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Note

The preparation and crystal structure of $(\eta^5\text{-}C_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$

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Abstract

The reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ with $p\text{-}CH_3C_6H_4S(O)_2O(CH_2)_3C_6H_5$ produces $(\eta^5\text{-}C_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$. This is only the second structurally characterized organometallic species in which an aromatic moiety is separated by three or more methylene groups. The alkyl chain adopts a staggered conformation, the Mo–C(1)–C(2)–C(3)–C(4) unit is nearly coplanar, and the alkyl chain eclipses the *trans*-carbonyl group on Mo. NMR evidence indicates that this conformation is preserved in solution.
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1. Introduction

$(\eta^5\text{-}C_5H_5)(OC)_3Mo\text{–}R$ complexes are precursors to organomolybdenum dioxo species that are active epoxidation catalysts [1]. Recently, there has been interest in grafting the $(\eta^5\text{-}C_5H_5)(OC)_3Mo$- group to a solid support through the R group, thus forming precursors to heterogeneous catalysts [1–3]. To a large extent these studies have focused on R groups that terminate in siloxane functionalities. However, such compounds have proven to be sensitive and somewhat difficult to handle [4]. As an alternative, we are interested in complexes that contain a $(\eta^5\text{-}C_5H_5)(OC)_3Mo$-fragment separated from an aromatic moiety by a flexible methylene chain. These species should be relatively easily manipulated and could be heterogenized by attachment to a support through substituents on the aromatic ring.

We were surprised that metal complexes containing several methylene groups bonded to an aromatic ring are rare. The only structurally characterized example that contains three or more methylene groups is $(R_3P)_2(Br)Pd\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}C_6H_5$ [5]. In fact, $(\eta^5\text{-}C_5H_5)(OC)_3M\text{–}(CH_2)_n\text{–}C_6H_5$, derivatives with more than a single methylene group are unknown for Mo or Cr. With W the compound with two methylene groups is known [6], but not with three or more. Moreover, there are only limited reports on $(\eta^5\text{-}C_5H_5)(OC)_3M\text{–}R$ (M = Cr, Mo, or W) where R is the *n*-propyl or a longer chain *n*-alkyl and there are no structures except for $(\eta^5\text{-}C_5H_5)(OC)_3W(CH_2)_3Br$ [7], $(\eta^5\text{-}C_5H_5)(OC)_3W(CH_2)_5I$ [7], $(\eta^5\text{-}C_5H_5)(OC)_3W(CH_2)_3CO_2H$ [8], and the related $(\eta^5\text{-}C_5H_5)(OC)_2(Ph_3P)Mo(CH_2)_3I$ [7]. In the course of our studies, we have prepared $(\eta^5\text{-}C_5H_5)(OC)_3Mo\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}C_6H_5$. As this complex is the model for a series of related derivatives that should be amendable to being heterogenized, we report its preparation and structure.

2. Experimental

2.1. Materials and methods

Infrared (IR) spectra were obtained as KBr pellets using an MIDAC Corporation M2000 FTIR. Nuclear Magnetic Resonance spectra were obtained with Bruker-Ace 200 and 400 MHz spectrometers. Chemical shifts for ^1H NMR and

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^{13}C NMR were reported in ppm downfield from tetramethylsilane (δ scale). Reactants and reagents were obtained from Aldrich Chemical Company. Solvents were dried and purified by appropriate means before use. All manipulations were performed under a dry nitrogen or argon atmosphere in a Vacuum Atmosphere Dry Box or by using Schlenk techniques. Since several of the reagents and the product are somewhat light sensitive, light was excluded whenever possible.

