TABLE VIII

BOND LENGTHS IN TRANSITION METAL ALKYLS AND FLUOROALKYLS

Complex	Metal coord no.	Bond	Length, A	M–C_α–C_β angle, deg	Ref
$(OC)_2Fe(\pi\text{-}C_5H_4)CH_2Fe(CO_4)$	6	$Fe^{I}–CH_2$	2.123 ± 0.015	95.1	40a
$\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$	6	$Fe^{II}–CH$	2.11 ± 0.02	112.5 (av)	40b
$(OC)_4Fe(CF_2CF_2H)_2$	6	$Fe^{II}–CF_2$	2.068 ± 0.014	121.2 (av)	7
DBC coenzyme	6	$Co^{III}–CH_2$	2.05 ± 0.05	130	41
$[Co(CN)_5CF_2CF_2H]^{3-}$	6	$Co^{III}–CF_2$	1.990 ± 0.014	119.7	5
$C_5F_6Co_2(CO)_7$	5	$Co^{I}–CF$	1.97 ± 0.03	?	*a*
$\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$	7	$Mo^{II}–CH_2$	2.397 ± 0.019	120.9	13
$\pi\text{-}C_5H_5Mo(CO)_3C_3F_7$	7	$Mo^{II}–CF_2$	2.288 ± 0.013	123.3	*b*
$\pi\text{-}C_5H_5Rh(CO)(C_2F_5)I$	6	$Rh^{III}–CF_2$	2.08 ± 0.03	116.4	6
$\pi\text{-}C_5H_5Re(CH_3)_2(C_6H_5CH_3)$	8	$Re^{V}–CH_3$	2.25 ± 0.03	. . .	*c*

[a] P. B. Hitchcock and R. Mason, *Chem. Commun.*, 503 (1966). [b] This work. [c] N. W. Allcock, *Chem. Commun.*, 177 (1965).

has been explained.[45] In saturated systems, the only fluorinated carbon–carbon bond that may be *longer* than the normal sp^3–sp^3 distance is that in $C_6F_8Fe(CO)_3$ where a $–CF_2–CF_2–$ linkage is forced into the eclipsed configuration due to a metal–"butadiene" interaction.[42–44]

The thermal parameters for the atoms constituting the terminal $–CF_3$ on the perfluoropropyl group indicate that the ligand is affected by substantial librational motions. Previous experience with perfluoromethyl groups[46–50] has indicated that they may often oscillate through a substantial angle. All bond lengths within the C_3F_7 ligand in the present molecule were therefore corrected for thermal motion (see Table IV) in such a way as to assume always that the outer atoms were rolling over the inner atoms. The success of this approximation is shown in the corrected bond lengths, which now are all in substantial agreement with literature values.

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(45) D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

(46) C. J. Spencer and W. N. Lipscomb, *Acta Cryst.*, **14**, 250 (1961).

(47) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 365 (1963).

(48) M. Gerloch and R. Mason, *Proc. Roy. Soc.* (London), **A279**, 170 (1964).

(49) N. A. Bailey and R. Mason, *Acta Cryst.*, **21**, 652 (1966).

(50) M. R. Churchill and R. Mason, *Proc. Roy. Soc.* (London), **A292**, 61 (1966).

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The Pentacarbonyls of Ruthenium and Osmium.
I. Infrared Spectra and Reactivity

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The existence of pentacarbonylruthenium and pentacarbonylosmium has been confirmed and their infrared spectra in the carbonyl stretching region have been measured. The two carbonyls have two infrared-active CO stretching vibrations. This suggests a trigonal-bipyramidal configuration of symmetry D_{3h}. The reactions of the two pentacarbonyls with halogens have also been investigated. Pentacarbonylruthenium gives dihalogenotetracarbonyls of the formula $RuX_2(CO)_4$ (X = Br, I) as slightly colored solids, sublimable *in vacuo*. The infrared spectra suggest a *cis* octahedral configuration in solution for the dihalogeno complexes.

