Contribution from the Research Department,
The Standard Oil Company (Ohio), Cleveland, Ohio

Bis(acrolein)molybdenum Dicarbonyl

By D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll

Received March 15, 1965

The preparation and properties of bis(acrolein)molybdenum dicarbonyl, $(CH_2CHCHO)_2Mo(CO)_2$, are described. A polymeric structure involving bridging acrolein groups is suggested from solubility properties and coordination requirements of the metal and is supported by spectral data. Similar structures are proposed and discussed for related complexes of acrylonitrile.

Introduction

Several modes of coordination are possible for unsaturated organic carbonyl compounds in their complexes with the transition metals. Acrolein and cinnamaldehyde complexes of Fe(0) have been reported,[1] (ligand)$Fe(CO)_4$, for which spectroscopic evidence and coordination requirements of the metal support strong interaction only with the carbon–carbon double bond with relatively little involvement of the aldehydic carbonyl. In particular, a strong band was observed for the acrolein complex at 1680 cm.$^{-1}$ in the infrared which is very close to the aldehydic carbonyl absorption for the free ligand in the liquid state (1675 cm.$^{-1}$), and the n.m.r. line for the aldehydic proton was shifted upfield only 0.13 p.p.m. from its normal location for the free ligand. A somewhat different situation was found in the acrolein complex of nickel, $(CH_2CHCHO)_2Ni$,[2] and in cinnamaldehyde iron tricarbonyl,[3] for which spectroscopic evidence and coordination requirements of the metal indicate involvement of both the carbon–carbon double bond and the aldehydic carbonyl in bonding with the metal.

We have prepared a diamagnetic[4] complex of zerovalent molybdenum, $(CH_2CHCHO)_2Mo(CO)_2$ (I), that is in principle similar to bis(acrolein)nickel. Solubility properties and infrared and nuclear magnetic resonance data suggest that the structure is a coordination polymer with both bonding sites on the ligand bridging adjacent metal atoms. Coordination polymers have recently been described for a mesityl oxide complex of Pt(II)[5] and for complexes of dinitriles with Sn(IV).[6]

Structural analogs of the acrolein complex are also reported here for the ligands methyl vinyl ketone and crotonaldehyde. Bis(acrylonitrile)molybdenum dicarbonyl, first reported by Massey and Orgel,[7] has been prepared and can be interpreted to possess the same type of structure as proposed for I.

Experimental

$(CH_2CHCHO)_2Mo(CO)_2$ (I).—$(CH_3CN)_3Mo(CO)_3$[8] (10 g.) was stirred with freshly distilled acrolein (50 ml.) for 18 hr. under nitrogen at room temperature. The filtered solution was evaporated under reduced pressure to give a red, amorphous solid (8.7 g.) which was purified by crystallizing from acetone. The orange powder thus obtained was not soluble in any of the common organic solvents and decomposed slowly above 100°.

Anal. Calcd. for $C_8H_8MoO_4$: C, 36.38; H, 3.05; O, 24.23; Mo, 36.33; N, 0.00. Found[9]: C, 35.74 ± 1.1; H, 3.56 ± 0.1; O, 24.52 ± 0.3; Mo, 33.45 ± 1.5; N, 0.62 ± 0.1.

Oxidation with excess I_2 in refluxing ethanol evolved 1.75 equiv. of CO based on a molecular weight of 264.

When I (0.3 g.) and triphenyl phosphite (0.5 ml.) under nitrogen were heated at 100° for 15 min., a strong odor of acrolein was observed. Upon dilution with benzene, and analyzing by vapor phase chromatography, approximately 0.08 g. of acrolein (62%) was found

$(CH_3CHCHCHO)_2Mo(CO)_2$ (II).—$(CH_3CN)_3Mo(CO)_3$[8] (10 g.) was stirred with crotonaldehyde (35 ml.) for 18 hr. under nitrogen at room temperature. The orange solid (1 g.) which precipitated was filtered off and washed repeatedly with acetone. The solid was insoluble in any of the common organic solvents. The filtrate was evaporated under reduced pressure to yield a red solid (6.75 g.) which was dissolved in acetone and precipitated with *n*-hexane. Infrared analysis showed that both compounds had essentially the same spectrum, but that the minor product was of a greater purity.

The red solid decomposed around 173°. Upon contact with air, the complex spontaneously ignited.

Anal. Calcd. for $C_{10}H_{12}MoO_4$: C, 41.11; H, 4.14; N, 0.00. Found: C, 37.41, 37.35; H, 4.02, 4.04; N, 0.85, 0.85.

Oxidation with excess I_2 in refluxing ethanol evolved 1.84 equiv. of CO based on a molecular weight of 292.

