

Transition Metal Carbonyl Compounds Containing Intramolecular Nucleophiles: Crystal Structure of $[(\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2)_3\text{-OH)Mo(CO)}_3]_2$

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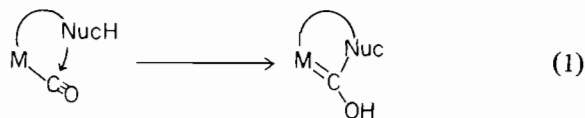
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Abstract

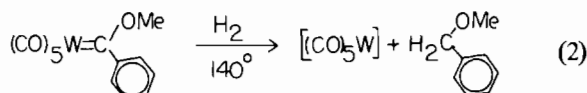
Compounds of the form $[(\eta^5\text{-C}_5\text{H}_4\text{R)Mo(CO)}_3]_2$, where R is a pendant alcohol (or its triphenylmethyl ether), were synthesized. There is no indication of nucleophilic interaction between the alcohol and the carbonyl ligands. The X-ray structure of the compound, where R = $-(\text{CH}_2)_3\text{-OH}$, was solved by heavy atom and Fourier methods (space group $P\bar{1}$, $a = 7.487(3)$ Å, $b = 7.713(3)$ Å, $c = 10.902(7)$ Å, $\alpha = 99.36(4)^\circ$, $\beta = 81.46(4)^\circ$, $\gamma = 115.26(3)^\circ$, $V = 563.0(10)$ Å³, $Z = 1$), and refined by full-matrix least-squares to S (goodness of fit) = 1.47 and $R = 0.057$ (3087 reflections). The alcohol group was found to be situated away from the carbonyl groups, involved in a weak intermolecular hydrogen bond.

Introduction

In an effort to explore the possibilities of activation of coordinated carbon-monoxide to reduction, bifunctional catalysts are attractive. The intramolecular delivery of a nucleophile to a coordinated carbonyl ligand may result in a system in which organic products may be obtained under relatively mild conditions. In particular, the reaction of a tethered nucleophile to give a carbene product is of interest (eqn. 1).



It is known that organometallic carbenes may be hydrogenated to yield the reduced CO derived fragment as in the reaction of a W carbene (eqn. 2) to form benzylmethyl ether [1].



Results and Discussion

A reasonable means of incorporating a nucleophile into a transition metal carbonyl compound is by the use of substituted cyclopentadienyl complexes. Some work has been done utilizing substituted arene chromium tricarbonyl compounds but no evidence for intramolecular nucleophilic attack at CO was observed [2]. Additionally, reaction of the arene ligands was observed in one case to occur most probably via reductive coupling [2]. As such cyclopentadienyl compounds were chosen because of their general stability upon metal complexation, as well as there being numerous Cp complexes known that undergo nucleophilic attack at the carbonyl ligands [3]. The cyclopentadienyl complex is also attractive in that numerous examples of the synthesis of substituted Cp ligands and their transition metal complexes exist [4]. The range of these Cp-transition metal compounds is wide, thus offering many avenues to explore.

In the present work the nucleophiles under consideration are oxygen-containing. The first complexes examined were $[\text{CpR}(\text{Mo}(\text{CO})_3)_2]$ compounds where R = $-(\text{CH}_2)_2\text{-OH}$ and $-(\text{CH}_2)_3\text{-OH}^\dagger$. The syntheses are straightforward and yield suitable amounts of the desired material (the yields are somewhat lower than that of the parent compound owing to the use of one equivalent of $\text{C}_5\text{H}_5\text{R}$ rather than excess). Unfortunately, the infra-red spectra in the carbonyl stretching range reveals nothing indicative of a nucleophilic interaction between

[†]Group VI is a viable choice since numerous examples of Cp compounds, including those containing carbenes, are known. Recently several bimetallic compounds containing a carbene were reported including the complex, $\text{Cp}(\text{CO})_3\text{Mo}-\text{MoCp}(\text{CO})_2(=\text{CO}-\text{CH}_2)_3$ [5].

