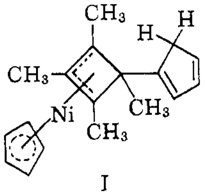
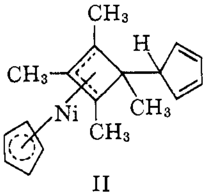
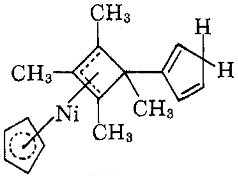


I



II



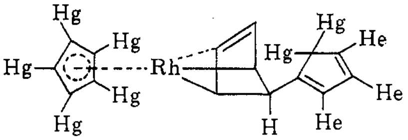
III

TABLE VII

DIHEDRAL ANGLES BETWEEN PLANES DEFINED IN TABLE VI

Planes	Angles, deg.
b, c	0.7
g, h	16.5
h, i	16.4
g, i	2.2
c, k	24.9

with the known X-ray structure[31] of $(C_5H_5)(1\text{-}exo\text{-}C_6H_5C_5H_5)Co$, structure IV was proposed, but a tentative assignment of the positions of the double bonds in the 1-*exo*-cyclopentadiene ring was not possible.[31] The n.m.r. spectrum of structure IV shows the typical resonances due to π-cyclopentadienyl (H_a) and cyclopentadiene (H_e, H_g) hydrogens as observed in $[(CH_3)_4C_4C_5H_5]NiC_5H_5$. For comparison these τ values are listed in Table VIII together with the corresponding values found in $[(CH_3)_4C_4C_5H_5]NiC_5H_5$. The close agreement of the observed τ values for the H_g and H_e hydrogens in the two complexes strongly supports the postulated configuration and suggests that the 1-*exo*-cyclopentadiene ring in $(C_5H_5)(1\text{-}exo\text{-}C_6H_5C_5H_5)Rh$ is also bonded through the 2-position as in the case of $[(CH_3)_4C_4C_5H_5]NiC_5H_5$. However, before more definite conclusions can be drawn, the n.m.r. spectra of the two complexes should be measured and compared under identical conditions in the same solvent.



IV

TABLE VIII

	$(C_5H_5)(1\text{-}exo\text{-}C_6H_5C_5H_5)Rh^a$	$[(CH_3)_4C_4C_5H_5]NiC_5H_5^b$
H_e	3.69–4.35 (multiplet)	3.79–4.25 (multiplet)
H_a	4.96 (doublet)	4.94 (singlet)
H_g	7.46 (multiplet)	7.25 and 7.45

[a] Measured in C_6D_6. [b] Measured in CS_2.

Acknowledgments.—We wish to thank both the United States Atomic Energy Commission and the National Science Foundation for financial support of this work. W. O. wishes to acknowledge Procter and Gamble for a fellowship (1963–1964). The computations were carried out on both an IBM 704 computer at MURA (under the Atomic Energy Commission) and on a CDC 1604 computer at the Numerical Analysis Laboratory (University of Wisconsin).

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Mass Spectrometric Studies of Chromium, Molybdenum, and Tungsten Hexacarbonyls[1]

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The appearance potentials of positive ions from chromium hexacarbonyl, molybdenum hexacarbonyl, and tungsten hexacarbonyl have been determined. The experimental data have been used to derive the heats of formation of various ionic species. The ionization potentials determined for the hexacarbonyls of chromium, molybdenum, and tungsten are 8.15 ± 0.17, 8.23 ± 0.12, and 8.56 ± 0.13 e.v., respectively. Comparisons of the energetics of the three compounds in the series are made along with their fragmentation schemes. From the determined energetic data, second ionization potentials have been calculated for a number of $M(CO)_x$ species.

Introduction

The increase in interest in the transition metal carbonyls over the past decade has arisen partly as a result of the discovery of many organometallic compounds in which the metal carbonyl system forms an integral part of the structure. The hexacarbonyls of chromium, molybdenum, and tungsten are well known. Infrared, Raman, electron diffraction, and X-ray measurements have shown that these compounds possess octahedral structures. Because an

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electron impact investigation may provide further insight into the nature of the bonding in these carbonyls, along with valuable information as to the nature of the gaseous ionic species produced by low-energy electron bombardment, we have studied these three carbonyls and report here our results.

