Reactions of Mercury Halides with CO, NO, N_2, and Unsaturated Hydrocarbons in Argon Matrices

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Abstract: A series of novel complexes of the type HgX_2L (X = F, Cl, Br, or I; L = CO, NO, N_2, C_2H_4, C_3H_6, and 1,3-C_4H_6) has been prepared through the reaction of HgX_2 vapor directly with the respective ligands in argon matrices. For L = CO, NO, and N_2, the ligand vibrations (except for L = N_2) are shifted to higher whereas the Hg–X vibrations are shifted to lower frequencies by complex formation. For L = C_2H_4, C_3H_6, C_6H_6, and 1,3-C_4H_6, the out-of-plane bending vibrations are shifted to higher frequencies, the in-plane bending vibrations unshifted, and the Hg–Cl vibrations are shifted to lower frequencies upon complexation. For L = C_3H_6 and 1,3-C_4H_6, the C=C stretching vibration shifted to a lower frequency. Evidence is presented to show that butadiene may form a 2:1 ($HgCl_2/C_4H_6$) complex if relatively high concentrations of $HgCl_2$ and butadiene are reacted. The structure of these complexes and the nature of the metal-olefin bonding are discussed based on infrared spectra.

Recently, a number of novel coordination compounds of the ML_n type (M = Ni, Pd, Pt etc.; L = CO, N_2, O_2, NO, PF_3 etc.; $n = 1 \sim 4$) have been prepared, and their vibrational spectra were analyzed in inert gas matrices.[1] Van Leirsburg and DeKock[2] have reacted metal dihalide (MX_2) molecules with ligands such as CO, NO, and N_2, and measured the infrared spectra of the MX_2L complexes in inert gas matrices. We have also studied the reactions between bent triatomic molecules such as $SnCl_2$ and PbX_2 (X = F, Cl, Br, and I) and the ligands such as CO, NO, and N_2 in argon and nitrogen matrices by infrared spectroscopy.[3] Now, our studies have been extended to include the reactions between linear triatomic molecules HgX_2 (X = F, Cl, Br, and I) and the ligands such as CO, NO, N_2, C_2H_4, C_3H_6, C_6H_6, and 1,3-C_4H_6. Thus far, there have been no reports on the formation of the HgX_2(olefin) type complexes except for our preliminary report on the $HgX_2C_2H_4$ series.[4] Our investigations show that the major products formed by these reactions are 1:1 complexes of the MX_2L type since both components are in high dilution in inert gases. In the case of 1,3-butadiene, however, there is a possibility of forming a 2:1 ($HgCl_2/C_4H_6$) complex since 1,3-butadiene is known to form such a complex with Pt(II) by utilizing its two C=C bonds.[5]

Experimental Section

Compounds. Mercury halides were purchased from Ventron Corp., Danvers, Mass. Argon, nitrogen, nitric oxide, carbon monoxide, ethylene, propylene, and 1,3-butadiene were purchased from Matheson Gas Products, Joliet, Ill. ^{13}CO (95% enriched) was purchased from Merck & Co., St. Louis, Mo. Anhydrous thiophene-free benzene (from Fisher) was dried over sodium and benzophenone before use. C_6D_6 was obtained from Wilmad Glass Co. and distilled prior to use. C_2D_4 was obtained from Phillips Petroleum Co. and frozen at 77 K to remove volatiles before use. All gas samples were prepared on a glass vacuum line using standard procedures.

Measurements of Infrared Spectra in Argon Matrices. Matrix reactions were performed by cocondensing mercury halide vapor with the reactant such as CO, NO, N_2, or olefin diluted in argon (dilution ratio, 1/200 to 1/2000) on a ~10 K CsI window cooled by a Cryogenic Technology Model 21 refrigerator. Detailed description of our apparatus is given in our previous paper.[3] Infrared spectra were measured during and after sample deposition on a Beckman IR-12 infrared spectrophotometer. High resolution spectra were recorded using a 10 or 20 cm^{-1} per in. chart expansion and a 4 or 8 cm^{-1} per min chart speed. Calibration of frequency readings was made using the rotation-vibration bands of standard molecules. Reproducibility of the spectra was checked by running the spectra several times. The error in frequency reading was always within ± 0.3 cm^{-1}. In Figures 1–7, the optical density of the strongest bands ranged from 0.6 to 0.7.

Computer Simulation of Spectra. In the case of $HgCl_2CO$ complex (Figure 4), computer-simulation spectra were obtained by using a program which plots the sum of Gaussian bands of given frequencies, intensities, and widths.[3]

Results and Discussion

(1) **Free HgX_2.** The infrared spectra of mercury halides in krypton matrices have been observed by Loewenschuss et al.[6,7] Figure 1 illustrates the infrared spectra of HgF_2, $HgCl_2$, $HgBr_2$, and HgI_2 observed in argon matrices, and Table I lists the observed frequencies for the monomeric species. Previous workers[6,7] observed three bands at 660.5, 641.5, and 639.0 cm^{-1} for matrix-isolated HgF_2 molecules, and assigned the last two bands to monomeric HgF_2 (split by the site effect) while the first band was left unassigned. In our case, the assignment is straightforward since only one band was observed at 645.9 cm^{-1}.

For $HgCl_2$, Loewenschuss et al.[6,7] report four bands at 411.5, 407.5, 402.5, and 398.0 cm^{-1} in a krypton matrix. The first band was attributed to an extra band due to a site effect whereas the remaining three bands were assigned to $Hg^{35}Cl_2$, $Hg^{35}Cl^{37}Cl$, and $Hg^{37}Cl_2$, respectively. In an argon matrix, we observed three bands at 416.3, 412.0, and 407.6 cm^{-1} which are assigned to the three isotopic species mentioned above. However, the last band is stronger than that expected for the 9:6:1 intensity pattern of the dichloro compound.[8] This is probably due to the overlap of a broad weak dimer band around 407 cm^{-1}.