Introduction

The monomeric pentacarbonyls of ruthenium[1] and osmium,[2] $Ru(CO)_5$ and $Os(CO)_5$, have been reported in the literature some 30 years ago as volatile, colorless liquids. These compounds, however, were not fully characterized at that time, although their formulas were well established. To the best of our knowledge, no reports, since those of the early discoverers, have appeared concerning the status of these two compounds, their properties, and their structure. This was mainly due to experimental difficulties connected with the high volatility of the compounds and their instability with respect to the corresponding trimers $M_3(CO)_{12}$. It therefore appeared interesting to run some carbonylations of ruthenium and osmium and then investigate the freshly prepared solutions by infrared spectroscopy in order to detect the two penta-

(1) W. Manchot and W. J. Manchot, *Z. Anorg. Allgem. Chem.*, **226**, 385 (1936).

(2) W. Hieber and H. Stallmann, *Z. Elektrochem.*, **49**, 288 (1943).

carbonyls among the volatile products and hopefully assign a structure to them. Two configurations—tetragonal pyramidal (C_{4v} symmetry) and trigonal bipyramidal (D_{3h} symmetry)—are possible for the two pentacarbonyls and the infrared spectrum in the CO stretching region is, in principle, capable of distinguishing between the two possibilities.

As a result of the present investigation, we confirm the existence of $Ru(CO)_5$ and $Os(CO)_5$, as originally formulated by Manchot and Hieber and their co-workers. We also report some of their properties and reactions and suggest that the two pentacarbonyls both have trigonal-bipyramidal structures in solution.

Experimental Section

Unless otherwise stated all of the operations were carried out in an atmosphere of prepurified nitrogen.

The infrared spectra were measured with a Perkin-Elmer instrument, Model 521, equipped with grating. Each spectrum was calibrated with CO, so that the limit of accuracy is believed to be ± 0.5 cm^{-1} for narrow bands. The infrared spectra in the gas phase were measured in a 10-cm gas cell. During the measurements of the light-sensitive pentacarbonyls in solution the samples were protected from the visible radiation of the light source with a silicium filter. The carbonylation reactions were carried out in a 250-ml stainless steel autoclave heated in a thermostated oil bath. Carbon monoxide was prepurified by treatment with a solution of iodine in 2,2'-diethoxydiethyl ether (bp 187°). Ruthenium was determined by decomposition of the samples with concentrated sulfuric acid, followed by oxidation to the volatile tetroxide RuO_4. The latter was steam distilled into a solution of potassium iodide and the liberated iodine was titrated with thiosulfate.[3]

(1) **Ruthenium Carbonyls.** (a) **Pentacarbonylruthenium.**—This compound was obtained by the method used by Pino and co-workers[4] for preparing $Ru_3(CO)_{12}$ but using heptane as solvent rather than methanol. The starting material was tris(acetylacetonato)ruthenium(III), which was carbonylated in *n*-heptane with a mixture of carbon monoxide and hydrogen, the latter acting as reducing agent. The temperature was 180°, the pressure 200 atm of CO and H_2 in a ratio 2:1, and the reaction time about 8 hr. At the end of the reaction the autoclave was cooled down slowly to room temperature and the gas vented. The pentacarbonyl and the solvent were condensed *in vacuo* under exclusion of light into a flask maintained at Dry Ice temperature.

In a typical experiment tris(acetylacetonato)ruthenium(III) (1.0 g, 2.51 mmoles) dissolved in 50 ml of anhydrous heptane was treated as described above with CO and H_2. On distillation, a colorless heptane solution containing about 0.31 g of $Ru(CO)_5$ was obtained, corresponding to a yield of 51.1%. This solution showed two bands in the carbonyl stretching region at 2035 and 1999 cm^{-1} together with a weak band at 2060 cm^{-1} owing to a small amount of $Ru_3(CO)_{12}$ (see Figure 1A and Table I).

