by the greatest molar absorptivity and thus becomes "more allowed" than the $^4B_{1g} \rightarrow {}^4B_{2g}$ transition.

In the case where propanediamine was the ligand added to the starting material, an alcohol-soluble product could also be isolated. This material analyzed the same as the trans isomer insoluble in alcohol, but the electronic absorption spectrum consisted of only two bands and the molar absorptivities were about twice those exhibited by the trans isomer. The two-band spectrum and enhanced molar absorptivities are consistent with a cis structure. Thus complexes 11 and 12 are assigned cis structures since the spectra are consistent with that of *cis*-$[Cr(en)_2F_2]I$ which has been shown by other methods to have a cis arrangement of the two fluoro ligands.[7]

The amount of trans isomer formed in the synthetic scheme appeared to vary with the nature of the diamine being added to the starting complex. When ethylenediamine was used, an 80% yield of trans isomer was obtained; the percentage of trans isomer decreased to 56% with propanediamine and to 30% with trimethylenediamine.

Treatment of *trans*-$[Cr(pn)(en)F_2]Br$ or *trans*-$[Cr(pn)(tmd)F_2]Br$ with 72% perchloric acid produced the corresponding fluoroaquo complexes, *e.g.*, *trans*-$[Cr(pn)(en)F(OH_2)](ClO_4)_2$, as orange products, along with some green solid. The nature of the green product will be discussed in a following publication. The fluoroaquo complexes all chromatographed as single spots and the electronic spectra of three bands are consistent with a trans structure. Thus, the replacement of one fluoro ligand in the mixed ligand complexes by concentrated perchloric acid takes place with retention of configuration.

Registry No. $[Cr(pn)_2F_2][Cr(pn)F_4]$, 40946-18-7; $Na[Cr(pn)F_4]\cdot 1.15NaClO_4$, 40961-77-1; $[Cr(pn)F_2(OH_2)_2]I$, 40902-38-3; $[Cr(pn)F_2(OH_2)_2]Br$, 40902-39-4; *trans*-$[Cr(pn)_2F_2]Br$, 40902-40-7; *trans*-$[Cr(pn)(en)F_2]Br$, 40902-41-8; *trans*-$[Cr(pn)(tmd)F_2]Br$, 40902-42-9; $[Cr(pn)_2F_2]Br$, 40902-44-1; $[Cr(pn)(dach)F_2]Br$, 40902-43-0; *trans*-$[Cr(en)(pn)F(OH_2)](ClO_4)_2$, 40902-45-2; *trans*-$[Cr(pn)(tmd)F(OH_2)](ClO_4)_2$, 40902-46-3; $[Cr(pn)(en)_2]Br_3$, 40902-47-4; $[Cr(pn)F_2(OH)_2Br]$, 40902-48-5; en, 107-15-3.

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Spectroscopic Studies of Metal-Metal Bonding. IV. Absorption and Laser Raman Spectra and Vibrational Analyses of $[(OC)_5Mn\text{-}M'(CO)_5]^-$ (M' = Cr, Mo, W)[1]

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Received December 28, 1972

The infrared (33-2200 cm^{-1}), laser Raman (0-2200 cm^{-1}), and uv-visible (20,000-35,000 cm^{-1}) spectra of the compounds $A[MnM'(CO)_{10}]$, where M' = Cr, Mo, W and $A^+ = (C_6H_5)_4As^+$ or $(C_2H_5)_4N^+$, are reported. The vibrational spectra have been assigned on the basis of C_{4v} symmetry, normal-coordinate analyses based on these assignments have been performed, and the values of k(Mn-M') have been found to be in the order k(Mn-W) > k(Mn-Mo) > k(Mn-Cr). For isoelectronic pairs, k(Mn-Re) > k(Mn-W), and k(Mn-Mn) > k(Mn-Cr). The resultant appropriate eigenvectors show that currently employed simplified models for estimation of intermetallic forces are inadequate to predict correctly the magnitude of k(Mn-M'). The bonding implications of these variations in metal-metal bond strengths are discussed.

Introduction

The monoanions $[(OC)_5Mn\text{-}M'(CO)_5]^-$ (M' = Cr, Mo, W) prepared by Anders and Graham[3] form part of the $MM'(CO)_{10}$ series of metal-metal bonded compounds in which changes in metal-metal bond strength, k(M-M'), can be studied as a function of both M and M'. The complete series includes $M_2(CO)_{10}$ (M = Mn, Tc, Re), $MM'(CO)_{10}$ (M = Re; M' = Mn), $MM'(CO)_{10}^-$ (M = Mn, Re; M' = Cr, Mo, W), and $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W), among which there are a number of useful relationships to study. For example, $MnCr(CO)_{10}^-$ is isoelectronic with both the neutral $Mn_2(CO)_{10}$ and the dianion $Cr_2(CO)_{10}^{2-}$, and $MnW(CO)_{10}^-$ is isoelectronic and isostructural with $MnRe(CO)_{10}$. Through vibrational analysis of the anions presented here we may expect then to observe how changing the nuclear charge distribution affects k(Mn-M') in several cases and how strong is the effect on k(Mn-M') on going from first- to second- to third-row transition metal, M', bound to the same metal, Mn. To develop this approach more fully, the vibrational analysis of the series $[(OC)_5Re\text{-}M'(CO)_5]^-$ (M' = Cr, Mo, W) will be reported in a subsequent publication.[4]

Several spectroscopic investigations of metal-metal bonded carbonyls of the type $MM'(CO)_{10}$ have been reported.[3,5-20]

[1] Presented in part at the 3rd Annual Northeast Regional Conference of the American Chemical Society, Providence, R. I., Oct 1970.

[2] Abstracted in part from the Ph.D. thesis of J. R. Johnson, Brown University, which is to be submitted for publication.

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Vibrational assignments for the infrared and Raman spectra of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$ have been published,[3,5-10,12,14-16,20] and in one study an approximate normal-coordinate analysis of the low-frequency modes of the three decacarbonyls was carried out by Spiro and Quicksall.[7] Edgell and Paauwe[21] have studied the vibrational spectra of $Cr_2(CO)_{10}^{2-}$ and related the assignments to those of $Mn_2(CO)_{10}$, in addition to elucidating the important counterion and solvent effects in the spectra.

The potential of vibrational analysis for determining such bond strength measures as k(M-M′) is well recognized, but it has been realized only for a few small molecules. For large, complex metal-metal bonded compounds spectral treatments must be made at one of various levels of approximation, as discussed in the reviews of Watters and Risen[22] and Spiro.[23] In order to obtain reasonable bonding information with as little uncertainty as possible arising from the vibrational analysis, we find it particularly helpful to study a series of closely related compounds. We report in this paper the complete infrared and laser Raman spectra of the five salts $Et_4NMnCr(CO)_{10}$, $Et_4NMnMo(CO)_{10}$, $Et_4NMnW(CO)_{10}$, $Ph_4AsMnCr(CO)_{10}$, and $Ph_4AsMnMo(CO)_{10}$, their vibrational assignments and normal-coordinate analyses, and the bonding implications of the results.

Experimental Section

The compounds $A[(OC)_5Mn-M'(CO)_5]$ where M′ = Cr, Mo, or W and $A^+ = Ph_4As^+$ or Et_4N^+, except the Ph_4As^+ salt of the MnW molecule, were prepared by the method of Anders and Graham,[3] with slight modification. All carbonyls were sublimed before use, and all solvents were carefully purified by distilling them from CaH_2 under N_2 and vacuum deaerating them. The syntheses were modified by not allowing the reaction temperature to exceed 140 ± 5° and by not allowing the reaction to proceed for longer than 2 hr at that temperature.

The purity of each compound was determined by elemental analysis (Baron Consulting Co., Midwest Microlab, Inc.) and spectral analysis (5 μ, ir). Calculated values of the elemental compositions agreed to within 0.3% for C, H, N, O, and As and 1.0% for the transition metals.

