the lower frequency peak displaying a shoulder on the low frequency side. Table 1 also shows the infrared carbonyl stretching frequencies of several dimeric complexes related to **2** and **3**. We have previously commented on the electron donating ability of the 1,2-di-*tert*-butylcyclopentadienyl ligand based upon carbonyl stretching frequencies [2]. As expected, the mono-*tert*-butyl-, 1,3-di-*tert*-butyl- and 1,2-di-*tert*-butyl-cyclopentadienyl ligands are very similar in their electron donating ability, as illustrated by the similarities of the carbonyl stretching frequencies in complexes of this type.

The  $^1\text{H}$  NMR spectra of **2** and **3** are virtually identical, with each displaying a singlet for the methyl groups of the *tert*-butyl groups and a triplet–doublet pattern for the remaining cyclopentadienyl ring protons. However, the  $^{13}\text{C}$  NMR spectra of **2** and **3** are significantly different. While the tungsten complex **3** shows the expected two different environments for the carbonyl ligands in a 1:2 ratio at 227.1 and 217.6 ppm, the  $^{13}\text{C}$

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Scheme 1. (i) Refluxing diglyme; (ii) acetic acid– $\text{Fe}_2(\text{SO}_4)_3 \cdot g\text{H}_2\text{O}$ – $\text{H}_2\text{O}$  solution; (iii) acetic acid, air; (iv) air; (v)  $\text{Br}_2$ .

NMR spectrum of the molybdenum analogue **2** is devoid of any carbonyl signals, although the three CO ligands are clearly present according to the infrared data (see above), and in the crystal structure (see below). Attempts to freeze out a coalescence phenomenon corresponding to a site exchange process were unsuccessful. In our hands, the  $^{13}\text{C}$  NMR spectrum of the parent hexacarbonyl dimer  $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$  also did not display carbonyl signals under the same conditions, and a search of the literature revealed a noteworthy absence of reported CO resonances for other cyclopentadienyl-molybdenum hexacarbonyl dimers. For example, for the closely related hexacarbonyl dimers containing the 1,3-di-*tert*-butylcyclopentadienyl or mono-*tert*-butylcyclopentadienyl ligands,  $[\text{Mo}(1,3\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3]_2$  and  $[\text{Mo}(\text{C}_5\text{H}_4\text{Bu})(\text{CO})_3]_2$ , Scheer et al. do not report the  $^{13}\text{C}$  NMR carbonyl resonances [6]. In contrast, CO resonances are observed for the corresponding tetracarbonyl dimers  $[\text{Mo}(1,3\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_2]_2$  and  $[\text{Mo}(\text{C}_5\text{H}_4\text{Bu})(\text{CO})_2]_2$  [6].

The mononuclear complex  $[\text{Mo}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3\text{Br}]$  (**5**) was prepared from **2** by the addition of  $\text{Br}_2$  in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  (Scheme 1). This direct oxidation method is in contrast to the typical literature preparation of  $[\text{Mo}(\text{Cp})(\text{CO})_3\text{Br}]$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) which is usually prepared by the addition of *N*-bromosuccinimide to the hydride complex  $[\text{Mo}(\text{Cp})(\text{CO})_3\text{H}]$  [7]. The reaction of dimer  $[\text{Mo}(\text{Cp})(\text{CO})_3]_2$  with  $\text{Br}_2$  reportedly results in more extensive oxidation and formation of  $[\text{Mo}(\text{Cp})(\text{CO})_2\text{Br}_3]$  via the tricarbonylmonobromide complex [8–10]. That this is not the case in the preparation of **5** is evidenced by the accurate elemental analysis, and the two observed carbonyl resonances in a 1:2 ratio observed in the  $^{13}\text{C}$  NMR spectrum. Unlike the parent dimer **2**, **5** clearly shows the carbonyl resonances in the  $^{13}\text{C}$  NMR spectrum. The  $^1\text{H}$  NMR spectrum of **5** is also straightforward, with a singlet observed for the *tert*-butyl groups and a triplet–doublet pattern for the

cyclopentadienyl ring protons. The infrared spectrum of **5** also exhibits three carbonyl stretching frequencies at 2043, 1969, and  $1945\text{ cm}^{-1}$ , while the aforementioned  $[\text{Mo}(\text{Cp})(\text{CO})_2\text{Br}_3]$  shows only two carbonyl stretches at 2095 and  $2060\text{ cm}^{-1}$  in the infrared spectrum [8].