$(CH_3COCHCH_2)_2Mo(CO)_2$ (III).—$(CH_3CN)_3Mo(CO)_3$[8] (10 g.) was stirred with freshly distilled methyl vinyl ketone (50 ml.) for 18 hr. under nitrogen at room temperature. The orange solid (6 g.) was filtered off and purified by washing repeatedly with acetone. The solid was insoluble in any of the common organic solvents. The filtrate when evaporated yields a small amount (about 0.5 g.) of dark brown solid. The major product when purified decomposes at 167–169°.

Anal. Calcd. for $C_{10}H_{12}MoO_4$: C, 41.11; H, 4.14; O, 21.91; Mo, 32.84; N, 0.00. Found[9]: C, 37.40 ± 0.9; H, 3.95 ± 0.1; O, 23.94 ± 0.2; Mo, 36.18 ± 0.7; N, 0.18 ± 0.1.

Oxidation with excess I_2 in refluxing ethanol evolved 1.65 equiv. of CO based on a molecular weight of 292.

When 3 g. of the complex and 10.5 ml. of triphenyl phosphite under nitrogen were refluxed in acetone overnight, approximately 0.886 g. of methyl vinyl ketone was identified in the reaction mixture (60% recovery) by vapor phase chromatography.

---

[1] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

[2] H. P. Fritz and G. N. Schrauzer, *Ber.*, **94**, 650 (1961).

[3] K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch.*, **19b**, 284 (1964).

[4] Measurement by H. D. Kaesz and M. L. Maddox of the University of California, Los Angeles.

[5] G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, **1**, 896 (1962).

[6] M. Kubota and S. R. Schulze, *ibid.*, **3**, 853 (1964).

[7] A. G. Massey and L. E. Orgel, *Chem. Ind.* (London), 436 (1961).

[8] D. P. Tate, J. M. Augl, and A. Buss, *Inorg. Chem.*, **2**, 427 (1963).

[9] Analyses were performed by Huffman Laboratories Inc., Wheatridge, Colo. Average values of 3–5 determinations are reported since the deviation between calculated and observed values is of the order of the repeatability of the determination. If a correction is made for the amount of starting acetonitrile complex still present based on the N value, the agreement between calculated and found values is good.

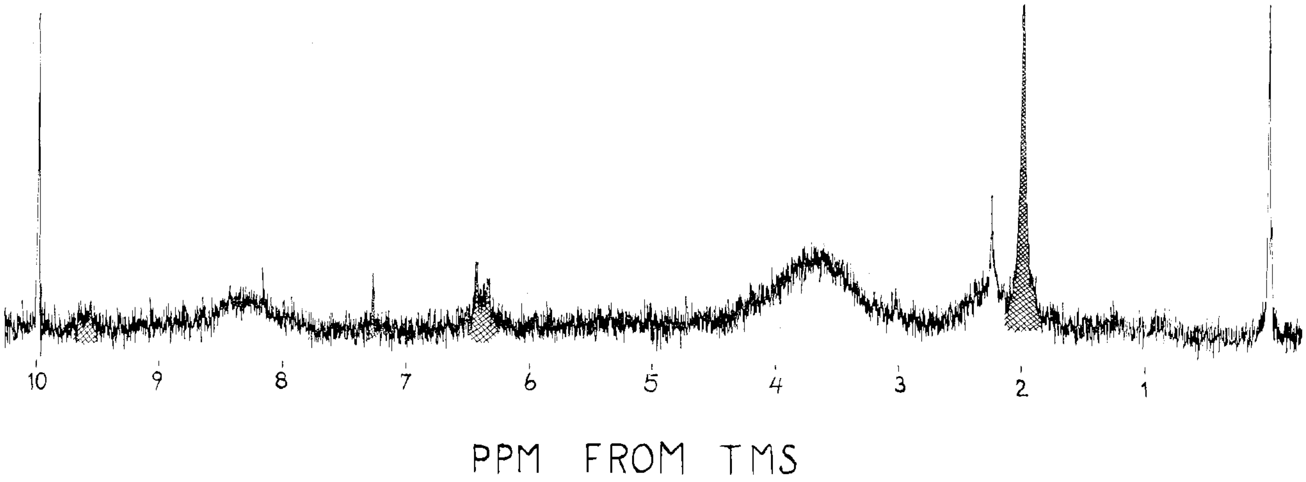


Figure 1.—Nuclear magnetic resonance spectrum of $(CH_2CHCHO)_2Mo(CO)_2$ (I).

$(CH_2CHCN)_2Mo(CO)_2$.—This material was prepared by the method of Massey and Orgel[7] and was identified by its infrared spectrum.