Solutions for spectral measurements were prepared and handled under an inert atmosphere or *in vacuo* using dried and deaerated solvents and were placed in infrared or Raman cells which had been purged with dry N_2 and then sealed. Infrared cells with KBr, CsI, and high-density polyethylene windows, along with standard glass capillary, single-pass, and multipass Raman cells, were used where appropriate.

These compounds decompose slowly in the air and upon standing in solution. Therefore, as a check on the purity of the solutions used, their 5-μ infrared spectra were recorded before, after, and from time to time during the measurement of the reported spectra. The reported spectra were reproduced several times on each of several different samples.

Infrared spectra were measured on a Beckman IR-11 or IR-12 spectrometer with a resolution and accuracy of *ca.* 1 cm^{-1} as determined by standard resolution tests and wave number calibration.[24] The laser Raman spectra were measured on the Jarrell-Ash laser Raman system, with He-Ne laser excitation, with an accuracy of *ca.* 1 cm^{-1} and a resolution of *ca.* 3 cm^{-1}. Visible-uv spectra were recorded on a Cary 15 spectrometer.

Spectral Results and Assignments

The crystal structures of $M_2(CO)_{10}$ molecules, where M = Mn, Tc, or Re, and of $M_2(CO)_{10}^{2-}$ compounds, where M = Cr or Mo, have been reported.[25-29] The point group essentially proper to the discrete $M_2(CO)_{10}$ molecules is D_{4d}. By analogy with these structures, the mixed-metal anions MnM′-$(CO)_{10}^-$ (M′ = Cr, Mo, W) are expected to show the same structural arrangement of carbonyl groups around the metal atoms resulting in C_{4v} symmetry for the anions. Thus, six terminal carbonyl stretches should be observable in the 2000-cm^{-1} region of the infrared solution spectra of these anions. In both the previously reported spectra of Anders and Graham and this work six well-resolved infrared bands were observed in the 5-μ region. These anions are, therefore, taken to possess C_{4v} point group symmetry. This is illustrated in Figure 1 which also contains a description of the internal valence coordinates.

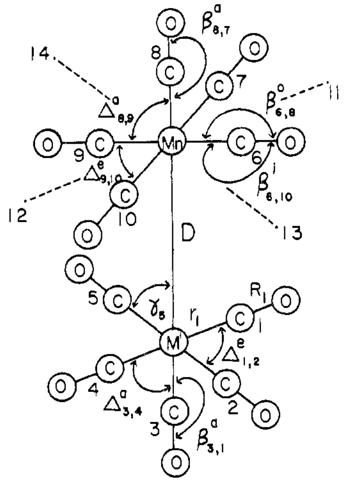

Figure 1. Idealized molecular geometry of the $MnM'(CO)_{10}^-$ anions (C_{4v}) including internal valence coordinates, defined as follows: $R_j = C_j\text{-}O$; $r_j = C_j\text{-}M$; $\beta_{j,k} = \delta(M\text{-}C_j\text{-}O)$ in the $C_j\text{-}M\text{-}C_k$ plane with C_j displaced toward k in $+\beta_{j,k}$; $\Delta_{j,k}{}^e = \delta(C_j\text{-}M\text{-}C_k)$ with both carbon atoms in the equatorial carbonyl plane, positive when opening; $\gamma_j = \delta(M\text{-}M\text{-}C_j)$ where C_j is an equatorial carbon atom, positive when opening; $\Delta_{j,k}{}^a = \delta(C_j\text{-}M\text{-}C_k)$ where one carbon is axial, along the C_4 axis, and one is equatorial, positive when opening.

For these anions the vibrational representation is Γ_{VIB} = 13 A_1(ir, R, pol) + 3 A_2(ia) + 6 B_1(R, depol) + 6 B_2(R, depol) + 16 E(ir, R, depol). The 60 normal modes occur at 44 frequencies of which 12 are Raman active only and 29 are both Raman and infrared allowed. The B modes are unique to the Raman spectra. Table I gives the distribution of vibrational mode symmetries over the internal coordinates for these anions.

In the normal-coordinate analyses, to be discussed below, values for bond lengths were obtained from a consideration of the known distances for $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ and those of the recently completed $M_2(CO)_{10}^{2-}$ dianions where M = Cr or Mo. Thus, the Mn-Cr distance was taken as 2.92 Å, and the metal-metal distances in $MnMo(CO)_{10}^-$ and MnW-$(CO)_{10}^-$ were taken as 2.94 and 2.96 Å, respectively. The last two values were estimated from the sum of the covalent radii for the appropriate metals taking into account the reported structural information for related compounds,[25-29] and the formal oxidation states of the metals involved. The M-C and C-O distances were also estimated from the structures of $M_2(CO)_{10}$ species and from those of the chromium, molybdenum, and tungsten hexacarbonyls. All angles were

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Table I. Symmetries of the Vibrational Modes for $[(OC)_5MnM'(CO)_5]^-$ (C_{4v})[a]

C-O str	$4\ A_1 + B_1 + B_2 + 2\ E$
M-C str	$4\ A_1 + B_1 + B_2 + 2\ E$
M-C-O def	$2\ A_1 + 2\ A_2 + 2\ B_1 + 2\ B_2 + 6\ E$
Eq C-M-C def	$B_1 + B_2 + 2\ E$
Ax C-M-C def[b]	$2\ A_1 + B_1 + B_2 + 2\ E$
M-M-C def[b,c]	$2\ A_1 + B_1 + B_2 + 2\ E$
Mn-M′ str	A_1
Torsion	A_2

[a] Abbreviations: eq, both M-C bonds are equatorial; ax, one M-C bond is axial; def, deformation; str, stretch. [b] The ax C-M-C def and M-M-C def contain $2\ A_1 + B_1 + B_2$ redundancies between them. [c] The carbon of the M-M-C def is in an equatorial position.

idealized to 90 or 180°, which is approximately true in the related compounds.

It is convenient to discuss the spectra of the $MnM'(CO)_{10}^-$ species in three separate regions: 5 μ (1800-2200 cm^{-1}), in which basically ν(C-O) modes occur; 300-800 cm^{-1}, in which largely δ(M-C-O) and ν(M-C) modes occur; 30-300 cm^{-1}, in which ν(M-M′) and several types of skeletal deformations occur. Table II contains all assigned fundamentals, their symmetry, depolarization ratios, and a partial description of the motions involved. An extensive table of band positions, intensities, states, and assignments for each of the compounds included in this study is available.[30]

Spectra in the Region 1800-2200 cm^{-1}. Table I indicates that six infrared ($4\ A_1 + 2\ E$) and eight Raman ($4\ A_1 + B_1 + B_2 + 2\ E$) fundamental frequencies are expected in this region: the four A_1 modes consist of two equatorial C-O stretches and two axial C-O stretches; the two E modes are both due to equatorial C-O stretches, as are the modes of B symmetry. Half of the above modes may be seen to arise from coordinates on the $M'(CO)_5$ portion of the molecule with the remainder from the $Mn(CO)_5$ moiety. The Raman spectra show clearly that the two highest frequency bands in this region are strongly polarized for all three anions and must be of A_1 symmetry. They are assigned as the two equatorial C-O stretches, with the lower frequency band resulting from the $M'(CO)_5$ moiety since its position shifts on going through the series. This assignment is in agreement with previous work.[3,5,10,13,14,31] The Raman bands at 1961 and 1941 cm^{-1} for the Mn-Cr anion, at 1959 and 1935 cm^{-1} for the Mn-Mo anion, and at 1961 and 1935 cm^{-1} for the Mn-W species are assigned as B modes since they are depolarized and are absent from the corresponding infrared spectra. The observed fundamentals in the infrared spectra at 1954, 1948, and 1951 cm^{-1} for these anions, respectively, along with corresponding depolarized Raman bands, are E modes on the basis of their strong infrared intensities and low intensities in the Raman spectra. The lowest frequency 5-μ region vibrations as well as those observed at *ca.* 1925 cm^{-1} are assigned as A_1 carbonyl stretches of axial character. This is substantiated by the depolarization ratios that are measurable and by the work of Clark and Crosse.[14] This then leaves the remaining fundamentals at 1894, 1906, and 1899 cm^{-1} for the Cr, Mo, and W anions to be of E symmetry. This is reasonable since the Cr and W infrared bands are strong and the corresponding Raman solution bands are weak, as expected from considerations of dipole moment and polarizability changes for the normal vibrations. This last assignment is consistent with the depolarization ratio of the 1894-cm^{-1} Mn-Cr anion band. Figure 2 shows a correlation diagram of the observed fundamentals for these three anions in the 5-μ region along with their symmetries.

