

Reactions of $\text{SmI}_2(\text{THF})_x$ with $[\text{Cp}'\text{Mo}(\text{CO})_3]_2\text{Hg}$ ($\text{Cp}' = \text{C}_5\text{H}_5^-$ or C_5Me_5^-): crystal and molecular structures of $[(\text{THF})_4\text{I}_2\text{Sm}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ and $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2$

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Abstract

The reactions of $\text{SmI}_2(\text{THF})_x$ with $[\text{Cp}'\text{Mo}(\text{CO})_3]_2\text{Hg}$ ($\text{Cp}' = \text{C}_5\text{H}_5^-$ or C_5Me_5^-) in THF at ambient temperature have been investigated. In the case of $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$, a new complex of $[(\text{THF})_4\text{I}_2\text{Sm}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ **1** was afforded. However, in the reaction involving $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$ the analog cannot be obtained, but instead the dimeric $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2$ **2**. Both complexes **1** and **2** have been characterized by X-ray crystallography. In **1** the cooperative activation of CO between Sm^{3+} and Mo was observed. The structure of complex **1** is the first example containing the "Sm($\mu\text{-OC}$)Mo" fragment.

Keywords: Samarium; Carbonyl; Molybdenum; Crystal structure

1. Introduction

There is considerable current interest in heterobimetallic complexes due to the search for homogeneous counterparts of Fischer–Tropsch catalysts [1–14]. In this context, the preparation and chemistry of complexes containing lanthanide and late d-block transition metal (LTM) have attracted appreciable attention. To date, many different types of LTM complex have been synthesized, and most of them have been structurally characterized [15–21]. Of LTM complexes, those with d-block transition metal carbonylate moiety are the predominant majority. Structurally characterized examples include: $[(\text{EtOH})(\text{H}_2\text{O})_4\text{Er}(\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5))_3]$ [19], $[(\text{HMPA})_4\text{Yb}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)_2]$ [21], $[(\text{HMPA})_5\text{Yb}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)][(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2 \cdot \text{THF}$ [21], $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-OC})_2\text{Fe}(\text{C}_5\text{Me}_5)_2]$ [22], $[(\text{C}_5\text{Me}_5)_2\text{Yb}(\mu\text{-OC})\text{Co}(\text{CO})_3(\text{THF})]$ [23], $[(\text{C}_5\text{Me}_5)_2\text{Yb}]_2[\text{Fe}_3(\text{CO})_{11}]$ [24], $[(\text{C}_5\text{Me}_5)_2\text{Yb}(\mu\text{-OC})_2\text{Mn}(\text{CO})_3]_2$ [25], $[(\text{C}_5\text{Me}_5)_2\text{Yb}(\mu\text{-OC})_3\text{Mn}(\text{CO})_2]_x$ [25], $[(\text{C}_5\text{Me}_5)_2\text{Yb}]_2[\text{Co}_3(\text{C}_5\text{H}_4\text{SiMe}_3)_2(\mu_3\text{-CO})_4]$ [26] and $(\text{THF})_5\text{La}[(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]_3 \cdot \text{THF}$ [27]. All of them consist of a transition metal carbonyl fragment and a lanthanide moiety bridged together via Ln–O–C–M (Ln =

lanthanide and M = transition metal) isocarbonyl linkages. All the above complexes containing ytterbium metal were prepared by redox reaction involving divalent ytterbium species and corresponding metal carbonyl compounds. As divalent samarium derivatives are stronger reducing agents and more oxophilic compared with the corresponding divalent ytterbium compounds, however, there are very few similar molecular structures containing samarium [22]. Herein, we report an example of a molecular structure containing "Sm–O–C–Mo" isocarbonyl linkage.

2. Experimental details

All manipulations were routinely conducted under a dinitrogen atmosphere using the vacuum line technique unless otherwise indicated. Solvents were thoroughly dried over sodium benzophenone ketyl and distilled under nitrogen immediately prior to use. Reagents $\text{Mo}(\text{CO})_6$ and $\text{C}_5\text{Me}_5\text{H}$ were purchased from the Aldrich Chemical Co. and used as received. Compounds $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$ [28], $\text{SmI}_2(\text{THF})_x$ [29] and KC_5Me_5 [30] were prepared by the published procedures. IR spectra were recorded on a Biorad FTS-7 IR spectrophotometer and ^1H and ^{13}C NMR spectra on a Jeol GSX 270FT spectrometer with $\text{Si}(\text{CH}_3)_4$ as references.

