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Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Studies on Main-Group Metal–Transition Metal Bonded Compounds. 5. Structure of $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$

DAVID E. CROTTY, THOMAS J. ANDERSON, MILTON D. GLICK, and JOHN P. OLIVER*

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The crystal and molecular structure of $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$ has been determined from single-crystal x-ray data collected by counter methods. The adduct crystallizes in the space group $P2_1/c$ with four molecules per unit cell of dimensions $a = 13.189$ (4) Å, $b = 7.825$ (2) Å, $c = 16.531$ (4) Å, and $\beta = 99.55$ (2)°. Full-matrix least-squares refinement gave discrepancy factors $R_1 = 0.054$ and $R_2 = 0.097$ for 1568 independent diffractometer data for which $I > 2.5\sigma(I)$. The structure contains a tetrahedral zinc atom coordinated to two bromine atoms, one oxygen atom, and one molybdenum atom. The molybdenum atom is sandwiched between two cyclopentadienyl groups which are tilted up from the zinc (dihedral angle = 36.6°). The hydrogen atoms, as located in the final difference map, form an asymmetric bridge between the Mo and Zn atoms, and it is proposed that this interaction leads to the stabilization of the complex. The complex is prepared from the reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ and EtZnBr in which $ZnBr_2$, formed from the self-proportionation equilibrium $2EtZnBr \rightleftharpoons Et_2Zn + ZnBr_2$, coordinates preferentially with the transition metal moiety or alternatively is prepared from the direct reaction of the hydride with $ZnBr_2$. Similar complexes are prepared using other group 2B metal halides.

Introduction

The structure[1] of Cp_2MoH_2 ($Cp = \eta^5\text{-}C_5H_5$) consists of a molybdenum atom sandwiched between two cyclopentadienyl rings; the normals from the centers of each ring pass through the molybdenum atom, although the rings are tilted to form a dihedral angle of 34.1°. This description is qualitatively consistent with a theoretical model proposed by Ballhausen and Dahl,[2] in which three localized orbitals are sandwiched between the rings (Figure 1). The hydrogen atoms are expected to reside at the two outer orbitals leaving a lone pair of electrons between these ligands which may serve as a basic site.

Alternatively Alcock[3] has suggested that the lone pair of electrons resides principally in a d orbital orthogonal to this axis and possesses no directional character (Figure 1). This model is consistent qualitatively with the structure and better accounts for the relatively small L–M–L bond angles observed in a wide number of related molecules and with the decrease in angle on proceeding from d^0 to d^1 to d^2 electronic configurations as indicated by Prout et al.[4] Dahl and co-workers in several papers[4-6] have proposed a bonding model similar in many respects to that of Alcock[3]—with most of the electron density in d^1 and d^2 systems located in an orbital orthogonal to the axis suggested by Ballhausen and Dahl.[2] The stereochemical effect results in the reduction of the L–M–L bond angle for the $(\eta^5\text{-}C_5H_5)_2ML_2$ systems as the number of electrons increases from 0 to 1 to 2. Finally Lauher and Hoffmann[7] have provided an extensive treatment of the bonding in these and other bis(cyclopentadienyl) complexes and have concluded that the various models proposed result from different linear combinations of the atomic orbitals, with each model emphasizing a particular facit of the possible modes of bonding.

The preponderance of evidence now indicates that the unshared pair of electrons resides in an orbital orthogonal to that proposed by Ballhausen and Dahl;[2] however, this electron pair does serve as a base as amply demonstrated by protonation,[8] by the formation of BF_3 adducts,[9,10] and by characterization of the aluminum adducts $Cp_2MH_2\cdot AlR_3$ (M = Mo, W; R = CH_3, C_2C_5, C_6H_5)[11,12] and $Cp_2ReH\cdot Al(CH_3)_3$.[11] Unfortunately no structures of these adducts have been determined. Rather the structures of the polymeric crystalline materials resulting from the elimination reactions of Al_2Me_6,[13,14] cyclohexylmagnesium bromide,[15] butyllithium,[16] or diethylzinc[17] with Cp_2MoH_2 have appeared. The structures of these materials, with the exception of the product resulting from the reaction with diethylzinc, have been determined by x-ray methods and reveal the presence of metal–metal bonding but do not show the formation of the simple adduct or its structure.