2.1.1. Synthesis of 3-phenylpropyl p-toluenesulfonate

A modification of the procedure described by Dishong was used [9]. In a nitrogen atmosphere, *p*-toluenesulfonylchloride (2.9 g, 15 mmol) was dissolved in 3 mL pyridine. This solution was cooled in an ice bath for 15 min and added to 3-phenyl-1-propanol (2.0 g, 15 mmol) in a 50 mL round bottomed flask. After stirring for 1 h the resulting solution was transferred to a 125 mL separatory funnel, 3 mL water was added, and the mixture extracted with dichloromethane (3 × 5 mL). Following extraction with ice cold 6 N HCl (3 × 5 mL) and 10 mL ice cold saturated NaCl solution, the organic phase was dried over magnesium sulfate. Following filtration, the solvent was evaporated under vacuum leaving a clear oil of 3-phenylpropyl *p*-toluenesulfonate (3.8 g, 13 mmol, 89% yield). ^{13}C ($CDCl_3$) δ: 21.7 ($–CH_2\mathit{C}H_2CH_2–$); 30.5 ($\mathit{C}H_3$); 31.9 ($Ar–\mathit{C}H_2–$); 69.7 ($\mathit{C}H_2–OTs$); 126.2, 127.9, 128.4, 128.5, 129.9, 133.1, 140.4, 144.9 (C_{Ar}). ^1H ($CDCl_3$) δ: 2.0 (m, $–CH_2C\mathit{H}_2CH_2OTs$, $^3J = 7.7$ Hz, $^3J = 6.3$ Hz); 2.5 (s, $C\mathit{H}_3$); 2.7 (t, $C\mathit{H}_2CH_2CH_2OTs$, $^3J = 7.7$ Hz); 4.1 (t, $CH_2CH_2C\mathit{H}_2OTs$, $^3J = 6.3$ Hz); 7.1–7.8 (m, Ar).

Table 1
Crystal data and structure refinement for $(\eta^5-C_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$

Empirical formula	$C_{17}H_{16}MoO_3$
Formula weight	364.24
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *P*bca
Unit cell dimensions	
a (Å)	9.8238(15)
b (Å)	17.8302(18)
c (Å)	17.9747(18)
Volume (Å^3)	3148.5(7)
Z, calculated density (Mg/m^3)	8, 1.537
Absorption coefficient (mm^{-1})	0.839
F(000)	1472
Crystal size (mm)	0.94 × 0.39 × 0.08
θ Range for data collection (°)	3.07–25.00
Limiting indices	$-11 <= h <= 3$, $-21 <= k <= 1$, $-21 <= l <= 2$
Reflections collected/unique [R_{int}]	3699/2759 [0.0161]
Completeness to theta = 25.00	99.6%
Absorption correction	SADABS
Maximum and minimum transmission	0.97 and 0.77
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2759/0/190
Goodness-of-fit on F^2	0.897
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0237$, $wR_2 = 0.0550$
R indices (all data)	$R_1 = 0.0357$, $wR_2 = 0.0577$
Largest difference in peak and hole (e A^{-3})	0.300 and −0.622

2.1.2. Synthesis of $(\eta^5-C_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$(12)

In a 250 mL three necked round bottomed flask, 100 mL freshly distilled THF, 2 M sodium cyclopentadienylide (7.5 mL, 15 mmol), and molybdenum hexacarbonyl (3.8 g, 15 mmol) were added sequentially. The reaction

Table 2
Bond lengths (Å) and angles (°) for $(\eta^5-C_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$