Loewenschuss et al.[6,7] report three bands at 293.0, 285.5, and 270 cm^{-1} for $HgBr_2$ in a krypton matrix, and assigned them to the monomer, dimer, and polymer in the same order of frequency. These assignments were confirmed by the observation that the polymer band disappears almost completely in the double-oven experiment. As is shown in Figure 1, we have observed three bands at 297.0 (strong, sharp), 290.3 (weak, sharp), and 281 (medium, broad) cm^{-1}, and assigned them to the monomer, dimer, and polymer, respectively, as suggested by the previous workers.

Previously, Loewenschuss et al.[6,7] reported four bands at 237.5 (monomer), 229 (dimer), 220 (polymer), and 234.5 cm^{-1} (unassigned) for HgI_2 in a krypton matrix. As is shown in Figure 1, we observed one sharp band at 234.8 cm^{-1} and one broad band of equal intensity at 228.3 cm^{-1}, and assigned them to the monomer and polymer (including dimer), respectively. Since the concentration of the polymer is rather high for HgI_2, it was not possible to make clear-cut assignments for the HgI_2–CO system (vide infra).

Table I. HgX_2 and Ligand Frequencies of HgX_2L in Argon Matrices (cm^{-1})

		$\nu(HgX_2)$			$\nu(L)$		
X	L	Free	Complex	Shift	Free	Complex	Shift
F	N_2	645.9	643.2	−2.7	—	—	—
	NO	645.9	641.7	−4.2	1875.0	1891.6	+16.6
	CO	645.9	638.3	−7.6	2138.0	2160.6	+22.6
	C_2H_4[a]	645.9	620.9	−25.0	946.8	972.6	+25.8
^{35}Cl	CO	416.3	412.0	−4.3	2138.0	2156.9	+18.9
	^{13}CO	416.3	412.0	−4.3	2092.7	2109.9	+17.2
	C_2H_4[a]	416.3	404.7	−11.6	946.8	957.6	+20.8
	C_2D_4[a]	416.3	404.7	−11.6	719.6	733.5	+13.9
Br	CO	297.0	—	—	2138.0	2153.1	+15.1
	C_2H_4[a]	297.0	—	—	946.8	965.5	+18.7
I	CO	234.8	—	—	2138.0	—[b]	—
	C_2H_4[a]	234.8	—	—	946.8	960.1	+13.3

[a] Only the CH_2 wagging band is listed. [b] Probably hidden under the strong band at 2149 cm^{-1}.

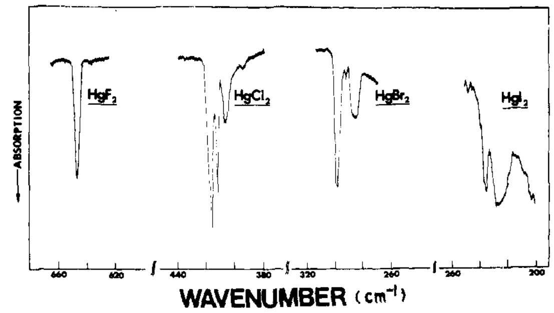


Figure 1. Infrared spectra of HgX_2 (X = F, Cl, Br, and I) isolated in argon matrices.

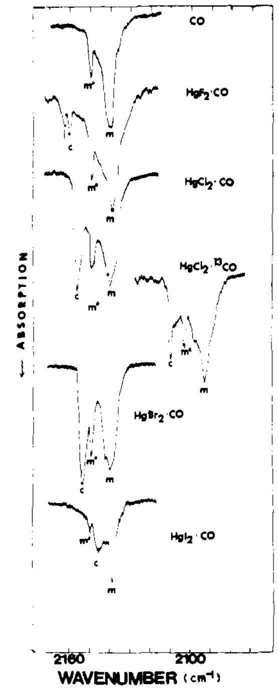


Figure 2. Matrix-isolation infrared spectra of CO and HgX_2CO (X = F, Cl, Br, and I) in the CO stretching region. m, m*, c, and i denote monomeric CO, CO–H_2O, HgX_2CO, and HF–CO, respectively.

(2) HgX_2CO Complexes. Figure 2 illustrates the infrared spectra (CO stretching region) of the HgX_2CO complexes (X = F, Cl, Br, and I) in argon matrices at ~10 K. As stated in our previous paper,[3] the bands at 2149 (marked by m*) and 2138 cm^{-1} (marked by m) are due to CO–H_2O and monomeric CO, respectively.[9] The m* band can be eliminated by using very fast deposition rates. If the slow spray-on method is used, these two bands are always observed in the spectra of the HgX_2–CO systems and their relative intensity varies depending upon the experimental condition. In the HgF_2–CO system, two new bands are observed at 2162 (marked by i) and 2160.6 cm^{-1} (marked by c). The former is due to the CO complex with HF which was produced by the reaction of HgF_2 with traces of H_2O in the system,[2] whereas the latter is assigned to the HgF_2CO complex. In the low-frequency region, a new band appears at 638.3 cm^{-1} in addition to the Hg–F stretching band of free HgF_2 at 645.9 cm^{-1} (second trace of Figure 3). This new band can be assigned to the HgF_2CO complex. Then, the Hg–F stretching band has been shifted by 7.6 cm^{-1} to lower frequency by complexation.

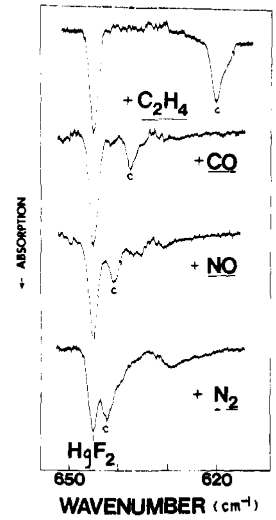


Figure 3. Matrix-isolation infrared spectra of HgF_2L (L = C_2H_4, CO, NO, and N_2) in the Hg–F stretching region. c denotes the band due to HgF_2L in each case.