Formation of addition compounds which contain metal–metal bonds has been reported in a number of cases and, in the instance of $(CO)_4CoHgX_2$ species, the structure clearly shows metal–metal bonding.[18] There has, however, been only a very limited amount of work on systems other than those involving mercury species and to the best of our knowledge no structural studies involving main group adducts of Cp_2MoH_2, Cp_2WH_2, or CpReH have appeared.

Experimental Section

Solvents were dried over $LiAlH_4$ and were used immediately or stored in evacuated vessels. The WCl_6, $ZnBr_2$, and $MoCl_6$ were obtained from RIC/ROC, opened and stored in an argon filled drybox, and used without further purification. Et_2Zn was obtained from Ethyl Corp. and distilled under vacuum as it was used.

Preparation of EtZnBr. An excess of Et_2Zn was distilled onto $ZnBr_2$ and mixed for 2 or 3 h. The excess Et_2Zn was distilled from the solid which was subsequently dissolved in diethyl ether. The concentration of EtZnBr was determined by measuring the partial pressure of ethane evolved from hydrolysis of the solution. The solution was stored under argon in a septum bottle at −20 °C.

Reaction of EtZnBr with Cp_2MoH_2. On addition of 2.0 mL of 1.4 × 10^{-1} M EtZnBr to 0.064 g of Cp_2MoH_2 (0.014 mol) a yellow solid precipitated immediately with no apparent evolution of gases. The

Table I. Analytical Data for Adducts of $(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo, W) and Group 2B Halides[a]

	Calcd			Obsd		
Compd	% C	% H	% X[b]	% C	% H	% X[b]
$(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnCl_2\cdot THF$	32.97	3.29	19.50	32.25	3.63	16.79
$(\eta^5\text{-}C_5H_5)_2MoH_2\cdot CdCl_2\cdot THF$	34.76	4.14	14.69	35.94	3.09	9.55
$(\eta^5\text{-}C_5H_5)_2MoH_2\cdot HgCl_2\cdot THF$	29.41	3.50	12.41	25.01	3.02	13.22
$(\eta^5\text{-}C_5H_5)_2WH_2\cdot ZnBr_2\cdot THF$	27.14	3.23	25.81	27.01	3.30	33.65

[a] See ref 19. [b] X is a halide.

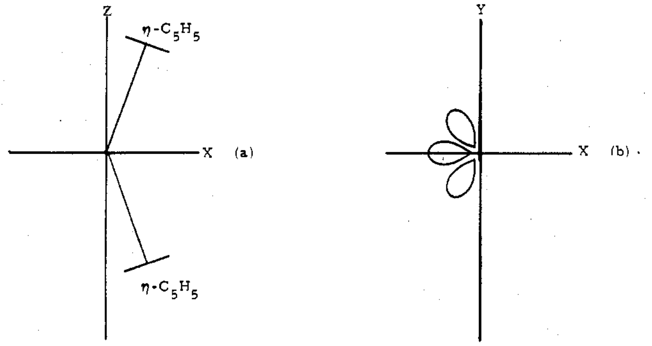


Figure 1. Disposition of the cyclopentadienyl rings and available metal orbitals for bis(cyclopentadienyl)–transition metal complexes.

solid was filtered, washed with ether, and dissolved in dimethylformamide (DMF). Partial removal of solvent by evaporation followed by storage at −20 °C for an extended period yielded crystals (mp 244–250 °C dec) which were used for the x-ray structural determination and proved to be $Cp_2MoH_2\cdot ZnBr_2\cdot DMF$.

Reaction of Group 2B Halides with Cp_2MH_2 (M = Mo, W). Equimolar amounts of the metal halide and the dihydride were weighed and mixed in the drybox. Upon addition of THF, an insoluble precipitate formed which was filtered, washed with THF, and dried under vacuum. Due to the difficulty in dissolving $CdCl_2$, this halide was first dissolved in THF and then the solution added to the dihydride. Chemical analyses,[19] Table I, indicate that the products may be formulated as $Cp_2MH_2\cdot EX_2\cdot THF$ (M = Mo, W; E = Zn, Cd, Hg; X = Cl, Br). All products melt with decomposition in the range of 240–250 °C.