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TABLE I. IR Stretching Frequencies of $[(\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2\text{)}_n\text{-OHMo(CO)}_3)_2]$.

n	ν_{CO} , (cm ⁻¹) ^a		
Parent	2020(w)	1955(s)	1915(s)
2	2002(w)	1953(s)	1908(s)
3	2000(w)	1955(s)	1912(s)
2 (trityl ether)	2040(w)	1955(s)	1915(s)

^aCH₂Cl₂ solution.

the alcohol and the Mo(CO)₃ fragment. In fact, the $\nu(\text{CO})$ region looks quite similar for the parent compound, the alcohol substituted compounds and the triphenylmethyl ether of the ethanol substituted complex (Table I). As such it appears that no significant interaction has occurred.

In an effort to generate a stronger nucleophile and thereby induce attack at the carbonyl, the hydroxyethyl-cyclopentadienyl compound was treated with bases such as sodium hydride and sodium methoxide. The only observed product was the tri-carbonyl anion obtained from simple reductive

TABLE III. Atom Coordinates ($\times 10^4$) and U_{eq} 's ($\text{\AA}^2, \times 10^4$).

	x	y	z	U_{eq}
Mo	4111.5(4)	126.9(4)	1430.3(3)	370
C(1)	1849(5)	-1132(5)	383(3)	450
O(1)	439(4)	-1904(4)	-134(2)	637
C(2)	5625(5)	2738(5)	908(3)	468
O(2)	6485(4)	4330(4)	728(2)	651
C(3)	2441(5)	1453(5)	2194(3)	485
O(3)	1493(4)	2259(4)	2685(3)	720
C(4)	-2508(8)	-4042(9)	4028(5)	965
O(41)	-2765(10)	-5098(10)	4870(7)	807 ^a
O(41)	-3082(15)	-2813(15)	4362(9)	954 ^a
O(43)	-4023(27)	-4827(24)	3627(16)	908 ^a
C(5)	-522(6)	-3512(7)	3233(4)	771
C(6)	1203(6)	-2157(6)	3933(3)	582
C(7)	3192(5)	-1573(5)	3171(3)	474
C(8)	3801(5)	-2693(5)	2187(3)	491
C(9)	5835(6)	-1640(6)	1848(3)	513
C(10)	6497(5)	126(6)	2602(4)	534
C(11)	4878(6)	179(5)	3417(3)	521

^aRefined Using Isotropic U 's. The populations were: O41, 44.0%; O42, 35.7%; O43, 20.3%.

TABLE II. Summary of Data Collection and Refinement Parameters.

Formula	C ₂₂ H ₂₂ O ₈ Mo ₂	
Formula weight	606.30	
Space group	$P\bar{1}$	
<i>a</i>	7.487(3) Å	
<i>b</i>	7.713(3) Å	
<i>c</i>	10.902(7) Å	
α	99.36(4) ^o	
β	81.46(4) ^o	
γ	115.26(3) ^o	
<i>V</i>	563.0(10) Å ³	
<i>Z</i>	1	
<i>D_{calc}</i>	1.789 g/cm ³	
Crystal size	0.050 × 0.250 × 0.800 mm	
λ	0.7107 Å	
μ	5.10 mm ⁻¹	
2 θ limits	4–56 ^o	56–60 ^o
Scan rate	2.02 ^o /min	0.99 ^o /min
Bkgrd-to-scan time ratio	1.0	0.5
Scan width	1.1 ^o	1.2 ^o above $K\alpha_2$
	1.1 ^o	1.2 ^o below $K\alpha_1$
Number of reflections	5780	1198
Total number of averaged data	3283	
Final agreement ^a		
R_F	0.057(3087)	
R'_F	0.039(2374)	
<i>S</i>	1.47(3283)	

^aDefined in the experimental section; number of reflections given in parentheses.

