

and 2.04 (3) Å in PtCl(OCH₃)(1,5-C₈H₁₂)(pyridine).⁴⁴ Thus in general M–C(olefin) distances may not be much different from M–C (σ-bonded) distances. There are bound to be many exceptions though since both M–C(olefin) and σ-M–C distances are influenced by substituent effects. Consider (C₅H₅)Rh(C₂F₄)(C₂H₄),³⁰ for example, where Rh–C(C₂F₄) is 2.024 (2) Å and Rh–C(C₂H₄) is 2.167 (2) Å; the Rh^{III}–σ-C distance is about 2.07 Å.³⁶

The current bonding ideas in bis(cyclopentadienyl)–transition metal complexes will be outlined very briefly with respect to the model in Figure 6. Ballhausen and Dahl⁴ suggested that ligands in (C₅H₅)₂MX₂ complexes would use orbitals ψ₁ and ψ₃ for ligand bonding and ψ₂ for lone pairs. Alcock⁵ suggested a similar model except that ψ₄ would be used for lone pairs instead of ψ₃. Green, *et al.*,² developed a model in MO terms extrapolated from the ferrocene model by “bending” the ferrocene MO’s under C_{2v}(2mm) symmetry. They proposed that either ψ₂ or ψ₄ might be used depending on the number of ligand orbitals and electrons available for bonding. The structure of (C₅H₅)₂Nb(C₂H₅)(C₂H₄)

(44) C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani, and U. Belluco, *Chem. Commun.*, 187 (1969).

can be rationalized in the simplest possible way in terms of the original Ballhausen–Dahl model using only one metal orbital for bonding to ethylene. However, the Green, *et al.*, model is more attractive in that it allows more flexibility in the bonding description. Accordingly we can use ψ₁ to bond to C₂H₅ and ψ₃ for the σ bond to C₂H₄. Then ψ₂ and ψ₄ are available for possible Nb–π* back-bonding to C₂H₄; both ψ₂ and ψ₄ are of the same symmetry under the local C_s(m) point symmetry. As discussed above, this could provide an electronic reason for favoring the olefin configuration in the molecular plane. Further MO calculations³ on (C₅H₅)₂MX₂ complexes are in progress which might shed more light on the nature of the bonding in these complexes.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5420.

Preparation and Structural Characterization of Transition Metal–Zinc Chloride Derivatives. The Crystal and Molecular Structure of [π-C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂ and [π-C₅H₅(CO)₃Mo]₂Zn

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Abstract: The preparation and characterization of compounds of the general formula [π-C₅H₅(CO)₃MZnCl·O(C₂H₅)₂]₂ and [π-C₅H₅(CO)₃MZnCl]_x (M = Mo, W) are reported. The structures of [π-C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂ and of [π-C₅H₅(CO)₃Mo]₂Zn have been determined from single-crystal X-ray data collected by counter methods. [π-C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂ crystallizes in space group *P* $\bar{1}$ with one dimer molecule per unit cell of dimensions *a* = 8.524 (3) Å, *b* = 9.090 (3) Å, *c* = 13.152 (4) Å, α = 56.03 (2)°, β = 110.13 (2)°, and γ = 103.96 (2)°. Full-matrix least-squares refinement gave final discrepancy factors of *R*₁ = 0.043 and *R*₂ = 0.052 for 2578 data having *F*² > 3σ(*F*²). The molecular structure consists of a centrosymmetric dimer with chloride atoms bridging the zinc atoms and a π-C₅H₅(CO)₃Mo ligand and a diethyl ether molecule completing the four-coordination sphere of each zinc atom. The molybdenum–zinc bond distance is 2.632 (1) Å. [π-C₅H₅(CO)₃Mo]₂Zn crystallizes in space group *P*2₁/*n* with two centrosymmetric molecules per unit cell of dimensions *a* = 11.101 (4) Å, *b* = 7.548 (2) Å, *c* = 11.726 (4) Å, and β = 64.43 (2)°. Full-matrix least-squares refinement gave discrepancy factors of *R*₁ = 0.040 and *R*₂ = 0.058 for 2101 reflections with *F*² > 3σ(*F*²). The molecule has a linear molybdenum–zinc–molybdenum bond with a molybdenum–zinc distance of 2.538 (1) Å. The solvated derivatives may be converted to the nonsolvated species of the general formula [π-C₅H₅(CO)₃MZnCl]_x (M = Mo, W) by heating under a dynamic vacuum. Infrared spectral data are interpreted in terms of a polymeric structure with carbonyl oxygen–zinc interactions supporting a polymer framework for the nonsolvated compounds.

The organometallic structural chemistry of complexes containing group II or group III metals and transition metal carbonyl derivatives has recently taken on importance because of the recognized ability of the transition metal moiety to exhibit two different modes of bond formation with a main group metal.

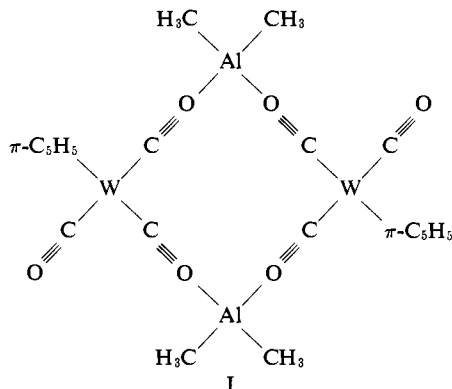
The first mode of bonding, exemplified by Zn[Co(CO)₄]₂¹ and [π-C₅H₅(CO)₃Mo]₃Tl² involves direct metal–metal bonding. Many complexes of this type

(1) B. Lee, J. M. Burlitch, and J. L. Hoard, *J. Amer. Chem. Soc.*, **89**, 6362 (1967).

(2) J. Rajaram and J. A. Ibers, *Inorg. Chem.*, **12**, 1313 (1973).

are known, particularly for the main group metals of zinc, cadmium, mercury,³⁻⁷ indium,^{8,9} and thallium.^{8,10}

The second type of bonding involves a main group metal and transition metal moiety bound through a $MC\equiv O-M'$ bridge. A compound exhibiting this bond type is $[\pi-C_5H_5(CO)_2Fe]_2 \cdot 2Al(C_2H_5)_3$.¹¹ The triethylaluminum species are bound to the bridged carbonyl oxygens by aluminum-oxygen bonds. More recently, X-ray structure determinations for $Al[\pi-C_5H_5(CO)_3W]_3 \cdot 3THF$ ¹² (THF = tetrahydrofuran) and $Mg[\pi-C_5H_5(CO)_3Mo]_2 \cdot 4py$ ¹³ (py = pyridine) have been described. In both cases the molecular framework is characterized by carbonyl oxygen-metal bonds. In the complex $[\pi-C_5H_5(CO)_3WAl(CH_3)_2]_2$ ¹⁴ similar bonding supports a dimeric unit as shown in I.



In this paper the initial results of an investigation into the synthesis and characterization of organo-transition metal zinc halide derivatives are presented. A single-crystal X-ray structure determination of a representative member of the series is reported and, for comparison, the X-ray structure of $[\pi-C_5H_5(CO)_3Mo]_2Zn$ is also reported here.

Solid state ir spectral data are presented for the halide and related derivatives. Shifts in the carbonyl frequencies are interpreted in terms of $Zn-O\equiv CM$ interactions in the species of general formula $[\pi-C_5H_5(CO)_3MZnCl]_x$.