$[(C_6H_5O)_3P]_4Mo(CO)_2$.—This derivative was obtained from the acrolein, crotonaldehyde, and methyl vinyl ketone complexes, I, II, and III, respectively, and from bis(acrylonitrile)molybdenum dicarbonyl. Derivatives of I and II were obtained by stirring the complexes in an acetone solution with triphenyl phosphite under nitrogen at room temperature, and that of III and bis(acrylonitrile)molybdenum dicarbonyl by refluxing. No gas evolution was observed. The mixture melting point (180–182°) and infrared spectra of all the derivatives were identical.

The products were identified as the *cis*, C_{2v}, isomer by the appearance of the strong A_1 and B_1 metal carbonyl stretching bands in the infrared spectrum at 1940 and 1880 cm.$^{-1}$. Splitting of the lower frequency band may be due to interaction of the ligands with some distortion of the octahedron.

Anal. Calcd. for $C_{74}H_{60}P_4MoO_{14}$: C, 63.80; H, 4.34; P, 8.89. Found: C, 63.29, 63.56; H, 4.43, 4.38; P, 8.15, 8.30.

Prolonged heating of the *cis* phosphite derivative at approximately 150–180° rearranged the complex to a *trans* configuration. The change during heating was observed in the infrared spectrum. The infrared spectrum shows a single strong metal carbonyl stretching band for the A_{2u} mode at 1970 cm.$^{-1}$.

The *trans* D_{4h} isomer of the phosphite derivative was also obtained from the methyl vinyl ketone complex, III, by heating the reaction mixture for 1 hr. at about 100° after the evaporation of the acetone solvent. The residue was dissolved in benzene and crystallized from warm ethanol. The white crystals had a melting point of 136–138°.

Infrared Spectra.—The infrared spectra were recorded on a Perkin-Elmer 221 double-beam infrared spectrophotometer with a prism-grating interchange. The complexes were examined from 3950 to 650 cm.$^{-1}$ as halocarbon oil–Nujol mulls prepared in a nitrogen atmosphere. Absorptions attributed to impurities and to the medium are cross-hatched. Bands are reproducible within 3 cm.$^{-1}$.

The triphenyl phosphite derivatives were examined from 3950 to 650 cm.$^{-1}$ as halocarbon oil–Nujol mulls taking no precautions against sample deterioration except to avoid prolonged exposure to light.

Nuclear Magnetic Resonance.—Proton magnetic resonances were observed with a fully equipped Varian DP-60 spectrometer. Samples were examined as saturated solutions (5–10 wt. %) in $CDCl_3$ with $(CH_3)_4Si$ as internal reference. Radiofrequency power was held well below saturation intensity and a sweep rate of approximately 1.0 c.p.s./sec. was employed. The sample temperature was 25.0 ± 0.5°, and the spectrum was calibrated by the usual side-band technique. Line positions were reproducible to ±0.01 p.p.m. or better.

Magnetic Susceptibility.[4]—The magnetic susceptibility of the solid was measured under an inert atmosphere by the Gouy method. The measurements were carried out at 25.5° over a range of field strengths. The standard used was $Hg[Co(SCN)_4]$, assuming a gram susceptibility of 16.44×10^{-6} at 20°. Found for $(CH_2CHCHO)_2Mo(CO)_2$ (I), $\chi_{\text{mole}}^{298} = +31.7 \pm 13 \times 10^{-6}$ cm.^{3}/mole.

Results

Acrolein reacts smoothly with $(CH_3CN)_3Mo(CO)_3$[8] to give $(CH_2CHCHO)_2Mo(CO)_2$ (I). When freshly isolated by evaporation of excess acrolein, I is soluble in benzene, chloroform, acrolein, and other oxygenated solvents. Upon standing in solution, however, I precipitates and cannot be redissolved. Attempted recrystallization invariably gives an insoluble product whose elemental analysis and infrared spectrum are basically unchanged.

Upon stirring I with triphenyl phosphite in acetone at room temperature, *cis*-$[(C_6H_5O)_3P]_4Mo(CO)_2$ is formed and acrolein can be identified in the supernatant liquid.

Corresponding complexes of Mo(0) were prepared from methyl vinyl ketone and crotonaldehyde. The compounds have analogous infrared spectra, exhibit the same solubility properties as I, and, with triphenyl phosphite, give *cis*-$[(C_6H_5O)_3P]_4Mo(CO)_2$.

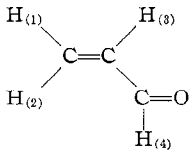
$(CH_2CHCN)_2Mo(CO)_2$, prepared by the method of Massey and Orgel,[7] is insoluble and also reacts with triphenyl phosphite to give $[(C_6H_5O)_3P]_4Mo(CO)_2$. Preparation of the phosphite derivative, however, requires more vigorous treatment, and the higher temperature results in isomerization to the *trans*, D_{4h}, form. A metastable soluble form as found for the acrolein complex (I) was not isolated for the acrylonitrile complex.