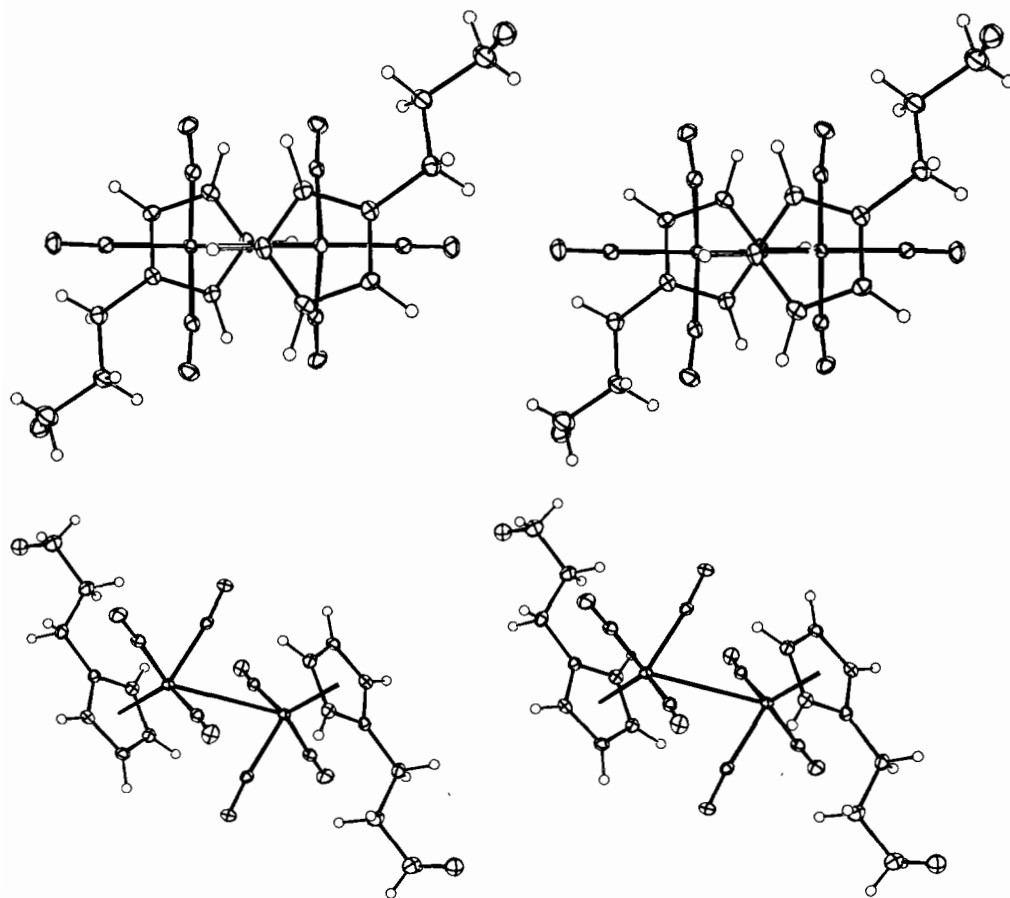


Fig. 1. Stereoview of ORTEP of $[(\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2)_3\text{OH)Mo(CO)}_3]_2$. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

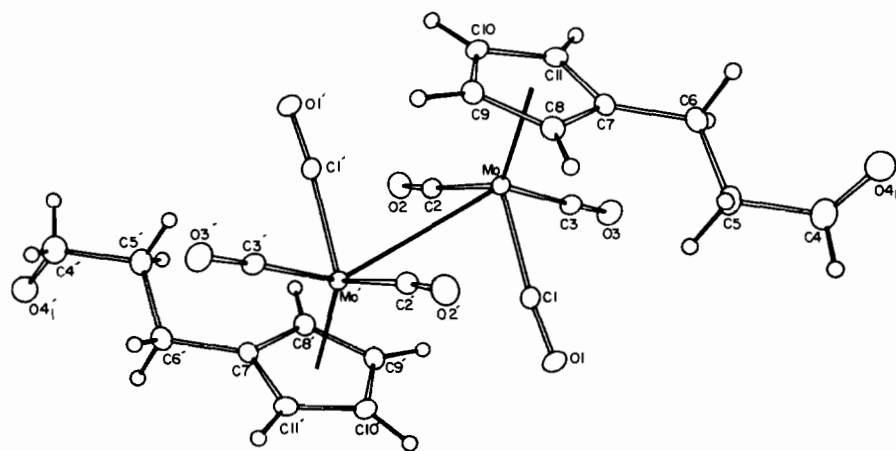


Fig. 2. Atom labelling scheme for $[(\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2)_3\text{OH)Mo(CO)}_3]_2$.

cleavage of the metal-metal bond in a manner similar to the well known amalgam reduction.