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2.1. Synthesis of $[(\text{THF})_4\text{I}_2\text{Sm}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ 1

A powder of $\text{Hg}[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_2$ (0.24 g, 0.348 mmol) was added to the solution of SmI_2 in THF (0.1 M, 7 ml) with vigorous stirring at room temperature. The dark blue solution turned yellow in seconds and mercury metal droplets were observed. The reaction was stirred overnight. A bright yellow solution was obtained after removing the insoluble materials by centrifugation. Orange powder was isolated after evaporating all solvent in vacuo in ca. 70% yield based on $\text{Hg}[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_2$. IR (Nujol mull on NaCl): 2027(s) and 1942(vs) cm^{-1} . Crystals suitable for X-ray analysis were grown from saturated THF solution at -20°C .

Table 1
Crystallographic data for 1 and 2^a

	1	2
Empirical formula	$\text{SmMoC}_{24}\text{H}_{37}\text{O}_7\text{I}_2$	$\text{C}_{26}\text{H}_{30}\text{O}_6\text{Mo}_2$
Color; habit	Orange; block	Red; plate
Crystal size (mm^3)	$0.23 \times 0.28 \times 0.38$	$0.22 \times 0.22 \times 0.33$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell dimensions		
a (Å)	10.122(1)	9.409(3)
b (Å)	18.396(2)	9.118(2)
c (Å)	16.933(3)	15.595(2)
β (°)	96.55(1)	97.38(2)
Volume (Å ³)	3132.3(7)	1327.0(5)
Z	4	2
Formula weight	937.70	630.40
Density (calc.) (g cm^{-3})	1.988	1.578
Absorption coefficient (cm^{-1})	42.68	9.80
$F(000)$	1788	636
2θ range (°)	2–40	2–50
Scan range ω	$1.00 + 0.35 \tan \theta$	$0.68 + 0.35 \tan \theta$
Number of reflections collected	2720	2674
Number of independent reflections	2500	2513
Number of observed reflections	1422 ($I > 3\sigma(I)$)	1191 ($I > 3\sigma(I)$)
R ; R_w (observed data)	0.045; 0.044	0.034; 0.032
Goodness of fit	2.221	1.370
Largest Δ/σ	0.09	0.02
Number of parameters	161	154
Residual extrema in the final difference map (e Å^{-3})	1.12 to -0.64	0.60 to -0.40

^a Data in common: radiation Mo K α ($\lambda = 0.71073$ Å); temperature (K) 298; scan type ω - 2θ ; scan speed ($^\circ \text{min}^{-1}$) 16.0 (up to four scans); background measurement 25% at both ends; absorption correction (ψ scan method; refinement method full-matrix least-squares; weighting scheme $w = 1/\sigma^2(F_o^2)$).

Table 2
Atomic coordinates and isotropic displacement coefficients B_{eq} for 1

Atom	x	y	z	B_{eq} (Å ²)
Sm(1)	0.9843(2)	0.19638(7)	0.36101(8)	3.00(4)
I(1)	1.1655(2)	0.2478(1)	0.2395(1)	4.68(6)
I(2)	0.8272(2)	0.1364(1)	0.4891(1)	5.31(6)
Mo(1)	0.6267(3)	0.4021(1)	0.3766(1)	3.91(7)
O(1)	1.094(2)	0.2780(8)	0.4600(9)	4.3(4)
O(2)	1.183(2)	0.1332(8)	0.4292(9)	3.9(4)
O(3)	0.981(2)	0.0736(8)	0.3059(9)	3.9(4)
O(4)	0.798(2)	0.1888(9)	0.2550(9)	4.5(4)
O(5)	0.868(2)	0.3108(8)	0.3514(8)	4.0(4)
O(6)	0.527(2)	0.264(1)	0.453(1)	9.1(7)
O(7)	0.773(2)	0.440(1)	0.541(1)	7.6(6)
C(1)	1.031(3)	0.316(2)	0.520(2)	6.3(8)
C(2)	1.109(4)	0.386(2)	0.528(2)	9(1)
C(3)	1.248(4)	0.365(2)	0.515(2)	9.1(10)
C(4)	1.228(4)	0.304(2)	0.458(2)	9.4(10)
C(5)	1.208(3)	0.117(1)	0.515(2)	5.2(7)
C(6)	1.349(4)	0.094(2)	0.525(2)	8.5(9)
C(7)	1.386(3)	0.067(2)	0.449(2)	7.6(9)
C(8)	1.297(3)	0.110(2)	0.389(2)	6.4(8)
C(9)	0.982(3)	0.005(2)	0.347(2)	7.2(8)
C(10)	1.012(4)	$-0.050(2)$	0.291(2)	9(1)
C(11)	0.988(3)	$-0.020(2)$	0.215(2)	8.1(9)
C(12)	0.968(3)	0.057(2)	0.221(2)	6.9(8)
C(13)	0.674(3)	0.157(2)	0.270(2)	7.3(9)
C(14)	0.570(3)	0.198(2)	0.215(2)	8.7(10)
C(15)	0.637(4)	0.240(2)	0.162(2)	10(1)
C(16)	0.783(3)	0.236(2)	0.184(2)	6.4(8)
C(17)	0.772(3)	0.347(1)	0.363(1)	3.0(6)
C(18)	0.561(4)	0.317(2)	0.426(2)	8.0(9)
C(19)	0.714(3)	0.427(1)	0.479(2)	5.4(7)
C(20)	0.582(3)	0.456(2)	0.248(2)	5.9(8)
C(21)	0.598(3)	0.513(1)	0.303(2)	4.9(7)
C(22)	0.501(3)	0.513(2)	0.357(2)	6.4(8)
C(23)	0.417(3)	0.457(2)	0.331(2)	6.7(8)
C(24)	0.465(3)	0.422(1)	0.266(2)	5.2(7)