Experimental Section

All preparations and subsequent manipulations were carried out under high vacuum conditions and/or under an argon or nitrogen atmosphere utilizing Schlenk tube and drybox techniques.¹⁵ All solvents, with the exception of THF, were dried over Na/K alloy and were degassed prior to use. THF was dried over $LiAlH_4$. Infrared data were obtained on a Perkin-Elmer Model 267 spec-

trophotometer on fluorocarbon mulls prepared in the drybox. The spectra were recorded immediately after preparation of the mulls. The samples showed no decomposition until the plates were separated and cleaned with solvent. The spectra were calibrated using the 1601.4 cm^{-1} absorption of polystyrene film. Nmr spectra were recorded on a Varian A60A spectrometer at a probe temperature of 35° . The cyclopentadienyltricarbonylhydrides of molybdenum and tungsten were prepared by literature methods¹⁶ and doubly sublimed prior to use. Molybdenum and tungsten hexacarbonyl were obtained from Pressure Chemical Co. and used as received. Diethylzinc¹⁷ and ethylzinc chloride¹⁸ were prepared by reported procedures. Analyses were obtained from Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

Preparation of $[\pi-C_5H_5(CO)_3MoZnCl \cdot O(C_2H_5)_2]_2$ (I). $\pi-C_5H_5(CO)_3MoH$ (0.56 g, 2.28 mmol) was dissolved in 3 ml of toluene. An equimolar quantity of C_2H_5ZnCl in a diethyl ether solution (4 ml) was added to the hydride solution at room temperature.

A nmr sample of the reaction solution was taken immediately and degassed and sealed. The nmr sample exhibited two sharp resonance absorptions in the $\pi-C_5H_5$ region. The resonance attributable to the hydride species decreased in intensity and disappeared after 30 min. The second $\pi-C_5H_5$ resonance increased in intensity throughout the reaction period. A third upfield singlet was observed and identified as ethane by the resonance position (δ 0.78 ppm).

The macro reaction, originally yellow in color, gradually became colorless and deposited white crystals after 2 hr. The crystals were isolated by filtration and suction dried. Recrystallization was not attempted due to molecular rearrangements which occur in solution,¹⁹ mp 236° dec.

Anal. Calcd for $[\pi-C_5H_5(CO)_3MoZnCl \cdot O(C_2H_5)_2]_2$: C, 34.3; H, 3.61; Cl, 8.44. Found: C, 32.3; H, 3.21; Cl, 9.9; C, 31.2; H, 3.07; Cl, 8.4.

Preparation of $[\pi-C_5H_5(CO)_3WZnCl \cdot O(C_2H_5)_2]_2$ (II). $\pi-C_5H_5(CO)_3WH$ (0.443 g, 1.16 mmol) was dissolved in 4 ml of toluene. An equimolar quantity of C_2H_5ZnCl in a diethyl ether solution (4 ml) was added to the hydride solution at room temperature. A nmr sample was taken immediately, and the observations were completely analogous to the molybdenum reaction. The macro reaction was likewise analogous, and white crystals were obtained. Recrystallization was not attempted due to molecular rearrangements which occur in solution,¹⁹ mp 282° dec.

Anal. Calcd for $[\pi-C_5H_5(CO)_3WZnCl \cdot O(C_2H_5)_2]_2$: C, 28.4; H, 2.98; Cl, 7.0. Found: C, 27.5; H, 2.97; Cl, 7.8.

Preparation of $\pi-C_5H_5(CO)_3MoZnCl$ (III). (a) $\pi-C_5H_5(CO)_3MoH$ (0.44 g, 1.79 mmol) was dissolved in 5 ml of benzene. An equimolar quantity of C_2H_5ZnCl in a benzene solution (5 ml) was added to the hydride solution at room temperature. Gas evolution was apparent and a white precipitate appeared after 5-10 min. The reaction was allowed to continue for 1 hr; however, gas evolution ceased well before this time. The white solid was isolated by filtration and suction dried, mp 240° dec.

Anal. Calcd for $\pi-C_5H_5(CO)_3MoZnCl$: C, 27.8; H, 1.46; Cl, 10.3. Found: C, 28.4; H, 2.14; Cl, 10.7.

(b) A sample of I (0.354 g, 0.42 mmol) was placed in a 25-ml flask and attached to a high vacuum line and heated to 50° with an oil bath under a dynamic vacuum. Diethyl ether, as identified from a nmr spectrum, was evolved. After 2 hr weight measurements revealed a weight loss of 0.060 g. Theoretical weight loss for complete removal of ether is 0.062 g. Ir spectra for the compounds generated by methods (a) and (b) were identical.

Preparation of $\pi-C_5H_5(CO)_3WZnCl$ (IV). (a) A benzene solution of $\pi-C_5H_5(CO)_3WH$ was prepared by mixing 0.445 g (1.3 mmol) of the hydride in 5 ml of solvent. An equimolar quantity of C_2H_5ZnCl in benzene (5 ml) was added to the hydride solution at room temperature. The observations and isolation of a white solid was completely analogous to the molybdenum reaction, mp 285° dec.

Anal. Calcd for $\pi-C_5H_5(CO)_3WZnCl$: C, 22.2; H, 1.16, Cl, 8.2. Found: C, 22.7; H, 1.49, Cl, 9.1.

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(17) A. H. Blatt, Ed., "Organic Synthesis," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 184.

(18) A. N. Nesmeyanov and K. A. Kocheshkov, Ed., "Methods of Elemento-Organic Chemistry," Vol. 3, World Publishing Co., New York, N. Y., 1967, p 27.

(19) The etherate derivatives of this class undergo irreversible molecular rearrangements when introduced into solution. A report dealing with this aspect of the chemistry will be available elsewhere.

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 (4) M. J. Mays and J. D. Robb, *J. Chem. Soc. A*, 329 (1968).
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 (15) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1968.

(b) A weighed sample of II (0.1605 g, 0.16 mmol) was treated in an identical manner as detailed for the molybdenum analog in (b) above. Experimental weight loss was determined to be 0.0235 g; theoretical weight loss was 0.0237 g. The ir spectra of compounds generated by methods (a) and (b) were identical.

Preparation of $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot 2,2'\text{-bipy}$ (V). A 1/1 toluene-diethyl ether solution of III (0.251 g, 0.59 mmol) was combined with a toluene solution of 2,2'-bipy (bipy = bipyridyl) (0.09 g, 0.60 mmol) at room temperature. An immediate reaction occurred and a yellow-orange precipitate formed. The crystalline product was isolated by filtration, washed with cyclopentane, and suction dried. Recrystallization could not be achieved due to the insolubility of the complex in all common solvents, mp 285° dec.

Anal. Calcd for $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot \text{N}_2\text{C}_{10}\text{H}_8$: C, 43.1; H, 2.62; Cl, 7.1. Found: C, 43.6; H, 3.00; Cl, 7.4.

Preparation of $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WZnCl}\cdot 2,2'\text{-bipy}$ (VI). A 1/1 benzene-diethyl ether solution of V (0.201 g, 0.46 mmol) was combined with a benzene solution of 2,2'-bipy (0.72 g, 0.46 mmol). An immediate reaction occurred and a lemon yellow precipitate was isolated. This complex is insoluble in all solvents, and recrystallization was not attempted, mp 305° dec.

Anal. Calcd for $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WZnCl}\cdot \text{N}_2\text{C}_{10}\text{H}_8$: C, 36.6; H, 2.22; Cl, 6.0. Found: C, 37.9; H, 2.61; Cl, 6.1.

Preparation of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$ (VII). $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoH}$ (0.39 g, 1.6 mmol) was dissolved in 10 ml of toluene and the reaction vessel attached to a high vacuum line. Excess diethylzinc (0.42 g, 3.4 mmol) was condensed into the reaction vessel at -196°. The reaction vessel was warmed to room temperature. Gas evolution was evident in the temperature range of -10 to 0° and was identified as ethane from its nmr spectrum. A cream colored precipitate formed concurrently with the evolution of ethane. Reaction was complete in 15-20 min. Excess diethylzinc and solvent were removed by high vacuum distillation, and the solid product was recrystallized from a saturated toluene solution by dilution with cyclopentane. The ir spectrum in toluene was in agreement with that previously reported,⁷ mp 190-193° (lit.⁷ 194-196°).

Anal. Calcd for $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$: C, 34.6; H, 1.82. Found: C, 35.3; H, 2.10.