Even though no direct nucleophilic interaction occurs, the substituted dimers provide a system in which the preferred orientation of an unconstrained substituted Cp in a 'four-legged piano stool' complex

may be examined. With this in mind, a single crystal of $[\text{Cp}-(\text{CH}_2)_3\text{-OHMo(CO)}_3]_2$ was obtained and an X-ray structure determined. The pertinent collection data are given in Table II and the atom coordinates are given in Table III. Figure 1 shows a stereoview of the complex and Figs. 2 and 3 show

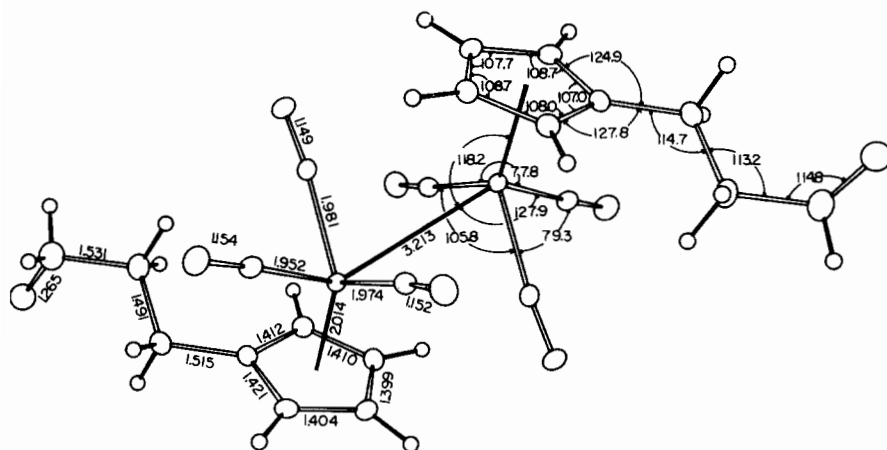


Fig. 3. Selected bond lengths and angles for the structure of $[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{OH})\text{Mo}(\text{CO})_3]_2$ (esd's are approx. 0.008 Å and 0.4° respectively).

TABLE IV. Best Least Square Plane and Torsion Angles.

Atom	Dev. ^a
C(7)	0.003
C(8)	-0.002
C(9)	0.001
C(10)	0.000
C(11)	-0.002
Mo	-2.013
C(6)	0.136
Atoms	Angle ($^\circ$)
C(8)-C(7)-C(6)-C(5)	-33.4(6)
C(11)-C(7)-C(6)-C(5)	153.7(4)
C(7)-C(6)-C(5)-C(4)	-179.0(4)
C(6)-C(5)-C(4)-O(41)	-69.7(7)
C(6)-C(5)-C(4)-O(42)	67.5(9)
C(6)-C(5)-C(4)-O(43)	168.1(12)

^aDeviation in Å from best Cp plane (C(7) through C(11)).

the atom labelling scheme and bond lengths and angles.

The structural framework is similar to that of the parent compound [6]. The cyclopentadienyl ligand is tipped only slightly (1.61°) with respect to the Cp centroid-Mo axis and there is little deviation of the ring carbons (≤ 0.003 Å) or C(6) (0.146 Å) from planarity (Table IV). Additionally, the pendent arm has adopted a low energy staggered conformation with a C(7)-C(6)-C(5)-C(4) torsion of $179.0(4)^\circ$ (Table IV). The hydroxyl groups form an intermolecular chain with hydrogen bonds directed approximately parallel to the x-axis and $\text{O}\cdots\text{O}'$ contacts ranging from 2.69 to 3.38 Å [7].

The arm connecting the alcohol to the Cp is of sufficient length to span the distance to the carbonyl ligands, and implies that the driving force is insuffi-

cient to induce nucleophilic attack. Surprisingly, an infra-red dilution study shows the presence of no intramolecular H bonding to the metal-carbonyl moiety. A neutral chromium indanol complex has been shown to possess just such an interaction between the alcohol and carbonyl groups (Fig. 5) [8, 9]*. Perhaps the length of the pendant arm is too great for a favorable interaction since many orientations are possible; the orientation of the chromium complex is well suited to interaction of the two groups. In related cationic complexes cyclic metallo-lactones can be prepared, but even in those cases it appears that the $-(\text{CH}_2)_3-$ arm is too long for significant interaction.