The complete assignment for the 2000-cm^{-1} fundamentals is in agreement with infrared studies on $M(CO)_5X$ molecules[31] which indicate the frequency ordering of their bands to be A_1(equatorial) > B_1(equatorial) > E(equatorial) > A_1(axial). Taking the halves of the anions, the $M'(CO)_5$ and $Mn(CO)_5$ portions, we find that this ordering agrees with the assignments made here.

Two weak Raman bands occurring in all three anions between 1880 and 1890 and between 1910 and 1920 cm^{-1} are assigned as $^{13}C-O$ vibrations. The area between 1840 and 1870 cm^{-1} for the Raman solid spectra shows two to three bands depending on the anion and the particular salt. These observations are in contrast to the Raman and infrared solution results which show one band only. The occurrence of multiple bands in the Raman solid spectra is undoubtedly a result of solid-state effects, but since the space groups of these molecules are unknown, no further discussion of the origin of these bands will be brought forward here. The positions of the expected B type (C-O) stretches may be calculated readily from our assignments of the A_1 and E modes using approximate treatments,[32] and these are in general close to the observed B frequencies.

Spectra in the Region 300-800 cm^{-1}. The M-C stretching motions and M-C-O deformations are expected for this region. The ν(M-C) motions give rise to the same symmetry species as the ν(C-O) vibrations and the δ(M-C-O) vibrations are of ($2\ A_1 + 2\ A_2 + 2\ B_1 + 2\ B_2 + 6\ E$) character with 8 ir-active ($2\ A_1 + 6E$) and 12 Raman-allowed fundamentals ($2\ A_1 + 2\ B_1 + 2\ B_2 + 6\ E$). The M-C-O deformation motions can be described as of the equatorial (β_i), out-of-plane (β_o), or axial (β_a) type. These M-C-O bending motions are usually observed in the 500-800-cm^{-1} part of this region, while the metal-carbon stretching modes are normally in the lower frequency portion from 300 to 500 cm^{-1}, although the actual frequency ranges for these two types of motion overlap and considerable mixing of them is expected.[32a] Certain types of cation vibrations also occur in this region and make the interpretation of the anion spectra more difficult.

Dipole moment and polarizability change considerations suggest that several of the M-C-O deformation modes should be strong in the infrared spectra and most should be weak in the Raman spectra. The three highest frequency modes in this region, which are observed at 670, 665, and 660 cm^{-1} for the Cr anion, 673, 666, and 616 cm^{-1} for the Mo anion, and 671, 663, and 603 cm^{-1} for the W anion, are therefore assigned as δ(M-C-O) vibrations. Figure 3 illustrates these bands. The two highest frequency modes in each set arise on the Mn end of the molecule, with the highest frequency mode being of A_1 symmetry. These assignments are supported by depolarization measurements. The second

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

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(32a) Note Added in Proof. Jones, *et al.*,[35] have assigned a F_{1g} δ(MCO) band in each of the analogous $M(CO)_6$ compounds in the 345-370-cm^{-1} region, supported partly on the basis of overtone and combination assignments. It has been suggested to us that an antisymmetric δ(MCO) mode should be observed for the present compounds in this region. We find no basis in our measurements reported here for such an assignment, and although a small change in the force field (interactions) could cause an unobserved mode to be calculated there, we have not done so because (1) no spectral evidence requires it, and (2) it would have no significant effect on the paper's primary result, which is the ordering in k(M-M′), because such a change would still leave the presently transferable (constant) portions of the force field both transferable and little different from those reported here.