Structural Determination. A suitable crystal of $Cp_2MoH_2\cdot ZnBr_2\cdot DMF$ was sealed in a thin-walled glass capillary and mounted on a Syntex $P2_1$ four-circle x-ray diffractometer. Rotation and axial photographs together with a small set of counter data were used to determine the monoclinic group, $P2_1/c$, which was confirmed by the complete set of intensity data. Fifteen reflections with 2θ between 11 and 20° (Mo Kα) were centered with a programmed centering routine and were used in a least-squares determination of cell parameters and errors. A summary of data collection and crystal parameters is given in Table II.

Intensity data were collected by the θ–2θ scan technique with Mo Kα radiation which had been diffracted by a highly oriented graphite monochromator whose diffraction vector was parallel to the diffraction vector of the sample. Backgrounds were measured at each end of the scan for a total time equal to half of the scan time. During data collection, the intensities of three standard reflections were monitored every 97 reflections and indicated no decomposition or movement of the crystal. The data were reduced to I and $\sigma(I)$ and standard deviations were assigned as

$$\sigma(I) = [\sigma^2_{\text{counter}} + (0.04I)^2]^{1/2}$$

where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, and K = ratio of scan time to background time.[20] Absorption corrections ranging between 2.6 and 3.9 were applied to I. A total of 1568 data for which $I > 2.5\sigma(I)$ were used in the solution and refinement of the structure.

Solution and Refinement of Structure. This structure was solved by iterative application of the $\sum 2$ relationship using 296 normalized structure factors of magnitude 1.3 or greater. An E-map based upon the phases of the solution with the largest consistency index (0.985) yielded the positions of the molybdenum atom, zinc atom, and one of the bromine atoms. Subsequent Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. Inclusion of idealized hydrogen positions (C–H = 1.0 Å) for the DMF and for the cyclopentadienyl fragments and full-matrix refinement with anisotropic thermal parameters for all nonhydrogen atomic parameters yielded final discrepancy factors of

Table II. Physical Constants and Experimental Data for $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$

Space group	$P2_1/c$	
a, Å	13.189 (4)	
b, Å	7.825 (2)	
c, Å	16.531 (4)	
β, deg	99.55 (2)	
Calcd density,[a] g/cm³	2.074	
2θ scan range, deg	Mo Kα_1 − 1.0° to Mo Kα_2 + 1.0°	
2θ scan rate, deg/min	2.0	
No. of data examined	2507	
No. of data for which $I > 2.5\sigma(I)$	1641	
2θ(max), deg	50	
Residual nonmetal electron density, e/Å³	1.11	
Error of fit	3.20	
Crystal faces and distances to center of crystal, mm	$(\bar{2},\bar{1},10)$	0.29
	$(\bar{3}0\bar{2})$	0.11
	$(\bar{3}0\bar{1})$	0.11
	$(\bar{2},0,\overline{11})$	0.29
	(100)	0.11
	(010)	0.08
	$(0\bar{1}0)$	0.08

[a] Density measurement prevented.

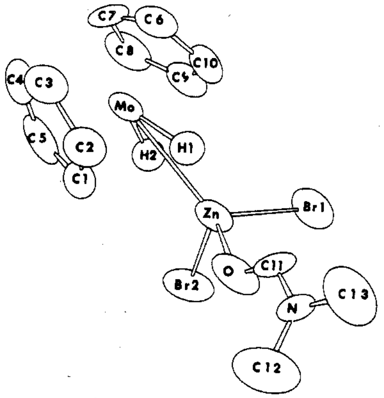


Figure 2. A view of $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$ with the atomic labeling scheme.