Preparation of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Zn}$ (VIII). In a manner completely analogous to the molybdenum hydride-diethylzinc reaction $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WH}$ (0.386 g, 1.2 mmol) and diethylzinc (0.30 g, 2.4 mmol) were combined and a white solid isolated. The ir spectrum of a toluene solution exhibited carbonyl absorptions identical with previously reported data for this derivative,⁷ mp 200-203° (lit.⁷ 203-205°).

Anal. Calcd for $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Zn}$: C, 26.3; H, 1.38. Found: C, 25.5; H, 1.45.

X-Ray Data Collection for $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$ and $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot \text{O}(\text{C}_2\text{H}_5)_2]_2$. A summary of data collection and crystal parameters for both compounds is given in Table I. The following procedures were used for both compounds. Suitable crystals were sealed in thin-walled glass capillaries under a N₂ atmosphere and mounted directly on a Syntex P2₁ four-circle dif-

fractometer. Air sensitivity of the crystals precluded a density determination. Rotation and axial photographs and counter data were adequate to determine space groups which were later confirmed by successful solution of the structure. Fifteen reflections with 2 θ between 6 and 19° were centered using a programmed centering routine. Cell constants and errors were obtained by least-squares refinement of these angles.

Intensity data were collected using Mo K α radiation which had been monochromatized using a highly oriented graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. The θ -2 θ scan technique was used with scan rates which varied between 1.94 and 14.6°/min to obtain comparable counting statistics for all data. Backgrounds were measured at each end of the scan for a total time equal to one-half the scan time.

During data collection, the intensities of three standard reflections were measured every 50 reflections with no decomposition being observed. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.²⁰ Standard deviations were assigned as follows

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

where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counting time, and K is the ratio of scan time to background time. No correction for absorption was made. Only those data for which $F^2 \geq 3\sigma(F^2)$ were used in the structure solution and refinement.

Structure Determination of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot \text{O}(\text{C}_2\text{H}_5)_2]_2$. Three-dimensional Patterson techniques gave the position of the Mo, Zn, and Cl atoms. A difference Fourier map then gave all of the non-hydrogen atoms except the ethyl groups of the ether. An additional structure factor calculation followed by a difference Fourier map was necessary to define the ethyl groups.

Least-squares refinement of all non-hydrogen atomic positions gave

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.043$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.052$$

for the model with anisotropic thermal parameters and anomalous scattering effects included for Mo, Zn, and Cl. The error of fit was 1.65. The highest residual electron density in a final difference map was 0.31 e/Å³. Table II is a list of atomic coordinates and thermal parameters. A listing of observed and calculated structure factors is available.²¹

Structure Determination of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$. Solution of the three-dimensional Patterson function resulted in the position of the Mo atom relative to the Zn atom which is crystallographically required to be at the origin.

Least-squares refinement of all atomic parameters with the ring hydrogens included as fixed contributions gave $R_1 = 0.040$ and $R_2 = 0.058$ for the model with anisotropic thermal parameters and anomalous scattering corrections included for Mo and Zn. The error of fit was 2.02. The highest residual electron density in a final difference map was 0.59 e/Å³. The largest nonmetal residual was 0.46 e/Å³. Table III contains a listing of atomic coordinates with thermal parameters. A listing of calculated and observed structure factors is available.²¹

Results

Preparation and Characterization of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MZnCl}\cdot \text{O}(\text{C}_2\text{H}_5)_2]_2$ and $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MZnCl}]_x$ (M = Mo, W). The syntheses of the transition metal zinc chloride derivatives were carried out by an extension of the method of Carey and Noltes.²² The method in-

(20) (a) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models. (b) Scattering factors, including anomalous dispersion corrections for Mo, Zn, and Cl, were taken from "The International Tables for X-Ray Crystallography," Vol. III, C. H. MacGillavry, G. D. Reich, and K. Lonsdale, Ed., Kynoch Press, Birmingham, England, 1962, p 201.

(21) See paragraph at end of paper regarding supplementary material.

(22) N. A. D. Carey and J. G. Noltes, *Chem. Commun.*, 1471 (1968).

Table I. Physical Constants and Experimental Data

	$[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$	$[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot \text{O}(\text{C}_2\text{H}_5)_2]_2$
Space group	$P2_1/n$	$P\bar{1}$
<i>a</i>	11.101 (4)	8.524 (3)
<i>b</i>	7.548 (2)	9.092 (3)
<i>c</i>	11.726 (4)	13.152 (4)
α	90.00	56.03 (2)
β	64.43 (2)	110.13 (2)
γ	90.00	103.96 (2)
Density (calcd)	2.08	1.76
Crystal size	0.113 × 0.169 × 0.26 mm	0.12 × 0.15 × 0.19 mm
Linear absorption coefficient	13.34 cm ⁻¹	25.02 cm ⁻¹
2 θ scan range (deg)	2 θ Mo K α_1 - 0.7 to 2 θ Mo K α_2 + 0.7	2 θ Mo K α_1 - 0.8 to 2 θ Mo K α_2 + 0.8
Deviation of 3 standards during data collection	3%	4%
Data collected	2920	5433
Data > 3 σ	2101	2578
2 θ (max)	60	60

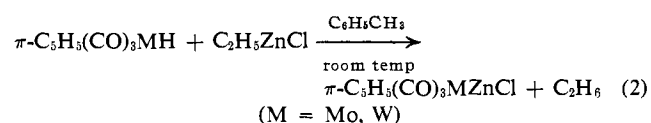
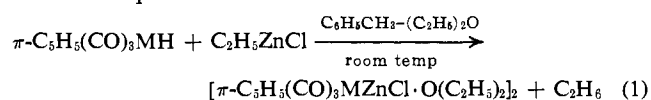
Table II. Atomic Coordinates and Anisotropic Thermal Parameters for $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2^a$

	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.2291 (1)	0.1412 (1)	0.2616 (1)
Zn	0.0414 (1)	-0.0199 (1)	0.1413 (1)
Cl	-0.1607 (2)	0.1275 (2)	-0.0595 (2)
O4	-0.1150 (6)	-0.2419 (6)	0.2322 (5)
C8	0.4956 (11)	0.2207 (13)	0.2276 (12)
C9	0.3882 (15)	0.2734 (15)	0.1116 (11)
C10	0.2914 (13)	0.4036 (12)	0.0812 (9)
C11	0.3410 (14)	0.4312 (12)	0.1843 (13)
C12	0.4738 (13)	0.3146 (15)	0.2815 (11)
C1	-0.0099 (9)	0.1744 (10)	0.2079 (7)
O1	-0.1496 (7)	0.2064 (8)	0.1762 (6)
C2	0.2550 (9)	-0.1137 (10)	0.3564 (7)
O2	0.2849 (8)	-0.2627 (7)	0.4170 (6)
C3	0.2045 (10)	0.0796 (10)	0.4286 (9)
O3	0.1951 (10)	0.0484 (11)	0.5201 (6)
C4	-0.1375 (13)	-0.4019 (12)	0.2250 (9)
C5	-0.0325 (16)	-0.5418 (12)	0.3383 (11)
C6	-0.2108 (14)	-0.2493 (13)	0.3096 (11)
C7	-0.3781 (13)	-0.1836 (17)	0.2244 (16)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	105 (1)	130 (1)	79 (1)	7 (1)	14 (1)	-58 (1)
Zn	123 (1)	151 (2)	79 (1)	9 (1)	18 (1)	-64 (1)
Cl	140 (3)	201 (4)	83 (2)	66 (3)	6 (2)	-69 (2)
O4	170 (10)	160 (10)	115 (6)	-28 (8)	59 (6)	-70 (6)
C8	135 (16)	259 (22)	203 (15)	-2 (15)	75 (13)	-62 (16)
C9	282 (25)	307 (26)	168 (13)	-75 (21)	127 (16)	-111 (16)
C10	260 (22)	193 (19)	142 (12)	-51 (17)	58 (13)	-45 (13)
C11	240 (21)	152 (16)	289 (19)	-82 (16)	134 (17)	-137 (16)
C12	201 (20)	369 (29)	199 (15)	-158 (20)	73 (15)	-178 (19)
C1	152 (14)	184 (15)	95 (7)	18 (11)	25 (8)	-77 (9)
O1	136 (10)	282 (14)	158 (7)	68 (9)	15 (7)	-124 (9)
C2	156 (14)	183 (15)	90 (7)	21 (12)	14 (8)	-67 (9)
O2	279 (14)	161 (11)	136 (7)	73 (11)	0 (8)	-52 (8)
C3	137 (14)	199 (17)	156 (11)	36 (12)	6 (10)	-100 (12)
O3	196 (15)	284 (19)	48 (6)	55 (13)	20 (8)	-84 (9)
C4	287 (22)	216 (18)	137 (10)	-61 (16)	63 (13)	-116 (12)
C5	419 (32)	198 (20)	216 (16)	67 (21)	74 (18)	-117 (16)
C6	276 (23)	258 (22)	210 (15)	-27 (18)	125 (16)	-133 (16)
C7	149 (19)	427 (34)	456 (30)	-21 (20)	56 (19)	-317 (28)