Nuclear Magnetic Resonance.—The proton n.m.r. spectrum of I (Figure 1), obtained before it irreversibly precipitates from solution, strongly suggests π-complexing through both the aldehyde carbonyl group and the carbon–carbon double bond. The notably broadened bands preclude the extraction of any useful spin-coupling data. Free acrolein and acetone are responsible for bands at approximately 9.6, 6.4, and 2.0 p.p.m.,

TABLE I

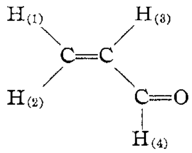
CHEMICAL SHIFTS (P.P.M. FROM TMS) OF FREE AND COMPLEXED LIGANDS

$(CH_2CHCHO)_2Mo(CO)_2$ (in $CDCl_3$)



	Free ligand	Complexed ligand	Δδ
$H_{(1)}$	6.39	3.67	2.72
$H_{(2)}$	6.39	2.24	4.15
$H_{(3)}$	6.39	3.67	2.72
$H_{(4)}$	9.55	8.28	1.27

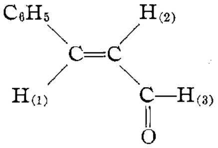
$(CH_2CHCHO)Fe(CO)_4$[a] (in acetone-d_6)



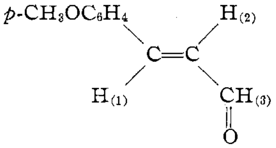
	Free ligand	Complexed ligand	Δδ
$H_{(1)}$	6.60	3.03	3.57
$H_{(2)}$	6.25	2.99	3.26
$H_{(3)}$	6.25	3.95	2.30
$H_{(4)}$	9.58	9.45	0.13

$RFe(CO)_3$[b]

R



	Free ligand		Complexed ligand		Δδ
	(Acetone-d_6)	($CDCl_3$)	(Acetone-d_6)	(CCl_4)	(Acetone-d_6)
$H_{(1)}$	7.63	7.52	6.52	5.95	1.11
$H_{(2)}$	6.78	6.71	3.30	3.13	3.48
$H_{(3)}$	9.75	9.71	7.78	7.52	1.97



	Free ligand		Complexed ligand		Δδ	
	(Acetone-d_6)	(CCl_4)	(Acetone-d_6)	(CCl_4)	(Acetone-d_6)	(CCl_4)
$H_{(1)}$	7.61	7.32	6.69	5.97	0.92	1.35
$H_{(2)}$	6.62	6.61	3.34	3.32	3.28	3.29
$H_{(3)}$	9.67	9.60	7.73	7.52	1.94	2.08
CH_3O	3.93		3.77			

[a] Values taken from ref. 1. [b] Values taken from ref. 3.

which are cross-hatched in Figure 1. Bands from I appear at 8.28, 3.67, and 2.24 p.p.m. (see Table I) in the approximate relative intensity 1:2:1, although the presence of impurities, especially acetone, prevents an exact integration.

Infrared.—The infrared spectra of the acrolein, crotonaldehyde, and methyl vinyl ketone complexes, I, II, and III, respectively, are shown in Figure 2a–c. The shift of the C═O and C═C frequencies to lower values from those for the free ligands gives strong evidence that the ligands are bound to the metal atom through both coordination sites (Table II).

TABLE II

INFRARED ABSORPTIONS FOR FREE AND CHELATED LIGANDS (IN CM.$^{-1}$)

	$\nu_{C=C}$	$\nu_{C=O}$
$CH_2CHCHO(l)$	1620	1700 (broad)
$(CH_2CHCHO)_2Mo(CO)_2$ (I)	1595	1550
$(CH_2CHCHO)_2Ni$[a]	1605	1518
$CH_3CHCHCHO(l)$	1657	1698
$(CH_3CHCHCHO)_2Mo(CO)_2$ (II)	1595	1560
$CH_3COCHCH_2(l)$	1621	1682
$(CH_3COCHCH_2)_2Mo(CO)_2$ (III)	1601	1562

[a] Values taken from ref. 2.

The spectrum of $(CH_2CHCN)_2Mo(CO)_2$[7] appears in Figure 2d.

The two carbonyl groups of all the complexes examined are mutually *cis* as indicated by the appearance of two strong, broad bands above 1900 cm.$^{-1}$ representing the A_1 and B_1 metal–carbonyl stretching modes of the *cis* (C_{2v}) structure. No bands ascribable to bridging carbonyls, M–CO–M, are observed.