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.054$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.096$$

The bridging hydrogen atoms appeared in the final Fourier difference map and these positions are included in Table III with the atomic coordinates and thermal parameters of the other atoms. Table IV lists bond distances and bond angles. Figure 2 identifies the atoms in a single molecule and Figure 3 is a stereoscopic view of the packing. A listing of calculated and observed structure factors and amplitudes and a stereoscopic view of a single molecule are available.[21]

Structure of $Cp_2MoH_2\cdot ZnBr_2\cdot DMF$. This structure consists of a $ZnBr_2$ moiety coordinated to Cp_2MoH_2 and DMF such that the

Table III. Atomic Coordinates[a] and Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$ with Estimated Standard Deviations of the Least Significant Figures in Parentheses

Atom	x	y	z	Atom	x	y	z
Mo(1)	0.6640 (1)	0.6649 (2)	−0.0721 (1)	C(5)	0.6190 (16)	0.9502 (23)	−0.0965 (12)
Br(1)	0.9039 (2)	0.3312 (3)	0.0604 (1)	C(6)	0.7057 (17)	0.3975 (25)	−0.1193 (12)
Br(2)	0.6833 (2)	0.4495 (3)	0.1851 (1)	C(7)	0.7799 (13)	0.5115 (25)	−0.1406 (11)
Zn(1)	0.7730 (2)	0.5385 (3)	0.0751 (1)	C(8)	0.7278 (16)	0.6289 (26)	−0.1944 (11)
O(1)	0.8573 (8)	0.7364 (16)	0.1363 (7)	C(9)	0.6204 (18)	0.5899 (27)	−0.2052 (10)
N(1)	0.9940 (10)	0.9113 (18)	0.1526 (8)	C(10)	0.6051 (15)	0.4446 (26)	−0.1589 (12)
C(1)	0.6774 (14)	0.9419 (22)	−0.0161 (12)	C(11)	0.9377 (15)	0.7880 (22)	0.1143 (10)
C(2)	0.6221 (14)	0.8374 (24)	0.0300 (12)	C(12)	0.9623 (16)	1.0012 (28)	0.2204 (12)
C(3)	0.5309 (15)	0.7824 (26)	−0.0190 (14)	C(13)	1.0866 (14)	0.9666 (27)	0.1267 (13)
C(4)	0.5287 (15)	0.8541 (25)	−0.0987 (14)	H(1)*	0.780	0.650	−0.004
				H(2)*	0.664	0.559	−0.004

Atom	β_{11} (B)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.0047 (1)	0.0067 (3)	0.0021 (1)	−0.0001 (1)	0.0009 (1)	−0.0001 (1)
Br(1)	0.0088 (2)	0.0185 (5)	0.0043 (1)	0.0057 (2)	0.0009 (1)	−0.0002 (2)
Br(2)	0.0078 (2)	0.0242 (5)	0.0027 (1)	−0.0050 (2)	0.0012 (1)	−0.0002 (2)
Zn(1)	0.0054 (1)	0.0102 (4)	0.0026 (1)	−0.0004 (2)	0.0010 (1)	−0.0005 (2)
O(1)	0.0053 (8)	0.0133 (24)	0.0033 (6)	−0.0029 (13)	0.0016 (6)	−0.0018 (10)
N(1)	0.0040 (10)	0.0137 (29)	0.0014 (5)	−0.0002 (14)	−0.0012 (6)	−0.0005 (11)
C(1)	0.0061 (13)	0.0093 (34)	0.0034 (9)	−0.0013 (18)	−0.0008 (9)	−0.0018 (14)
C(2)	0.0051 (13)	0.0153 (39)	0.0031 (8)	0.0024 (20)	−0.0001 (9)	−0.0005 (16)
C(3)	0.0064 (15)	0.0133 (41)	0.0056 (11)	0.0028 (20)	0.0033 (11)	0.0003 (18)
C(4)	0.0058 (15)	0.0109 (38)	0.0059 (12)	0.0042 (20)	−0.0005 (11)	−0.0019 (18)
C(5)	0.0085 (17)	0.0082 (34)	0.0038 (9)	0.0010 (21)	0.0002 (10)	−0.0005 (15)
C(6)	0.0096 (19)	0.0116 (37)	0.0036 (9)	0.0039 (23)	0.0012 (11)	−0.0020 (16)
C(7)	0.0057 (14)	0.0164 (43)	0.0037 (9)	0.0038 (22)	0.0015 (10)	0.0009 (17)
C(8)	0.0083 (17)	0.0156 (41)	0.0026 (8)	0.0017 (23)	0.0016 (10)	0.0014 (16)
C(9)	0.0117 (21)	0.0157 (42)	0.0010 (7)	0.0051 (25)	−0.0017 (10)	−0.0014 (15)
C(10)	0.0066 (16)	0.0145 (42)	0.0043 (10)	−0.0046 (21)	0.0009 (11)	−0.0050 (18)
C(11)	0.0065 (14)	0.0100 (35)	0.0013 (7)	0.0013 (18)	−0.0015 (8)	0.0001 (13)
C(12)	0.0091 (18)	0.0204 (48)	0.0037 (10)	−0.0053 (25)	0.0003 (10)	−0.0016 (19)
C(13)	0.0052 (13)	0.0198 (46)	0.0052 (11)	−0.0027 (22)	0.0010 (10)	−0.0025 (19)