$$B_{\text{eq}} = \frac{1}{3} \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha).$$

2.2. Synthesis of $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$

This compound was prepared by the procedure of King and Stone [28] by substituting $\text{C}_5\text{Me}_5\text{K}$ for $\text{C}_5\text{H}_5\text{Na}$ in ca. 70% yield based on $\text{C}_5\text{Me}_5\text{K}$. IR (Nujol mull on NaCl): 1947(vs), 1889(sh) and 1873(vs) cm^{-1} . ^1H NMR (CDCl_3): 1.57 ppm (s, CH_3). ^{13}C NMR (CDCl_3): 11.73 ppm (s, CH_3), 104.13 ppm (s, ring carbons).

2.3. Preparation of $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2$ 2

A powder of $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$ (0.208 g, 0.25 mmol) was added to the solution of SmI_2 (0.1 M, 5 ml) in THF at room temperature. The mixture was stirred overnight. A transparent orange solution was obtained after removing insoluble mercury by centrifugation. After evaporating all solvent, an oily residue was left. Extraction with 10 ml of dimethoxyethane (DME) pro-

Table 3
Atomic coordinates and isotropic displacement coefficients B_{eq} for 2

Atom	x	y	z	B_{eq} (\AA^2)
Mo(1)	0.03660(6)	0.00031(9)	0.39987(4)	2.57(1)
O(1)	0.2329(7)	0.2513(7)	0.4817(4)	6.0(2)
O(2)	-0.0393(7)	0.2626(7)	0.2767(4)	5.7(2)
O(3)	-0.2928(6)	0.0402(6)	0.3947(3)	4.5(2)
C(1)	0.1549(9)	0.1582(9)	0.4578(5)	4.0(2)
C(2)	-0.0122(9)	0.1680(10)	0.3232(5)	3.3(2)
C(3)	-0.1731(9)	0.0242(9)	0.4069(5)	3.7(2)
C(4)	0.0385(8)	-0.1395(9)	0.2773(5)	3.1(2)
C(5)	0.0103(8)	-0.2401(9)	0.3427(5)	2.7(2)
C(6)	0.1325(8)	-0.2468(8)	0.4058(4)	2.7(2)
C(7)	0.2372(8)	-0.1476(9)	0.3805(5)	2.9(2)
C(8)	0.1792(8)	-0.0837(8)	0.3008(5)	3.2(2)
C(9)	-0.0539(10)	-0.117(1)	0.1915(5)	5.2(3)
C(10)	-0.1160(9)	-0.3415(9)	0.3374(5)	4.4(2)
C(11)	0.1555(9)	-0.3526(9)	0.4793(5)	4.2(2)
C(12)	0.3891(9)	-0.136(1)	0.4207(5)	4.7(2)
C(13)	0.2599(9)	0.012(1)	0.2458(5)	5.2(2)

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

ceeded to give a red solution. The single crystals of $[(C_5Me_5)Mo(CO)_3]_2$ suitable for X-ray analysis were grown from this solution at -25°C in 30% yield based on $[(C_5Me_5)Mo(CO)_3]_2Hg$.