The carbonyls of nickel and iron have been investigated previously.[2] Baldock and Sites[3] reported the mass spectral cracking pattern for tungsten hexacarbonyl at 50 e.v. Vilesov and Kurbatov[4] recently reported ionization potentials determined by photoionization for these group VIA hexacarbonyls; however, there has been no detailed investigation made of the appearance potentials and heats of formation of the various ionic products of the ionization and dissociation processes. This paper reports the information obtained from our appearance potential studies. Mass spectral cracking patterns for these compounds along with ionization and appearance potential data for the principal ions formed from these three carbonyls have been determined. A number of doubly-charged ions have been observed also, and we report their appearance potentials. From the experimentally determined energetic data the heats of formation of many ionic species are calculated in accordance with the proposed breakdown processes. Second ionization potentials are presented from normal thermochemical calculations. The suggested successive dissociations subsequent to ionization are discussed and compared to those found earlier in the study of nickel and iron carbonyls.[2] The possibility of the metal ions being formed in excited states is discussed.

Experimental

The mass spectra and appearance potentials reported here were obtained with a Bendix Model 12-100 time-of-flight mass spectrometer. The instrumentation has been described previously.[5]

The samples of chromium hexacarbonyl, molybdenum hexacarbonyl, and tungsten hexacarbonyl were obtained from commercial sources. No significant amounts of impurities were noted from the mass spectra in any of the samples.

Mass spectra were determined at nominal electron energies of 70 e.v. Appearance potentials were determined from the ionization efficiency curves using the technique of extrapolated voltage differences described by Warren[6] and the technique of Lossing, Tickner, and Bryce.[7] The energy compensation method[8] was used to check the determinations of the ionization potentials. Because these carbonyls have very low vapor pressures[9] at room temperature, we were prevented from using a noble gas for calibration purposes, and therefore mercury background (from the diffusion pump) was used to calibrate the ionizing voltage scale. The spectroscopic value for the ionization potential of mercury (10.43 e.v.[10]) was used for calibration. Appearance potential measurements were made utilizing the major isotope of each of the metal-containing species (except for the WC^+ ion) in order to achieve the maximum sensitivity possible.

Due to the nature of the hexacarbonyls studied, replacement of the tungsten filament was necessary several times during the course of the study. These filament replacements did not affect the results obtained, since the ionization and appearance potentials were reproducible with the different filaments within the quoted errors.

Results

The appearance potentials for the ions studied in each carbonyl are summarized in the third column of Tables I–III. The probable processes by which the various ions are formed, consistent with the measured (and, in some cases, estimated) energetics, are given in the fourth column. The calculated heats of formation for the ions are given in the last column. A number of doubly-charged ions were observed in the spectra of these compounds. Appearance potentials for the doubly-charged ions from molybdenum carbonyl are given in Table II.

Table I

Appearance Potentials and Heats of Formation of the Principal Ions of Chromium Hexacarbonyl

Ion	70-e.v. relative abundance	Appearance potential, e.v.	Probable neutral product(s) in addition to ion	ΔH_f (ion), kcal./mole
CrC^+	4.2	(24.7)	$CO_2 + 4CO$ (?)	(530)
Cr^+	100.0	17.7 ± 0.3	6CO	326
$CrCO^+$	74.0	14.9 ± 0.2	5CO	235
$Cr(CO)_2^+$	48.8	13.1 ± 0.2	4CO	167
$Cr(CO)_3^+$	1.3	(12.0)	3CO	(115)
$Cr(CO)_4^+$	0.3	(10.7)	2CO	(60)
$Cr(CO)_5^+$	0.2	(9.5)	CO	(5)
$Cr(CO)_6^+$	18.9	8.15 ± 0.17		−52

Table II

Appearance Potentials and Heats of Formation of the Principal Ions of Molybdenum Hexacarbonyl