To conclude, it has been demonstrated that well defined systems containing intramolecular nucleophiles are available. The electronic situation is such, however, in the present molybdenum dimers as to disfavor nucleophilic attack at CO either by the alcohol or by an alkoxide. The metal-metal bond is the most reactive site present. Work on other systems possessing no metal-metal bond as well as a cationic charge on the metal center possess more promising characteristics, such as higher CO stretching frequencies, and will be reported elsewhere [11].

Experimental

$\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ were purchased from the Pressure Chemical Company. All reactions were carried out using standard Schlenk techniques. Argon used in Schlenk work was purified by passage

*Normally free -OH exhibits a stretch at $3650\text{--}3584\text{ cm}^{-1}$ [10].

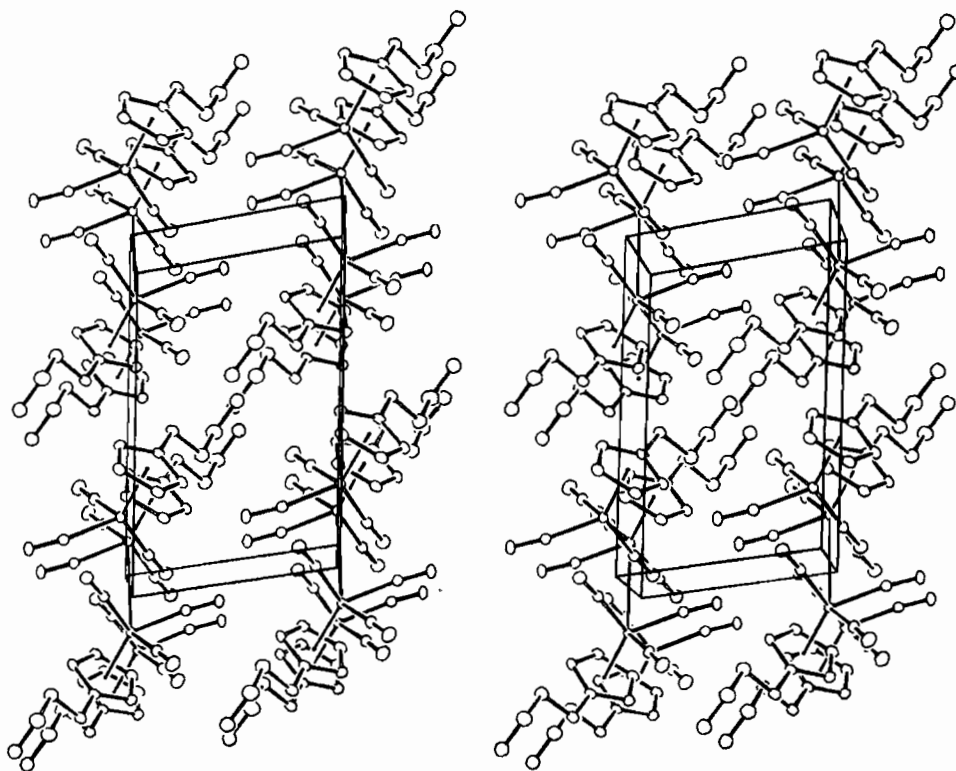


Fig. 4. Stereoview of ORTEP diagram showing the unit cell of $[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{OH)Mo(CO)}_3]_2$.

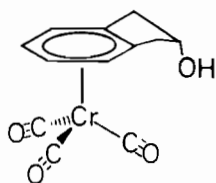


Fig. 5. A chromium indanol complex.

through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. Manipulations were also performed using a Vacuum Atmospheres dry box with nitrogen atmosphere. Toluene, benzene and THF were vacuum transferred from sodium-benzophenone ketyl. Methylene chloride was stirred over P_2O_5 and acetone was dried over 4 Å molecular sieves prior to use. Infra-red spectra were obtained from a Perkin-Elmer 257 grating instrument and a Beckman model IR 4240 spectrometer referenced to the 1601 cm^{-1} stretch of polystyrene. FT IR spectra obtained for the dilution study were recorded on a Mattson Sirius 100 instrument. Continuous wave NMR spectra were recorded on a Varian EM-390 instrument with an ambient probe temperature of 34°C . Fourier transform ^1H spectra were taken on a JEOL FX-90Q spectrometer operating at 89.56 MHz with a probe temperature of 25°C . Melting points were obtained from a Büchi melting

point apparatus with all samples placed in glass capillaries under a nitrogen atmosphere and sealed. No temperature corrections were made. Elemental analyses were performed by Schwarzkopf Micro-analytical of Woodside, New York.