^a Standard deviation from the full variance-covariance matrix is given in parentheses for the least significant digit(s). The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The β 's are multiplied by 10^4 .

volves reaction between the appropriate organo-transition metal hydride and ethylzinc chloride as shown in eq 1 and 2.



The reagents are combined in solution at room temperature, and a smooth reaction starts immediately as evidenced by the evolution of ethane. For the generation of the ether complex the toluene/diethyl ether ratio is quite critical with regard to the rate of crystallization. After repeated trials a 1/1 solvent ratio was found to be optimum and produced well-formed crystalline products after 2–3 hr. In a large excess of toluene, crystallization does not occur, and attempts to induce precipitation by solvent reduction were unreliable. In a large excess of ether a microcrystalline product is produced by rapid precipitation. For preparative purposes, however, the synthesis of this complex in a pure ether solvent produces a suitable product identical with that produced in the cosolvent. Reaction 2 is

carried out in the absence of ether and a microcrystalline polymeric product precipitates 10–15 minutes after the reaction begins.²³

All complexes are white solids which decompose slowly upon exposure to air, discoloration being noticeable after 2–3 hr of exposure. The compounds may be stored under an inert atmosphere and after a period of 1 year the complexes remain intact. The derivatives decompose prior to melting. The etherate products are curiously insoluble in ethereal solvents; however, they show appreciable solubility in aromatic solvents.¹⁹ The nonetherate products are soluble in ethereal solvents and insoluble in hydrocarbon and aromatic solvents.

The ether complexes may be readily converted to the nonetherate analogs by heating under a dynamic vacuum. Diethyl ether removal is quantitative and complete after approximately 2 hr at 50°.

The 2,2'-bipy adducts of the zinc halide derivatives are easily prepared by the addition of the complexing

(23) The standard preparation for the analogous cadmium and mercury complexes (TmMX) (Tm = transition metal moiety, e.g., $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}$, $(\text{CO})_5\text{Co}$; M = Hg, Cd) is an exchange reaction between a bis metal derivative (Tm_2M) and a heavy metal halogen (MX_2).^{4,5} This method has been quite successful for mercury and cadmium complexes; however, limited work using this technique has consistently failed to produce the desired zinc compounds.

Table III. Atomic Coordinates and Anisotropic Thermal Parameters for $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}^a$

	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.0283 (0)	-0.0217 (0)	0.2031 (0)
Zn	0.0 (0)	0.0 (0)	0.0 (0)
C3	-0.0393 (5)	-0.2132 (7)	0.3309 (4)
O3	-0.0743 (4)	-0.3267 (6)	0.4023 (3)
C2	0.0944 (5)	-0.2318 (6)	0.0938 (4)
O2	0.1371 (5)	-0.3567 (5)	0.0331 (4)
Cl	-0.1609 (6)	-0.0064 (7)	0.2355 (5)
O1	-0.2719 (4)	0.0107 (7)	0.2612 (5)
C4	0.2387 (6)	0.1029 (9)	0.1518 (8)
C5	0.1712 (7)	0.0968 (9)	0.2822 (7)
C6	0.0610 (7)	0.2065 (10)	0.3195 (7)
C7	0.0576 (7)	0.2816 (8)	0.2168 (9)
C8	0.1697 (8)	0.2195 (10)	0.1086 (7)
H1 ^b	0.3333 (59)	0.0313 (64)	0.1101 (56)
H2 ^b	0.2008 (59)	0.0211 (65)	0.3319 (56)
H3 ^b	0.0169 (56)	0.1928 (78)	0.3939 (52)
H4 ^b	0.0082 (54)	0.3669 (77)	0.1955 (49)
H5 ^b	0.1956 (61)	0.2463 (76)	0.0401 (53)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	68 (0)	117 (1)	55 (0)	-3 (0)	-34 (0)	2 (0)
Zn	110 (1)	160 (2)	55 (1)	-25 (1)	-53 (1)	23 (1)
C3	93 (5)	184 (9)	64 (4)	-000 (5)	-38 (4)	14 (5)
O3	156 (6)	248 (9)	85 (4)	-17 (6)	-45 (4)	54 (5)
C2	120 (6)	149 (8)	68 (4)	-16 (6)	-38 (4)	14 (5)
O2	222 (8)	150 (7)	102 (4)	18 (6)	-44 (5)	-34 (4)
Cl	94 (5)	214 (11)	97 (5)	-16 (6)	-56 (4)	39 (6)
O1	78 (5)	459 (16)	162 (6)	-15 (6)	-57 (4)	84 (7)
C4	80 (6)	202 (12)	198 (10)	-10 (7)	-51 (6)	-65 (9)
C5	154 (9)	222 (13)	184 (10)	-16 (8)	-133 (9)	-13 (9)
C6	144 (9)	293 (15)	106 (6)	-29 (9)	-45 (6)	-73 (8)
C7	141 (9)	126 (10)	254 (13)	11 (7)	-121 (9)	-24 (9)
C8	198 (11)	253 (15)	124 (7)	-129 (11)	-86 (8)	65 (9)

^a Standard deviations from the full variance-covariance matrix are given in parentheses for the least-significant digit(s). The form of the anisotropic temperature factor is $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$. The β 's are multiplied by 10^4 . ^b Hydrogen atoms were added as fixed contributions and assigned an isotropic temperature factor of 2.0.

agent to a toluene-diethyl ether solution of the corresponding derivatives. Alternatively, reaction 1 or 2 may be carried out in the presence of 2,2'-bipy and precipitation of the addition complex occurs immediately. The complexes are highly colored and are only very slightly soluble in common solvents. The colored nature of the complexes is similar to that exhibited by the 2,2'-bipy adducts of zinc alkyls.²⁴

Infrared Spectral Characteristics. All products have been characterized by ir spectroscopy in the solid state as Fluorocarbon mulls. The ir data are presented in Table IV for all compounds and the spectra for derivatives I, II, III, IV, VII and VIII are reproduced in Figures 1 and 2.²⁵

An outstanding characteristic with regard to the chloride etherate and nonetherate complexes is the occurrence of prominent common absorptions. Within the accuracy of the measurements, common bands in I and III occur at 1754, 1891, and 1920 cm^{-1} . For II and IV identical absorptions appear at 1752, 1881, and 1975 cm^{-1} . With the exception of the absorption at 1975 cm^{-1} in II and IV, the common absorptions in the etherate complexes can be described as weak to medium intensity and upon removal of ether become medium to strong. Also, some absorptions disappear by conversion to the nonetherate, most notably the shoulder at 1882 cm^{-1} in I and the shoulder at 1872 cm^{-1} in III.