Ion	70-e.v. relative abundance	Appearance potential, e.v.	Probable neutral product(s) in addition to ion	ΔH_f (ion), kcal./mole
$MoCO^{+2}$	16.8	34.5 ± 0.5	5CO	709
$Mo(CO)_2^{+2}$	18.2	30.8 ± 0.5	4CO	597
$Mo(CO)_3^{+2}$	13.2	29.1 ± 1.2	3CO	532
MoC^+	25.0	27.2 ± 0.4	$CO_2 + 4CO$ (?)	608
Mo^+	100.0	20.7 ± 0.5	6CO	417
$MoCO^+$	81.5	18.1 ± 0.3	5CO	331
$Mo(CO)_2^+$	63.1	15.6 ± 0.3	4CO	247
$Mo(CO)_3^+$	88.5	13.7 ± 0.3	3CO	177
$Mo(CO)_4^+$	9.1	11.9 ± 0.2	2CO	109
$Mo(CO)_5^+$	4.0	9.80 ± 0.15	CO	34
$Mo(CO)_6^+$	32.1	8.23 ± 0.12		−29

Each of the three molecules fragments upon electron bombardment to produce ions of the general formula $M(CO)_x^+$, where $x = 0, 1, 2, \ldots, 6$. Similar ions also were observed in the mass spectra of nickel tetra-

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we have estimated the heats of formation of $Cr(CO)_3^+$, $Cr(CO)_4^+$, and $Cr(CO)_5^+$ to be 115, 60, and 5 kcal./mole, respectively. Applying these estimated values to the processes proposed for the formation of the ions (Table I), appearance potentials of 12.0, 10.7, and 9.5 e.v. were obtained for the chromium tri-, tetra-, and pentacarbonyl ions, respectively. These estimated values are enclosed in parentheses in Table I. The estimated appearance potential of 24.7 e.v. and the heat of formation of 530 kcal./mole of CrC^+ were obtained in a similar manner.

Molybdenum Hexacarbonyl.—The energetic data for the fragment ions produced from molybdenum hexacarbonyl are tabulated in Table II.

Energetics obtained for both the +1 and +2 ions of a specific species, *i.e.*, $M(CO)_x^+$ and $M(CO)_x^{+2}$, allows the second ionization potential to be calculated.

$$M(CO)_x^+ \longrightarrow M(CO)_x^{+2} + e \qquad (1)$$

If the heats of formation of both species are known, the heat of reaction can be obtained readily. This is then the second ionization potential of the species $M(CO)_x$. Using the appearance potentials given in Table II, the second ionization potentials for MoCO, $Mo(CO)_2$, and $Mo(CO)_3$ are calculated to be 16.4, 15.2, and 15.4 e.v., respectively.

Many other ions were also investigated in molybdenum hexacarbonyl; however, no further comments will be made concerning the thermochemical properties of these ions here since these data are conveniently summarized in Table II.

Tungsten Hexacarbonyl.—The heats of formation of WC^+ and WC_2O^+ are calculated to be 654 and 561 kcal./mole, respectively, as shown in Table III. However, processes for the formation of these ions cannot be assigned with certainty (and therefore are noted by a question mark in Table III). Further studies on other systems yielding similar ions must be made before the processes can be substantiated. The use of a double ionization chamber (so that the neutral fragments formed might be studied) would be of aid in understanding these fragmentation processes.

A number of doubly-charged ions were observed in the spectra of tungsten hexacarbonyl; however, due to the very low vapor pressure of this carbonyl[9] under the conditions of our experiments, no energetic investigations of these species were made.

The appearance potentials determined for the metal ions (Cr^+, Mo^+, and W^+) yield heats of formation (Tables I–III) significantly greater than the presently accepted values[12] (237, 327, and 387 kcal./mole, respectively, for Cr^+, Mo^+, and W^+). The discrepancies between the experimentally determined heats of formation of the gaseous metal ions and the literature values are larger than could reasonably be attributed to kinetic energies. It is suggested that the metal ions are produced in excited states dependent upon the electronic configurations originally present in the carbonyls.