Bond lengths			
Mo–C(16)	1.982(3)	C(3)–C(4)	1.501(3)
Mo–C(15)	1.983(3)	O(3)–C(17)	1.142(3)
Mo–C(17)	1.988(3)	C(4)–C(5)	1.379(3)
Mo–C(13)	2.321(2)	C(4)–C(9)	1.395(3)
Mo–C(14)	2.323(2)	C(5)–C(6)	1.388(4)
Mo–C(10)	2.339(3)	C(6)–C(7)	1.384(4)
Mo–C(1)	2.341(2)	C(7)–C(8)	1.379(4)
Mo–C(12)	2.355(2)	C(8)–C(9)	1.377(3)
Mo–C(11)	2.360(3)	C(10)–C(14)	1.407(4)
O(1)–C(15)	1.144(3)	C(10)–C(11)	1.418(4)
C(1)–C(2)	1.511(3)	C(11)–C(12)	1.382(4)
O(2)–C(16)	1.142(3)	C(12)–C(13)	1.402(4)
C(2)–C(3)	1.540(3)	C(13)–C(14)	1.399(4)
Bond angles			
C(16)–Mo–C(15)	105.98(10)	C(16)–Mo–C(11)	120.70(12)
C(16)–Mo–C(17)	78.27(10)	C(15)–Mo–C(11)	115.26(11)
C(15)–Mo–C(17)	80.50(11)	C(17)–Mo–C(11)	146.58(10)
C(16)–Mo–C(13)	139.69(10)	C(13)–Mo–C(11)	57.60(10)
C(15)–Mo–C(13)	109.80(9)	C(14)–Mo–C(11)	58.04(9)
C(17)–Mo–C(13)	89.81(10)	C(10)–Mo–C(11)	35.14(10)
C(16)–Mo–C(14)	106.16(9)	C(1)–Mo–C(11)	79.64(9)
C(15)–Mo–C(14)	144.46(9)	C(12)–Mo–C(11)	34.09(10)
C(17)–Mo–C(14)	91.55(9)	C(2)–C(1)–Mo	122.70(15)
C(13)–Mo–C(14)	35.07(9)	C(1)–C(2)–C(3)	112.23(19)
C(16)–Mo–C(10)	96.74(10)	C(4)–C(3)–C(2)	111.54(19)
C(15)–Mo–C(10)	150.36(10)	C(5)–C(4)–C(9)	117.8(2)
C(17)–Mo–C(10)	123.42(10)	C(5)–C(4)–C(3)	121.0(2)
C(13)–Mo–C(10)	58.32(10)	C(9)–C(4)–C(3)	121.0(2)
C(14)–Mo–C(10)	35.14(9)	C(4)–C(5)–C(6)	121.5(2)
C(16)–Mo–C(1)	74.55(9)	C(7)–C(6)–C(5)	119.7(3)
C(15)–Mo–C(1)	72.10(9)	C(8)–C(7)–C(6)	119.4(2)
C(17)–Mo–C(1)	133.72(9)	C(9)–C(8)–C(7)	120.4(3)
C(13)–Mo–C(1)	134.16(9)	C(8)–C(9)–C(4)	121.1(2)
C(14)–Mo–C(1)	131.66(9)	C(14)–C(10)–C(11)	107.0(3)
C(10)–Mo–C(1)	96.61(9)	C(14)–C(10)–Mo	71.82(15)
C(16)–Mo–C(12)	153.74(12)	C(11)–C(10)–Mo	73.24(15)
C(15)–Mo–C(12)	96.19(10)	C(12)–C(11)–C(10)	108.5(2)
C(17)–Mo–C(12)	119.95(11)	C(12)–C(11)–Mo	72.76(16)
C(13)–Mo–C(12)	34.88(10)	C(10)–C(11)–Mo	71.62(15)
C(14)–Mo–C(12)	58.04(9)	C(11)–C(12)–C(13)	108.2(2)
C(10)–Mo–C(12)	57.92(10)	C(11)–C(12)–Mo	73.15(15)
C(1)–Mo–C(12)	99.84(9)	C(13)–C(12)–Mo	71.25(14)
C(14)–C(13)–C(12)	108.2(2)		
C(14)–C(13)–Mo	72.54(14)		
C(12)–C(13)–Mo	73.87(14)		
C(13)–C(14)–C(10)	108.0(2)		
C(13)–C(14)–Mo	72.39(13)		
C(10)–C(14)–Mo	73.04(14)		
O(1)–C(15)–Mo	176.8(2)		
O(2)–C(16)–Mo	178.6(2)		
O(3)–C(17)–Mo	178.8(2)		