If $HgCl_2$ is reacted with CO in an argon matrix, a new band appears at 2156.9 cm^{-1} together with those due to CO–H_2O (m*) and monomeric CO (m) (Figure 2). This new band is assigned to the $HgCl_2CO$ complex. All three bands are shifted to 2109.9 (c), 2102.7 (m*), and 2092.7 (m) cm^{-1} when ^{13}CO is reacted with $HgCl_2$. The observed shift of 47.0 cm^{-1} from $HgCl_2{}^{12}CO$ to $HgCl_2{}^{13}CO$ is close to that expected for free diatomic CO (48.3 cm^{-1}), indicating that the electronic structure of CO has been only slightly perturbed by the interaction with $HgCl_2$.

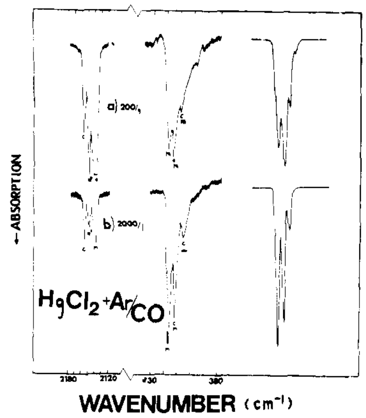


Figure 4. Matrix-isolation infrared and computer-simulation spectra of the $HgCl_2$-CO system. Left, CO stretching region; center, Hg-Cl stretching region; right, computer-simulation spectrum in the Hg-Cl stretching region. The upper (a) and lower (b) curves were obtained with the Ar/CO ratios of 200/1 and 2000/1, respectively.

When $HgCl_2$ is reacted with CO in a relatively high concentration (CO/Ar = 1/200), four bands are observed at 416.3, 412.0, 407.6, and 403.2 cm^{-1} as is shown by the upper center trace of Figure 4. The first band is definitely due to unreacted $Hg^{35}Cl_2$. However, the second and third bands are stronger than that expected for the 9:6:1 intensity pattern[8] of free $HgCl_2$. This result can only be explained if we assume that the bands due to $HgCl_2CO$ (at 412.0, 407.6, and 403.2 cm^{-1}) are overlapped on those of free $HgCl_2$. These assignments are supported by a computer-simulation spectrum shown in the upper right trace of Figure 4. This was obtained with the assumptions that both $HgCl_2$ and $HgCl_2CO$ exhibit three bands at the frequencies mentioned above with the 9:6:1 intensity ratio and that the relative concentration of free and complexed $HgCl_2$ is 6:4 (the half-bandwidth of each band was taken to be 3.4 cm^{-1}). The upper left trace of Figure 4 shows the spectrum of the same matrix in the CO stretching region. It is seen that the concentration of free CO is rather high since this experiment was carried out with excess CO.

If a similar experiment is carried out with excess $HgCl_2$ (CO/Ar = 1/2000), the spectrum shown by the lower center trace of Figure 4 is obtained. It is very similar to that of free $HgCl_2$ although the intensity ratio of the three peaks is not exactly 9:6:1. A computer-simulation spectrum (lower right trace of Figure 4) reveals that only 6% of $HgCl_2$ is complexed to CO in this case. The lower left trace of Figure 4 shows the spectrum of the same matrix in the CO stretching region. It is seen that the intensity of the free CO band (m) is close to that of $HgCl_2CO$ (c). Since the concentration of CO is relatively low, about a half of the CO was reacted with $HgCl_2$ in this experiment.

When $HgBr_2$ is reacted with CO in an argon matrix, a new band appears at 2153.1 cm^{-1} due to complex formation (Figure 2). A similar experiment with HgI_2 produces a new band at ca. 2145 cm^{-1} which is between the CO-H_2O (m*) band at 2149 cm^{-1} and the free CO band (m) at 2138 cm^{-1}. Thus far, the CO stretching bands of HgX_2CO have been assigned at HgF_2CO, 2160.6 > $HgCl_2CO$, 2156.9 > $HgBr_2CO$, 2153.1. If we assign the 2145-cm^{-1} band to HgI_2CO, the shift of the CO stretching band from the bromide to the iodide (ca. 8 cm^{-1}) is too large compared with those from the fluoride to the chloride (3.7 cm^{-1}) and from the chloride to the bromide (3.8 cm^{-1}). Thus it is most reasonable to assume that the HgI_2CO band is hidden under the CO-H_2O (m*) band near 2149 cm^{-1}. The 2145-cm^{-1} band is probably due to the CO complexed with polymeric HgI_2.

Although we have interpreted our results in terms of complex formation, we realize that an alternate explanation would treat the observed effects as nearest-neighbor interactions. We prefer the former interpretation due to the following reasons: (1) We find higher concentrations of $HgCl_2CO$ than statistically predicted by completely random orientation of the two components. For example, in a 2000/1 (Ar/CO) reaction with $HgCl_2$, statistics predicts ca. 0.6% of $HgCl_2$ to have nearest neighbor interactions if we assume 12 nearest neighbors for each $HgCl_2$ molecule. On the other hand, we found ca. 6% of $HgCl_2$ reacted with CO as determined by the relative intensities of ν(HgCl, complex)/ν(HgCl, free) (vide infra). (2) We find that the bands are rather sharp (half-bandwidth, ca. 2.0 cm^{-1} for ν(CO) and less than 3.5 cm^{-1} for ν(HgCl)) in the $HgCl_2$-CO system. If what we observed was a "nearest neighbor interaction", we would have expected to see rather broad bands due to the many possible orientations and $HgCl_2$-CO distances. Furthermore, a $HgCl_2$-CO experiment in a Kr matrix showed almost no differences in bandwidths or frequency shifts, whereas these would be expected in the case of a "nearest neighbor interaction".