Discussion

Acrolein and Related Complexes.—Instances of π-complexing through the carbon–carbon double bond with metal carbonyl compounds are very common, but little has been reported on the nature of metal-to-ligand bonds in which an aldehyde carbonyl group is involved as a coordination site. Nuclear magnetic resonance for I indicates that the C═O is π-complexed to the metal atom (Figure 1). The aldehyde proton n.m.r. band for I has been shifted upfield 1.27 p.p.m. from its position in the free ligand. Stark, *et al.*,[3] noted shifts of approximately 1.9 to 2.1 p.p.m. (solvent dependent) of the aldehyde proton resonance in cinnamaldehydeiron tricarbonyl, while a shift of only 0.13 p.p.m. was noted for the aldehyde proton in acroleiniron tetracarbonyl[1] and 0.53 p.p.m. for the cinnamaldehydeiron tetracarbonyl[1] aldehyde proton resonance. This evidence indicates that the aldehyde carbonyl group was not involved in the latter cases, while it was in the former and in I.

The broad band centered at 3.67 p.p.m. in I (see Table I) is assigned to $H_{(1)}$ and $H_{(3)}$ since it is believed that they should exhibit approximately the same chemical shift in the complexed ligand. This repre-

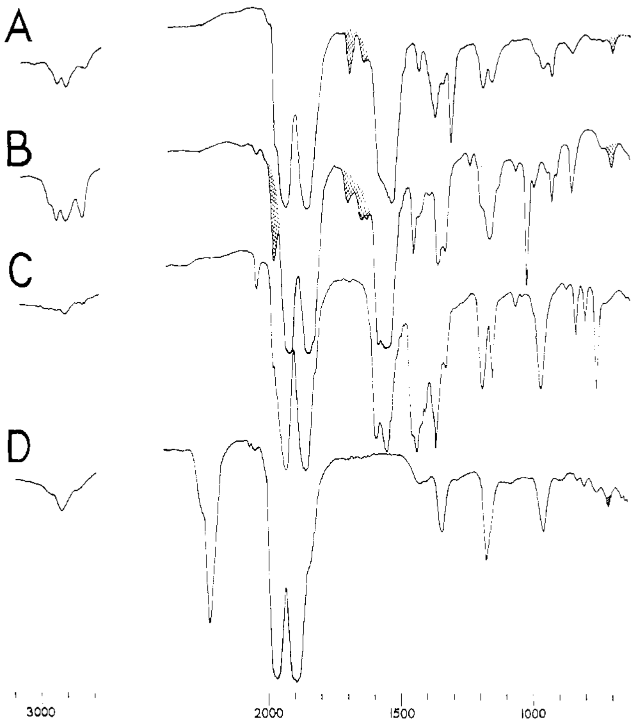


Figure 2.—Infrared spectra of complexes, halocarbon oil–Nujol mulls: A, $(CH_2CHCHO)_2Mo(CO)_2$ (I); B, $(CH_3CHCHCHO)_2Mo(CO)_2$ (II); C, $(CH_3COCHCH_2)_2Mo(CO)_2$ (III); D, $(CH_2CHCN)_2Mo(CO)_2$.

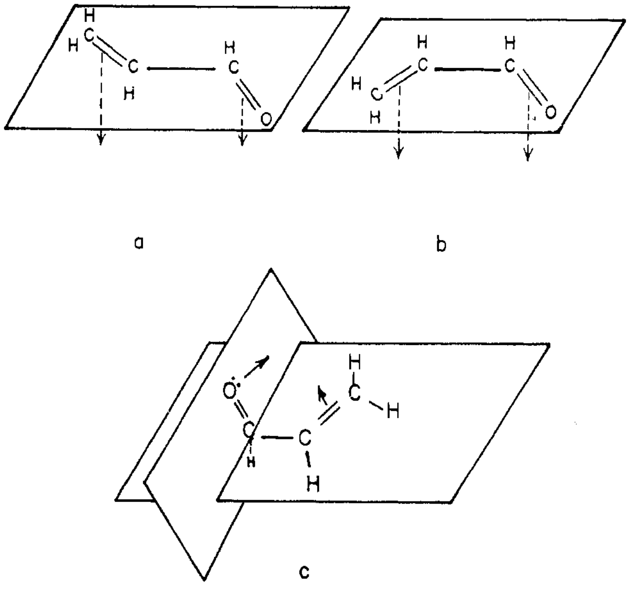


Figure 3.—Possible conformation of the ligand in $(CH_2CHCHO)_2Mo(CO)_2$ (I).