Hydroxyethylcyclopentadiene

The method of Schröder was used with the substitution of potassium tert-butoxide for potassium in tert-butanol [12].

To a mixture of 5.61 g of potassium t-butoxide (0.05 mol) in 100 ml of t-butanol (dried over MgSO_4) in a large Schlenk flask under argon was added 0.5 mol of freshly distilled cyclopentadiene (41.14 ml). To this mixture, one equivalent of ethylene oxide in 20 ml of t-butanol was slowly added, the temperature of the reaction mixture being maintained at $20\text{--}25^\circ\text{C}$ by means of a water bath. The mixture was then stirred at room temperature for 4 h, during which time the color changed from red to dark gray. Following this, the reaction mixture was neutralized with 5% H_2SO_4 and extracted twice with 50 ml of petroleum ether. The extracts were then washed once with water and dried over Na_2SO_4 . A yellow solution was obtained. Solvent was then removed under reduced pressure and the resulting yellow oil was purified by Kugelrohr. The desired product was collected at

40 °C and 5 μ of Hg (5.6 g, 10.2%): ^1H NMR (CDCl_3), $\text{C}_5\text{H}_5\text{R}$ (alkenyl) 6.5–6.0 (m, 3H), $-\text{CH}_2-\text{O}$ 3.7 (t, 2H), $\text{C}_5\text{H}_5\text{R}$ (alkyl) 2.9 (d, 2H), $\text{C}_5\text{H}_5\text{CH}_2-$ 2.6 (m, 2H), $-\text{OH}$ variable (s, 1H).

Hydroxypropylcyclopentadiene

To a mixture of 0.5 mol of NaH (20 g of 60% dispersion in oil) in 150 ml of THF in a large Schlenk flask under argon was added one equivalent of freshly distilled cyclopentadiene (41.1 ml). The mixture was stirred and cooled during the addition. One equivalent of 3-bromopropanol (45.2 ml) was then added to the NaCp mixture as quickly as possible while continuing stirring and cooling. The mixture was then stirred for 2 h at room temperature, after which 150 ml of petroleum ether were added followed by slow addition of 150 ml of water. The two layers were separated and the aqueous layer was extracted twice with 50 ml of petroleum ether, these being added to the original petroleum ether layer. The combined petroleum ether fraction was then washed twice with 50 ml of water and dried over Na_2SO_4 . Solvent was then removed under reduced pressure and the resulting material was vacuum distilled. The desired product was collected at 70 °C and 1 μ of Hg (9.3 g, 15%): ^1H NMR (CDCl_3), $\text{C}_5\text{H}_5\text{R}$ (alkenyl) 6.5–5.9 (m, 3H), $-\text{CH}_2-\text{O}$ 3.6 (t, 2H), $\text{C}_5\text{H}_5\text{R}$ (alkyl) 2.9 (d, 2H), $\text{C}_5\text{H}_5-\text{CH}_2-$ 2.4 (m, 2H), $-\text{CH}_2-$ 1.8 (m, 2H), $-\text{OH}$ variable (s, 1H).

$[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_n\text{OH})\text{Mo}(\text{CO})_3]_2$ ($n = 2, 3$)

The method of King was followed with the substitution of one equivalent of the substituted cyclopentadiene for excess cyclopentadiene [13].