As stated in our previous paper,[3] the CO stretching frequency of MX_2CO is governed by the σ donation from CO to the metal. Since this donation originates in the 5σ of CO which is slightly antibonding, the CO stretching frequency becomes higher as the degree of σ donation increases. Thus, in the above HgX_2CO series, σ donation from CO decreased in the order F > Cl > Br > I. The same order of the halogens was noted previously for the PbX_2CO series.[3] It should be noted, however, that there are rather large gaps in the CO frequencies between PbX_2CO and HgX_2CO. Thus, the order of the CO stretching frequencies are: CuF_2CO, 2210 > NiF_2CO, 2200 > CrF_2CO, 2188 > MnF_2CO, 2183 > PbF_2CO, 2176 > HgF_2CO, 2160.6; $NiCl_2CO$, 2189 > $SnCl_2CO$, 2176 $\approx$ $PbCl_2CO$, 2176 > $HgCl_2CO$, 2157. This result can only be explained if we assume that the degree of σ donation in HgX_2CO is much less than that in PbX_2CO. Alternatively, we may conclude that π-back-bonding is more extensive in HgX_2CO than in PbX_2CO since it tends to decrease the CO stretching frequency. As stated in our previous paper, the shift of the M-X stretching band to a lower frequency is proportional to the degree of σ donation from CO to the metal. Namely, the M-X stretching frequency decreases as the metal accepts more electrons. In PbF_2CO,[3] the antisymmetric Pb-F stretching band of free PbF_2 at 507.2 cm^{-1} is shifted by -10.9 cm^{-1} whereas the antisymmetric Hg-F stretching band of HgF_2 at 645.9 cm^{-1} is shifted by -7.6 cm^{-1} by complexation with CO. Then, the percentage shift for PbF_2CO (10.9/507.2) is much larger than that for HgF_2CO (7.6/645.1). This again suggests that σ donation is much less in HgF_2CO than in PbF_2CO. The same trend is found in the M-X stretching frequencies of $HgCl_2CO$ and $PbCl_2CO$.

(3) HgF_2L Complexes (L = CO, NO, N_2, and C_2H_4). In the previous section, we have discussed the spectrum of HgF_2CO. Since HgF_2 exhibits a sharp single Hg-F stretching band, we have chosen the HgF_2L system to study the effect of changing the ligand (L) on the Hg-F frequency. When HgF_2 is reacted with NO, three bands are observed at 1891.6, 1875.0, and 1866 cm^{-1} which can be assigned to HgF_2NO, monomeric NO, and dimeric NO (cis), respectively.[10] In this case, the NO stretching band has been shifted by +16.6 cm^{-1} by complex formation (for $HgCl_2NO$, the shift was +14.5 cm^{-1}). Figure 3 shows the spectrum of the HgF_2-NO system in the low frequency region. A new band at 641.7 cm^{-1} is definitely assignable to HgF_2NO. A similar experiment with N_2 gives a new band at 643.2 cm^{-1} (HgF_2N_2). However, no new bands were observed when HgF_2 was reacted with O_2 in a rather high concentration (2% in argon). We have previously reported the spectrum of $HgF_2(C_2H_4)$.[4] As is shown in Figure 3, this complex exhibits a new band at 620.9 cm^{-1}. If we arrange

Table II. Vibrational Frequencies of Ethylene, Benzene, and 1,3-Butadiene and Their $HgCl_2$ Complexes (cm^{-1})

C_2H_4 gas[a]	C_2H_4 Ar-matrix[b]	C_2H_4 Ar-matrix[c]	$HgCl_2(C_2H_4)$ Ar-matrix[c]	Assignment[h]
1444	1440	1441.3	1441.3	ν_{12}, CH_2 bend (ip)
949	946	946.8	967.6	ν_7, CH_2 wag (op)
810	807	—	—	ν_{10}, CH_2 rock (ip)
C_6H_6 gas[d]	C_6H_6 Ar-matrix[e]	C_6H_6 Ar-matrix[c,f]	$HgCl_2(C_6H_6)$ Ar-matrix[c]	
1485	1480.5	1484.4	1484.4	ν_{13}, ring def (ip)
1037	1038	1041.4 1039.8	1041.4 1039.8	ν_{14}, CH bend (ip)
671	682.5	675.5	685.2	ν_4, CH bend (op)
C_4H_6 gas[g]		C_4H_6 Ar-matrix[c]	$HgCl_2(C_4H_6)$ Ar-matrix[c]	
1599		1596.7	1581.7	ν_8, C=C str (ip)
1385		1380.3	—	ν_{10}, CH_2 bend (ip)
1013		1022.6	1027.3	ν_{14}, CH_2 twist (op)
909		906.0	922.0	ν_{18}, CH_2 wag (op)

[a] T. Shimanouchi, *J. Chem. Phys.*, **26**, 594 (1957). [b] Reference 12. [c] Present work. [d] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1945, p 365. [e] Reference 16. [f] Only monomer bands are listed (see text). [g] Reference 19. [h] Key: ip, in-plane mode; op, out-of-plane mode.

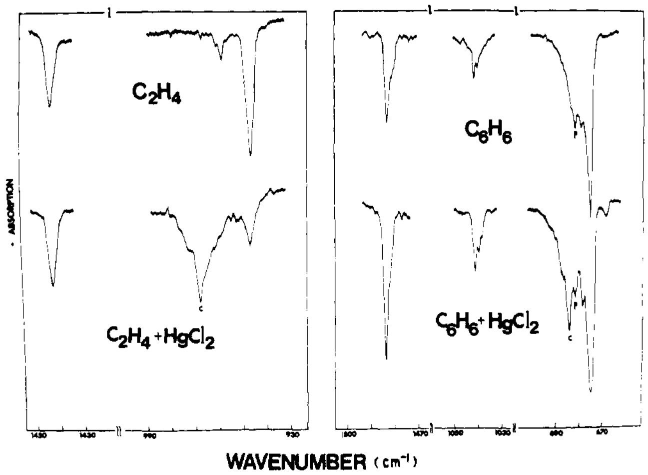


Figure 5. Matrix-isolation infrared spectra of C_2H_4 and $HgCl_2(C_2H_4)$ (left) and of C_6H_6 and $HgCl_2(C_6H_6)$ (right). c and p denote the bands due to $HgCl_2L$ (L = C_2H_4 or C_6H_6) and $(C_6H_6)_x$, respectively.

these five ligands in the order of the Hg-F stretching frequency, the following order is obtained:

$$\begin{array}{lccccc} L = & \text{free} \approx O_2 & N_2 & NO & CO & C_2H_4 \\ \nu(\text{Hg-F}), cm^{-1} & 645.9 > & 643.2 > & 641.7 > & 638.3 \gg & 620.9 \end{array}$$

Similar orders of the ligands have been obtained previously for the NiF_2L[2] and $SnCl_2L$ series.[3] For the $HgCl_2L$ series, we obtain the order:

$$\begin{array}{lccc} L = & \text{free} & CO & C_2H_4 \\ \nu(Hg^{35}Cl_2), cm^{-1} & 416.3 > & 412.0 \gg & 404.7 \end{array}$$

As discussed in our previous paper,[3] the M-X stretching frequency is lowered as the metal accepts more electrons from the ligand. Thus, the above series indicates that the degree of electron donation follows the order: $C_2H_4 \gg CO > NO > N_2 > O_2$. Again a rather large gap is noted between C_2H_4 and CO in this series. The reason for this will be discussed in the following section.