2.4. X-ray analyses of complexes 1 and 2

Both orange block crystals of complex 1 and red plate crystals of complex 2 were mounted in glass capillaries under deoxygenated paraffin oil. Crystal intensity data were collected at ambient temperature on a Rigaku AFC7R diffractometer using Mo K α radiation

($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz and polarization effects and absorption by the ψ scan method [31]. Structures were solved by direct methods (SIR 88) [32] and refined by full-matrix least-squares analysis. Hydrogen atoms were placed at idealized positions and included in structure factor calculations but not refined. All calculations were performed on a Silicon-Graphics computer using the TeXsan package from MSC [33].

The pertinent crystallographic data for both 1 and 2 are listed in Table 1. Coordinates of non-hydrogen atoms and selected bond distances and angles in 1 and 2 are summarized in Tables 2, 3, 4 and 5 respectively. Complete lists of bond lengths and angles and tables of hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Center.

3. Results and discussion

Samarium diiodide is a strong one-electron reducing agent. There have been intensive investigations on its application in organic synthesis [29,34,35]. Interactions of SmI_2 with transition metal complexes very often lead to redox reaction rather than formation of heterobimetallic complexes. Evans et al. [36] reported the reaction of $SmI_2(THF)_x$ with $Co_2(CO)_8$ to give the $[(THF)_5SmI_2]^+[Co(CO)_4]^-$ ion pair instead of the bimetallic compound $[(THF)_xI_2Sm(\mu-OC)Co(CO)_3]$.

The reaction of $SmI_2(THF)_x$ with $[(C_5H_5)Mo(CO)_3]_2Hg$ is rapid and gives only one isolated product $[(THF)_4I_2Sm(\mu-OC)Mo(CO)_2(C_5H_5)]$ 1 in high yield. Complex 1 is exceedingly air- and moisture-sensitive. It

Table 4
Selected bond distances (\AA) and angles ($^\circ$) in 1

Distances					
Sm(1)–I(1)	3.058(2)	Sm(1)–I(2)	3.039(2)	Sm(1)–O(1)	2.42(2)
Sm(1)–O(2)	2.49(2)	Sm(1)–O(3)	2.44(1)	Sm(1)–O(4)	2.46(2)
Sm(1)–O(5)	2.41(2)	Mo(1)–C(17)	1.82(3)	Mo(1)–C(18)	1.93(3)
Mo(1)–C(19)	1.91(3)	Mo(1)–C(20)	2.40(3)	Mo(1)–C(21)	2.38(3)
Mo(1)–C(22)	2.40(3)	Mo(1)–C(23)	2.40(3)	Mo(1)–C(24)	2.38(3)
O(5)–C(17)	1.22(2)	O(6)–C(18)	1.14(3)	O(7)–C(19)	1.17(3)
Angles					
I(1)–Sm(1)–I(2)	174.35(8)	I(1)–Sm(1)–O(1)	90.6(4)		
I(1)–Sm(1)–O(2)	86.6(4)	I(1)–Sm(1)–O(3)	90.7(4)		
I(1)–Sm(1)–O(4)	89.8(4)	I(1)–Sm(1)–O(5)	90.6(4)		
I(2)–Sm(1)–O(1)	88.1(4)	I(2)–Sm(1)–O(2)	87.7(4)		
I(2)–Sm(1)–O(3)	87.2(4)	I(2)–Sm(1)–O(4)	94.6(4)		
I(2)–Sm(1)–O(5)	94.2(4)	O(1)–Sm(1)–O(2)	71.7(5)		
O(1)–Sm(1)–O(3)	145.3(5)	O(1)–Sm(1)–O(4)	142.6(5)		
O(1)–Sm(1)–O(5)	71.8(5)	O(4)–Sm(1)–O(5)	70.8(5)		
C(17)–Mo(1)–C(18)	85(1)	C(17)–Mo(1)–C(19)	86(1)		
C(18)–Mo(1)–C(19)	86(1)	Sm(1)–O(5)–C(17)	149(1)		
Mo(1)–C(17)–O(5)	177(1)	Mo(1)–C(18)–C(6)	175(3)		
Mo(1)–C(19)–O(7)	176(2)				