mixture was refluxed for approximately 4.5 h under a dinitrogen atmosphere and in the absence of light. A color change from light pink to translucent orange was observed before reflux. After cooling 3-phenylpropyl *p*-toluenesulfonate (3.8 g, 13 mmol) in 20 mL THF was added dropwise over a period of a several minutes. During the addition the color changed from orange to red–orange. After stirring overnight, the THF was evaporated. The resulting viscous liquid was purified by chromatography through an alumina column using 80/20 hexanes/ethyl acetate. Following evaporation of the solvent from the red fraction, the resulting solid was washed with hexanes to yield yellow $(\eta^5\text{-C}_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$ (2.0 g, 5.4 mmol, 41%). ^{13}C (THF-d_8) δ: 1.5 (Mo*C*H_2); 38.7 ($MoCH_2$*C*H_2); 41.7 ($MoCH_2CH_2$*C*H_2–); 93.1 (C_{CP}); 125.3–166.7 (C_{Ar}); 228.2 (CO_{cis}); 240.4 (CO_{trans}). ^1H (THF-d_8) δ: 1.7 (m, MoC*H*$_2$); 2.0 (m, $MoCH_2C$*H*$_2$); 2.7 (t, $MoCH_2CH_2C$*H*$_2$); 5.4 (s, Cp); 7.2–7.7 (m, Ar). The Mo–CH_2–CH_2–CH_2 portion of the ^1H spectrum can be closely simulated [10] as $AA'BB'C_2$ spin system with the following parameters: $\delta_A = \delta_{A'} = 1.7$ ppm, $\delta_B = \delta_{B'} = 2.0$ ppm, $\delta_C = 2.7$ ppm, $J_{AA'} = -19$ Hz, $J_{AB} = 3$ Hz, $J_{AB'} = 10$ Hz, $J_{AC} = J_{A'C} = 0$ Hz, $J_{BB'} = -14$ Hz, $J_{BC} = J_{B'C} = 7$ Hz, $J_{CC} = -15$ Hz. IR: 1920 (C≡O); 2014 (C≡O) cm^{-1}. X-ray quality crystals were obtained by recrystallization from hexanes. (Considerably lower yields of $(\eta^5\text{-C}_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$ were obtained from reactions of $Na[CpMo(CO)_3]$ with $X(CH_2)_3C_6H_5$ where X = Cl or Br [11].)

2.1.3. Single crystal X-ray diffraction

The measurement was performed using a Siemens SMART CCD system with Mo K_α X-radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Selected crystals of $(\eta^5\text{-C}_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$ were coated with mineral oil, mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment). Data were collected at 173 K. A full hemisphere of the reciprocal space was scanned by ω in three sets of frames of 0.3°. As an absorption correction the SADABS routine was applied. The structures were solved by direct methods using SHELXTL and refined using SHELX-97 [12,13]. Refinement was by full-matrix least-squares on F^2. The crystal, data collection and refinement information are summarized in Table 1 and bond lengths and bond angles in Table 2. A perspective drawing of the molecule is shown in Fig. 1.

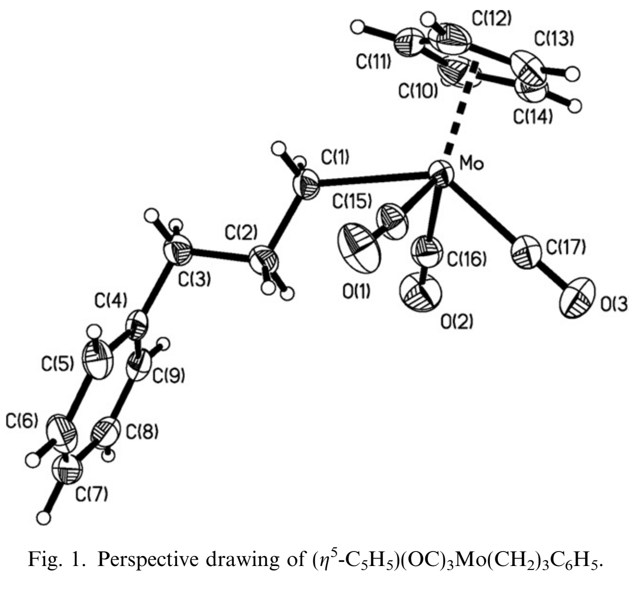
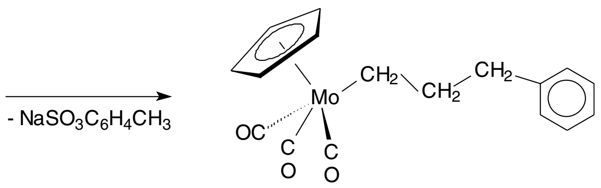