sents an upfield shift from their position in free acrolein of 2.72 p.p.m. The olefinic proton, $H_{(2)}$, in I is expected to exhibit a greater upfield shift, owing to its position relative to the metal in the complex, and is therefore assigned to the band at 2.24 p.p.m., indicating a shift of 4.15 p.p.m. upfield. These shifts are in general agreement, but on the low side, with what can be expected for olefin π-complexes of metal carbonyls.[10] Note that the analog of $H_{(2)}$ in I, labeled $H_{(1)}$, in the cinnamaldehyde complexes with iron tricarbonyl of Stark, *et al.*,[3] has been shifted only 0.92 to 1.35 p.p.m. (solvent dependent) upfield. This anomalously small shift may be due to the orientation of the phenyl ring and its consequent anisotropic paramagnetic deshielding of the $H_{(1)}$ proton in the complex, or the ring may be acting as a π-electron sink.

We postulate coordination of the aldehyde group through π-complexing of C═O rather than lone-pair coordination through oxygen. This is based in part on the shift of the aldehydic hydrogen *upfield* by 1.27 p.p.m. from its resonance in the free ligand. This is somewhat analogous to the upfield shift observed for similarly situated protons in olefins which are π-complexed to the metal.[10,11] The shift direction is the same, although in the case of the aldehyde proton it is probably due to a reduction of its anisotropic deshielding.[12] Coordination through the oxygen lone pair would be expected to lead to a *downfield* shift for the aldehydic proton, as a result of the deshielding inductive effect from the donation of electrons to the metal. This is also somewhat analogous to the downfield shift observed for the methyl hydrogens of acetonitrile in $(CH_3C{\equiv}N)M(CO)_5$, M = Cr, W,[10] and for the H_x olefin hydrogen in $(CH_2CH_xCN)_2W(CO)_4$,[10] in which it was postulated that the ligand is coordinated through the lone pair on nitrogen. In the case of cinnamaldehydeiron tricarbonyl,[3] the upfield shift of the aldehyde proton is almost twice that observed for I, which suggests that the carbonyl involvement is greater than in I. This can be explained in the cinnamaldehyde complex if the π-orbitals of the carbon–carbon double bond and the carbonyl bond are in the same plane and can experience maximum coupling; the ligand would then have an allylic structure. One can reason that in I the geometry of the carbonyl is such that its π-orbitals are somewhat out of the plane of the π-orbitals of the carbon–carbon double bond, thus preventing maximum coupling and allowing distinct coordination at both sites in the ligand.

Of the three most probable conformations that the ligand might assume in I, a near-planar arrangement is favored (Figure 3). In structures a and b all atoms of the ligand lie in a plane above the metal atom. The staggered conformation, c, would place the π-orbitals of the aldehyde group in a geometrically unfavorable position to form a good π-bond to the metal. This arrangement would more likely result in bonding through the lone-pair electrons on oxygen and would also uncouple the two π-bonded systems. The near-planar arrangement is consistent with n.m.r. measurements as discussed above.

---

(10) B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).

(11) See references such as (a) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961); (b) R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3600 (1961); (c) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961); (d) J. R. Holmes, H. D. Kaesz, and S. L. Stafford, "Advances in Organometallic Chemistry," R. West and F. G. A. Stone, Ed., Academic Press, Inc., in press.

(12) It has been pointed out by Gutowsky and Jonáš that bond anisotropy, in addition to π-electron localization or delocalization, must be considered in interpreting chemical shifts due to π-complexing. See H. S. Gutowsky and J. Jonáš, *Inorg. Chem.*, **4**, 430 (1965).

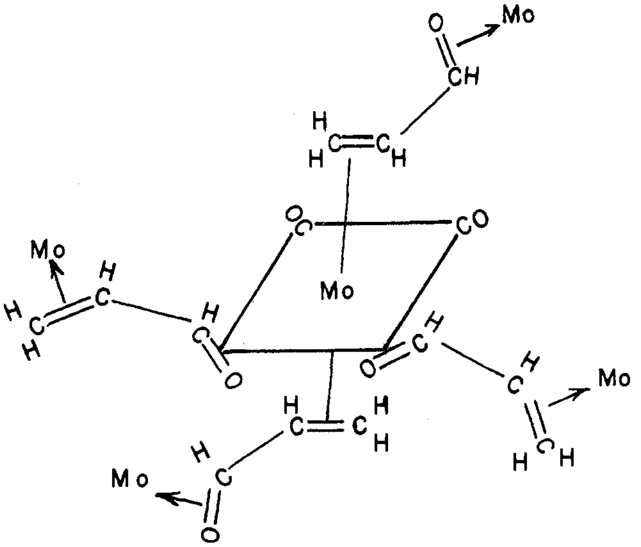


Figure 4.—Proposed structure for polymeric $(CH_2CHCHO)_2Mo(CO)_2$ (I).