If the reaction of anion **1** with  $\text{Mo}(\text{CO})_6$  with subsequent acidification with glacial acetic acid is followed by oxidation with ambient air, rather than with  $\text{Fe}(\text{III})$ , a different reaction ensues. No formation of **2** is observed, and the orange, crystalline oxo complex  $[\text{Mo}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2\text{O})_2(\mu^2\text{-O})_2]$  (**4**) is the only isolable product (Scheme 1). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4** are rather unremarkable, with the expected resonances observed, and characteristic oxo bands at  $938$  (vs,  $\nu_{\text{Mo}=\text{O}}$ ),  $916$  (s,  $\nu_{\text{Mo}=\text{O}}$ ), and  $720$  (w,  $\nu_{\text{Mo}-\text{O}-\text{Mo}}$ )  $\text{cm}^{-1}$  are present in the infrared spectrum. These values correlate well with those molybdenum–oxo stretches found in  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5\text{O})_2(\mu^2\text{-O})_2]$  ( $\nu_{\text{Mo}=\text{O}}$  925,  $901\text{ cm}^{-1}$ ) [11],  $[\text{Mo}(\eta^5\text{-C}_5\text{Me}_5\text{O})_2(\mu^2\text{-O})_2]$  ( $\nu_{\text{Mo}=\text{O}}$  917  $\text{cm}^{-1}$ ) [12], and in the related oxo complex  $[\text{Mo}(\eta^5\text{-C}_5\text{Me}_5\text{O})_2(\mu^2\text{-O})]$  ( $\nu_{\text{Mo}=\text{O}}$  912,  $771\text{ cm}^{-1}$ ) [13]. The oxo complex **4** is indeed formed by air oxidation of the hexacarbonyl complex **2** under the same conditions. The facility of formation of **4** is notable in comparison with the more vigorous conditions required for oxidation of  $[\text{Mo}(\text{Cp})(\text{CO})_3]_2$  to the corresponding oxo complex [11]. The tungsten analogue **3** is unreactive towards air under these conditions.

## 2.2. Solid state structures

X-ray quality crystals of **2** and **4** were easily obtainable and the two molecules were subjected to single crystal X-ray diffraction analyses. Table 2 provides a summary of the structure determinations, crystal data, data collection, solution and refinement. Fractional atomic coordinates for **2** and **4** are provided in Tables 3 and 4 respectively; bond distances and angles for **2** and **4** are in Tables 5 and 6 respectively.

An ORTEP of the structure of **2** is shown in Fig. 1. Interestingly, the steric bulk of the *tert*-butyl groups

Table 1  
Infrared stretching frequencies of CO ligands in  $[\text{M}(\text{cyclopentadienyl})(\text{CO})_3]_2$  (M = Mo, W)

Metal: cyclopentadienyl	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )	Solvent	Ref.
Mo: $\text{C}_5\text{H}_5$	1964, 1920, 1913	hexanes	
Mo: $\text{C}_5\text{H}_4\text{Me}$	1954, 1913	$\text{CCl}_4$	[4]
Mo: $\text{C}_5\text{Me}_5$	1933, 1898	tetradecane	[5]
<b>2</b>	1950, 1914, 1898	hexanes	
Mo: $\text{C}_5\text{H}_4^t\text{Bu}$	1950, 1912	$\text{CH}_2\text{Cl}_2$	[6]
Mo: $1,3\text{-C}_5\text{H}_3^t\text{Bu}_2$	1944, 1900	$\text{CH}_2\text{Cl}_2$	[6]
<b>3</b>	1944, 1905, 1880	$\text{CHCl}_3$	
W: $\text{C}_5\text{Me}_5$	1920, 1893	tetradecane	[5]
W: $\text{C}_5\text{H}_4\text{Me}$	1956, 1908, 1895	$\text{CHCl}_3$	[3]
W: $\text{C}_5\text{H}_5$	1952, 1903	benzene	[4]

does not have much of an effect on the length of the Mo–Mo bond. At 3.253(1) Å, the Mo–Mo bond in **2** is not significantly longer than the corresponding distance in  $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$  (3.235(1) Å) [14] and is actually

somewhat shorter than the distance in the pentamethylcyclopentadienyl analogue  $[\text{Mo}(\text{C}_5\text{Me}_5)(\text{CO})_3]_2$  (3.281(1) Å) [15]. In **2** the cyclopentadienyl ligands are oriented so as to minimize steric interactions between

Table 2  
Crystallographic determinations for **2** and **4**

	<b>2</b>	<b>4</b>
<i>Crystal data</i>		
Empirical formula	$\text{C}_{32}\text{H}_{42}\text{Mo}_2\text{O}_6$	$\text{C}_{26}\text{H}_{44}\text{Mo}_2\text{O}_4$
Color; habit	red block	orange-brown block
Crystal size ( $\text{mm}^3$ )	$0.40 \times 0.42 \times 0.40$	$0.10 \times 0.28 \times 0.48$
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pccn$
Unit cell dimensions		
<i>a</i> (Å)	7.470(3)	12.886(3)
<i>b</i> (Å)	8.658(3)	16.877(5)
<i>c</i> (Å)	13.319(6)	12.316(3)
$\alpha$ (deg)	84.16(3)	
$\beta$ (deg)	80.26(3)	
$\gamma$ (deg)	75.04(3)	
Volume (Å <sup>3</sup> )	818.8(6)	2678.6(12)
Z	1	4
Formula weight	714.5	612.5
Density (calc.) ( $\text{g cm}^{-3}$ )	1.449	1.524
Absorption coefficient ( $\text{mm}^{-1}$ )	0.800	0.967
<i>F</i> (000)	366	1264
<i>Data collection</i>		
Diffraction used	Siemens P4	Siemens P4
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
Temperature (K)	296	296
Monochromator	Highly oriented graphite crystal	Highly oriented graphite crystal
2 $\theta$ Range (deg)	4.0–52.0	4.0–43.0
Scan type	Wyckoff	Wyckoff
Scan speed (deg min <sup>-1</sup> )	Variable; 3.08 to 29.30 in $\omega$	Variable; 3.08 to 29.30 in $\omega$
Scan range ( $\omega$ ) (deg)	1.00	1.00
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time	Stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 197 reflections	3 measured every 197 reflections
Index ranges	$-9 \leq h \leq 9, -10 \leq k \leq 10, 0 \leq l \leq 16$	$-14 \leq h \leq 0, 0 \leq k \leq 19, 0 \leq l \leq 14$
Reflections collected	3373	2449
Independent reflections	3226 ( $R_{\text{int}} = 1.97\%$ )	2097 ( $R_{\text{int}} = 4.76\%$ )
Observed reflections	2831 ( $F > 4.0\sigma(F)$ )	1516 ( $F > 5.0\sigma(F)$ )
Absorption correction	N/A	N/A
<i>Solution and refinement</i>		
System used	Siemens SHELXTL PLUS (PC version)	Siemens SHELXTL PLUS (PC version)
Solution	Direct methods	Patterson methods
Refinements method	Full-matrix least squares	Full-matrix least squares
Quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic <i>U</i>	Riding model, fixed isotropic <i>U</i>
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of parameters refined	181	145
Final <i>R</i> indexed (obs. data)	$R = 3.44\%, wR = 3.61\%$	$R = 3.46\%, wR = 5.00\%$
Indices (all data)	$R = 4.06\%, wR = 4.06\%$	$R = 5.21\%, wR = 5.74\%$
Goodness-of-fit	0.85	1.12
Largest and mean $\Delta/\sigma$	0.002, 0.000	0.004, 0.001
Data-to-parameter ratio	15.6:1	10.5:1
Largest difference peak ( $\text{e \AA}^{-3}$ )	1.57	0.47
Largest difference hole ( $\text{e \AA}^{-3}$ )	-0.46	-0.59