[a] The form of the anisotropic thermal parameters for both compounds is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; the hydrogen atoms were located 1.0 Å from the attached atom with isotropic thermal parameters (B) set to 10% greater than the equivalent B for the attached atom.

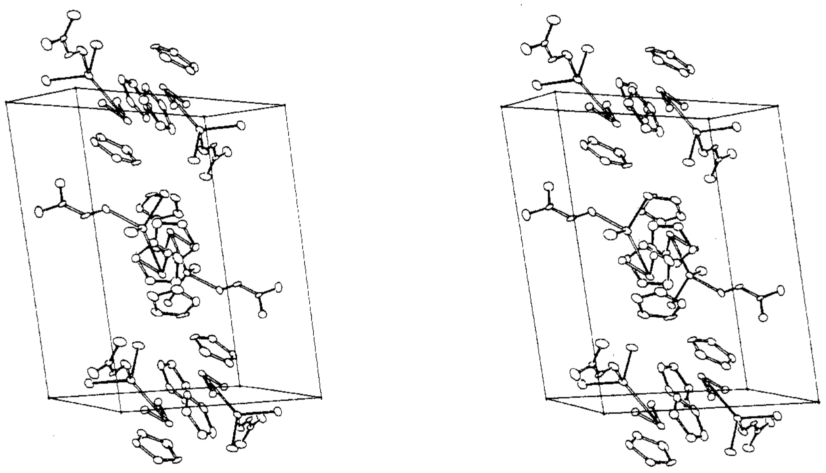


Figure 3. Stereoscopic view of the packing of $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$.

bromine atoms, oxygen atom, and molybdenum atom are approximately tetrahedral about the zinc atom. The Cp_2MoH_2 moiety binds to the zinc atom via a Mo–Zn bond with two weak Zn–H interactions, while the DMF is coordinated through the aldehyde oxygen.

If one ignores the Zn–H interactions, the zinc atom, Figure 4a, is tetrahedrally coordinated to two bromine atoms (2.420 (3) Å average), one oxygen atom (2.070 (11) Å) and the molybdenum atom (2.793 (3) Å). This metal-metal distance is somewhat greater than the molybdenum-zinc distance of 2.711 (1), 2.632 (1), and 2.538 (1) Å reported for $Cp(CO)_3MoZnBr\cdot 2THF$,[22] $[Cp(CO)_3MoZnCl\cdot Et_2O]_2$,[23] and $[Cp(CO)_3Mo]_2Zn$,[23] respectively. The Zn–Br distance is slightly shorter than the 2.433 (2) Å reported[22] for $Cp(CO)_3MoZnBr\cdot 2THF$. The angles about the zinc atom, again ignoring Zn–H interactions, average 109° and range from 97.9 (3) to 120.6 (1)°. The Zn–H distances of 1.59 and 1.78 Å are only approximate but may represent significant interactions.

The coordination sphere about the molybdenum atom includes two cyclopentadienyl groups (Mo–C, 2.315 (18) Å average), a zinc atom (2.793 (3) Å) and two hydrogen atoms (1.76 and 1.40 Å). If one presumes Mo–H bonding and attributes three coordination sites to each cyclopentadienyl group, then the molybdenum atom may be thought of as nine-coordinate.