The large downward shift in stretching frequency of the aldehyde carbonyl in the infrared spectra of I–III (Figure 2a–c) and the related bis(acrolein)nickel (Table II) is of the magnitude observed for the C=C stretching frequency in π-complexes of olefins. It is attributed to a decrease in the C=O bond order due to back donation of electrons from the metal into the vacant antibonding orbitals of this group. This ability to accept charge may be aided by the presence of the C=C bond, since complexes of the zerovalent metals have previously been reported only with saturated organic carbonyls in solution.[13] If this is the case, very low-energy vacant orbitals in the aldehyde C=O into which much of the charge from the metal is drained are available leaving a stable metal-to-olefin bond with more σ-character than usually observed for olefin π-complexes. This effect would also account for the somewhat smaller perturbation of the olefinic protons noted by n.m.r. The relatively smaller decrease in the C=C stretching frequencies is shown in Table II. In addition, the effectiveness of the carbonyls on the metal in accepting charge in I, thereby reducing the amount of back donation from the metal to the aldehyde bonding site, is demonstrated in the smaller downward shift of the aldehyde carbonyl for I than for bis(acrolein)nickel, see Table II.

Partially ionic structures as proposed by Schrauzer for the Ni complexes[2] are unlikely since I is diamagnetic.[4] The possibility of complete charge transfer in the formation, for instance, of $[Mo(CO)_2]^{2+}$ + 2-$(CH_2CHCHO)^-$ is also ruled out by the magnetic properties. It is difficult to imagine any kind of spin pairing in the ligands which, as one-electron reduction species in a fully ionic complex, would each contribute an unpaired electron in the molecule. Furthermore, it is difficult to imagine spin pairing for the four d electrons of Mo(II); this would only occur in the presence of a strong tetrahedral field, which is unlikely in the present complex. Recovery of the acrolein unchanged by displacement with other ligands tends to support a nonionic structure.

The solubility properties, elemental analyses, and infrared spectra of I suggest that a low molecular weight species of $(CH_2CHCHO)_2Mo(CO)_2$ is formed initially which slowly forms intermolecular bonds and becomes a coordination polymer (Figure 4). The number of units in the soluble form of I is not known since molecular weight determinations could not conveniently be made (the soluble form is isolated as the crude material). The absence of differences between the infrared spectra of the soluble and insoluble forms of I suggests that the ligand possesses the same conformation in both. We would favor an essentially *cisoid* arrangement, consistent with previously reported 1,3-diene complexes.[14] The proposed structure thus assumes no unusual coordination states and accounts for the solubility properties. Molybdenum(0), with an atomic number 42, is able to achieve the E.A.N. of krypton; the two acrolein ligands, either chelating or bridging, supply 4 electrons each, and the two carbonyl groups supply an additional 4 to make a total of 12 electrons donated (in a formal sense).

Acrylonitrile and Related Complexes.—Through analogous arguments, we arrive at the same structure for bis(acrylonitrile)molybdenum dicarbonyl as for I, namely, a coordination polymer in which each metal has achieved a coordination number of six and the E.A.N. through the use of bridging bidentate acrylonitrile ligands. The following remarks can also easily be applied to $(CH_2CHCN)_2Ni$.[2] In these compounds, however, involvement of the nitrile group is through the lone-pair electrons on the nitrogen (in contrast to the π-complexed C=O in I).

The present suggestion differs from previous ones concerning these complexes[2,7,15] basically in the interpretation of the almost unchanged value of the C≡N stretching frequency. The band appears 15 cm.$^{-1}$ lower than in free acrylonitrile, 2235 cm.$^{-1}$ (Figure 2d). That this does not positively rule out involvement of the C≡N groups was recognized by previous workers[7] and can be rationalized in the following way.

A number of cases are known in which the C≡N group is coordinated through its nitrogen lone pair, and in all of these a shift to higher frequency is observed.[6,10] In the absence of inductive effects by a charged metal atom, this increase in C≡N bond order reflects the degree of charge removal from the metal by donation of electrons into the antibonding orbitals of the nitrile group. As can be noted from a comparison of the upward shifts of the C≡N frequency for acetonitrile complexes [+23 cm.$^{-1}$ for $(CH_3CN)W(CO)_5$[10]] with those of acrylonitrile complexes [+4 cm.$^{-1}$ for $(CH_2CHCN)W(CO)_5$[10]] of M(0), the presence of a

---

[13] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 1264 (1963).

[14] E. O. Fischer, H. P. Kögler, and P. Kuzel, *Ber.*, **93**, 3006 (1960); O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960).