Table I summarizes the observed frequencies of the HgX_2L complexes and the shifts of HgX_2 and L vibrations upon complex formation.

(4) **$HgCl_2$ Complex with Ethylene.** In the previous communication,[4] we have briefly reported the infrared spectra of the $HgX_2(C_2H_4)$ series. A more complete report including the C_2D_4 complexes will be made below.

The infrared spectrum of ethylene in an argon matrix has been reported by Barnes and Howells.[11] Below 2000 cm^{-1}, they observed three bands at 1440 (ν_{12}, B_{3u}, CH_2 bend), 946 (ν_7, B_{1u}, CH_2 wag), and 807 cm^{-1} (ν_{10}, B_{2u}, CH_2 rock). As is shown in Figure 5, we observed two strong bands at 1441.3 (ν_{12}) and 946.8 cm^{-1} (ν_7) in an argon matrix. The 807-cm^{-1} band (ν_{10}) reported by previous workers was too weak to be observed. When ethylene was reacted with $HgCl_2$, no changes were observed in the CH stretching region and the 1441.3-cm^{-1} band did not shift while a new band appeared at 967.6 cm^{-1}. Lack of shifts in the CH stretching region is common to all other systems studied in this paper. The 967.6-cm^{-1} band (marked by c in Figure 5 bottom left) has been assigned to the ν_7 ethylene mode of $HgCl_2(C_2H_4)$ since its frequency is sensitive to the change in the halogen.[4] Then. the CH_2 wagging mode has been shifted by +20.8 cm^{-1} to a higher frequency upon complexation. This assignment is also supported by an isotopic study of ethylene where the ν_7 mode of free C_2D_4 in argon is at 719.6 cm^{-1}. When C_2D_4 was reacted with $HgCl_2$, a new band appeared at 733.5 cm^{-1} which was assigned to the ν_7 mode of $HgCl_2(C_2D_4)$. The ratio, $\nu_7(C_2H_4)/\nu_7(C_2D_4)$ is almost the same for free ethylene (1.316) and the complexed ethylene (1.319). This result also implies that no drastic changes in electronic structure occurred by the complexation of ethylene to $HgCl_2$. Table II summarizes the observed frequencies of C_2H_4 and $HgCl_2(C_2H_4)$.

As reported previously,[4] free $HgCl_2$ in an argon matrix exhibits three bands at 416.3 ($Hg^{35}Cl_2$), 412.0 ($Hg^{35}Cl^{37}Cl$), and 407.6 cm^{-1} ($Hg^{37}Cl_2$) with an intensity ratio of about 9:6:1. When $HgCl_2$ was reacted with ethylene, two new bands were observed at 404.7 and 399.6 cm^{-1}.[4] These bands can be assigned to $Hg^{35}Cl_2(C_2H_4)$ and $Hg^{35}Cl^{37}Cl(C_2H_4)$, respectively. The $Hg^{37}Cl_2(C_2H_4)$ band is too weak to be observed.

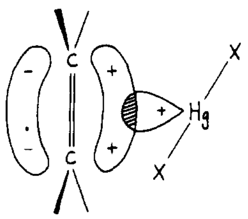
Table III. Observed Frequencies[d] and Band Assignments of C_3H_6 and $HgCl_2(C_3H_6)$ in Argon Matrices (cm^{-1})

C_3H_6 gas[a]	C_3H_6 Ar-matrix[b]	C_3H_6 Ar-matrix[c]	$HgCl_2(C_3H_6)$ Ar-matrix[c]	Band assignment[b]
1652	1650 (s)	1655.2 (m) 1652.0 (m)	1636.7 (m)	ν_6, A′, C=C str
1474	1453 (vs)	1454.4 (vs)	1454.4 (vs)	ν_7, A′, CH_3 asym def
1443	1439 (s)	1440.1 (s)	1440.1 (vs)	ν_{16}, A″, CH_3 asym def
1419	1415 (m)	1416.7 (w)	1416.7 (w)	ν_8, A′, CH bend
1378	1373 (w)	1375.2 (w)	1375.2 (w)	ν_9, A′, CH_3 sym def
1298	—	—	—	ν_{10}, A′, CH_2 bend
1229	1212 (m)	—	—	ν_{11}, A′, CH_2 wag
1172	—	—	—	ν_{12}, A′, CH_3 rock
1045	1043 (s)	1044.1 (m)	1046.2 (m)	ν_{17}, A″, CH_3 rock
991	998 (s)	997.9 990.7	1004 (w, br)	ν_{18}, A″, CH bend
920	932 (m)	932 (m)	932 (m)	ν_{13}, A′, CC str
912	908 (vs)	909.9 (vs)	930.1 (vs)	ν_{19}, A″, CH_2 wag
578	578 (s)	578.9 (m)	579.9 (m, br)	ν_{20}, A″, CH_2 twist

[a] Reference 15. [b] Reference 12. [c] This work. [d] Intensity designation: vs, very strong; s, strong; m, medium; w, weak; br, broad.

The average shift of the two bands observed is $-12.0\ cm^{-1}$. These frequencies are not sensitive to the deuteration of ethylene.