The two planar cyclopentadienyl moieties are tilted away from the zinc atom with a dihedral angle of 36.6°. The plane consisting of the two hydrogen atoms, the molybdenum atom, and the zinc atom is sandwiched between the two rings, forming a dihedral angle of 15.7° with the C(1)···C(5) ring and 21.9° with the C(6)···C(10) ring. The metal–hydrogen plane is approximately perpendicular (87.5°) to the plane of the DMF oxygen and the two bromines. The potential mirror symmetry of the O–Zn–Mo plane is destroyed by the asymmetry about the zinc atom as demonstrated by the O–Zn–Br angles of 102.5 (3) and 97.9 (3)°.

Table IV. Bond Distances and Angles for $(\eta^5\text{-}C_5H_5)_2MoH_2{\cdot}ZnBr{\cdot}DMF$

Distances, Å		Angles, deg	
Mo-C(1)	2.352 (17)	Br(1)-Zn-Br(2)	109.1 (1)
Mo-C(2)	2.299 (18)	Br(1)-Zn-Mo	115.1 (1)
Mo-C(3)	2.282 (17)	Br(1)-Zn-O(1)	102.5 (3)
Mo-C(4)	2.304 (18)	Br(2)-Zn-Mo	120.6 (1)
Mo-C(5)	2.328 (18)	Br(2)-Zn-O(1)	97.9 (3)
Mo-C(6)	2.331 (18)	Mo-Zn-O(1)	108.5 (4)
Mo-C(7)	2.373 (17)	C(5)-C(1)-C(2)	106.5 (16)
Mo-C(8)	2.332 (17)	C(1)-C(2)-C(3)	109.8 (17)
Mo-C(9)	2.258 (17)	C(2)-C(3)-C(4)	107.3 (18)
Mo-C(10)	2.295 (17)	C(3)-C(4)-C(5)	107.4 (18)
Mo-Zn	2.793 (3)	C(4)-C(5)-C(1)	109.0 (18)
Zn-Br(1)	2.410 (3)	C(10)-C(6)-C(7)	106.8 (17)
Zn-Br(2)	2.430 (3)	C(6)-C(7)-C(8)	110.7 (18)
Zn-O(1)	2.070 (11)	C(7)-C(8)-C(9)	104.6 (17)
C(1)-C(2)	1.403 (25)	C(8)-C(9)-C(10)	109.5 (17)
C(2)-C(3)	1.403 (25)	C(9)-C(10)-C(6)	108.4 (17)
C(3)-C(4)	1.427 (26)	Zn-O(1)-C(11)	121.0 (11)
C(4)-C(5)	1.404 (26)	O(1)-C(11)-N(1)	122.6 (15)
C(5)-C(6)	1.403 (25)	C(11)-N(1)-C(12)	121.3 (15)
C(6)-C(7)	1.411 (27)	C(11)-N(1)-C(13)	121.4 (15)
C(7)-C(8)	1.427 (27)	C(12)-N(1)-C(13)	117.3 (15)
C(8)-C(9)	1.404 (28)	Mo-H(1)-Zn	113.7
C(9)-C(10)	1.431 (29)	Mo-H(2)-Zn	122.5
C(10)-C(6)	1.380 (25)	H(1)-Mo-H(2)	63.8
O(1)-C(11)	1.244 (20)	H(1)-Zn-H(2)	59.8
N(1)-C(11)	1.315 (21)		
N(1)-C(12)	1.442 (24)		
N(1)-C(13)	1.427 (22)		
Mo-H(1)	1.76		
Mo-H(2)	1.40		
Zn-H(1)	1.59		
Zn-H(2)	1.78		