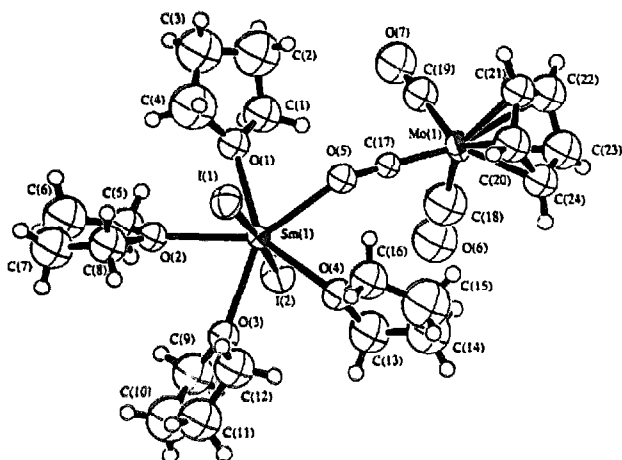


Fig. 1. A perspective view of the structure of $[(\text{THF})_4\text{I}_2\text{Sm}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ **1** with atomic numbering scheme.

has been characterized by both spectroscopic and crystallographic methods. A perspective view of complex **1** is presented in Fig. 1. The central samarium atom is coordinated to five oxygen atoms, of which four come from THF molecules and one isocarbonyl ligand. Together with two iodide ligands, they form a pentagonal-bipyramidal structure surrounding the samarium atom with the oxygen atoms in the equatorial pentagonal plane and the iodide ligands in two apical positions. The average bond distances $\text{Sm}-\text{I}$ [3.048(2) Å] and $\text{Sm}-\text{O}(\text{THF})$ [2.45(2) Å] are significantly shorter than the corresponding average bond distances in complexes $\text{SmI}_2(\text{THF})_2(\text{DME})_2$ [3.246(1) and 2.530(5) Å] and $\text{SmI}_2(\text{THF})_3(\text{DME})$ [3.233(1) and 2.571(4) Å] [37], which provides further evidence that the samarium ion in **1** is trivalent. The five oxygen atoms and Sm^{3+} are almost coplanar, with maximum deviation 0.08 Å. The $\text{I}-\text{Sm}-\text{I}$ angle is essentially linear [174.35(8)°], and 10 $\text{I}-\text{Sm}-\text{O}$ angles fall into a narrow range of 86.6(4)°–94.6(4)°, close to 90°. The five $\text{O}-\text{Sm}-\text{O}$ angles for adjacent oxygen atoms are in the range 70.8(5)°–73.8(5)°, with mean value 72.04°. The bond distance $\text{Sm}-\text{O}(5)$ [isocarbonyl 2.41(2) Å] is slightly shorter than other bond distances $\text{Sm}-\text{O}(1-4)$ [ranging from 2.42(2)

to 2.49(2) Å, average value 2.45(2) Å], and the distance $\text{C}(17)-\text{Mo}(1)$ [1.82(3) Å] is also shorter than $\text{C}(19)-\text{Mo}(1)$ [1.91(3) Å] and $\text{C}(18)-\text{Mo}(1)$ [1.93(3) Å]. The distance $\text{O}(5)-\text{C}(17)$ [1.22(2) Å] is elongated compared with $\text{C}(18)-\text{O}(6)$ [1.14(3) Å] and $\text{C}(19)-\text{O}(7)$ [1.17(3) Å]. This suggests weakening of the CO bond upon coordination to both samarium and molybdenum centers. Similar observations have been made in other complexes containing an isocarbonyl linkage [3,27]. The distance $\text{O}(5)-\text{C}(17)$ is also slightly longer than the corresponding bond distances in $[(\text{HMPA})_4\text{Yb}(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ **3** [mean value 1.17(3) Å] and $[\text{Yb}(\text{HMPA})_3(\mu\text{-OC})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)][(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2 \cdot \text{THF}$ **4** [1.15(3) Å], probably because of the stronger oxophilicity of Sm^{3+} in **1** than that of the Yb ion in **3** and **4**.

To investigate if this method is applicable to other Cp derivatives, we have prepared the compound $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$ by a modified procedure [28] and studied its reaction with $\text{SmI}_2(\text{THF})_x$. However, the reaction is relatively slow and gives $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2$ **2** in moderate yield (30%) instead of the expected isocarbonyl linked analog of **1**. The homogeneity of bulk material in **2** was checked by solution IR spectroscopy. The complex **2** has been synthesized through reacting $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2]_2$ with carbon monoxide in isooctane solution [38]. However, its crystal and molecular structure remain unknown. Therefore, single crystals of **2** have been subjected to X-ray analysis.