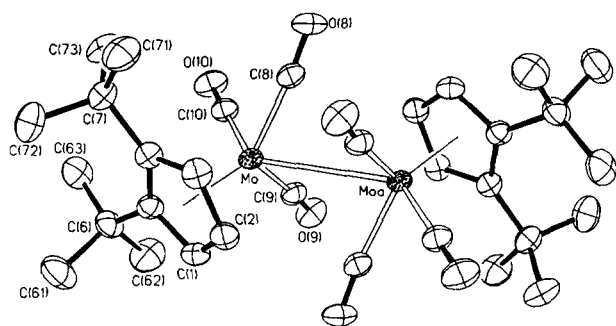


Fig. 1. Molecular structure of  $[\text{Mo}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3]_2$  (**2**) drawn with 35% thermal ellipsoids.

tert-butyl groups; therefore, steric contacts between tert-butyl groups on neighboring rings do not have a significant effect on the Mo–Mo distance. Unfortunately, comparison X-ray data are not available for  $[\text{Mo}(1,3\text{-C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3]_2$  and  $[\text{Mo}(\text{C}_5\text{H}_4\text{Bu})(\text{CO})_3]_2$  [6].

The characterization of the oxo complex **4** was also confirmed crystallographically. The ORTEP (Fig. 2) illustrates the dimeric structure with a metal–metal bond (2.597(2) Å) flanked by two oxo bridges (Mo–O: 1.925(4) Å; Mo–O–Mo 84.5(2)°). A terminal oxo ligand (Mo–O: 1.686(4) Å) and a 1,2-di-tert-butylcyclopentadienyl ring on each metal atom complete the structure. The two cyclopentadienyl ligands are both on the same side of the  $\text{Mo}_2\text{O}_2$  core, with the overall symmetry of the molecule being  $C_2$  owing to the orientation of the tert-butyl groups.

Table 3  
Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$  for **2**)

Atom	x	y	z	$U_{\text{eq}}^a$
Mo	317.8(4)	4197.4(4)	1134.8(2)	35(1)
C(1)	–2448(5)	3478(5)	1871(3)	50(2)
C(2)	–1848(6)	2701(5)	959(3)	49(2)
C(3)	–105(6)	1638(5)	1033(3)	47(1)
C(4)	408(5)	1689(4)	2015(3)	42(1)
C(5)	–1106(5)	2891(5)	2553(3)	43(1)
C(6)	–1677(6)	3362(6)	3673(3)	54(2)
C(7)	2097(6)	411(5)	2356(3)	50(1)
C(8)	2779(5)	3878(5)	241(3)	44(1)
C(9)	–749(5)	6539(5)	1221(3)	44(1)
C(10)	1870(5)	4820(5)	1998(3)	45(1)
C(61)	–3059(8)	2359(8)	4177(4)	82(3)
C(62)	–2701(8)	5141(7)	3720(4)	84(2)
C(63)	–103(7)	3096(6)	4319(3)	66(2)
C(71)	3136(7)	–611(6)	1454(4)	73(2)
C(72)	1320(8)	–737(6)	3167(4)	72(2)
C(73)	3557(6)	1065(6)	2733(4)	68(2)
O(8)	4272(4)	3589(4)	–218(2)	61(1)
O(9)	–1390(5)	7875(4)	1370(3)	63(1)
O(10)	2760(4)	5223(4)	2500(3)	62(1)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 4  
Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for **4**