(24) J. G. Noltes and J. W. G. Van Den Hurk, *J. Organometal. Chem.*, **3**, 222 (1965).

(25) Spectra for V and VI are reproduced in the microfilm edition of this journal. See paragraph at end of paper regarding supplementary material.

Table IV. Infrared Data in the Carbonyl Region for Transition Metal-Zinc Derivatives^a

Compound	ν_{CO} (cm^{-1})
I	1993 (sh, m), 1980 (sh, s), 1969 (s), 1920 (w), 1895 (sh, m), 1882 (sh, s), 1855 (st), 1758 (w)
II	1991 (sh, m), 1975 (s), 1912 (w), 1881 (sh, m), 1872 (sh, m), 1847 (s), 1752 (m)
III	1996 (sh, m), 1980 (s), 1919 (w), 1891 (m), 1864 (m), 1754 (m)
IV	1988 (sh, s), 1975 (s), 1907 (w), 1883 (s), 1852 (s), 1751 (s)
V	1946 (s), 1860 (s), 1830 (sh, m), 1816 (s), 1789 (sh, w)
VI	1942 (s), 1848 (s), 1812 (s), 1785 (sh, w)
VII	1968 (s), 1894 (s), 1867 (s)
VIII	1978 (sh, s), 1961 (s), 1910 (sh, m), 1900 (m), 1871 (sh, m), 1850 (sh, s), 1836 (v s)

^a Infrared spectra were obtained as Fluorocarbon mulls and recorded on a Perkin-Elmer Model 267 spectrometer. Spectra were calibrated against the 1601.4- cm^{-1} band of polystyrene film.

A second notable feature in the ir is the complexity of the spectra for the chloride derivatives compared to the bis compounds. Three fundamental carbonyl modes are expected based on local symmetry and the bis derivatives exhibit "ideal" spectra.²⁶ Based on a comparison of the crystal structures, reported below, the etherate complexes should exhibit ir spectra similar

(26) Prominent shoulder absorptions are quite evident for the tungsten complex. This characteristic may be ascribed to coupling across the heteroatom or, alternatively, to conformational effects. See, for example, J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1875 (1967), and references therein.

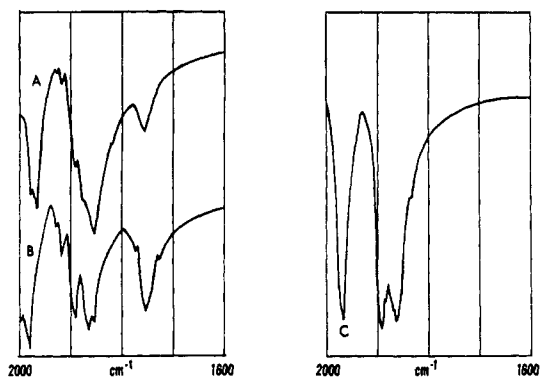


Figure 1. Infrared spectra in the carbonyl region for (A) $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2$, (B) $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}]_2$, and (C) $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$.

to the bis complexes. In the absence of any significant differences in the structural parameters of the transition metal moieties the complexity of the spectra is believed to be a consequence of a nonetherate impurity. Due to the lability of the ether species, the act of mulling drives off some of the ether resulting in an ir sample containing a mixture of etherate and nonetherate. This behavior gives rise to common absorptions which become more intense with total removal of diethyl ether.

In an attempt to understand the complex spectra of the nonetherate complexes the 2,2'-bipy adducts were prepared and mull spectra were obtained for these derivatives. With the formation of the adducts the complexity of the spectra is reduced, and three strong carbonyl absorptions are evident and shifted to lower energy. The shift to lower energy is consistent with the redistribution of electron density into the carbonyl groups. The similarity of these spectra to the bis derivatives implies that the chloride adducts and bis derivatives contain stereochemically identical transition metal moieties. A structure for the adducts consistent with the observed spectra are tetrahedral monomeric species with the 2,2'-bipy base completing the coordination sphere of zinc.

Crystal Structure of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2$. The crystal structure of I consists of discrete dimeric units. There appears to be no interaction between molecular units, the shortest intermolecular distance being 3.15 Å between C₉ and C₁₁. A stereoscopic view of a single molecule is given in Figure 3 and stereo packing drawing of the unit cell is shown in Figure 4. A full view of the molecular structure, excluding hydrogen atoms, is shown in Figure 5 with the labeling scheme. Bond distances and angles are given in Table V.

The molecular framework is structured on a zinc-chlorine bridge system. The bridge system is planar, as required by the crystallographic center of inversion, and unsymmetrical with zinc-chlorine distances of 2.401 (2) and 2.359 (2) Å. These distances are considerably longer than the zinc-chlorine distances in coordinated zinc chloride. The 1,10-phenanthroline complex of ZnCl₂ exhibits a Zn-Cl distance of 2.20 Å.²⁷ Other Zn-Cl distances in similar ZnCl₂ complexes

(27) C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).

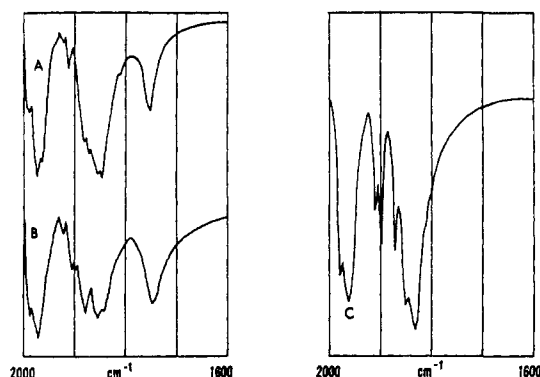


Figure 2. Infrared spectra in the carbonyl region for (A) $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2$, (B) $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WZnCl}]_2$, and (C) $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Zn}$.

Table V. Interatomic Distances (Å) and Angles (deg) for $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2^a$

Atom	Distance	Atom	Angles
Mo-Zn	2.632 (1)	Zn-Mo-Cl	65.3 (2)
Mo-C1	1.952 (8)	Zn-Mo-C2	66.0 (2)
Mo-C2	1.951 (7)	Zn-Mo-C3	122.0 (2)
Mo-C3	1.951 (7)	C1-Mo-C2	107.3 (3)
Mo-C8	2.331 (9)	C1-Mo-C3	82.3 (3)
Mo-C9	2.363 (10)	C2-Mo-C3	81.3 (3)
Mo-C10	2.352 (9)	Mo-Zn-Cl	123.2 (1)
Mo-C11	2.314 (8)	Mo-Zn-Cl'	121.0 (1)
Mo-C12	2.324 (8)	Mo-Zn-O4	119.2 (1)
Zn-Cl	2.401 (2)	Cl-Zn-O4	96.9 (2)
Zn-Cl' ^b	2.359 (2)	Cl'-Zn-O4	99.8 (2)
Zn-O4	2.093 (5)	Cl-Zn-Cl'	90.3 (1)
Zn-Cl ^c	2.538 (7)	Zn-Cl-Zn'	89.7 (1)
Zn-C2 ^c	2.560 (7)	Zn-O4-C4	123.3 (5)
O4-C4	1.476 (10)	Zn-O4-C6	121.9 (5)
O4-C6	1.472 (9)	C4-O4-C6	114.9 (6)
C4-C5	1.467 (14)	O4-C4-C5	111.1 (7)
C6-C7	1.486 (16)	O4-C6-C7	107.1 (10)
C1-O1	1.169 (8)	Mo-C1-O1	174.6 (7)
C2-O2	1.164 (8)	Mo-C2-O2	174.1 (7)
C3-O3	1.151 (7)	Mo-C3-O3	178.1 (10)
C8-C9	1.352 (15)	C8-C9-C10	109.0 (10)
C9-C10	1.399 (15)	C9-C10-C11	108.2 (10)
C10-C11	1.420 (15)	C10-C11-C12	108.3 (10)
C11-C12	1.452 (15)	C11-C12-C8	103.5 (9)
C12-C8	1.453 (15)	C12-C8-C9	111.0 (10)

^a Number in parentheses represents the estimated standard deviations of the least significant digit. ^b The primed atoms in this table correspond to inversion related atoms. ^c These values represent nonbonded distances.

range from 2.24 to 2.32 Å.^{28,29} In all these complexes the Zn-Cl distance apparently depends upon the nature of the coordinating agent. The distances in the present complex may be a consequence of the bridge system. Bond lengths involving bridging atoms are usually longer than analogous terminal distances.³⁰

The coordination of zinc is completed by a $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}$ moiety and a diethyl ether species. The zinc to ethereal oxygen distance is 2.093 (5) Å and is comparable to the Zn-O distance (2.07 Å) in $(\text{MeZn-OMe})_2$.³¹ The zinc-molybdenum distance of 2.632

(28) B. K. S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1961).