Table II. Observed and Calculated Fundamentals

$\mathrm{MnCr(CO)_{10}^-}$						$\mathrm{MnMo(CO)_{10}^-}$						$\mathrm{MnW(CO)_{10}^-}$					
ν_i,[a] cm^{-1}	ρ_{obsd}	Γ	ν_{obsd},[b] cm^{-1}	ν_{calcd}, cm^{-1}	Description[c]	ν_i,[a] cm^{-1}	ρ_{obsd}	Γ	ν_{obsd},[b] cm^{-1}	ν_{calcd}, cm^{-1}	Description[c]	ν_i,[a] cm^{-1}	ρ_{obsd}	Γ	ν_{obsd},[b] cm^{-1}	ν_{calcd}, cm^{-1}	Description[c]
ν_1	0.21	A_1	2065	2065	$\nu_{\text{C-O(eq)Mn}} + \nu_{\text{C-O(ax)Mn}}$	ν_1	0.05	A_1	2067	2067	$\nu_{\text{C-O(eq)Mn}} + \nu_{\text{C-O(ax)Mn}}$	ν_1	0.06	A_1	2068	2068	$\nu_{\text{C-O(eq)Mn}} + \nu_{\text{C-O(ax)Mn}}$
ν_2	0.22	A_1	1991	1991	$\nu_{\text{C-O(eq)Cr}}$	ν_2	0.24	A_1	2007	2007	$\nu_{\text{C-O(eq)Mo}}$	ν_2	0.23	A_1	2009	2009	$\nu_{\text{C-O(eq)W}} + \nu_{\text{C-O(ax)W}}$
ν_{14}	0.81	B	1961	1961	$\nu_{\text{C-O(eq)Mn}}$	ν_{14}	0.74	B	1959	1959	$\nu_{\text{C-O(eq)Mn}}$	ν_{14}	0.79	B	1961	1961	$\nu_{\text{C-O(eq)Mn}}$
ν_{20}		E	1952	1952	$\nu_{\text{C-O(eq)Mn}}$	ν_{20}	>0.75	E	1946	1946	$\nu_{\text{C-O(eq)Mn}}$	ν_{20}	0.80	E	1950	1950	$\nu_{\text{C-O(eq)Mn}}$
ν_{36}	0.81	B	1941	1941	$\nu_{\text{C-O(eq)Cr}}$	ν_{36}		B	1935	1935	$\nu_{\text{C-O(eq)Mo}}$	ν_{36}	0.78	B	1935	1935	$\nu_{\text{C-O(eq)W}}$
ν_3	0.72	A_1	1927	1927	$\nu_{\text{C-O(ax)Mn}} + \nu_{\text{C-O(eq)Mn}}$	ν_3	0.68	A_1	1923	1923	$\nu_{\text{C-O(ax)Mn}} + \nu_{\text{C-O(eq)Mn}}$	ν_3	0.72	A_1	1929	1929	$\nu_{\text{C-O(ax)Mn}} + \nu_{\text{C-O(eq)Mn}}$
ν_{21}	0.75	E	1894	1894	$\nu_{\text{C-O(eq)Cr}}$	ν_{21}		E	1906	1906	$\nu_{\text{C-O(eq)Mo}}$	ν_{21}		E	1899	1899	$\nu_{\text{C-O(eq)W}}$
ν_4	0.63	A_1	1865	1865	$\nu_{\text{C-O(ax)Cr}}$	ν_4	0.52	A_1	1866	1866	$\nu_{\text{C-O(ax)Mo}}$	ν_4	0.63	A_1	1863	1863	$\nu_{\text{C-O(ax)W}} + \nu_{\text{C-O(eq)W}}$
ν_5	0.25	A_1	670	674	$\delta_{\text{Mn-C-O(op)}} + \delta_{\text{Cr-C-O(op)}}$	ν_5	0.00	A_1	673	672	$\delta_{\text{Mn-C-O(op)}}$	ν_5	0.00	A_1	671	668	$\delta_{\text{Mn-C-O(op)}}$
ν_{22}		E	665	664	$\delta_{\text{Mn-C-O(ax)}} + \delta_{\text{C-Mn-C(ax)}}$	ν_{22}		E	666	666	$\delta_{\text{Mn-C-O(ax)}} + \delta_{\text{C-Mn-C(ax)}}$	ν_{22}		E	663	663	$\delta_{\text{Mn-C-O(ax)}} + \delta_{\text{C-Mn-C(ax)}}$
ν_6	0.24	A_1	660	656	$\delta_{\text{Cr-C-O(op)}} + \delta_{\text{Mn-C-O(op)}}$	ν_6		A_1	616	616	$\delta_{\text{Mo-C-O(op)}}$	ν_6		A_1	603	603	$\delta_{\text{W-C-O(op)}}$
ν_{23}		E		636	$\delta_{\text{Cr-C-O(ax)}} + \delta_{\text{C-Cr-C(ax)}}$	ν_{23}		E	598	598	$\delta_{\text{Mo-C-O(ax)}} + \delta_{\text{C-Mo-C(ax)}}$	ν_{23}		E	589	589	$\delta_{\text{W-C-O(ax)}} + \delta_{\text{C-W-C(ax)}}$
ν_{15}		B		560	$\delta_{\text{Mn-C-O(op)}}$	ν_{42}		A_2		572	$\delta_{\text{Mn-C-O(eq)}}$	ν_{42}		A_2		575	$\delta_{\text{Mn-C-O(eq)}}$
ν_{42}		A_2		559	$\delta_{\text{Mn-C-O(eq)}}$	ν_{43}		A_2		571	$\delta_{\text{Mo-C-O(eq)}}$	ν_{37}		B		566	$\delta_{\text{Mn-C-O(eq)}} + \delta_{\text{C-Mn-C(eq)}}$
ν_{24}		E	551	553	$\delta_{\text{Mn-C-O(eq)}} + \nu_{\text{Mn-C(eq)}}$	ν_{37}		B		563	$\delta_{\text{Mn-C-O(eq)}} + \delta_{\text{C-Mn-C(eq)}}$	ν_{43}		A_2		562	$\delta_{\text{W-C-O(eq)}}$
ν_{37}		B		549	$\delta_{\text{Mn-C-O(eq)}} + \delta_{\text{C-Mn-C(eq)}}$	ν_{15}		B		561	$\delta_{\text{Mn-C-O(op)}}$	ν_{15}		B		558	$\delta_{\text{Mn-C-O(op)}}$
ν_{43}		A_2		538	$\delta_{\text{Cr-C-O(eq)}}$	ν_{24}		E	558	559	$\delta_{\text{Mn-C-O(eq)}} + \nu_{\text{Mn-C(eq)}}$	ν_{24}		E	556	557	$\delta_{\text{Mn-C-O(eq)}} + \nu_{\text{Mn-C(eq)}}$
ν_{25}		E	535	536	$\delta_{\text{Cr-C-O(eq)}} + \nu_{\text{Cr-C(eq)}}$	ν_{16}		B		558	$\delta_{\text{Mo-C-O(eq)}} + \delta_{\text{C-Mo-C(eq)}}$	ν_{16}		B		549	$\delta_{\text{W-C-O(eq)}} + \delta_{\text{C-W-C(eq)}}$
ν_{38}		B		528	$\delta_{\text{Cr-C-O(op)}}$	ν_{25}		E	543	543	$\delta_{\text{Mo-C-O(eq)}}$	ν_{25}		E		529	$\delta_{\text{W-C-O(eq)}}$
ν_{16}		B		527	$\delta_{\text{Cr-C-O(eq)}}$	ν_{38}		B		518	$\delta_{\text{Mo-C-O(op)}}$	ν_{38}		B		514	$\delta_{\text{W-C-O(op)}}$
ν_{26}		E		498	$\delta_{\text{Mn-C-O(op)}} + \delta_{\text{Mn-C-O(ax)}}$	ν_{26}		E		499	$\delta_{\text{Mn-C-O(op)}} + \delta_{\text{Mn-C-O(ax)}}$	ν_{26}		E		500	$\delta_{\text{Mn-C-O(op)}} + \delta_{\text{Mn-C-O(ax)}}$
ν_{27}		E		493	$\delta_{\text{Cr-C-O(op)}} + \delta_{\text{Cr-C-O(ax)}}$	ν_7	0.23	A_1	496	496	$\nu_{\text{Mn-C(ax)}}$	ν_7	0.10	A_1	493	493	$\nu_{\text{Mn-C(ax)}}$
ν_7	0.00	A_1	492	492	$\nu_{\text{Mn-C(ax)}}$	ν_{27}		E		481	$\delta_{\text{Mo-C-O(op)}} + \delta_{\text{Mo-C-O(ax)}}$	ν_{27}		E		471	$\delta_{\text{W-C-O(op)}} + \delta_{\text{W-C-O(ax)}}$
ν_{28}	0.82	E	467	464	$\nu_{\text{Cr-C(eq)}} + \delta_{\text{Cr-C-O(eq)}}$	ν_{28}		E	457	456	$\nu_{\text{Mn-C(eq)}} + \delta_{\text{Mn-C-O(eq)}}$	ν_{28}		E	450	450	$\nu_{\text{Mn-C(eq)}} + \delta_{\text{Mn-C-O(eq)}}$
ν_{29}	0.83	E	456	454	$\nu_{\text{Mn-C(eq)}} + \delta_{\text{Mn-C-O(eq)}}$	ν_8	0.07	A_1	422	422	$\nu_{\text{Mn-C(eq)}} + \nu_{\text{Mn-C(ax)}}$	ν_8	0.05	A_1	438	438	$\nu_{\text{W-C(ax)}} + \nu_{\text{W-C(eq)}}$
ν_8	0.06	A_1	434	435	$\nu_{\text{Cr-C(ax)}}$	ν_9	0.21	A_1	411	412	$\nu_{\text{Mo-C(ax)}} + \nu_{\text{Mo-C(eq)}}$	ν_9	0.06	A_1	421	421	$\nu_{\text{Mn-C(eq)}} + \nu_{\text{Mn-C(ax)}}$
ν_9	0.11	A_1	418	418	$\nu_{\text{Mn-C(eq)}} + \nu_{\text{Mn-C(ax)}}$	ν_{29}		E	401	400	$\nu_{\text{Mo-C(eq)}}$	ν_{29}		E		409	$\nu_{\text{W-C(eq)}}$
ν_{10}	0.18	A_1	400	400	$\nu_{\text{Cr-C(eq)}}$	ν_{10}	0.31	A_1	383	382	$\nu_{\text{Mo-C(eq)}} + \nu_{\text{Mo-C(ax)}}$	ν_{10}	0.33	A_1	388	388	$\nu_{\text{W-C(eq)}} + \nu_{\text{W-C(ax)}}$
ν_{17}		B		361	$\nu_{\text{Mn-C(eq)}}$	ν_{39}		B		367	$\nu_{\text{Mo-C(eq)}}$	ν_{39}		B		379	$\nu_{\text{W-C(eq)}}$
ν_{39}		B		351	$\nu_{\text{Cr-C(eq)}}$	ν_{17}		B		361	$\nu_{\text{Mn-C(eq)}}$	ν_{17}		B		362	$\nu_{\text{Mn-C(eq)}}$
ν_{11}	0.26	A_1	153	153	$\nu_{\text{Mn-Cr}} + \delta_{\text{C-Cr-C(ax)}}$	ν_{11}	0.31	A_1	150	150	$\nu_{\text{Mn-Mo}} + \delta_{\text{C-Mn-C(ax)}}$	ν_{11}	0.27	A_1	149	149	$\nu_{\text{Mn-W}} + \delta_{\text{C-Mn-C(ax)}}$
ν_{30}		E		125	$\delta_{\text{C-Cr-C(ax)}} + \delta_{\text{C-Cr-C(eq)}}$	ν_{30}		E		122	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{C-Mn-C(eq)}}$	ν_{30}		E		125	$\delta_{\text{C-W-C(ax)}} + \delta_{\text{C-Mn-C(ax)}}$
ν_{31}		E		122	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{C-Mn-C(eq)}}$	ν_{31}		E		116	$\delta_{\text{C-Mo-C(ax)}} + \delta_{\text{C-Mo-C(eq)}}$	ν_{31}		E		121	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{C-W-C(ax)}}$
ν_{12}	0.00	A_1	122	120	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{C-Cr-C(ax)}}$	ν_{18}		B		111	$\delta_{\text{C-Mo-C(eq)}} + \delta_{\text{Mo-C-O(eq)}}$	ν_{12}		A_1	112	112	$\delta_{\text{C-W-C(ax)}} + \delta_{\text{Mn-W-C(eq)}}$
ν_{18}		B		107	$\delta_{\text{C-Cr-C(eq)}} + \delta_{\text{Cr-C-O(eq)}}$	ν_{12}	<0.75	A_1	110	111	$\delta_{\text{C-Mo-C(ax)}} + \delta_{\text{C-Mn-C(ax)}}$	ν_{18}		B		111	$\delta_{\text{C-W-C(eq)}} + \delta_{\text{W-C-O(eq)}}$
ν_{40}		B		107	$\delta_{\text{C-Mn-C(eq)}} + \delta_{\text{Mn-C-O(eq)}}$	ν_{40}		B		107	$\delta_{\text{C-Mn-C(eq)}} + \delta_{\text{Mn-C-O(eq)}}$	ν_{40}		B		108	$\delta_{\text{C-Mn-C(eq)}} + \delta_{\text{Mn-C-O(eq)}}$
ν_{32}		E		99	$\delta_{\text{C-Cr-C(eq)}} + \delta_{\text{C-Mn-C(eq)}}$	ν_{32}		E		99	$\delta_{\text{C-Mn-C(eq)}} + \delta_{\text{C-Mo-C(eq)}}$	ν_{32}		E		97	$\delta_{\text{C-Mn-C(eq)}} + \delta_{\text{C-W-C(eq)}}$
ν_{33}		E		91	$\delta_{\text{C-Mn-C(eq)}} + \delta_{\text{C-Cr-C(eq)}}$	ν_{33}		E		91	$\delta_{\text{C-Mo-C(eq)}} + \delta_{\text{C-Mn-C(eq)}}$	ν_{33}		E		90	$\delta_{\text{C-W-C(eq)}} + \delta_{\text{C-Mn-C(eq)}}$
ν_{41}		B		80	$\delta_{\text{C-Cr-C(ax)}} + \delta_{\text{Mn-Cr-C(eq)}}$	ν_{19}		B		81	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{Mo-Mn-C(eq)}}$	ν_{41}		B		89	$\delta_{\text{C-W-C(ax)}} + \delta_{\text{Mn-W-C(eq)}}$
ν_{19}		B		79	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{Cr-Mn-C(eq)}}$	ν_{41}		B		77	$\delta_{\text{C-Mo-C(ax)}} + \delta_{\text{Mn-Mo-C(eq)}}$	ν_{19}		B		77	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{W-Mn-C(eq)}}$
ν_{34}		E		60	$\delta_{\text{Mn-Cr-C(eq)}} + \delta_{\text{Cr-Mn-C(eq)}}$	ν_{34}		E		59	$\delta_{\text{Mo-Mn-C(eq)}} + \delta_{\text{Mn-Mo-C(eq)}}$	ν_{34}		E		62	$\delta_{\text{Mn-W-C(eq)}} + \delta_{\text{W-Mn-C(eq)}}$
ν_{13}		A_1		53	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{C-Cr-C(ax)}}$	ν_{13}		A_1		52	$\delta_{\text{C-Mo-C(ax)}} + \delta_{\text{C-Mn-C(ax)}}$	ν_{13}		A_1		55	$\delta_{\text{C-Mn-C(ax)}} + \delta_{\text{W-Mn-C(eq)}}$
ν_{35}		E		39	$\delta_{\text{Cr-Mn-C(eq)}} + \delta_{\text{Mn-Cr-C(eq)}}$	ν_{35}		E		38	$\delta_{\text{Mn-Mo-C(eq)}} + \delta_{\text{Mo-Mn-C(eq)}}$	ν_{35}		E		38	$\delta_{\text{W-Mn-C(eq)}} + \delta_{\text{Mn-W-C(eq)}}$
$\lvert\Sigma_{i=1}{}^{\alpha}\nu_{\text{calcd}} - \nu_{\text{obsd}}\rvert/\alpha = 1.0\ \text{cm}^{-1}$						$\lvert\Sigma_{i=1}{}^{\alpha}\nu_{\text{calcd}} - \nu_{\text{obsd}}\rvert/\alpha = 0.5\ \text{cm}^{-1}$						$\lvert\Sigma_{i=1}{}^{\alpha}\nu_{\text{calcd}} - \nu_{\text{obsd}}\rvert/\alpha = 0.3\ \text{cm}^{-1}$					