Atom	x	y	z	$U_{\text{eq}}^a$
Mo(1)	8072.3(4)	6865.7(3)	2135.6(4)	25(1)
O(1)	8310(3)	6645(3)	3449(3)	46(2)
O(2)	6603(3)	7035(2)	1883(3)	31(1)
C(1)	9240(4)	5746(3)	1717(4)	27(2)
C(2)	9556(4)	6437(3)	1100(4)	27(2)
C(3)	8723(5)	6595(3)	359(4)	31(2)
C(4)	7922(5)	6075(3)	527(5)	35(2)
C(5)	8211(4)	5565(3)	1377(5)	37(2)
C(6)	9790(5)	5188(3)	2527(5)	36(2)
C(7)	8971(6)	4741(4)	3229(6)	59(3)
C(8)	10378(6)	4565(4)	1850(6)	59(3)
C(9)	10520(5)	5580(4)	3337(5)	52(2)
C(10)	10586(4)	6900(3)	1048(5)	36(2)
C(11)	11479(5)	6353(4)	750(6)	55(3)
C(12)	10830(5)	7359(4)	2100(5)	46(2)
C(13)	10507(5)	7526(4)	143(6)	62(3)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

The solid state structure of the closely related molybdenum oxo complex,  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)\text{O}]_2(\mu^2\text{-O})_2$  has been determined by Couldwell and Prout [16] to be very similar to **4**. The Mo–Mo bond length of (2.602(1) Å) is nearly identical to that of **4**, as are the Mo–O distances in the oxo-bridged ligands (1.932(2) and 1.948(3) Å) and the terminal Mo–O distances (1.702(4), 1.695(4) Å). Even the bond angle subtended by the bridging oxo ligands is the same (Mo–O–Mo: 84.2°) as it is in **4**. The structure of the pentamethylcyclopentadienyl analogue  $[\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)\text{O}]_2(\mu^2\text{-O})_2$  [17] is also known and, again, the bond lengths and angles in the molybdenum–oxo core of this complex are nearly identical to those in **4**.

In both **2** and **4** some distortions of the cyclopentadienyl ring can be observed similar to those reported for 1,1',2,2'-tetra-tert-butylferrocene [1]. The distortion is manifested in a longer bond distance between the tert-butyl bearing carbon atoms in the ring. For example, in the structure of **4** the C1–C2 distance of 1.450(8) Å is significantly longer than the bond lengths between the other carbon atoms of the cyclopentadienyl ring

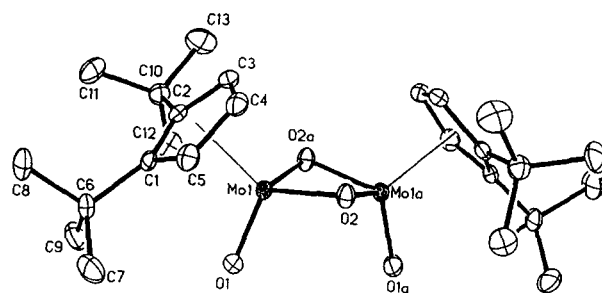


Fig. 2. Molecular structure of  $[\text{Mo}(\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{Bu}_2)\text{O}]_2(\mu^2\text{-O})_2$  (**4**) drawn with 35% thermal ellipsoids.

(1.422(8), 1.433(8), and 1.370(8) Å). In 1,1',2,2'-tetra-*tert*-butylferrocene this distance is 1.468(6) Å [1]. In addition to the lengthening of the C1–C2 bond length in **4**, an expansion of the C6–C1–C2 and C10–C2–C1 bond angles to an average of 133.3(2)° occurs to help relieve repulsions between the two adjacent *tert*-butyl groups. This is accompanied by a contraction of the C6–C1–C5 and C10–C2–C3 bond angles to an average of 120.3(5)°. In 1,1',2,2'-tetra-*tert*-butylferrocene, the corresponding angles of 133.4(2)° and 120.0(3)° are nearly identical to those in **4**. Similar distortions of the di-*tert*-butylcyclopentadienyl ring in **2** are also present (Fig. 1).

### 3. Experimental

Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried using Aquasorb®. Benzene, diethyl ether, diglyme, and tetrahydrofuran (THF) were distilled under nitrogen from sodium or potassium benzophenone ketyl; dichloromethane and hexanes from CaH<sub>2</sub>. <sup>1</sup>H NMR (300 MHz), and <sup>13</sup>C and <sup>13</sup>C{<sup>1</sup>H} (75 MHz) NMR spectra were recorded on a Varian UNITY plus 300 System in the solvent indicated. Chemical shifts are reported as ppm