(29) N. R. Kunchier and M. R. Truter, *J. Chem. Soc.*, 3478 (1958).

(30) For example, in Al_2Cl_6 and $\text{Al}_2(\text{CH}_3)_6$ terminal Al-Cl and Al-CH₃ distances are shorter than bridging Al-Cl and Al-CH₃ distances. "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11 (1958); R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962).

(31) H. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, 194 (1966).

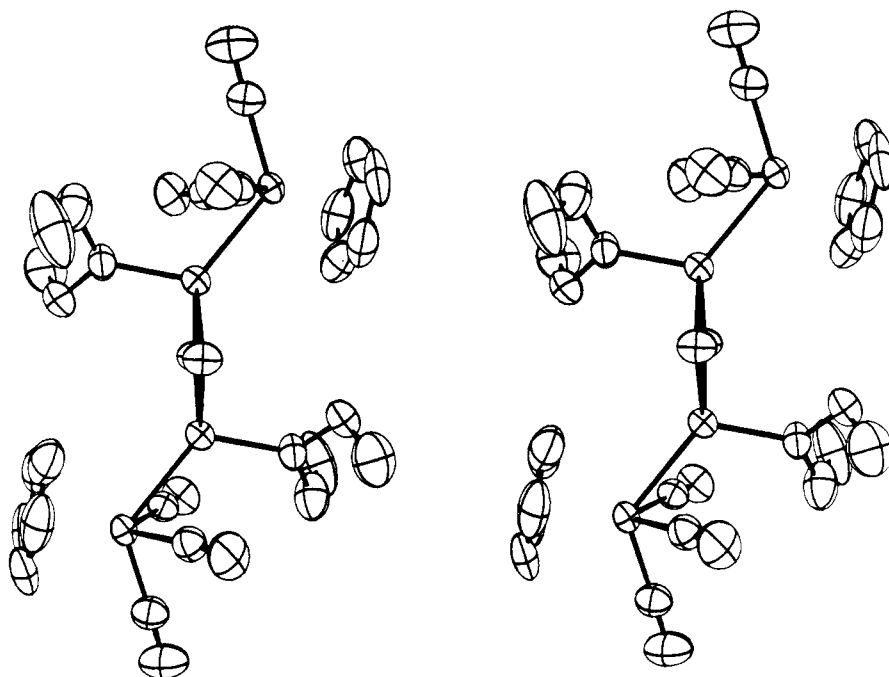


Figure 3. A stereoscopic view of the $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2$ molecule. The atoms are represented by 50% probability thermal ellipsoids.

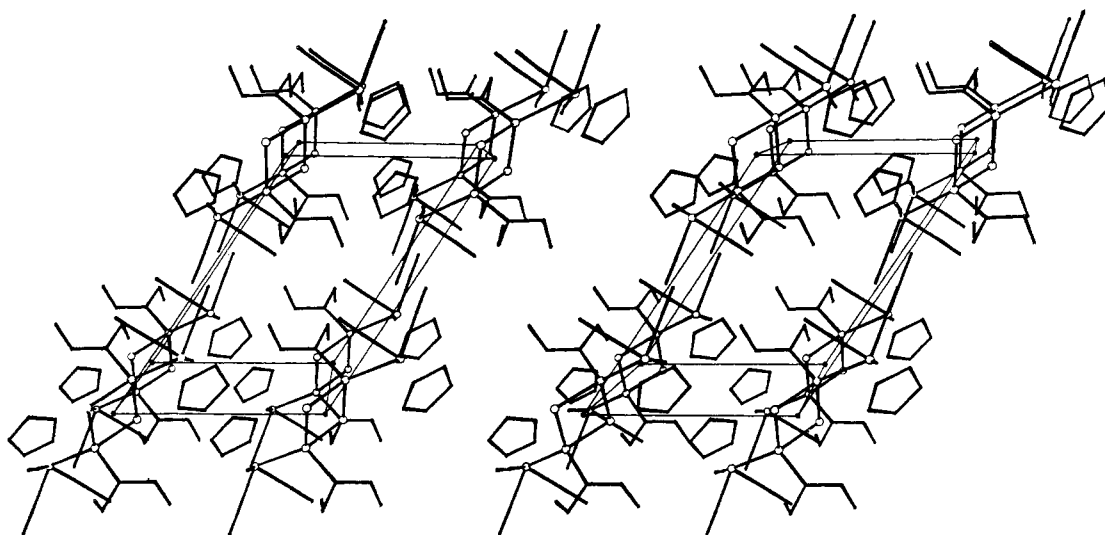


Figure 4. A stereoscopic view of the unit cell of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoZnCl}\cdot\text{O}(\text{C}_2\text{H}_5)_2]_2$ with the crystallographic a axis horizontal and the c axis vertical.

(1) Å is 0.09 Å longer than the analogous bond length in $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$ (2.538 (1) Å) but 0.15 Å shorter than the calculated single-bond distance.³² The stereochemistry about the zinc atoms may be described as highly distorted tetrahedra. The bond angles in the bridge system are close to 90° and the angles associated with the two remaining ligands are 120°. Presumably the stereochemical requirements of the bridge system are responsible for the distortions.

The coordinated ether groups exhibit normal C–O and C–C bond distances.³³ Stereochemically, the ethyl groups are arranged in a screw fashion to alleviate intramolecular contacts.

(32) Using the covalent radius of 1.62 Å for Mo(0) and 1.16 Å for Zn (taken from the Zn–C distance in $\text{Zn}(\text{CH}_3)_2$ and a carbon radius of 0.77 Å) a Mo–Zn single bond distance of 2.78 Å is calculated.

(33) Reference 20b.

The bond distances in the $\pi\text{-C}_5\text{H}_5(\text{CO})\text{Mo}$ groups are quite normal and show no unusual distances compared to other molecules incorporating this transition metal functionality. A comparison is provided by the data given in Table VI.

Crystal Structure of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$. The crystal structure of VII consists of the packing of discrete molecular units. Intermolecular distances are normal and no interactions are apparent. A stereoscopic view of a single molecule is shown in Figure 6 and a stereo packing diagram is given in Figure 7. A total view of the molecule, excluding hydrogen atoms, is shown in Figure 8 with the labeling scheme. Intramolecular bond distances and angles are given in Table VII.

The molecular framework consists of a linear molybdenum–zinc–molybdenum bond system with a center of symmetry at the zinc site. The molybdenum to zinc

Table VI. Average Distances in Å between Adjacent Atoms in the π -C₅H₅(CO)₃Mo Group of (A) [π -C₅H₅(CO)₃Mo]₂,^a (B) π -C₅H₅(CO)₃MoC₂H₅,^b (C) π -C₅H₅(CO)₃MoCl,^c (D) [π -C₅H₅(CO)₃Mo]₂Tl,^d (E) [π -C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂,^e and (F) [π -C₅H₅(CO)₃Mo]₂Zn^e

Atom	A	B	C	D	E	F
Mo-C (ring)	2.35	2.38 (2)	2.36	2.351 (9)	2.337 (10)	2.335 (6)
Mo-C (carbonyl)	1.96	1.96	1.99	1.968 (12)	1.951 (8)	1.974 (6)
C-O	1.16	1.15	1.16	1.154 (8)	1.161 (8)	1.146 (7)
C-C (ring)	1.42	1.43 (4)	1.36	1.42	1.42	1.39

^a F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957). ^b M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963). ^c S. Chaiwasie and R. H. Fenn, *Acta Crystallogr., Sect. B*, **24**, 525 (1968). ^d Reference 2. ^e This work.