[15] G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); G. N. Schrauzer, *Ber.*, **94**, 642 (1961); G. N. Schrauzer and S. Eichler, *ibid.*, **95**, 260 (1962); G. N. Schrauzer, S. Eichler, and D. A. Brown, *ibid.*, **95**, 2755 (1962); G. N. Schrauzer and S. Eichler, *Chem. Ind.* (London), 1270 (1961); D. A. Brown and G. N. Schrauzer, *Z. physik. Chem.* (Frankfurt), **36**, 1 (1963).

double bond in the ligand aids the nitrile group in back-accepting charge from the metal, resulting in a smaller increase in the CN stretching frequency. For $(CH_2CHCN)_2Mo(CO)_2$, one may note at least two effects which operate to *lower* the bond order of the CN group and thus offset any shift to high frequency which might have been brought about through coordination. In the first place, if the olefinic group of the acrylonitrile molecule is coordinated to a metal, this may improve its ability to enhance back acceptance by the coordinated nitrile group. Also, in bis(acrylonitrile)-molybdenum dicarbonyl there may be a greater amount of charge on the metal to back donate to the ligands owing to a reduced number of carbonyls compared to $(CH_2CHCN)W(CO)_5$.[10] For further illustration, one may consider bis(acrylonitrile)nickel, in which there are no carbonyls to serve as π-acceptors so the ligand must back accept all the charge from the metal, and the C≡N frequency reflects this by showing the greater shift to lower frequency (-35 cm.$^{-1}$).[2] The CN position in $(CH_2CHCN)_2Mo(CO)_2$ thus appears only slightly shifted to lower frequency, 2220 cm.$^{-1}$, compared to its position in the free ligand, 2235 cm.$^{-1}$, even though it is coordinated to the metal atom.

Conclusions

It is concluded that the structure of bis(acrolein)-molybdenum dicarbonyl is polymeric with the ligands bridging adjacent metal atoms by π-complexing through the C═C and C═O groups. A metastable soluble form, first obtained, readily polymerizes to an insoluble bridged structure. Spectral data suggest a near-planar configuration of the ligands.

The proposed structure is in keeping with the solubility properties, a reasonable coordination number of the metal, and reactivity of the compounds. The diamagnetism and infrared and nuclear magnetic resonance spectral evidence strongly support these conclusions and also permit explanation of the structures of previously reported bis(acrylonitrile)molybdenum dicarbonyl,[7] bis(acrylonitrile)nickel,[2] and bis-(acrolein)nickel.[2] In the acrylonitrile complexes it is proposed that the nitrile group involvement is through the nitrogen lone-pair electrons.

The relative shifts in the infrared stretching frequencies of the coordinated C═C, C═O, and C≡N groups may be explained qualitatively by consideration of the ability of the ligand to accept back-donation from the metal dπ orbitals in the various complexes.

Acknowledgment.—The authors are indebted to Professor Herbert D. Kaesz (Department of Chemistry, University of California, Los Angeles) for valuable discussions and encouragement and to Herbert Grossman for experimental assistance.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Vibrational Spectra and Bonding in Metal Carbonyls. IV. CO and Re–Re Stretching Modes in the Decacarbonyls of Rhenium and Manganese[1]

BY F. A. COTTON AND R. M. WING

Received April 12, 1965

The Raman spectrum of $Re_2(CO)_{10}$ has been recorded as well as the infrared spectra of both dimanganese and dirhenium decacarbonyls in the region of CO stretching overtones. With these data and the existing infrared data, the problem of interaction of CO stretching motions across the metal–metal bond has been examined. It has been found that the spectrum of CO stretching frequencies may be satisfactorily explained using a potential energy function based upon a simple physical model in which a repulsive interaction between the dπ electrons of the two metal atoms is invoked. The Re–Re stretching frequency is 120 cm.$^{-1}$, corresponding to a force constant of about 0.8 mdyne/Å.

Introduction

The question of the nature and magnitude of the interaction between the two $M(CO)_5$ halves of an $(OC)_5MM(CO)_5$ molecule or between the two $M(CO)_4L$ halves of an $L(OC)_4MM(CO)_4L$ molecule is an important and interesting one which has concerned us for some time. From a comparison of the infrared spectra[2,3] of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with those of corresponding $XM(CO)_5$ compounds[4] it is apparent that there are several characteristic differences, which are not so simple as a mere shifting of the pattern as a whole. These differences are, chiefly: (1) The highest frequency band is relatively very weak in $XM(CO)_5$ compounds, whereas it has an intensity intermediate between those of the other two bands in the dinuclear species. (2) The relative spacings of the three bands differ in the mononuclear and binuclear

---

[1] Supported by the National Science Foundation.

[2] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956).

[3] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).

[4] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *ibid.*, **1**, 933 (1962)