As shown in Fig. 2, the molecular geometry can involve a pseudo-square-pyramidal configuration with the C_5Me_5 ring occupying the apical position and three carbonyl ligands and the metal–metal bond completing the square base. The dimer is related by a crystallographic inversion center which requires an *anti* rotational configuration between the two “ $(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3$ ” units. The structural parameters of **2** are essentially identical to those in $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ [39], except for a slightly longer Mo–Mo distance (3.284(1) Å for **2**, 3.235(1) Å for $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$) and a small difference in the $\text{C}(1)-\text{Mo}(1)-\text{C}(3)$ angle (113.5(3)° in

Table 5
Selected bond distances (Å) and angles (°) in **2**

Distances					
$\text{Mo}(1)-\text{Mo}(1)^a$	3.284(1)	$\text{Mo}(1)-\text{C}(1)$	1.967(9)	$\text{Mo}(1)-\text{C}(2)$	1.959(9)
$\text{Mo}(1)-\text{C}(3)$	2.003(8)	$\text{Mo}(1)-\text{C}(4)$	2.300(7)	$\text{Mo}(1)-\text{C}(5)$	2.368(8)
$\text{Mo}(1)-\text{C}(6)$	2.424(7)	$\text{Mo}(1)-\text{C}(7)$	2.370(7)	$\text{Mo}(1)-\text{C}(8)$	2.303(7)
$\text{O}(1)-\text{C}(1)$	1.153(9)	$\text{O}(2)-\text{C}(2)$	1.134(9)	$\text{O}(3)-\text{C}(3)$	1.127(8)
Angles					
$\text{Mo}(1)^a-\text{Mo}(1)-\text{C}(1)$	74.9(2)	$\text{Mo}(1)-\text{Mo}(1)-\text{C}(2)$	121.4(2)		
$\text{Mo}(1)-\text{Mo}(1)-\text{C}(3)$	67.6(2)	$\text{C}(1)-\text{Mo}(1)-\text{C}(2)$	77.5(3)		
$\text{C}(1)-\text{Mo}(1)-\text{C}(3)$	113.5(3)	$\text{C}(2)-\text{Mo}(1)-\text{C}(3)$	78.1(3)		
$\text{Mo}(1)-\text{C}(1)-\text{O}(1)$	170.8(8)	$\text{Mo}(1)-\text{C}(2)-\text{O}(2)$	177.8(8)		
$\text{Mo}(1)-\text{C}(3)-\text{O}(3)$	167.1(7)				

^a Symmetry code $-x, -y, 1-z$.

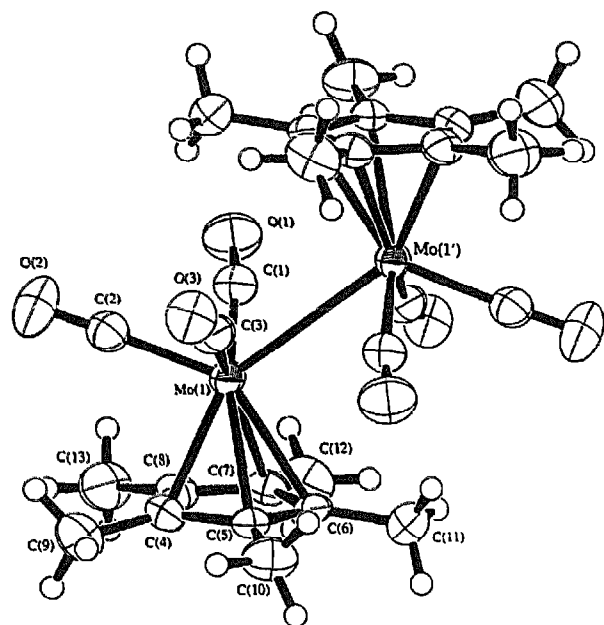


Fig. 2. The molecular structure of $[(C_5Me_5)Mo(CO)_3]_2$ **2** with atomic numbering scheme.

2, $105.9(1)^\circ$ in $[(C_5H_5)Mo(CO)_3]_2$). The formation of **2** probably occurs via the combination of " $[(C_5H_5)Mo(CO)_3]$ " radicals generated by the reduction. However, the marked difference in reactivity between $[(C_5H_5)Mo(CO)_3]_2Hg$ and $[(C_5Me_5)Mo(CO)_3]_2Hg$ is not fully understood.

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