Table 5  
Bond lengths (Å) and angles (deg) for **2**

Mo–C(1)	2.340 (4)	Mo–C(2)	2.371 (5)
Mo–C(3)	2.337 (5)	Mo–C(4)	2.351 (4)
Mo–C(5)	2.342 (4)	Mo–C(8)	1.985 (4)
Mo–C(9)	1.985 (4)	Mo–C(10)	1.964 (5)
C(1)–C(2)	1.399 (6)	C(1)–C(5)	1.428 (6)
C(2)–C(3)	1.400 (5)	C(3)–C(4)	1.432 (6)
C(4)–C(5)	1.464 (5)	C(4)–C(7)	1.547 (5)
C(5)–C(6)	1.546 (6)	C(6)–C(61)	1.543 (8)
C(6)–C(62)	1.535 (7)	C(6)–C(63)	1.529 (7)
C(7)–C(71)	1.541 (6)	C(7)–C(72)	1.535 (7)
C(7)–C(73)	1.525 (8)	C(8)–O(8)	1.155 (5)
C(9)–O(9)	1.156 (5)	C(10)–O(10)	1.153 (6)
C(1)–Mo–C(2)	34.5(1)	C(1)–Mo–C(3)	57.8(1)
C(2)–Mo–C(3)	34.6(1)	C(1)–Mo–C(4)	59.1(1)
C(2)–Mo–C(4)	58.8(1)	C(3)–Mo–C(4)	35.6(1)
C(1)–Mo–C(5)	35.5(1)	C(2)–Mo–C(5)	58.8(2)
C(3)–Mo–C(5)	59.2(1)	C(4)–Mo–C(5)	36.4(1)
C(1)–Mo–C(8)	154.0(2)	C(2)–Mo–C(8)	120.9(2)
C(3)–Mo–C(8)	96.7(2)	C(4)–Mo–C(8)	104.0(1)
C(5)–Mo–C(8)	138.2(1)	C(1)–Mo–C(9)	95.4(2)
C(2)–Mo–C(9)	115.2(2)	C(3)–Mo–C(9)	149.7(2)
C(4)–Mo–C(9)	144.1(1)	C(5)–Mo–C(9)	108.2(1)
C(8)–Mo–C(9)	107.7(2)	C(1)–Mo–C(10)	120.1(2)
C(2)–Mo–C(10)	148.8(2)	C(3)–Mo–C(10)	127.2(2)
C(4)–Mo–C(10)	94.1(2)	C(5)–Mo–C(10)	90.3(2)
C(8)–Mo–C(10)	77.9(2)	C(9)–Mo–C(10)	76.5(2)
Mo–C(1)–C(2)	74.0(3)	Mo–C(1)–C(5)	72.3(2)
C(2)–C(1)–C(5)	110.0(3)	Mo–C(2)–C(1)	71.5(3)
Mo–C(2)–C(3)	71.4(3)	C(1)–C(2)–C(3)	107.7(4)
Mo–C(3)–C(2)	74.0(3)	Mo–C(3)–C(4)	72.8(2)
C(2)–C(3)–C(4)	110.0(3)	Mo–C(4)–C(3)	71.7(2)
Mo–C(4)–C(5)	71.5(2)	C(3)–C(4)–C(5)	106.0(3)
Mo–C(4)–C(7)	129.6(3)	C(3)–C(4)–C(7)	119.7(3)
C(5)–C(4)–C(7)	133.5(4)	Mo–C(5)–C(1)	72.2(2)
Mo–C(5)–C(4)	72.2(2)	C(1)–C(5)–C(4)	106.3(3)
Mo–C(5)–C(6)	129.9(3)	C(1)–C(5)–C(6)	117.8(3)
C(4)–C(5)–C(6)	134.6(3)	C(5)–C(6)–C(61)	106.1(4)
C(5)–C(6)–C(62)	110.6(4)	C(61)–C(6)–C(62)	108.3(4)
C(5)–C(6)–C(63)	117.0(3)	C(61)–C(6)–C(63)	108.4(4)
C(62)–C(6)–C(63)	106.2(4)	C(4)–C(7)–C(71)	109.6(4)
C(4)–C(7)–C(72)	107.6(4)	C(71)–C(7)–C(72)	106.0(4)
C(4)–C(7)–C(73)	115.4(4)	C(71)–C(7)–C(73)	106.4(4)
C(72)–C(7)–C(73)	111.5(4)	Mo–C(8)–O(8)	174.0(3)
Mo–C(9)–O(9)	173.5(3)	Mo–C(10)–O(10)	178.4(3)

downfield of internal TMS. Infrared spectra were recorded on a Perkin–Elmer Model 1600 FT-IR spectrophotometer and are reported in reciprocal centimeters. Melting points of samples in capillaries open to the air were obtained using a Thomas Hoover device, and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY). All crystallographic software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (Sheldrick, Siemens XRD, Madison, WI).

W(CO)<sub>6</sub> (Pressure), Mo(CO)<sub>6</sub> (Strem), and

Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 9H<sub>2</sub>O (Baker) were purchased from commercial sources and used without further purification. Li[1,2-C<sub>5</sub>H<sub>3</sub>Bu<sub>2</sub>] (1) was prepared according to the literature procedure [1].

### 3.1. Preparation of [Mo(η<sup>5</sup>-1,2-C<sub>5</sub>H<sub>3</sub>Bu<sub>2</sub>)(CO)<sub>3</sub>]<sub>2</sub> (2)

Solid Li[1,2-C<sub>5</sub>H<sub>3</sub>Bu<sub>2</sub>] (0.348 g, 1.89 mmol) and Mo(CO)<sub>6</sub> (0.500 g, 1.89 mmol) were mixed in a Schlenk flask under N<sub>2</sub> and diglyme (40 ml) and hexanes (3 ml) were added. The heterogeneous mixture was heated to reflux for 1 h to give a yellow solution which was then