Fig. 1. Perspective drawing of $(\eta^5\text{-C}_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$.

3. Results and discussion

The reaction of $(\eta^5\text{-C}_5H_5)Mo(CO)_3^-$ with $p\text{-}CH_3C_6H_4S(O)_2O(CH_2)_3C_6H_5$ produces $(\eta^5\text{-C}_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$ in about 40% yield:

$Na[(\eta^5\text{-C}_5H_5)Mo(CO)_3] + p\text{-}CH_3C_6H_4S(O)_2O(CH_2)_3C_6H_5$



While the compound is stable for long periods when stored in the dark under an inert atmosphere, it slowly decomposes when exposed to light. In our hands, higher yields were obtained when the reaction was run in the dark.

The alkyl chain in $(\eta^5\text{-C}_5H_5)(OC)_3Mo(CH_2)_3C_6H_5$ adopts a staggered conformation, with Mo–C(1)–C(2)–C(3) and C(1)–C(2)–C(3)–C(4) dihedral angles of 178.03(16)° and 179.7(2)°, respectively. The phenyl ring is nearly perpendicular to the plane of aliphatic carbons with C(2)–C(3)–C(4)–C(5) and C(2)–C(3)–C(4)–C(9) dihedral angles of 89.1(3)° and 87.3(3)°, respectively. Notably, the C(17)–Mo–C(1)–C(2) dihedral angle of 2.5(3)° indicates that the alkyl chain eclipses the *trans*-carbonyl group. While there is a similar conformation in $(\eta^5\text{-C}_5H_5)(OC)_3W(CH_2)_5I$ [7], in the other structurally characterized complexes that contain a three carbon aliphatic chain: $(\eta^5\text{-C}_5H_5)(OC)_3W(CH_2)_3CO_2H$ [8], $(\eta^5\text{-C}_5H_5)(OC)_3W(CH_2)_3Br$ and *trans*-$(\eta^5\text{-C}_5H_5)(Ph_3P)(OC)_3Mo\ (CH_2)_3I$ [7], the plane of the alkyl chain is staggered with respect to the *trans* ligand.

The ^1H NMR spectrum of methylene chain appears as a $AA'BB'C_2$ pattern. If the conformation observed in the crystal structure is predominant in solution, even rapid rotation about the Mo–C and the C–C bonds would not exchange the two methylene protons on C(1) and on C(2). Thus, if the solid state conformation is preserved in solution an $AA'BB'C_2$ spectrum is expected. On the other hand, the protons within respective methylene groups would exchange during rapid rotation if the conformation is similar to the ones in $C_5H_5)(OC)_3W(CH_2)_3CO_2H$ [8], $(\eta^5\text{-C}_5H_5)(OC)_3W(CH_2)_3Br$ and *trans*-$(\eta^5\text{-C}_5H_5)(Ph_3P)(OC)_3Mo(CH_2)_3I$ [7]. Thus, the fact that a simple $A_2B_2C_2$ spectrum is not observed indicates that the conformation of the Mo–CH_2–CH_2–R moiety observed in the crystal structure likely is predominant in solution. Based on this conformation the most suitable congeners for heterogenizing may be ones with suitable para substituents.

4. Supplementary data

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 610219 for (η^5-C_5H_5)$(OC)_3Mo(CH_2)_3C_6H_5$. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44 1223 336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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