[a] The inactive A_2 torsion mode was not included in these calculations. [b] All observed band positions are reported for solution spectra except where bands were observed only in the solid state. Abbreviations: eq, equatorial; ax, axial; op, out of the equatorial plane.

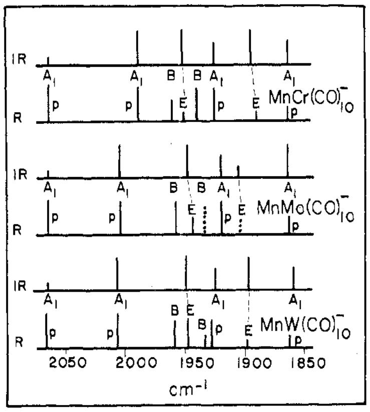

Figure 2. Correlation of observed ir and Raman fundamentals in the 5-μ (2000-cm^{-1}) region for the three anions. The symmetry types and polarizations are indicated. Dotted lines denote fundamentals observed only in the solid state, and dashed lines correlate the ir and Raman bands.

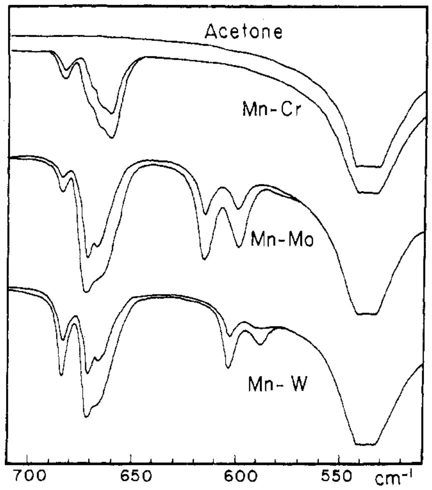

Figure 3. Infrared spectra of the tetraethylammonium salts of each anion in the 470-700-cm^{-1} region in acetone solution. The top spectrum in each set is at lower concentration than the bottom one. The uppermost spectrum is that of pure acetone. Vertical scale is transmittance, arbitrary units, with each compound offset.

band is of E symmetry since there cannot be two δ(M-C-O) modes of A_1 symmetry arising on the same half of the molecule. The two highest frequency bands in this region therefore are described as primarily A_1 (β_0) and E (β_a) motions. The modes at 660, 616, and 603 cm^{-1}, respectively, in these three anions are assigned as the remaining A_1 δ(M-C-O) vibration on the basis of the measured depolarization ratio for the Cr anion and the shift in frequency accompanying the change in M$'$. As mentioned, the spectral interpretation in this part of the middle-frequency region is complicated by the occurrence of Ph_4As^+ and Et_4N^+ cation bands. Thus, solid $(C_6H_5)_4AsCl$ has bands at 616 and 681 cm^{-1} in the infrared spectrum and at 614, 670, and 682 cm^{-1} in the Raman spectrum. Similarly, solid $(C_2H_5)_4NCl$ has observable bands at 618 and 679 cm^{-1} in the infrared spectrum and at 666 and 681 cm^{-1} in the Raman spectrum. Cation bands are distinguished from those belonging to the anion on the basis of both spectral intensities and positions.