Table 6  
Bond lengths (Å) and angles (deg) for 4

Mo(1)–O(1)	1.686 (4)	Mo(1)–O(2)	1.937 (4)
Mo(1)–C(1)	2.467 (5)	Mo(1)–C(2)	2.407 (6)
Mo(1)–C(3)	2.385 (6)	Mo(1)–C(4)	2.394 (6)
Mo(1)–C(5)	2.390 (6)	Mo(1)–Mo(1A)	2.597 (2)
Mo(1)–O(2A)	1.925 (4)	O(2)–Mo(1A)	1.925 (4)
C(1)–C(2)	1.450 (8)	C(1)–C(5)	1.422 (8)
C(1)–C(6)	1.542 (8)	C(2)–C(3)	1.433 (8)
C(2)–C(10)	1.540 (8)	C(3)–C(4)	1.370 (8)
C(4)–C(5)	1.404 (8)	C(6)–C(7)	1.558 (10)
C(6)–C(8)	1.539 (9)	C(6)–C(9)	1.521 (9)
C(10)–C(11)	1.519 (9)	C(10)–C(12)	1.540 (9)
C(10)–C(13)	1.537 (9)		
O(1)–Mo(1)–O(2)	111.3(2)	O(1)–Mo(1)–C(1)	85.4(2)
O(2)–Mo(1)–C(1)	132.4(2)	O(1)–Mo(1)–C(2)	107.3(2)
O(2)–Mo(1)–C(2)	137.2(2)	C(1)–Mo(1)–C(2)	34.6(2)
O(1)–Mo(1)–C(3)	140.6(2)	O(2)–Mo(1)–C(3)	102.9(2)
C(1)–Mo(1)–C(3)	56.5(2)	C(2)–Mo(1)–C(3)	34.8(2)
O(1)–Mo(1)–C(4)	133.2(2)	O(2)–Mo(1)–C(4)	82.6(2)
C(1)–Mo(1)–C(4)	56.7(2)	C(2)–Mo(1)–C(4)	57.3(2)
C(3)–Mo(1)–C(4)	33.3(2)	O(1)–Mo(1)–C(5)	99.1(2)
O(2)–Mo(1)–C(5)	98.4(2)	C(1)–Mo(1)–C(5)	34.0(2)
C(2)–Mo(1)–C(5)	57.2(2)	C(3)–Mo(1)–C(5)	56.0(2)
C(4)–Mo(1)–C(5)	34.1(2)	O(1)–Mo(1)–Mo(1A)	106.5(2)
O(2)–Mo(1)–Mo(1A)	47.6(1)	C(1)–Mo(1)–Mo(1A)	167.3(1)
C(2)–Mo(1)–Mo(1A)	134.2(1A)	C(3)–Mo(1)–Mo(1A)	110.9(1)
C(4)–Mo(1)–Mo(1A)	114.4(1)	C(5)–Mo(1)–Mo(1A)	142.9(1)
O(1)–Mo(1)–O(2A)	109.1(2)	O(2)–Mo(1)–O(2A)	92.5(2)
C(1)–Mo(1)–O(2A)	124.8(2)	C(2)–Mo(1)–O(2A)	91.8(2)
C(3)–Mo(1)–O(2A)	87.7(2)	C(4)–Mo(1)–O(2A)	114.8(2)
C(5)–Mo(1)–O(2A)	143.5(2)	Mo(1A)–Mo(1)–O(2A)	48.0(1)
Mo(1)–O(2)–Mo(1A)	84.5(2)	Mo(1)–C(1)–C(2)	70.4(3)
Mo(1)–C(1)–C(5)	70.0(3)	C(2)–C(1)–C(5)	106.2(5)
Mo(1)–C(1)–C(6)	127.7(4)	C(2)–C(1)–C(6)	134.4(5)
C(5)–C(1)–C(6)	119.1(5)	Mo(1)–C(2)–C(1)	75.0(3)
Mo(1)–C(2)–C(3)	71.8(3)	C(1)–C(2)–C(3)	105.8(5)
Mo(1)–C(2)–C(10)	123.6(4)	C(1)–C(2)–C(10)	132.2(5)
C(3)–C(2)–C(10)	121.6(5)	Mo(1)–C(3)–C(2)	73.4(3)
Mo(1)–C(3)–C(4)	73.7(3)	C(2)–C(3)–C(4)	110.4(5)
Mo(1)–C(4)–C(3)	73.0(3)	Mo(1)–C(4)–C(5)	72.8(3)
C(3)–C(4)–C(5)	107.8(5)	Mo(1)–C(5)–C(1)	76.0(3)
Mo(1)–C(5)–C(4)	73.1(3)	C(1)–C(5)–C(4)	109.6(5)
C(1)–C(6)–C(7)	110.0(5)	C(1)–C(6)–C(8)	107.0(5)
C(7)–C(6)–C(8)	107.6(5)	C(1)–C(6)–C(9)	116.2(5)
C(7)–C(6)–C(9)	105.3(5)	C(8)–C(6)–C(9)	110.4(5)
C(2)–C(10)–C(11)	110.7(5)	C(2)–C(10)–C(12)	113.3(5)
C(11)–C(10)–C(12)	110.7(5)	C(2)–C(10)–C(13)	108.7(5)
C(11)–C(10)–C(13)	107.0(5)	C(12)–C(10)–C(13)	106.1(5)