For $n = 2$, one equivalent of $\text{Mo}(\text{CO})_6$ and 2-hydroxyethylcyclopentadiene were refluxed in toluene under argon with stirring for 2.5 h. The mixture was then cooled to room temperature and the resulting liquid phase was transferred to another flask via a cannula, leaving unreacted hexacarbonyl behind. Solvent was removed under reduced pressure, at which point more hexacarbonyl sublimed out of the mixture. The resulting red oil was dissolved in a minimal amount of THF. Methylene chloride was then added (four times the THF volume) and the mixture was cooled to -20 °C overnight. The resulting red powder was isolated by Schlenk filtration and washed with CH_2Cl_2 followed by diethyl ether. Remaining solvent was removed under reduced pressure, leaving the product as a fine red powder (1.81 g, 17%): $n = 2$, M.P. = 155–157 °C: ^1H NMR ($(\text{CD}_3)_2\text{CO}$), CpR 5.37 (broad d, 4H), $-\text{CH}_2-\text{O}$ 3.62 (t, 2H), Cp- CH_2- 2.54 (t, 2H), $-\text{OH}$ variable (s, 1H); IR (CH_2Cl_2): ν_{CO} , 2002(w), 1953(s), 1908(s). *Anal.* Calcd. for $\text{C}_{20}\text{H}_{18}\text{Mo}_2\text{O}_8$: C 41.54; H 3.14. Found: C, 41.21; H, 3.26. $n = 3$, M.P. = 126–130 °C: ^1H NMR ($(\text{CD}_3)_2\text{CO}$), CpR 5.40 (broad d, 4H), $-\text{CH}_2-\text{O}$ 3.57 (t, 2H), Cp- CH_2- 2.53 (t, 2H),

$-\text{CH}_2-$ 1.72 (m, 2H), $-\text{OH}$ variable (s, 1H); IR (CH_2Cl_2): ν_{CO} , 1955(s), 1910(s). *Anal.* Calcd. for $\text{C}_{22}\text{H}_{22}\text{Mo}_2\text{O}_8$: C 43.58; H, 3.71. Found: C 43.93; H 3.86. $n = 2$, trityl ether* M.P. = 197–199 °C: ^1H NMR (C_6D_6), Ph 7.60–6.99 (m, 15H), CpR 4.84 (d of d, 4H), Cp- CH_2- 3.05 (t, 2H), $-\text{CH}_2-$ 2.35 (t, 2H), $-\text{OH}$ variable (s, 1H); IR (CHCl_3) ν_{CO} , 1955(s), 1915(s). *Anal.* Calcd. for $\text{C}_{58}\text{H}_{46}\text{Mo}_2\text{O}_8$: C 65.54; H, 4.17. Found: C 65.59; H 4.62.

$[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_n\text{OH})\text{Mo}(\text{CO})_3]^- \text{Na}^+$ ($n = 2, 3$)

For $n = 2$, a solution of 300 mg of $[(\text{CpCH}_2\text{-CH}_2\text{OH})\text{Mo}(\text{CO})_3]_2$ (0.52 mmol) in 60 ml of THF was stirred over excess sodium amalgam (2.1 mmol of Na in 1.5 ml of Hg) under argon at room temperature. After 75 min, the red solution had changed to a pale gold. The solution was transferred away from the amalgam *via* a cannula and filtered on a Schlenk frit. A clear yellow filtrate was obtained from which solvent was removed under reduced pressure. The remaining brown solid was dissolved in 5 ml of THF after which 30 ml of diethyl ether were added causing a pale precipitate to form. This was isolated by cannula filtration and upon removal of remaining solvent under reduced pressure, 231 mg of the desired product were obtained (75%): $n = 2$, ^1H NMR ($(\text{CD}_3)_2\text{CO}$), CpR 4.90 (AA'BB', 4H), $-\text{CH}_2-\text{O}$ 3.55 (t, 2H), Cp- CH_2- 2.46 (t, 2H), $-\text{OH}$ variable (s, 1H); IR (THF): ν_{CO} , 1900(s), 1795(s), 1750(s). $n = 3$: ^1H NMR ($(\text{CD}_3)_2\text{CO}$), CpR 4.88 (AA'BB', 4H), $-\text{CH}_2-\text{O}$ 3.57 (t, 2H), Cp- CH_2- 2.32 (t, 2H), $-\text{CH}_2-$ 1.75 (m, 2H), $-\text{OH}$ variable (s, 1H); IR (THF) ν_{CO} , 1900(s), 1795(s), 1742(s).