The highest frequency band below 500 cm^{-1} remains in approximately the same position on going from the Cr to the W anion. It is polarized and is assigned to the Mn-C axial stretching motion which is expected to be higher in frequency than the A_1 equatorial Mn-C vibration since the metal-carbon modes, to a first approximation, should show the reverse ordering of the C-O 5-μ stretching bands. The band at *ca.* 420 cm^{-1} for all three anions is polarized and assigned to the equatorial Mn-C stretching motion. The lowest frequency mode in the 300-800-cm^{-1} region which shifts from one anion to the next is assigned to an equatorial A_1 ν(M$'$-C) vibration. This assignment is supported by the change in frequency between anions and by the measured depolarization ratios. The remainder of the middle-frequency bands are assigned as shown in Table II. A comparison of the observed middle-frequency infrared and Raman fundamentals for each compound along with their symmetries is presented in Figure 4.

Spectra in the Region below 300 cm^{-1}. In this region $3\ A_1 + A_2 + 2\ B_1 + 2\ B_2 + 6\ E$ fundamentals are expected, of which 9 ($3\ A_1 + 6\ E$) are infrared allowed and all are Raman active except the A_2 vibration. The 3 A_1 modes in this region are based upon Mn-M$'$ stretching motion and the skeletal C-M-C^{ax} (Δ_a) and M-M-C^{eq} (γ_e) bending motions. The $2\ B_1 + 2\ B_2$ modes include C-M-C^{eq} (Δ_e), Δ_a, and γ_e deformations. This region is complicated by the possible occurrence of lattice modes, of mixing of lattice modes with one another and with the fundamentals, and of combinations between the fundamental vibrations, in addition to the anion fundamentals. Since these problems make any asignments speculative for the solid-state spectra, only those bands observed in Raman solution spectra with measured depolarization ratios will be discussed.

The bands observed at 153, 150, and 149 cm^{-1} in the solution spectra of the Cr, Mo, and W anions, respectively, are assigned as the modes composed chiefly of the metal-metal stretching vibration, ν(Mn-M$'$). These bands are strong and polarized in the Raman spectra and thus of A_1 symmetry, and they appear some 25-100 cm^{-1} higher than the skeletal deformation modes, which they therefore cannot be easily confused with as happens in other cases, *e.g.*, $Re_2(CO)_{10}$. The modes observed at 122 and 112 cm^{-1} for the Cr and Mo anions are polarized in the Raman spectra and are assigned as largely due to A_1 (Δ_a) motions. These two bands correspond to the 110-cm^{-1} vibration observed in the Raman spectrum of the solid $MnW(CO)_{10}^-$ salt. The depolarized Raman bands centered at *ca.* 90 cm^{-1} must be of E or B symmetry, and those found at 67, 69, and 71 cm^{-1} for the Cr, Mo, and W species are composed of γ_e and Δ_a deformations.

Spectra in the Uv-Visible Region. The uv-visible spectra of the $MnM'(CO)_{10}^-$ species in solution were each found to contain two absorption maxima in the near-ultraviolet spectra, with the higher frequency band of larger molar absorptivity. These bands can be assigned by direct analogy to those for $M_2(CO)_{10}$ (M = Mn, Tc, Re) molecules, which were assigned by Gray and coworkers.[20] In that study, preferential orientation of the molecules in a liquid-crystalline medium was employed to obtain polarization properties of the more intense of two overlapping bands. The higher frequency, more intense band was found to be polarized along the principal molecular axis. On the basis of this information and the known range of metal-ligand charge-transfer bands in metal carbonyls, the more intense band was assigned to the $A_1 \rightarrow B_2$ transition. This is the allowed transition between the metal-metal σ-bonding orbital, whose principal constituent is $[d_{z^2}(M_A) + d_{z^2}(M_B)]$, and its corresponding antibonding orbital: $[d\sigma(M\text{-}M) \rightarrow d\sigma^*(M\text{-}M)]$.

By close analogy, then band II in the Cr, Mo, and W series of anions studied here is also assigned to the $[d\sigma(Mn\text{-}M') \rightarrow d\sigma^*(Mn\text{-}M')]$ transition. The energy of this transition increases in the order W-Mn > Mo-Mn > Cr-Mn. Table III

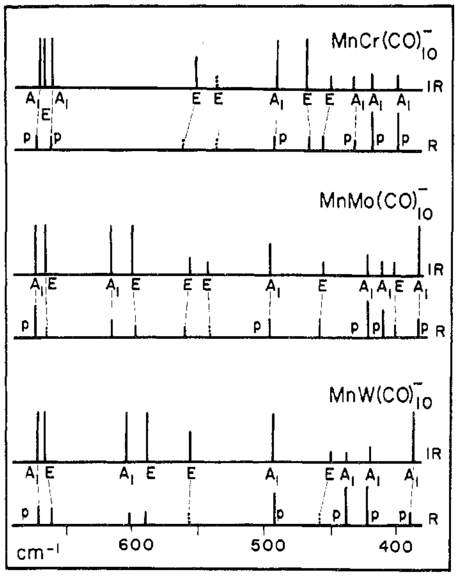

Figure 4. Correlation diagram of the observed ir and Raman fundamentals in the middle-frequency region for the three anions. The symmetry types and polarizations are indicated. Dotted lines denote fundamentals observed only in the solid state, and dashed lines correlate ir and Raman bands.

Table III. Visible-Uv Spectra of the MnM$'$(CO)$_{10}^-$ Anions[a, b]

Compd	State	Band I	Band II
$Et_4NMnCr(CO)_{10}$	*c*	24,300	29,300
$Ph_4AsMnCr(CO)_{10}$	*c*	24,300	29,300
$Et_4NMnMo(CO)_{10}$	*c*	26,900	30,400
$Ph_4AsMnMo(CO)_{10}$	*c*	26,900	30,400
$Et_4NMnW(CO)_{10}$	*c*	26,600	30,700
$Mn_2(CO)_{10}$	*d*		29,400[e]
$Tc_2(CO)_{10}$			31,700[e]
$Re_2(CO)_{10}$			32,300[e]

[a] All band positions are in cm^{-1}. [b] Quartz cells of 1-cm path length were used for tetrahydrofuran solutions. [c] Tetrahydrofuran solution of the compounds. [d] Nematic liquid-crystal solution of the compounds. [e] Results from the work of Gray, *et al.*[20]

lists the band positions for the anions studied here and those compounds investigated by Gray, *et al.*[20]

Vibrational Analysis. A normal-coordinate analysis was carried out for each of the MnM$'$(CO)$_{10}^-$ anions to derive the maximum information obtainable from the spectra regarding the strengths of the M$'$-Mn bonds and the forms of the vibrations involving the distentions of these bonds. Although highly approximate calculations of k(M$'$-Mn) are possible from only "ν(M$'$-Mn)," they ignore both other useful spectral information and force field data from related studies. In this study it is not possible to obtain complete, unique force fields, of course, but it is possible to obtain key force constants from calculations constrained by the requirements that the entire spectrum be fit closely by the calculated frequencies and that mode mixing be taken into account properly.