As stated in the previous section, the large gap of the HgX_2 stretching frequencies between the CO and C_2H_4 complexes suggests that electron donation from the ligand to the metal is much larger in $HgX_2(C_2H_4)$ than in HgX_2CO. In $HgX_2(C_2H_4)$, electron donation presumably occurs from its filled 2p π MO to the vacant metal 6p orbital.[12] If we assume a side-on structure in which ethylene is bonded to the metal with its plane parallel and its C=C axis perpendicular to the X-Hg-X axis, an appreciable overlap of the ethylene 2p π MO and the metal orbital is expected (see below). On the other hand, the overlap of the 5σ orbital of CO with the metal orbital would be less since significant 5σ electron density is restricted to a small volume around the carbon atom.[2] These differences in geometry and electronic structure of the complexes are probably responsible for the rather large gap of the frequencies discussed above.



The side-on structure shown above also accounts for the lack of shifts of the in-plane modes such as CH stretching and CH_2 bending and for the shift of the out-of-plane CH_2 wagging mode (ν_7) to a higher frequency. In this mode, all four hydrogen atoms vibrate in the direction perpendicular to the C_2H_4 molecular plane, and such a vibration requires more energy in the complex due to repulsive forces between these hydrogens and $HgCl_2$. A similar shift of ν_7 to a higher frequency was noted previously[13] for Zeise's salt, $K[PtCl_3(C_2H_4)]H_2O$. However, the shift in Zeise's salt ($+80\ cm^{-1}$) is much larger than that in $HgCl_2(C_2H_4)$ ($+20.8\ cm^{-1}$) since the M-C_2H_4 interaction is much stronger and ethylene is probably much closer to the metal in the former than in the latter complex.

Previously, Fredin and Nelander[14] prepared the $Cl_2(C_2H_4)$ complex in a nitrogen matrix, and proposed a C_{2v} structure in which the Cl-Cl bond coincides with the C_2 axis perpendicular to the ethylene plane. The C_{2v} structure of the complex was supported by the observation of a number of new bands which are forbidden under the V_h symmetry of free ethylene. In our case, the V_h symmetry of ethylene remains unchanged by complexation since the $HgCl_2$-C_2H_4 interaction is relatively weak. Thus no relaxation of the V_h selection rules was noted in the infrared spectrum of $HgCl_2(C_2H_4)$.

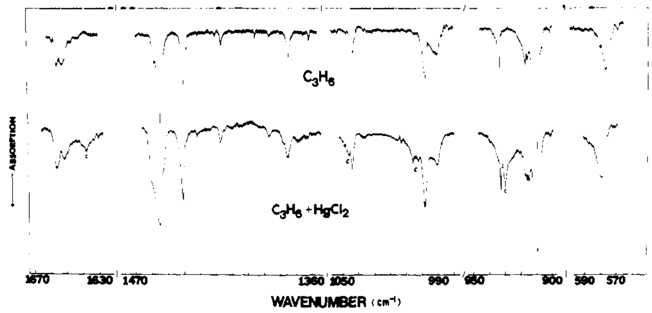


Figure 6. Matrix-isolation infrared spectra of propylene and $HgCl_2$-propylene in the 1700-550-cm^{-1} region. c denotes peaks due to $HgCl_2(C_3H_6)$.

(5) **$HgCl_2$ Complex with Propylene.** The infrared spectrum of propylene in an argon matrix has been reported by Barnes and Howells.[11] Figure 6 shows the infrared spectrum of propylene in an argon matrix in the 1700-550-cm^{-1} region. Table III compares our frequencies with those of previous investigators. Because of its low symmetry (C_s), propylene exhibits at least 12 bands in this region. When propylene was reacted with $HgCl_2$, the spectrum shown in the bottom of Figure 6 was obtained. The three bands at 1046.2 (ν_{17}), 1004 (ν_{18}), and 930.1 (ν_{19}) (all marked by c in Figure 6) newly appear in the complex, and all these bands are shifted to higher frequencies upon complexation, the largest shift being $+20.2\ cm^{-1}$ for the CH_2 wagging mode (ν_{11}). Although no new bands were observed for other out-of-plane (A″) modes such as ν_{16} and ν_{20}, the former became stronger and the latter shifted slightly (1.0 cm^{-1}) to higher frequency and its bandwidth increased. These results suggest the presence of unresolved complex bands at slightly higher frequencies than those of free propylene. Thus, it is concluded that all out-of-plane modes are more or less shifted to higher frequencies upon complexation with $HgCl_2$. This should be contrasted to the in-plane (A′) modes which do not show any shifts by complexation. The only exception is the ν_6 (C=C stretching) mode which was shifted by ca. 20 cm^{-1} to a lower frequency. Such a shift could not be observed previously for the ethylene complex because of its selection rules. It should be noted, however, that this shift (20 cm^{-1}) is much

smaller than that observed for other Pt(II)-olefin complexes (170-150 cm^{-1}).[15] In the low-frequency region, two new bands were observed at 405.3 and 401.0 cm^{-1} upon complexation of $HgCl_2$ with propylene. As expected, these frequencies are almost the same as those of $HgCl_2(C_2H_4)$.

The present results obtained for $HgCl_2(C_3H_6)$ are basically the same as those for $HgCl_2(C_2H_4)$. Thus, a side-on structure similar to that proposed for the ethylene complex is suggested. However, the present results provide more definitive support for such a structure since we observed that at least three out-of-plane bands were shifted to higher frequencies and the C=C stretching band was shifted to a lower frequency.

(6) **$HgCl_2$ Complex with Benzene.** Previous workers[16] reported three bands at 1480.5 (ν_{13}, E_{1u}, in-plane ring deformation), 1038 (ν_{14}, E_{1u}, in-plane CH bend), and 682.5 cm^{-1} (ν_4, A_{2u}, out-of-plane CH bend) for C_6H_6 diluted to 0.2-0.1% in argon. Using similar concentrations, we observed bands at 1484.4 (strong), 1041.4 (medium), 1039.8 (shoulder), 682.3 (strong), 679.8 (strong), and 675.5 (very strong) cm^{-1} (Figure 5). Upon annealing the matrix, the bands at 1484.4, 1041.4, 1039.8, and 675.5 cm^{-1} become weaker and the three bands reported by previous investigators at ca. 1480, 1038, and 682.5 cm^{-1} become stronger. We have, therefore, assigned these three bands to a benzene aggregate. According to our results, monomeric benzene in an argon matrix absorbs at 1484.4 (ν_{13}), 1041.4 and 1039.8 (ν_{14} split slightly by the matrix effect), and 675.5 cm^{-1} (ν_4), as is shown in Table II. The 679.8-cm^{-1} band in our spectrum is probably due to the dimeric species. Previous workers noted that their ν_4 frequency (682.5 cm^{-1}) is unusually high compared with its gas-phase value (671 cm^{-1}). According to our new assignments, ν_4 in an argon matrix is only 4.5 cm^{-1} higher than that in the gas phase.