cooled to room temperature. A solution of glacial acetic acid (10 ml),  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (10.0 g, 17.8 mmol), and  $\text{H}_2\text{O}$  (50 ml) was added to the solution, which turned purple immediately. This mixture was stirred for 48 h at room temperature. The solid was collected on a glass frit in air, dissolved in  $\text{CH}_2\text{Cl}_2$ , and dried over  $\text{MgSO}_4$ . After filtration the purple solid was applied to a  $2 \times 20$  cm silica gel chromatography column packed with hexanes. A reddish-purple band was eluted with  $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$  (1:1) and the solvent was removed by rotary evaporation to give a purple microcrystalline solid. The solid was washed with methanol, collected on a glass frit in air and dried in vacuo to give **2** (0.260 g, 38%) as a purple microcrystalline solid. X-ray quality crystals were grown by slow evaporation of  $\text{CH}_2\text{Cl}_2$  from a 1:1  $\text{CH}_2\text{Cl}_2:\text{MeOH}$  solution. M.p.: 150–170 °C (dec.).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  5.19 (d,  $^3J_{\text{HH}} = 3.17$  Hz, 2H, Cp-H), 4.90 (t,  $^3J_{\text{HH}} = 3.17$  Hz, 1H, Cp-H), 1.40 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  122.2 (s,  $\text{CC}(\text{CH}_3)_3$ ), 95.7 (s, CH–CH–CH), 94.0 (s, CH–CH–CH), 34.4 (s,  $\text{C}(\text{CH}_3)_3$ ), 34.0 (s,  $\text{C}(\text{CH}_3)_3$ ). IR (hexanes,  $\text{cm}^{-1}$ ): 1950 (vs, CO), 1914 (vs, CO), 1898 (s, CO). Anal. Found: C, 54.13; H, 6.09.  $\text{C}_{32}\text{H}_{42}\text{Mo}_2\text{O}_6$ . Calc.: C, 53.79; H, 5.92%.

### 3.2. Preparation of $[\text{W}(\eta^5-1,2-\text{C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3]_2$ (**3**)

Solid  $\text{Li}[1,2-\text{C}_5\text{H}_3\text{Bu}_2]$  (0.320 g, 1.74 mmol) and  $\text{W}(\text{CO})_6$  (0.611 g, 1.74 mmol) were mixed in a Schlenk flask under  $\text{N}_2$  and diglyme (100 ml) and hexanes (3 ml) were added. The heterogeneous mixture was heated to reflux for 40 min to give a yellow solution which was then cooled to room temperature. A solution of glacial acetic acid (10 ml),  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (10.0 g, 17.8 mmol), and  $\text{H}_2\text{O}$  (150 ml) was added to the solution, which immediately turned reddish-brown. This mixture was then allowed to stand for 3 days, over which time a reddish solid formed on the bottom of the flask. The solution was decanted and the solid dissolved in  $\text{CH}_2\text{Cl}_2$  (50 ml). The red solution was dried over  $\text{MgSO}_4$ , filtered, and the solvent was removed on a rotary evaporator. The solid was then applied to a  $2 \times 20$  cm silica gel chromatography column packed with hexanes. A yellow band was first eluted with hexanes and discarded, and then a reddish-purple band was eluted with  $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$  (1:1). The solvent was removed from the second band in vacuo to give a purple microcrystalline solid with some yellow oil. The solid was washed with hexanes ( $2 \times 10$  ml) and again dried in vacuo to give **3** (0.096 g, 12%) as a purple microcrystalline solid. M.p.: 196 °C (dec.).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  5.35 (dd,  $^3J_{\text{HH}} = 3.18$  Hz,  $^2J_{\text{WH}} = 0.73$  Hz, 2H, Cp-H), 5.07 (td,  $^3J_{\text{HH}} = 3.18$  Hz,  $^2J_{\text{WH}} = 0.73$  Hz, 1H, Cp-H), 1.44 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  226.2 (s, CO), 216.7 (s, CO), 119.8 (s,  $\text{CC}(\text{CH}_3)_3$ ), 97.1 (s, CH–CH–CH), 92.2 (s, CH–CH–CH), 34.3 (s,

$\text{C}(\text{CH}_3)_3$ ), 34.2 (s,  $\text{C}(\text{CH}_3)_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2000 (w, CO), 1943 (vs, CO), 1902 (vs, CO), 1879 (vs, CO). IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 1944 (vs, CO), 1905 (vs, CO), 1880 (vs, CO). Anal. Found: C, 43.12; H, 4.75.  $\text{C}_{32}\text{H}_{42}\text{O}_6\text{W}_2$ . Calc.: C, 43.17; H, 4.75%.