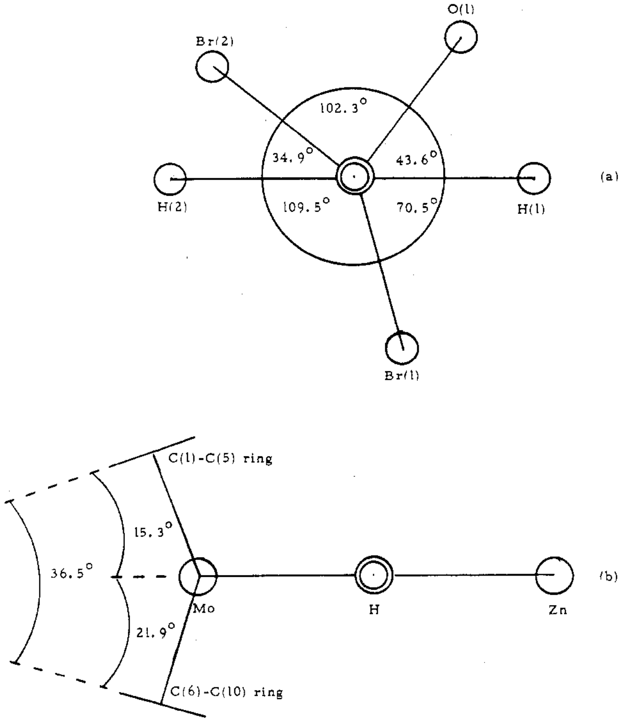


Figure 4. Schematic representation of $(\eta^5\text{-}C_5H_5)_2MoH_2{\cdot}ZnBr_2{\cdot}DMF$: (a) viewed down the zinc–molybdenum bond; (b) viewed down the normal to the metal–H–metal plane.

The 36.6° dihedral angle between the cyclopentadienyl rings is slightly larger than the 34.1° angle reported[1] for the free Cp_2 MoH_2. The ring carbon atoms are, on the average, 2.32 (2) Å from the molybdenum atom and 1.41 (3) Å from each other compared with 2.29 and 1.43 Å reported for the free dihydride.

The carbon–oxygen distance in the DMF moiety of 1.24 (2) Å is slightly longer than the average 1.235(5) Å reported for uncomplexed $O{=}CHNR_2$ molecules,[24] as expected if electron density is donated to the zinc.

Discussion

The reaction of a transition metal hydride, such as Cp_2MoH_2 with organozinc halide may proceed in one of several ways. The path is determined by reactivity of the metal hydride toward each of the components of the equilibrium mixture as described in eq 1 which lies to the right.[25] A typical

$$R_2Zn + ZnX_2 \leftrightharpoons 2RZnX \tag{1}$$

reaction is that described for $Cp(CO)_3MoH$ in which ethane is eliminated, yielding species of the form $Cp(CO)_3MZnX$ (M = Mo, W; X = Cl, I, Br).[22,23] In reactions with Cp_2MoH_2, this path would lead to the trimetallic species $Cp_2Mo(ZnX)_2$.

A second path is that in which the transition metal derivative forms a complex with the strongest Lewis acid in the system, presumably by use of its available electron pair. Several examples of this type of behavior have been cited in the Introduction, but only limited structural and spectroscopic data are available on these systems.

In the present study we have shown that the latter mode of reaction is preferred for the equilibrium mixture described by eq 1. Furthermore zinc, cadmium, and mercuric chlorides, as well as zinc bromide, all form complexes which may be formulated in the same manner as the product resulting from reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ with the alkyl–zinc halide equilibrium mixture (Table I).

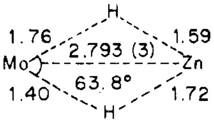
The lack of proton abstraction from $(\eta^5\text{-}C_5H_5)_2MoH_2$ by the equilibrium mixture is graphic evidence for the nonacidic nature of the hydrogen atoms, while the ready formation of the adducts, even in relatively basic solvent such as THF and DMF, shows the strong tendency of the transition metal complex to function as a base.