In the analyses a complete set of internal valence coordinates were defined, as in Figure 1, and were used to generate symmetry coordinates by standard techniques.[30] The eigenvalue calculations were carried out with both the TVP and SVEC programs of Edgell and Yantis[33] and the GMAT and VSEC programs of Schachtschneider.[34]

The force fields reported in Table IV were found by perturbing initial force fields to obtain agreement between the calculated and assigned spectra. The criteria for agreement were the closeness of fit between the calculated and observed frequencies and the accuracy of the calculated eigenvector representation of the motions assigned to the vibrational bands. Another criterion, based on the similarities between the spectra of the anions, is that the portion of the force fields proper to the Mn(CO)$_5$ moiety be essentially the same for each MnM$'$(CO)$_{10}^-$ species. It is evident from the observed spectra that this portion should be similar to but not identical with every other case. This is a useful criterion because it constrains the ranges of values through which other portions of the force fields may vary. Still another constraint is that the force fields be as small as is possible while retaining force constants whose values must be appreciably different from zero.

The initial force constants were estimated as follows. Those proper to the M$'$(CO)$_5$ moiety were transferred from the reported force fields for the parent M$'$(CO)$_6$ molecules,[35] and those proper to the Mn(CO)$_5$ moiety were obtained from studies on Mn(CO)$_5$X and Mn$_2$(CO)$_{10}$ species.[5,7,17,32] The initial values for k(Mn-M$'$) were calculated using our model approach (model 3, *vide infra*) and constants for the C-O stretches were approximated from an energy-factored vibrational analysis of the ν(C-O) spectra.

The results of the analyses are summarized in Table I, which gives a comparison of the calculated and observed frequencies. In all cases the agreement, defined by $\epsilon = |\Sigma_{i=1}{}^{\alpha}\nu_{\text{calcd}} - \nu_{\text{obsd}}|/\alpha$, is within 2 cm^{-1}. Refinement beyond this point is not justified for the spectra of such large molecules.

Model Calculations. It is often desirable to obtain approximate values for the magnitudes of metal-metal bond force constants without performing detailed normal-coordinate analyses of the molecules. Two common approaches for doing this involve making a pseudodiatomic approximation in which the pseudodiatoms are the metal atoms themselves (model 1) or the moieties of the actual molecule (model 2). These are occasionally generalized to polynuclear cluster species as well. They yield roughly limiting values, low and high, respectively. When the eigenvectors from the detailed analyses are considered, however, it is apparent that, for many cases, equally simple but more accurate values may be obtained by taking the mass of a metal pseudoatom to be the mass of that atom plus the weighted mass of each ligand atom attached to it and external to the intermetallic bond. The weighting of each is the projection of the bond length from the metal to the ligand onto the vibrational coordinate direction divided by the bond length itself. For the present cases, the mass of each pseudodiatom is the sum of the mass of the metal atom and that of the axial CO group. In Table V are presented the results of this model (model 3) and those from models 1 and 2 along with the values of k(M$'$-Mn) from the detailed vibrational analysis. It can be seen that the accuracy and ordering are good for these and closely related species. We shall discuss the basis and wider applications of this approach in a later paper.[36]

Discussion

The vibrational analyses of the MM$'$(CO)$_{10}^-$ compounds presented in this paper were performed to obtain bond

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(33) W. F. Edgell and R. L. Yantis, to be submitted for publication; see also R. L. Yantis, M.S. Thesis, Purdue University, 1964.

(34) J. H. Schachtschneider, Technical Reports No. 231-64 and No. 57-65, Shell Development Co., Emeryville, Calif., 1964 and 1965.

(35) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, 8, 2349 (1969).

(36) J. R. Johnson, K. L. Watters, and W. M. Risen, Jr., to be submitted for publication.

Table IV. Nonzero Force Field Elements for the $MnM'(CO)_{10}^-$ Species

A. Force Field Elements[a,b,f] Constant through the Series

β_a	0.43[c]	r_a	2.58	Δ_a'',Δ_a'' trans	−0.01
β_o	0.39	r'',R''	0.735	Δ_a'',Δ_a'' cis	−0.01
β_o'',β_o'' trans	0.04	r_a'',D	0.10	γ_e,γ_e' cis	−0.01[d]
β_i,β_i trans	0.04	Δ_e''	0.10	γ_e,γ_e' trans	−0.01[d]
β_i'',β_i'' cis	0.02	r_a,β_o	−0.07	r_e',Δ_e' cis	0.03[e]
β_i',β_i' trans	0.02	Δ_a	0.14	r_e,β_a	0.03
β_a',β_o'	0.02	Δ_e'',Δ_e'' trans	−0.01	r_e',Δ_e' trans	−0.03[e]
β_o'',β_o'' cis	0.027	Δ_e'',Δ_e'' cis	−0.01	r_a,γ_e	0.05[e]

B. Force Field Elements[a,b,f] Varied through the Series

	$MnCr(CO)_{10}^-$	$MnMo(CO)_{10}^-$	$MnW(CO)_{10}^-$		$MnCr(CO)_{10}^-$	$MnMo(CO)_{10}^-$	$MnW(CO)_{10}^-$
r_e	2.37	2.39	2.32	r_e'	2.20	2.08	2.40
r_a'	2.21	2.12	2.54	β_a'	0.41	0.37	0.35
R_e	15.89	15.83	15.91	R_e'	15.14	15.31	15.14
R_a	15.21	15.15	15.24	R_a'	14.27	14.34	14.23
β_i	0.33	0.35	0.35	β_i'	0.31	0.34	0.33
D	0.50	0.60	0.71	β_o'	0.31	0.32	0.31
γ_e	0.04	0.05	0.03	γ_e'	0.06	0.04	0.07
r_e,r_e cis	0.24	0.27	0.24	r_e',r_e' cis	0.16	0.09	0.12
r_e,r_a cis	0.18	0.20	0.17	r_e',r_a' cis	0.04	0.09	0.17
r_e,r_e trans	0.26	0.31	0.34	r_e',r_e' trans	0.17	0.33	0.23
R_e,R_e cis	0.29	0.29	0.30	R_e',R_e' cis	0.12	0.22	0.21
R_e,R_a cis	0.27	0.28	0.27	R_e',R_a' cis	0.21	0.23	0.27
R_e,R_e trans	0.35	0.38	0.35	R_e',R_e' trans	0.48	0.37	0.45
β_a,β_o	0.043	0.047	0.043	Δ_a'	0.15	0.12	0.15
β_o',γ_e' eq	0.030	0.00	0.00				

[a] All force field elements are in millidynes per angstrom. [b] All internal valence coordinates are defined as positive for bond stretching or angle opening; thus all force field elements have unique signs. [c] Primed and nonprimed valence force constants refer to the M′ and Mn ends of the molecules, respectively, whereas double-primed force constants are equivalent for both halves of a molecule. [d] The cis and trans designations of these valence force constants refer to the projection of the M–C bond of either γ_e or γ_e' onto the carbonyl plane of the opposite half of the molecule. In the cis notation there is 45° between the M–C projection of γ_e and the M–C of γ_e' whereas in the trans there is 135°. [e] These internal coordinates share a common carbon. [f] Some force field elements in this table have been rounded off for presentation. The precise final values used in the normal-coordinate analyses may be obtained by writing to the authors.

Table V. Comparison of Calculated Mn–M′ Force Constants[a]

Species	Model[b]	k(Mn–M′)	NCA k(Mn–M′)
$MnCr(CO)_{10}^-$	1	0.37	
	2	1.34	
	3	0.56	0.50[c]
$MnMo(CO)_{10}^-$	1	0.47	
	2	1.42	
	3	0.66	0.60[c]
$MnW(CO)_{10}^-$	1	0.55	
	2	1.59	
	3	0.78	0.71[c]
$MnMn(CO)_{10}$	1	0.41	
	2	1.47	
	3	0.63	0.59[d]
$MnRe(CO)_{10}$	1	0.62	
	2	1.78	
	3	0.87	0.81[d]

[a] All force constants are in millidynes per angstrom. [b] Models: 1, pseudodiatomic metal masses; 2, pseudodiatomic moiety masses; 3, symmetry-axis momentum conservation. [c] Result from a complete normal-coordinate analysis. [d] Values from the work of Quicksall and Spiro[7] for a normal-coordinate analysis of the low-frequency modes of each molecule.

strength information with which to elucidate the bonding of these species and the differences which result from changing the metal M′. The key results of these analyses are the values of k(M–M′) which indicate the ordering of metal-metal bond strengths to be Mn–W > Mn–Mo > Mn–Cr, with Mn–Mn > Mn–Cr and Mn–Re > Mn–W for isoelectronic pairs. A comparison of the magnitudes of $k_{C-O(eq)}$, $k_{C-O(ax)}$ and $k_{M-C(eq)}$, $k_{M-C(ax)}$ for the individual anions and their ordering through the series is also of interest.