Figure 5 shows that the only noticeable change resulting from the reaction of benzene with $HgCl_2$ is the appearance of a new strong band at 685.2 cm^{-1} (marked by c). This band is definitely assigned to the ν_4 vibration of $HgCl_2(C_6H_6)$ since its intensity increases as the concentration of $HgCl_2$ increases. Then, ν_4 of free C_6H_6 has been shifted +9.7 cm^{-1} by complex formation. A similar shift was observed for the ν_4 of free C_6D_6 at 497.7 cm^{-1} which was shifted to 506.0 cm^{-1} in $HgCl_2(C_6D_6)$. The ratio, $\nu_4(C_6H_6)/\nu_4(C_6D_6)$ is 1.357 for free benzene and 1.354 for complexed benzene. This again indicates that the complexation causes very little perturbation on the electronic structure of benzene. In the low-frequency region, two new Hg-Cl stretching bands were observed at 405.1 and 400.8 cm^{-1}. These frequencies are similar to those observed for the $HgCl_2$ complexes of other unsaturated hydrocarbons.

Our results mentioned above clearly indicate that two in-plane modes (ν_{13} and ν_{14}) are not shifted whereas one out-of-plane mode (ν_4) is shifted to a higher frequency by complexation with $HgCl_2$. This implies that the $HgCl_2$ molecule is probably located above the benzene plane. Furthermore, the fact that the 9:6 intensity ratio of two strong Hg-Cl stretching bands near 400 cm^{-1} remains unchanged after complexation with benzene seems to suggest the equivalence of the two chlorine atoms in the benzene complex. Thus, the Cl-Hg-Cl axis is probably parallel to the benzene plane although its exact location relative to the benzene nucleus cannot be deduced from the present work. It should be noted, however, that $HgCl_2$ is only very loosely bound to benzene since the infrared spectrum shows that the D_{6h} selection rules are still retained in the complex. Previously, Fredin and Nelander[17,18] studied the infrared spectra and structures of benzene complexed with Cl_2, Br_2, and ICl[17] and I_2[18] in nitrogen matrices. In the former three complexes, they observed that most benzene fundamentals become infrared active upon complex formation. Thus, they suggested an oblique coordination of the halogen molecule which interacts mainly with one of the C=C bonds of benzene. In the $I_2(C_6H_6)$ complex, only two forbidden fundamentals ($\nu_2(A_{1g})$ and $\nu_{11}(E_g)$) became infrared active by complexation. Thus, they proposed a structure in which the I-I axis coincides with the C_6 axis of benzene (axial coordination). Our results on $HgCl_2(C_6H_6)$ are different from either of these halogen-benzene complexes in that no violation of the D_{6h} symmetry selection rules is apparent.

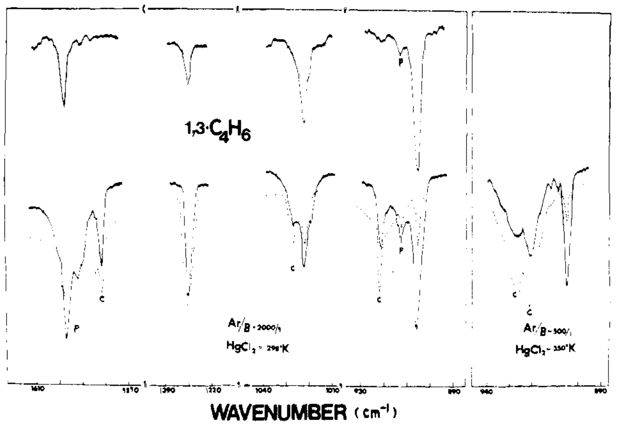


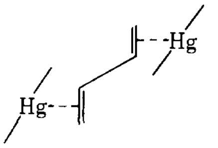
Figure 7. Matrix-isolation infrared spectra of 1,3-butadiene (top) and $HgCl_2(C_4H_6)$ (bottom). The left bottom curves indicate the results obtained by reacting relatively low concentrations of butadiene (Ar/C_4H_6 = 200/1) and $HgCl_2$ (vaporized at 298 K). The right bottom curve denotes the spectrum of the CH_2 wagging region obtained by reacting relatively high concentrations of butadiene (Ar/C_4H_6 = 500/1) and $HgCl_2$ (vaporized at 350 K). In both cases, the dotted lines indicate the spectra obtained after annealing. c, c', and p denote the bands due to $HgCl_2(C_4H_6)$, $(HgCl_2)_2(C_4H_6)$, and $(C_4H_6)_x$, respectively.

(7) **$HgCl_2$ Complexes with 1,3-Butadiene.** The infrared spectrum of 1,3-butadiene (C_4H_6) in the gaseous phase has been measured and assigned in terms of a symmetric-trans structure.[19] As is shown by the upper trace of Figure 7, four strong bands were observed at 1596.7 (C=C stretching), 1380.3 (CH_2 scissoring), 1022.6 (CH_2 twisting), and 906.0 cm^{-1} (CH_2 wagging) in an argon matrix. These frequencies are very close to those reported for the gaseous phase. Furthermore, no new bands were observed in an argon matrix. We, therefore, conclude that butadiene in an argon matrix is also symmetric-trans.