The formation of the monosolvated species under the conditions studied show the marked tendency for zinc, cadmium, and mercury to attain a coordination number of four. It is suggested that if less basic solvents were to be used, these metals will achieve the coordination by formation of metal–halogen–metal bridges as noted in other systems.[15,22]

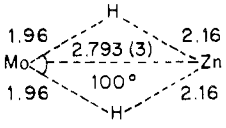
The solid-state structure of the adduct $Cp_2Mo{\cdot}ZnBr_2{\cdot}DMF$ is shown in Figures 2–4. These figures and the data collected in Table IV show that the coordinated DMF molecule is only altered slightly from that of the free molecule, and the cyclopentadienyl rings are tipped from 31.8° in the free Cp_2MoH_2 molecule to 36.5° on formation of the adduct. This value for the dihedral angle is substantially smaller than those observed for a variety of molybdenum derivatives as reported by Prout et al.[4] which range from 42 to 52°. The observed variation in angle is a function of the substituents on the molybdenum atom, which indicates an increase in steric interaction on complex formation with zinc bromide.

The most interesting feature in this structure is the coordination of the zinc to the molybdenum moiety since the stability of this complex implies the formation of a relatively strong bonding interaction between the zinc bromide and transition metal hydride.

Examination of the structure shows that the Zn–Mo distance (2.793 (3) Å) is larger than the reported Zn–Mo distances in compounds with direct metal–metal bonds which are respectively $Cp(CO)_3MoZnBr{\cdot}2THF$ (2.711 (1) Å),[22] $[Cp(CO)_3MoZnCl{\cdot}Et_2O]_2$ (2.632 (1) Å),[23] and $[Cp(CO)_3Mo]_2Zn$ (2.538 (1) Å).[23] This suggests that the stable bonding may result from causes other than the direct metal–metal interaction. Further one should note that there are two hydrogen atoms in the region between the molybdenum and zinc atoms which might serve as bridging groups. This situation is depicted in I with the hydrogens as located approximately in the present work (a) and as predicted from the approximate Mo–H distance in Cp_2MoH_2[26] from the calculations of Fenske et al.[6]



Ia



Ib

for the H–Mo–H angle of 100° (b). These two models bracket the observed metal–hydrogen distances obtained for a variety of transition metal hydrides from neutron diffraction studies[27] and the approximate value obtained for Mo–H distances obtained from x-ray data.[28] Further the rather sharp angle for the H–Mo–H angle of 64° is compatible with Mo–H–Zn bridge bond formation. These factors, i.e., the long Mo–Zn distance, the H–Mo and H–Zn distances, and the small H–Mo–H angle all suggest metal–hydrogen–metal bridge bonding at the expense of direct addition compound formation with metal–metal bonding. Unfortunately the crudeness of the data precludes a definitive answer to this question since the precise locations of the hydrogen atoms are unknown and therefore one cannot differentiate between the relative importance of these two modes of bonding in the zinc complex nor define effectively the relative stability of this species.

Studies are in progress to further differentiate between the two modes of reactions described, i.e., elimination vs. adduct formation, and to probe the relative contributions of the possible modes of bonding.

Registry No. $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnCl_2\cdot THF$, 63251-36-5; $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot CdCl_2\cdot THF$, 63251-34-3; $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot HgCl_2\cdot THF$, 63251-35-4; $(\eta^5\text{-}C_5H_5)_2WH_2\cdot ZnBr_2\cdot THF$, 63251-37-6; $(\eta^5\text{-}C_5H_5)_2MOH_2\cdot ZnCl_2\cdot DMF$, 63251-33-2; Cp_2MoH_2, 1291-40-3; EtZnBr, 6107-37-5.

Supplementary Material Available: Table V, a listing of observed and calculated structure amplitudes (×10), and Figure 5, a stereoscopic view of a single molecular unit (8 pages). Ordering information is given on any current masthead page.

References and Notes

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(19) Chemical analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.
(20) (a) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) NEWES, W. Schmonsees' program for generation of normalized structure factors; (3) REL, R. E. Long's program for phase determination by Sayre's method; (4) FORDAP, A. Zalkin's Fourier program; (5) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (6) ORTEP, C. K. Johnson's program for drawing crystal models; (7) ABSORB, L. K. Templeton's absorption correction program; (8) HFINDR, A. Zalkin's idealized hydrogen program, modified by T. J. Anderson. (b) Scattering factors for Mo, Zn, Br, O, N, C, and H including anomalous scattering for Mo, Zn, and Br were taken from J. A. Ibers and W. C. Hamilton, Ed., "International Tables for X-Ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, 1974.
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