Several years ago, Cotton, Fischer, and Wilkinson[13] suggested thot excited states of the metal atom and carbon monoxide might be involved in the bond rupture in the metal carbonyls. If we assume that a similar process might occur in the electron impact fragmentation, represented as

$$M(CO)_x \longrightarrow (M^+)^* + xCO + e \qquad (2)$$

then the thermochemical relation involving the appearance potential would be

$$\Delta H_f[(M^+)^*] \leqslant \Delta H_f[M(CO)_x] - x[\Delta H_f(CO)] + A[(M^+)^*] \qquad (3)$$

Since M^+ has the same *m/e* value as $(M^+)^*$, the measured appearance potential may well refer to the formation of an excited metal ion, in which case the heat of formation calculated would be for the excited metal ion.

In order to test if the heats of formation determined are those given by eq. 3, it is necessary to determine the excitation energy of the ion. In the diamagnetic chromium carbonyl, the CO ligands are involved in d^2sp^3 bonding. Since the ionization potential of $Cr(CO)_6$ is only slightly greater than the ionization potential of the chromium atom,[10] the electron withdrawn upon ionization may be considered to have been localized on the chromium atom. (Similar reasoning holds for the other hexacarbonyls studied.) If the six CO groups are removed from the $Cr(CO)_6^+$, the Cr^+ would have four electrons paired up in two d-orbitals and the fifth electron in a third d-orbital. Thus, if the electron configuration of the free chromium ion is the same as that in the $Cr(CO)_6^+$, the chromium ion would be in an excited state, $(Cr^+)^*$, described as d^5 ($^2I_{11/2}$). This state lies approximately 86 kcal./mole above the ground state of Cr^+.[10] Since ΔH_f (Cr^+) is 237 kcal./mole, $\Delta H_f[(Cr^+)^*] = 237 + 86 =$ 323 kcal./mole. This value is in good agreement with the value of 326 kcal./mole calculated from the experimental data (Table I).

In a similar manner, the expected excited states of the other metal ions, fragmented from the carbonyls of molybdenum and tungsten and from the nickel tetracarbonyl and iron pentacarbonyl,[2] may be determined and their heats of formation calculated. These are summarized in columns three to five of Table IV. A comparison of column five in Table IV with the data in the last column in Tables I–III indicates generally good agreement between the observed and calculated values for the heats of formation of the metal ions and therefore suggests that the metal ions, formed upon ionization and fragmentation subsequent to electron impact with these carbonyls, are produced in excited states.

For the molybdenum and tungsten carbonyls, the differences between column five in Table IV and the experimental data in Tables II and III may be attributed partially to kinetic energy and partially to experimental error. However, the agreement in the

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TABLE III

APPEARANCE POTENTIALS AND HEATS OF FORMATION OF THE PRINCIPAL IONS OF TUNGSTEN HEXACARBONYL

Ion	70-e.v. relative abundance	Appearance potential, e.v.	Probable neutral product(s) in addition to ion	ΔH_f (ion), kcal./mole
WC^+	14.2	28.8 ± 0.5	$CO_2 + 4CO$ (?)	654
WC_2O^+	11.5	25.9 ± 0.6	$CO_2 + 3CO$ (?)	561
W^+	63.3	22.9 ± 0.6	6CO	477
WCO^+	64.6	20.2 ± 0.3	5CO	388
$W(CO)_2^+$	57.4	17.6 ± 0.2	4CO	302
$W(CO)_3^+$	100.0	14.9 ± 0.2	3CO	213
$W(CO)_4^+$	52.2	12.7 ± 0.2	2CO	136
$W(CO)_5^+$	6.1	9.80 ± 0.17	CO	43
$W(CO)_6^+$	46.5	8.56 ± 0.13		−12

carbonyl and iron pentacarbonyl.[2] Baldock and Sites[3] were unable to detect the $W(CO)_5^+$ ion in their studies of the (50-e.v.) cracking pattern of tungsten hexacarbonyl. Although found to be present in a small amount, the existence of the $W(CO)_5^+$ ion was established (both by masses and isotopic abundances) in this study. All the remaining $M(CO)_x^+$ ions are rather abundant in the tungsten carbonyl spectrum. The relative abundance of all three of the $M(CO)_5^+$ ions is low. With an increase of the atomic number of the central metal atom in the group VIA carbonyls, the relative intensities of the $M(CO)_4^+$ and $M(CO)_3^+$ ions increase markedly. In the molybdenum carbonyl, the $Mo(CO)_5^+$ and $Mo(CO)_4^+$ ions are low in abundance, whereas in the chromium carbonyl the $Cr(CO)_5^+$, $Cr(CO)_4^+$, and $Cr(CO)_3^+$ ions have nearly disappeared from the mass spectra.