If 1,3-butadiene (0.05% in argon) is reacted with $HgCl_2$ vaporized at room temperature, the spectrum shown by the lower trace (solid curve) of Figure 7 is obtained. Three new bands (marked by c) are clearly visible at 1581.7, 1027.3, and 922.0 cm^{-1} which are assigned to the C=C stretching, CH_2 twisting, and CH_2 wagging modes of the $HgCl_2(C_4H_6)$ complex, respectively. If this matrix is warmed to 40 K followed by recooling to 10 K, the spectrum shown by the dotted line is obtained. It is seen that the three complex bands mentioned above become stronger relative to the free butadiene bands.

These results show that the C=C stretching band is shifted by −15 cm^{-1}, the in-plane CH_2 scissoring band is not shifted, and the two out-of-plane bending bands (CH_2 twisting and wagging) are shifted by +4.7 and +16.0 cm^{-1}, respectively, upon complexation with $HgCl_2$. Similar to the cases of other olefin complexes, the present results support a side-on coordination of $HgCl_2$ to one of the C=C bonds of 1,3-butadiene. Table II summarizes the observed frequencies of C_4H_6 and $HgCl_2(C_4H_6)$.

If a relatively high concentration of butadiene (0.2% in argon) is reacted with a relatively high concentration of $HgCl_2$ vaporized at 350 K, the spectrum shown on the right section of Figure 7 is obtained. In addition to the CH_2 wagging mode of the 1:1 complex at 922.0 cm^{-1} (marked by c), a new band emerges at 927.7 cm^{-1} (marked by c'). Warming this matrix to 40 K followed by cooling to 10 K caused a marked decrease in the intensity of the free butadiene band at 906.0 cm^{-1} and an increase in the intensities of both c and c′ bands. Since this experiment was carried out with a high concentration of $HgCl_2$, it is reasonable to assign the 927.7-cm^{-1} band (c′) to the 2:1 complex, $(HgCl_2)_2(C_4H_6)$. Bands characteristic of the 2:1 complex could not be observed in other regions of the spectra probably because other modes are much less sensitive to the coordination of the second $HgCl_2$ molecule. In the low-frequency region, the Hg–Cl stretching bands of these complexes were observed at 404.5 ($Hg^{35}Cl_2$) and 400.9 cm^{-1} ($Hg^{35}Cl^{37}Cl$). However, no spectral changes were noted by changing the relative concentration of $HgCl_2$. A possible structure of the 2:1 complex may be depicted as



since butadiene retains its symmetric-trans configuration and $HgCl_2$ coordinates to the C=C bond in a side-on fashion.

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The Addition of Alkyl Halides to Rhodium(I) Dithiolene Complexes. The Synthesis, Structure, and Chemical Properties of Rhodium(III) Acyl Species

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Abstract: The Rh(I) complex $[Rh(CO)(PPh_3)(mnt)]^-$ (mnt = maleonitriledithiolate) reacts with alkyl halides R–X (X = I, R = Me, Et, *n*-Pr, *n*-Bu, *n*-$C_{10}H_{21}$; X = Br, R = Bz) to form a series of stable Rh(III) acyl anions. The complexes have been characterized by IR and ^{1}H NMR spectroscopy, and the structure of a representative member of the series (R = Et) has been determined by single-crystal x-ray diffraction. In all of the complexes (except for R = Me) the α-methylene protons of the acyl ligand are magnetically nonequivalent indicating that the acyl group is bonded to a chiral center which is preserved on the NMR time scale. The structure determination of $(AsPh_4)[RhI(COEt)(PPh_3)(mnt)]$ shows the complex to crystallize in space group $P2_1/a$ ($C_{2h}{}^5$) in a cell of dimensions a = 18.466 (6), b = 13.608 (5), c = 19.088 (8) Å, β = 106.39 (1)° with four molecules per unit cell (ρ_{expt1} = 1.54 (2), ρ_{calcd} = 1.558 g/cm^3). The Rh(III) acyl anion adopts a square pyramidal structure with the acyl group occupying the apical position at a distance of 2.006 (14) Å from the Rh(III) ion. In the base of the square pyramid the Rh–S distances are unequal, reflecting the differing influence of the trans ligands (2.323 (3) Å trans to phosphine vs. 2.269 (3) Å trans to iodide). The structure determination thus affirms the diastereotopic nature of the α-methylene protons in the static structure. Addition of Ag^+ to solutions of the Rh(III) acyl anions results in the removal of iodide and the formation of neutral acyl species in which the α-methylene protons appear magnetically equivalent. Solvent exchange is presumed to ocur rapidly in these systems since neutral five-coordinate complexes can be isolated in the presence of coordinating solvents. Heating solutions of the neutral acyl species in THF or CH_2Cl_2 results in the migration of the R group (R = Me, Et, Bz) from the acyl carbon to one of the sulfur donor atoms of the dithiolene ligand to give S-alkylated Rh(I) complexes of the formula $[Rh(CO)(PPh_3)(R\text{-}mnt)]$. The reaction of $[Rh(CO)(PPh_3)(mnt)]^-$ with $OEt_3{}^+$ yields a mixture of the *S*-ethyl complex and the neutral propanoyl species which upon warming in THF converts entirely to the $Rh(CO)(PPh_3)(Et\text{-}mnt)$ complex. The dicarbonyl complex $[Rh(CO)_2(mnt)]^-$ is considerably less reactive than its monosubstituted triphenylphosphine derivative.

The formation of rhodium acyl species occurs in a variety of metal promoted and catalyzed reactions ranging from the decarbonylation of aldehydes and acid chlorides[1,2] to ketone syntheses,[3,4] hydroformylation[5,6] and the carbonylation of methanol to acetic acid.[7] In many of these studies the existence of Rh acyl intermediates has been established by observation of the characteristic carbonyl stretch around 1700 cm^{-1} but in others the transient acyl species are proposed based solely on the reaction products. In cases where stable Rh acyl complexes have been synthesized, their characterization has been mainly by IR and NMR spectroscopy.[1,2,8-10] Only one x-ray structure determination of a rhodium acyl complex has been reported to date.[11] Consequently there has been little systematic development of the structure–reactivity relationship for these chemically interesting systems.

In this paper, we report the synthesis and characterization