Metal-metal σ bonds in each of these anions are considered to be formed primarily from overlap of symmetry proper combinations of $(n + 1)$s, $(n + 1)p_z$, and nd_{z^2} orbitals on the metals, with the d_{z^2} orbitals being the prime contributors. The possibility of the metal-metal bond containing π character can also be envisioned. The degenerate (E) sets of metal valence orbitals nd_{xz}, nd_{yz} and $(n + 1)p_x$, $(n + 1)p_y$ are of correct symmetry for π overlap and bond formation; however the $(n + 1)p_x$, $(n + 1)p_y$ set, along with $(n + 1)p_z$, $nd_{x^2-y^2}$, and $(n + 1)$s on the M end, and the $(n + 1)p_x$, $(n + 1)p_y$ set, along with $(n + 1)p_z$, nd_{xy}, and $(n + 1)$s on the M′ end, are primarily involved in ligand-metal σ bonding. This therefore leaves only the nd_{xy}, nd_{yz} orbitals for π-bond formation. The d_{xz} and d_{yz} orbitals, filled on both metals, may overlap and they may be involved in π bonding to empty π^* orbitals on both the axial and equatorial CO ligands. As electron density is removed from the metals to the CO ligands, the possibility arises that some net π(M–M′) bonding may exist.

Naturally, the order of metal-metal bond strengths, Mn–W > Mn–Mo > Mn–Cr, can be understood by considering the energies and overlap of the basis orbitals. The energy ordering of the valence d orbitals for the uncharged M′ metals is found to be W > Cr > Mo, with all values falling in the range −6 to −8 eV.[37] Although these valence orbital energies do not apply directly to the atoms in their formally (1−) state, if they are in the same order, the metal-metal bond strength order would be Mn–Mo > Mn–Cr > Mn–W with constant overlap. This is not the k(M–M′) ordering, so the extent of overlap of Mn $3d_{z^2}$ orbital with the nd_{z^2} orbital of M′ must be of major importance. Since the nd_{z^2} orbitals become more extended through the Cr group, the overlap variation results in the observed Mn–W > Mn–Mo > Mn–Cr ordering. Thus, overlap changes are largely responsible for these variations in metal-metal bond strengths, with energy variations being present but of secondary importance.

Since the basis orbitals which combine in forming the Mn–Mn and Mn–Cr bonds have essentially the same extension,

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[37] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969).

the degree of overlap should be nearly the same in the two species. However, the orbital energies are lower for the Mn-Mn case, since the Cr$^-$ level is higher than the Mn^0 level, and a stronger bond is expected. The same argument holds for the pair Mn-Re, Mn-W.

The results discussed above are consistent with dissociation energies found for M-M bonds from electron impact measurements,[38,39] observations of mass spectral fragmentation patterns,[40-42] and previous force constant calculations[7] all of which indicate an increase in metal-metal bond strength as a row of the periodic table is descended.

Analysis of the $k_{\text{C-O}}$ and $k_{\text{M-C}}$ values reveals several interesting relationships. The $k_{\text{C-O(eq)}}$'s are larger than the corresponding $k_{\text{C-O(ax)}}$ values, and the reverse is true for the $k_{\text{M-C}}$ values. This follows from preferential back-donation into the π^*(CO) of the axial CO which is trans to the M'(CO)$_5$, since that increases the π character of the M-C axial bond and the π^* character of the axial CO bond, as is the general case in which the trans ligand acts as a weak π base.

Comparisons can also be made for $k_{\text{M'-C(eq)}}$ and $k_{\text{C-O(eq)}}$ between members of the M-M' series. The $k_{\text{C-O(eq)}}$ values are in the relationship $k_{\text{C-O(eq)}}(\text{Mo}) > k_{\text{C-O(eq)}}(\text{Cr}) \simeq k_{\text{C-O(eq)}}(\text{W})$ which indicates that the amount of π bonding between Mo and the equatorial ligands associated with it is lower than that for either Cr or W. This decrease in the π bonding for Mo is also reflected in the Mo-C equatorial force constant, which is the lowest of the three $k_{\text{M'-C(eq)}}$ values. This result is in agreement with recent vibrational analyses by Jones, *et al.*,[35] and the photoionization and bonding results of Schlag and Lloyd[37] on the metal hexacarbonyls.

Acknowledgment. We gratefully acknowledge support of this work under the Materials Science Program of Brown University with contract support by the Advanced Research Projects Agency (SD-86) and the National Science Foundation. A NASA fellowship to J. R. J. is gratefully acknowledged. The laser Raman instrument purchase was made possible in part through Grant GP-10187 from the National Science Foundation. The experimental assistance of Mr. D. M. Duggan and T. Del Donno is gratefully acknowledged.

Registry No. Et$_4$NMnCr(CO)$_{10}$, 40664-55-9; Ph$_4$AsMnCr(CO)$_{10}$, 40605-02-5; Et$_4$NMnMo(CO)$_{10}$, 40605-03-6; Ph$_4$AsMnMo(CO)$_{10}$, 40629-31-0; Et$_4$NMnW(CO)$_{10}$, 40605-04-7.

Supplementary Material Available. Table VI, a listing of band positions, intensities, physical states, and assignments for each compound studied, along with Table VII, a listing of normalized symmetry coordinates, 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, 20× 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 INORG-73-2349.

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Reactions of Halocarbonyls of Group VIb Elements. II. Complexes of Molybdenum and Tungsten Containing Group Va Donors or Phenyl Isocyanide

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Received February 8, 1973

Halocarbonyls of molybdenum and tungsten, Mo(CO)$_4$X$_2$ and W(CO)$_4$X$_2$ (X = Cl, Br), reacted with PEt$_3$, P(OEt)$_3$, AsEt$_3$, py, and CNPh to form substituted halocarbonyls, M(CO)$_x$L$_y$X$_2$ and W(CO)$_x$L$_y$X$_2$. The use of neat pyridine, 2,6-lutidine, and NCPh led in some cases to products containing no carbonyl groups. In such cases molybdenum underwent a facile disproportionation to produce compounds of Mo(0) and Mo(III). A similar disproportionation occurred much less readily in the case of tungsten halocarbonyl. With W(CO)$_4$Br$_2$ and NCPh, WBr$_2$(NCPh)$_2$ was produced. Complexes of various types containing 2,2'-bipyridine and 1,10-phenanthroline were obtained by reaction with MoBr$_3$(NCR)$_3$ or MoI$_3$. Compounds of mixed oxidation state, Mo$_3$Br$_8$(NCPh)$_6$ and W$_3$I$_8$(NCCH$_3$)$_6$, were obtained when trivalent and tetravalent compounds, respectively, were heated in the presence of a nitrile. Physical examination of some of the compounds is reported.

Introduction

There are two well-established methods for making substituted halocarbonyl complexes of the type M(CO)$_x$L$_y$X$_2$ where M = Mo or W, X = Cl, Br, or I. The first, introduced by Nyholm and coworkers,[1] involves treating the hexacarbonyl with a neutral electron donor L followed by halogen oxidation of the resulting substituted carbonyl.[1-7] A second method involves treatment of the halocarbonyl complexes M(CO)$_4$X$_2$ with the appropriate donor.[8-11] It has been reported recently that reduction of MoCl$_4$(PPh$_3$)$_2$ and WOCl$_4$

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