In the previous work on the carbonyls of nickel and iron,[2] it was noted that no ions were formed through cleavage of the C–O bonds. This is not found to be the case for the hexacarbonyls of chromium, molybdenum, and tungsten. Ions of the type MC^+ and MC_2O^+ were detected in the mass spectra. Here, too, the abundance of the MC^+ and the MC_2O^+ ions was found to increase with an increase in the atomic number of the central metal atom.

The monoisotopic relative abundances are given in column two of Tables I–III. The experimentally determined isotopic abundances agreed, to within the experimental error, with the accepted literature values in all three cases.

Figure 1 shows how the ion abundance varies for the $M(CO)_x^+$ type ions in each of the compounds studied as a function of the electron energy. These clastograms are very similar to those obtained for the iron and nickel carbonyls.[2] At low electron energies the parent molecule ion predominates. As the electron energy is increased the fragment ions "grow-in" in order of their appearance potentials, *e.g.*, $M(CO)_5^+$, $M(CO)_4^+$, etc. Subsequently, the abundances of each of these ions passes through a maximum (except for M^+ and MCO^+) and then decreases to a nearly constant value at higher electron energies. Further comments on these features will be discussed below. The heats of formation reported by Cotton, Fischer, and Wilkinson[11] for chromium hexacarbonyl, molybdenum hexacarbonyl, and tungsten hexacarbonyl were employed. These values are −240.4, −218.5, and −209.6 kcal./mole, respectively. Additional heats of formation which were used in the thermochemical calculations are as follows: CO, −26.4 kcal./mole[12]; CO_2, −94 kcal./mole.[12]

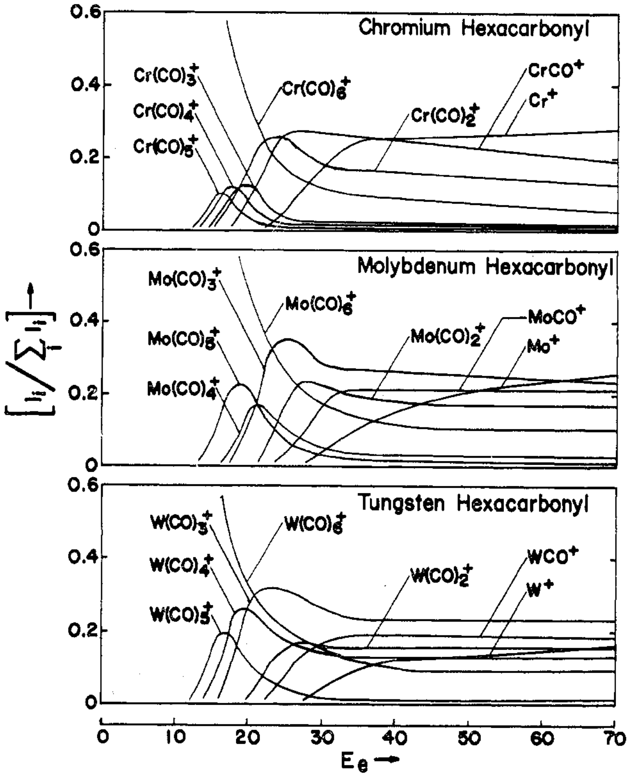

Figure 1.—Clastograms for chromium, molybdenum, and tungsten hexacarbonyls. (The energy axis has the units e.v.)

Discussion

The ionization potentials determined for the hexacarbonyls of chromium, molybdenum, and tungsten (8.15 ± 0.17, 8.23 ± 0.12, and 8.56 ± 0.13 e.v., respectively), agree with the photoionization values reported by Vilesov and Kurbatov[4] (8.03, 8.12, and 8.18 e.v., respectively).

Chromium Hexacarbonyl.—The energetics for the principal ions formed upon electron impact of the chromium hexacarbonyl are tabulated in Table I.