X-ray Structure Determination

A thin triangular crystalline plate of $[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{-OH})\text{Mo}(\text{CO})_3]_2$ (0.05 \times 0.25 \times 0.80 mm), obtained after allowing a reaction mixture to stand at room temperature under argon for a period of twelve months, was mounted in a glass capillary under N_2 . A series of oscillation and Weissenberg photographs suggested triclinic symmetry and the space group was assumed to be $P\bar{1}$; data were collected on a locally-modified Syntex $P2_1$ diffractometer with graphite monochromator and $\text{MoK}\alpha$ radiation. The unit cell parameters (Table II) were obtained by least-squares refinement of twelve reflections ($30 < 2\theta < 34^\circ$). The three check reflections indicated no decomposition. The data were reduced to F_o^2 ; the form factors from the 'International Tables for X-Ray Crystallography' [14] for the other atoms, and those for Mo were corrected for anomalous dispersion [15]. The details of data collection are included in Table II.

*The trityl ether of the starting substituted cyclopentadienyl was a gift from K. M. Doxsee.

The position of the Mo atom was derived from the Patterson map, and the Fourier map phased on Mo revealed the remainder of the complex. All H-atoms (except on OH) were introduced into the model with fixed coordinates at idealized positions and isotropic $U = 0.076 \text{ \AA}^2$. The alcohol oxygen (O4) was found to be three-fold disordered. The populations and coordinates of the three oxygen positions were obtained from difference Fourier maps. Least-squares refinement of the non-hydrogen atoms with anisotropic U_{ij} 's (O4 was refined with isotropic parameters), minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$, using all the data (3283 reflections) led to S (goodness of fit) = 1.47 and $R_F = 0.057$; final shift/errors < 0.01. The maximum deviations found in the $\Delta\rho$ map are close to Mo and are about 0.9 e \AA^{-3} . All calculations were carried out on a VAX 11/780 computer using the CRYRM system of programs.

Acknowledgement

Acknowledgement is made to the Department of Energy (Project # DEATO3-79ER1049) for financial support.

*The weights, $w = [s + r^2b + (0.02 \times s)^2]^{-1} (Lp/k^2)^2$, s = scan counts, r = scan-to-background time ratio, b = total background counts, k = scale factor of F_o ; $R_F = \sum |F_o - |F_c|| / \sum |F_o|$ (sums of reflections with $I > 0$); $R_F = R_F$ (sums of reflections with $I > 3\sigma_I$); $S = [\sum w(F_o^2 - (F_c/k)^2)^2 / (n - \nu)]^{1/2}$, n = number of reflections, ν = number of parameters.

Supplementary Material Available: Tables of H-Atom Coordinates (Table 5), Gaussian Amplitudes (Table 6) and Structure Factor Amplitudes (Table 7) have been deposited with the Editor (17 pages).

References

- 1 C. P. Casey, M. A. Andrews, D. R. McAlister and J. E. Rinz, *J. Am. Chem. Soc.*, **102**, 1927 (1980).
- 2 K. M. Doxsee, *Ph.D. Thesis*, California Institute of Technology, 1983.
- 3 H. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, *J. Am. Chem. Soc.*, **99**, 8323 (1977).
- 4 See for example, D. W. Macomber, W. P. Hart and M. D. Rausch, *Adv. Organomet. Chem.*, **21**, 1 (1982).
- 5 H. Adams, N. A. Bailey and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 273 (1984).
- 6 F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).
- 7 G. H. Stout and L. H. Jensen, 'X-Ray Structure Determination', Macmillan, New York, 1968, Table 12.1, p. 303.
- 8 W. R. Jackson and C. H. McMullen, *J. Chem. Soc.*, 1170 (1965).
- 9 B. Caro and G. Jaouen, *J. Organomet. Chem.*, **220**, 309 (1981).
- 10 R. M. Silverstein, G. C. Bassler and T. C. Morrill, 'Spectrophotometric Identification of Organic Compounds, 3rd edn.', Wiley, New York, 1974.
- 11 T. S. Coolbaugh, B. D. Santarsiero and R. H. Grubbs, *J. Am. Chem. Soc.*, accepted for publication.
- 12 V. R. Schröder, A. Striegler, G. Zimmerman and M. Mühlstädt, *J. Prakt. Chem.*, **315**, 958 (1973).
- 13 R. B. King, 'Organometallic Syntheses, Vol. I', Academic, New York, 1965.
- 14 'International Tables for X-Ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974, Table 2.2B, p. 99.
- 15 'International Tables for X-Ray Crystallography, Vol. IV', Kynoch Press, 1974, Table 2.3.1, p. 149.