### 3.3. Preparation of $[\text{Mo}(\eta^5-1,2-\text{C}_5\text{H}_3\text{Bu}_2)\text{O}]_2(\mu^2-\text{O})_2$ (**4**)

Solid  $\text{Li}[1,2-\text{C}_5\text{H}_3\text{Bu}_2]$  (0.500 g, 2.71 mmol) and  $\text{Mo}(\text{CO})_6$  (0.716 g, 2.71 mmol) were mixed in a Schlenk flask under  $\text{N}_2$  and THF (50 ml) was added. The heterogeneous mixture was heated to reflux for 20 h to give a yellow solution which was then cooled to room temperature. Glacial acetic acid (0.500 ml) was added via syringe and the solution immediately turned brown and a precipitate formed. This mixture was stirred 10 min and then air was bubbled through the mixture for 4 h to give a reddish brown solution. The solvent was removed under reduced pressure and the solid extracted with warm benzene ( $3 \times 20$  ml). The extracts were filtered through Celite, and again the solvent was removed under reduced pressure. The solid was then applied to a  $2 \times 20$  cm silica gel chromatography column packed with hexanes. A pink band was first eluted with hexanes, a yellow band was eluted with  $\text{Et}_2\text{O}$ , and finally another yellow band was eluted with  $\text{CH}_2\text{Cl}_2$ . The solvent was removed from the two yellow bands in vacuo to give orange solids which were identical by  $^1\text{H}$  NMR and IR spectra. The two solids were then combined for crystallization from hexane– $\text{Et}_2\text{O}$  to give  $[\text{Mo}(\eta^5-1,2-\text{C}_5\text{H}_3\text{Bu}_2)\text{O}]_2(\mu^2-\text{O})_2$  (0.097 g, 12%) as an orange microcrystalline solid. X-ray quality crystals were grown by layering hexane onto a concentrated dichloromethane solution of **4** and allowing the layers to diffuse together for 2 days at room temperature. M.p.: 140 °C (dec.).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{H}}$  5.98 (d,  $^3J_{\text{HH}} = 3.42$  Hz, 2H, Cp-H), 5.10 (t,  $^3J_{\text{HH}} = 3.42$  Hz, 1H, Cp-H), 1.64 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{C}}$  135.0 (s,  $\text{CC}(\text{CH}_3)_3$ ), 108.3 (s, CH–CH–CH), 105.5 (s, CH–CH–CH), 35.1 (s,  $\text{C}(\text{CH}_3)_3$ ), 33.3 (s,  $\text{C}(\text{CH}_3)_3$ ). IR ( $\text{CS}_2$ ,  $\text{cm}^{-1}$ ): 2962 (vs), 2922 (s), 1606 (w), 1489 (s), 1454 (s), 1406 (w), 1364 (s), 1307 (w), 1244 (s), 1160 (s), 970 (w), 938 (vs, Mo=O), 916 (s, Mo=O), 849 (w), 842 (w), 824 (s), 810 (w), 720 (w, Mo–O–Mo). Anal. Found: C, 50.61; H, 6.97.  $\text{C}_{26}\text{H}_{42}\text{Mo}_2\text{O}_4$ . Calc.: C, 51.15; H, 6.93%.

### 3.4. Preparation of $[\text{Mo}(\eta^5-1,2-\text{C}_5\text{H}_3\text{Bu}_2)(\text{CO})_3\text{Br}]$ (**5**)

A solution of **2** (0.115 g, 0.161 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was prepared and cooled to  $-78$  °C. 10 ml of a 0.15 M solution of  $\text{Br}_2$  in  $\text{CH}_2\text{Cl}_2$  was prepared and 1 ml of this was slowly added to the solution of **2** via syringe. The solution was warmed to room temperature and stirred for 1 h. An IR spectrum of a small aliquot

showed diminished peaks at 2003 and 1910  $\text{cm}^{-1}$  (due to **2**) and new peaks at 2044 and 1969  $\text{cm}^{-1}$ . More of the  $\text{Br}_2$  solution (250  $\mu\text{l}$ ) was then added and the solution was stirred for another hour. Again, IR of a small aliquot showed further disappearance of the peaks at 2003 and 1910  $\text{cm}^{-1}$ . A final portion of the  $\text{Br}_2$  solution (50  $\mu\text{l}$ ) was added and, after stirring 0.5 h, the solvent was removed under reduced pressure. The resulting oily residue was extracted twice with hexanes (20 ml) and filtered through a Celite plug on a Schlenk frit. The volume of the solvent was reduced to about 5 ml and then the solution was cooled at  $-60^\circ\text{C}$  overnight. The supernatant liquid was then decanted via cannula and the resulting red-orange solid was dried in vacuo to give **5** (0.076 g, 54%). M.p.: 59–60  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  4.90 (d,  $^3J_{\text{HH}} = 2.93$  Hz, 2H, CH–CH–CH), 4.82 (t,  $^3J_{\text{HH}} = 2.93$  Hz, 1H, CH–CH–CH), 1.06 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}}$  245.7 (s, CO), 225.8 (s, CO), 125.3 (s,  $\text{CC}(\text{CH}_3)_3$ ), 99.5 (s, CH–CH–CH), 93.2 (s, CH–CH–CH), 34.5 (s,  $\text{C}(\text{CH}_3)_3$ ), 34.0 (s,  $\text{C}(\text{CH}_3)_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2044 (vs, CO), 1969 (vs, CO), 1945 (vs, CO). Anal. Found: C, 43.84; H, 4.95.  $\text{C}_{16}\text{H}_{21}\text{BrMoO}_3$ . Calc.: C, 43.96; H, 4.84%.

### 3.5. Crystal structure of **2**

A suitable crystal was mounted on a glass fiber with epoxy cement. The unit-cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ( $20 \leq 2\theta \leq 25^\circ$ ). No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. *E*-statistics suggested a centrosymmetric space group and  $P\bar{1}$  was chosen. The space group choice was subsequently verified by chemically reasonable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least squares procedures. The compound molecule was located on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions.

### 3.6. Crystal structure of **4**

An orange-brown block specimen was mounted on a glass fiber with epoxy cement, and the Laue symmetry (*mmm*) and unit-cell parameters were obtained photographically. The unit-cell parameters were refined from the angular settings of 25 high-angle reflections. One octant of data was collected. Azimuthal scans indicated

a transmission factor of 1.08  $\text{cm}^{-1}$ ; accordingly, no correction for absorption was required. The unique metal atom was located from a Patterson map and the remaining non-hydrogen atoms were obtained from a subsequent difference map. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were idealized. The molecule resides on a crystallographic two-fold axis at the mid-point of the Mo(1)–Mo(1a) and O(2)–O(2a) vectors.

## 4. Supplementary material available

Listings of experimental and calculated structure factors for **2** and **4** (13 pages) are available.

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