The low abundances of $Cr(CO)_3^+$, $Cr(CO)_4^+$, and $Cr(CO)_5^+$ prevented the determination of their appearance potentials. However, since similar ions of the type $M(CO)_3^+$, $M(CO)_4^+$, and $M(CO)_5^+$ were studied in the investigations of both the molybdenum and tungsten carbonyls, and since energetic data on the remaining $Cr(CO)_x^+$ ions were obtained, interpolations and extrapolations may be made. In this way

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[12] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

TABLE IV

ENERGETIC DATA FOR TRANSITION METAL IONS PRODUCED FROM SOME METAL CARBONYLS

		Excited ion		
Ion	ΔH_f(ion),[12] kcal./mole	State	Excitation energy, kcal./mole	ΔH_f-$[(M^+)^*]$, kcal./mole
Cr^+	237	$d^5\ ^2I_{11/2}$	86	323
Mo^+	327	$d^5\ ^2I_{11/2}$	66	393
W^+	387	$d^5\ ^2I_{11/2}$	69	456
Fe^+	278	$d^7\ ^2H_{11/2}$	58	336
Ni^+	279			

nickel carbonyl case is less satisfactory and it appears reasonable to assume that only a portion of this is due to kinetic energy. (However, this may also reflect that an excited state is formed for the nickel case, but that the electronic configurations for the nickel in the ion and in the molecule ion are not the same.) A further study measuring the kinetic energy of the nickel ion produced from nickel carbonyl would be of significant interest.

Conclusions

In the earlier study of nickel and iron carbonyls,[2] we proposed that the fragmentation of the transition metal carbonyls occurs by successive removal of CO groups. The observed features of the clastograms obtained in the present study of the group VIA carbonyls lend further support to this proposal and make even more desirable a test of this proposal by use of the quasi-equilibrium theory.[14,15]

Ions of the type MC^+ and MC_2O^+ are found to be produced by electron impact in the chromium, molybdenum, and tungsten carbonyls; similar ions were not observed in the spectra of nickel tetracarbonyl and iron pentacarbonyl. No ions of the type MO^+ were detected in the spectra of either the group VIA carbonyls or the nickel and iron carbonyls.

We have observed that the relative abundances of the $M(CO)_x{}^+$ species, where x is 3, 4, or 5, increase as the atomic number of the metal atom increases. The same phenomenon is noted in the ions formed by cleavage of the C–O bond, *i.e.*, MC^+ and MC_2O^+.

The ionization potentials of the three hexacarbonyls are quite similar, but do show a slight increase with the atomic number of the central metal atom. This follows the trend in the variation of the ionization potential of the group VIA elements as the atomic number increases. Also, the ionization potentials of these carbonyls are not greatly different from the ionization potentials of the corresponding gaseous metals. It would appear, therefore, that the electron removed from the group VIA and VIII carbonyls upon ionization is one largely associated with the metal atom rather than with the carbonyl groups.

The large discrepancies between the experimentally determined heats of formation of the gaseous metal ions have been attributed to these ions being formed in excited states.

Several of these suggestions demand further investigation. It is anticipated that current studies in our laboratories on other carbonyls will aid in providing further insight into the bonding and stabilities of the transition metal carbonyls.

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Preparation and Properties of a Series of Halocarbonylrhodates

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Halocarbonyl anions of Rh(I) and Rh(III), of the formulas $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I), $[Rh_2(CO)_2X_4]^{-2}$ (X = Br, I), and $\{Rh(CO)I_4\}^-$, are reported. These anions were isolated as the tetrabutylammonium and tetraphenylarsonium salts, and their structures were deduced from magnetic, conductivity, and infrared absorption measurements.

Introduction

Halocarbonylmetalates are known[2-7] for several of the transition elements which form carbonyl halides. However, no halocarbonyl anions of rhodium have been reported, although its dimeric carbonyl halides, $[Rh_2(CO)_4X_2]$ (X = Cl, Br, I) have been known for more than 20 years[8] and extensively studied.[9] It was therefore of interest as part of an investigation on the coordination compounds of rhodium[10-14] to attempt the preparation of halocarbonylrhodates and to study

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[13] L. M. Vallarino, *J. Inorg. Nucl. Chem.*, **8**, 289 (1958).

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