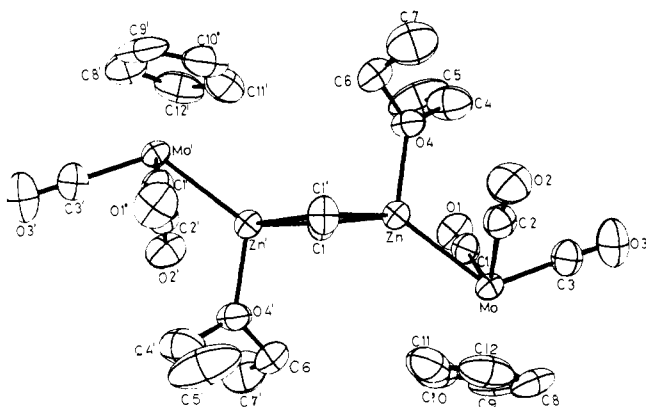


Figure 5. A perspective view of the [π -C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂] molecule with the labeling scheme. The atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Primed atoms correspond to inversion related atoms.

Table VII. Interatomic Distances (Å) and Angles (deg) for [π -C₅H₅(CO)₃Mo]₂Zn^a

Atom	Distance	Atom	Angle
Mo-Zn	2.538 (1)	Zn-Mo-C1	67.9 (2)
Mo-C1	1.969 (6)	Zn-Mo-C2	66.7 (1)
Mo-C2	1.971 (5)	Zn-Mo-C3	126.7 (1)
Mo-C3	1.982 (5)	C1-Mo-C2	103.9 (2)
Mo-C4	2.344 (6)	C1-Mo-C3	82.7 (2)
Mo-C5	2.335 (5)	C2-Mo-C3	79.5 (2)
Mo-C6	2.322 (6)	Mo-C1-O1	175.1 (6)
Mo-C7	2.328 (6)	Mo-C2-O2	176.4 (6)
Mo-C8	2.346 (6)	Mo-C3-O3	177.6 (8)
C1-O1	1.142 (7)	C4-C5-C6	108.3 (6)
C2-O2	1.152 (6)	C5-C6-C7	109.4 (6)
C3-O3	1.143 (6)	C6-C7-C8	107.9 (6)
C4-C5	1.383 (10)	C7-C8-C4	106.9 (6)
C5-C6	1.382 (10)	C8-C4-C5	107.5 (6)
C6-C7	1.346 (10)		
C7-C8	1.420 (10)		
C8-C4	1.397 (10)		
Zn-C1 ^b	2.561 (6)		
Zn-C2 ^b	2.522 (5)		
Zn-O1 ^b	3.243 (5)		
Zn-O2 ^b	3.198 (4)		

^a Number in parentheses represents the estimated standard deviations of the least significant digit. ^b These values represent non-bonded distances.

distance is 2.538 (1) Å and is 0.24 Å shorter than the calculated single-bond distance for Mo(0) and Zn.

The structural parameters of the π -C₅H₅(CO)₃Mo groups do not differ significantly from other derivatives involving this transition metal group (Table VI). With regard to bond angles and intramolecular non-bonding distances the π -C₅H₅(CO)₃Mo groups are identical with those in [π -C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂.

The C-C distances in the cyclopentadienyl rings show some irregularity (range 1.42–1.34 Å), but a consistent trend is not apparent and the differences are probably a consequence of vibrational motion.

Discussion

Structure and Bonding in [π -C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂] and [π -C₅H₅(CO)₃MoZnCl]₂. Four coordination with tetrahedral stereochemistry is dominant in organozinc halide chemistry. The structure of ethylzinc iodide has been reported and found to be polymeric with primary bonds supplemented by Zn-neighboring iodide interactions which make up the polymer framework and complete the tetrahedral symmetry around zinc.³⁴ Structural determinations have not been carried out for the chloride or bromide analogs; however, in nonpolar solvents these compounds are tetrameric.³⁵ Presumably, they contain four-coordinate zinc with structures similar to that of methylzinc methoxide.³¹

In the presence of basic coordinating compounds the alkylzinc halide derivatives can be isolated as monomeric species with two solvent molecules.³⁶ There is no evidence for halide bridged dimeric species in the solid state. Thus, the dimeric chlorine bridged complex is unique to organozinc halide structural chemistry. Apparently, electronic and steric effects of the transition metal moiety sufficiently alters the zinc site to stabilize the dimeric structure. The greater ionic character of the transition metal derivative compared to an alkyl group may be responsible. The structural characteristics of these derivatives are also probably dependent on the basicity of the coordinating molecule. Stronger monodentate bases (py, THF) may alter the structure and stabilize a tetrahedral monomeric species. Certainly, our work with 2,2'-bipy adducts suggests that monomeric species can be prepared when the ligand forms sufficiently strong bonds to the zinc.

The structure of the nonetherate species appears to be polymeric and its complete insolubility in noncoordinating solvents is consistent with this. The polymeric framework may be broken down with coordinating solvents which can interact with zinc.

The intermolecular interactions which support the polymer framework are structurally important and some information with regard to this feature may be deduced from the ir data. Low energy ir absorptions in complexes of this nature have been ascribed to carbonyl oxygen-metal interactions.³⁷ We propose that

(34) P. T. Moseley and H. M. M. Shearer, *J. Chem. Soc., Dalton Trans.*, 64 (1973).

(35) J. Boersma and J. G. Noltes, *Tetrahedron Lett.*, 1521 (1966).

(36) K. H. Thiele and P. Zdzunneck, *Organometal. Chem. Rev.*, **1**, 331 (1966).

(37) D. F. Shriver and Sr. A. Alich, *Coord. Chem. Rev.*, **8**, 15 (1972).

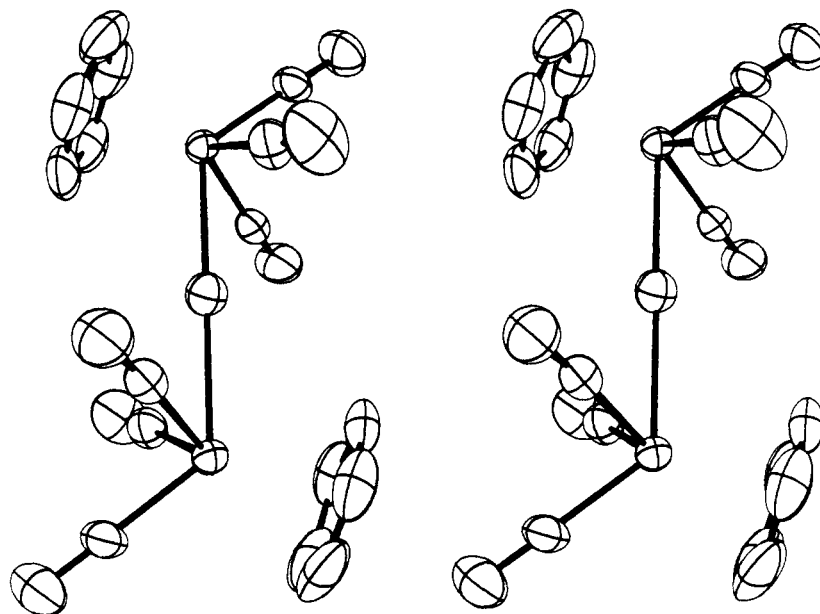


Figure 6. A stereoscopic view of the $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$ molecule. The atoms are represented by 50% probability thermal ellipsoids.

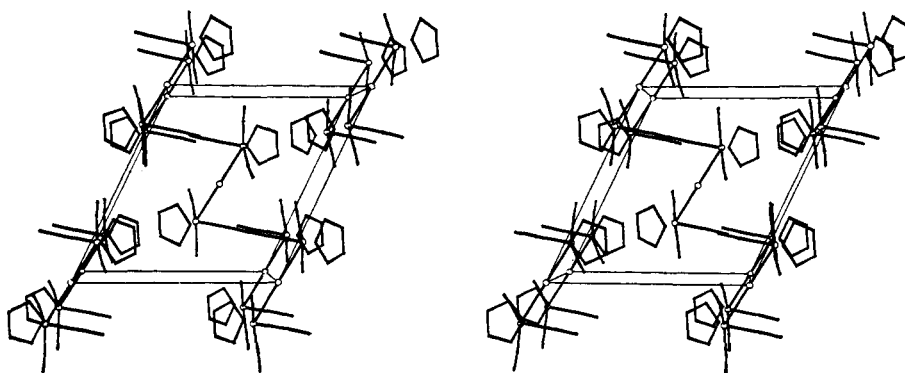
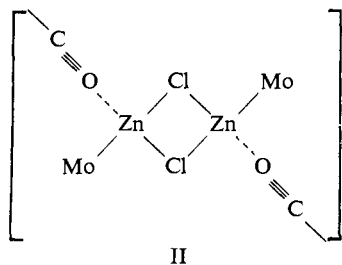


Figure 7. A stereoscopic view of the unit cell of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$ with the crystallographic a axis horizontal and the c axis vertical.

the absorption in the 1750-cm^{-1} region is the result of a $\text{C}\equiv\text{O}\text{---Zn}$ intermolecular interaction and further that the polymeric framework is made up of a continuous array of neighboring carbonyl oxygen–zinc associations. A possible polymeric unit is shown in II. Upon re-



moval of ether from the solvated derivative, the zinc atoms become coordinatively unsaturated. To maintain a pseudo-tetrahedral stereochemistry and full coordination neighboring carbonyl oxygen atoms take up the vacant positions.³⁸ This is similar to the neighboring iodide–zinc interactions in $(\text{EtZnI})_x$.³⁴

(38) The possibility of the presence of $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{M}$ ionic species has also been considered since the absorption at 1752 and 1891 cm^{-1} corresponds closely to the anion of the molybdenum species.³⁹ This possibility has been rejected, however, because these absorptions disappear in THF. Furthermore, formation of an appropriate counterion

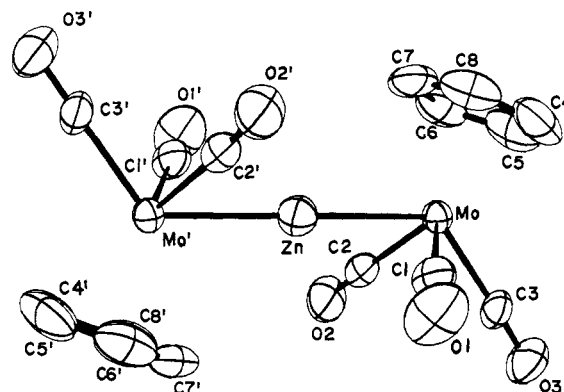


Figure 8. A perspective view of the $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2\text{Zn}$ molecule with the labeling scheme. The atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Primed atoms correspond to inversion related atoms.

The 2,2'-bipy adducts of the ether free derivative also lend support to this structural possibility. In the pres-

such as ZnCl^+ is unlikely. Representative samples have also been milled in cyclohexane and the resulting ir spectra are identical with fluorocarbon mulls, thus ruling out reaction with the mulling agent.

(39) R. B. King, K. H. Parnell, C. A. Eggers, and L. W. Hauk, *Inorg. Chem.*, 7, 2353 (1968).

ence of a strong coordinating base the coordination sites are satisfied and carbonyl interactions are not necessary. Thus, the ir spectra for these adducts are consistent with unperturbed carbonyl groups similar to the bis derivatives.

The bonding parameters in the etherate complexes are based on an sp^3 hybridization state for the zinc orbitals. Two of these orbitals are involved in the bridge bonding with appropriate molecular orbitals of the chlorine atoms. The two remaining hybrid orbitals are σ bonded to molybdenum and an ethereal oxygen, respectively.

The zinc-molybdenum bond distances reported above are shorter than the calculated single-bond distance. For the bis transition metal complex the contraction may be rationalized in terms of a π bonding contribution involving d electron density of the molybdenum atom and vacant p orbitals of zinc. For the four-coordinate sp^3 hybridized zinc complexes, this mode of bonding is excluded and therefore the short zinc-molybdenum distance in the halide complex cannot be a result of π bonding. An alternative explanation is available by consideration of the true oxidation state of zinc. In the transition metal derivatives, zinc more closely approaches the formal oxidation state of +2 (*i.e.*, is more ionic in character) compared to $(CH_3)_2Zn$. Thus, the use of a covalent radii, derived from bond distances in $(CH_3)_2Zn$ is inherently in error due to a difference between the apparent and real oxidation states. A trial calculation using the ionic radii of zinc (0.74 Å) predicts a zinc-molybdenum distance of 2.36 Å which is 0.18 Å less than the observed value. Thus, the observed value lies approximately half way between the two calculated values and shows the extreme dependence of bond distances on the true oxidation state. The short zinc-molybdenum distance in the bis complex may be ascribed to the inadequacy of the covalent radii for the purposes of calculation and need not be an indication of π bonding. The analogous bond in the halide complex is longer due to the expanded coordination sphere of zinc.

Based on the proposed structure for the nonsolvated complexes, the zinc sites remain sp^3 hybridized with the simple additional feature of carbonyl oxygen-zinc interactions. This interaction may be described as a simple acid-base interaction where the lone pair electrons of the oxygen are donated to an empty sp^3 orbital vacated by the removal of diethyl ether.

Comparison with Other Group II TmMX Derivatives (M = Mg, Cd, Hg). The synthesis and characterization

of transition metal-zinc chloride complexes completes the significant main group II metal series. Throughout this series the complete spectrum of bonding and association modifications is evident.

The magnesium compounds, as reported by Ulmer,⁴⁰ exhibit varied behavior highly dependent on the transition metal moiety. Compounds in this class were not well characterized in the solid state;⁴¹ however, evidence from the ir spectral studies supports carbonyl oxygen-magnesium interaction in THF solutions.

Mercury and cadmium halide complexes, on the other hand, have been well characterized for a large number of transition metal derivatives.⁴⁻⁶ In these complexes there is no evidence of association through metal carbonyl interactions or halogen bridging. The compounds appear as well-behaved covalent monomeric species both in solution and as solids.

The zinc complexes exhibit intermediate behavior with respect to the extremes shown by the magnesium complexes and the cadmium and mercury analogs. The structural characteristics of the zinc complexes are dominated by the tetrahedral coordination requirements of zinc which leads to carbonyl-oxygen coordination when other coordinating agents are not available to fill these positions.

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Supplementary Material Available. Structure factor tables and reproduced ir spectra will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$6.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5427.

(40) S. W. Ulmer, Ph.D. Thesis, Cornell University, 1972.

(41) During the preparation of this manuscript the first single-crystal X-ray structure determination of a transition metal-magnesium halide was reported. π -C₆H₅-bis(diphenylphosphino)ethane iron magnesium bromide · 3THF contains a tetrahedral magnesium atom with Fe-Mg, Br-Mg, and two O(THF)-Mg bonds. A third THF species is incorporated in the lattice as a molecule of crystallization. H. Felkin, P. J. Knowles, B. Meunier, A. Mitschler, L. Ricard, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 44 (1974).