The presence of the monomeric pentacarbonyl in the colorless heptane solutions was established by direct ruthenium and CO analyses, the latter carried out in the gas volumetric equipment described elsewhere.[5]

A solution (20 ml) of the carbonyl containing 0.0478 g of ruthenium (0.473 mg-atom) rapidly evolved 31.5 ml of CO (STP conditions; 1.406 mmoles) on treatment with iodine and pyridine. Treatment with additional iodine and pyridine for about 10 hr did not produce any significant gas evolution. Therefore 3 moles of CO was evolved according to the stoichiometry

$$n\mathrm{Ru(CO)_5} + n\mathrm{I_2} \xrightarrow{\text{pyridine}} [\mathrm{RuI_2(CO)_2}]_n + 3n\mathrm{CO} \qquad (1)$$

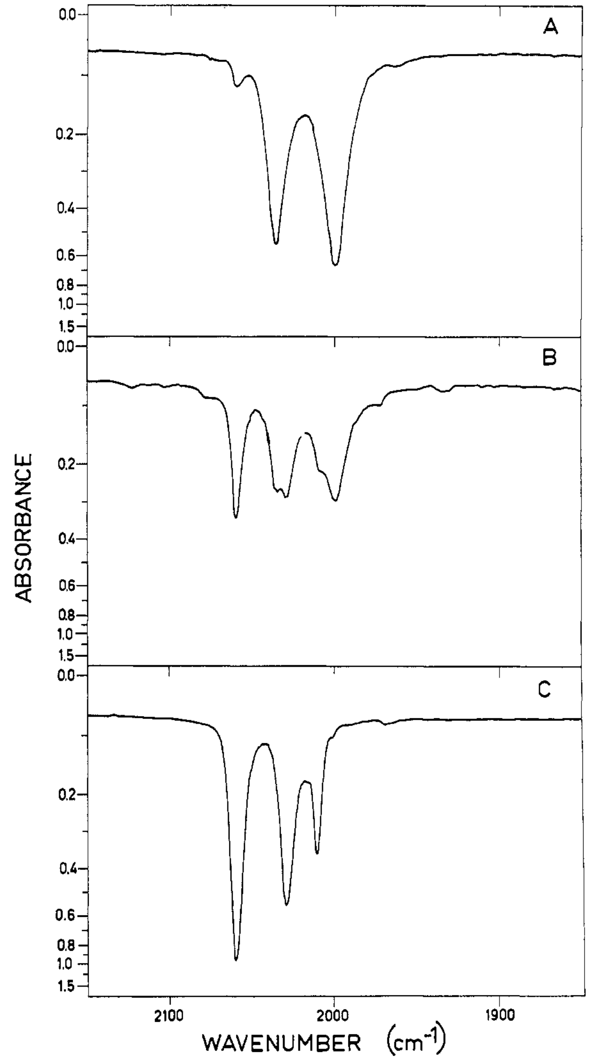

Figure 1.—A. Infrared spectrum of pentacarbonylruthenium in the carbonyl stretching region. Heptane solution, approximately 2×10^{-2} *M;* 0.1-mm cell. The band at 2060 cm^{-1} is due to small amounts of $Ru_3(CO)_{12}$. B. The same solution as A after 30-min exposure to sunlight. The band at 2060 cm^{-1} and the shoulders at 2029 and 2010 cm^{-1} indicate conversion of $Ru(CO)_5$ to the trimer. C. Infrared spectrum of $Ru_3(CO)_{12}$. Heptane solution; 0.1-mm cell.

The brown solid formed during the reaction with iodine was filtered and found to have infrared bands at 2056 and 1997 cm^{-1} in tetrahydrofuran solution. Irving[6] reports two bands at 2050 and 1995 cm^{-1} for the polymeric diiododicarbonyl $[RuI_2(CO)_2]_n$. Manchot and Manchot[1] also report the formation of the polymeric iodocarbonyl by treatment of the trimer $Ru_3(CO)_{12}$ with iodine under drastic conditions (250°).

The heptane solutions of pentacarbonylruthenium were handled under exclusion of air and light. On exposure to light, particularly ultraviolet, the solutions turned orange very readily with formation of $Ru_3(CO)_{12}$. The conversion of $Ru(CO)_5$ to $Ru_3(CO)_{12}$ was followed either spectroscopically (Figure 1A–C) or gas volumetrically. An approximately 1.5×10^{-2} *M* solution of the pentacarbonyl in heptane was converted into the trimer by irradiation with a mercury lamp in a Pyrex flask at 30° under an atmosphere of carbon monoxide. The conversion was practically complete in 6 hr as judged by the amount of CO evolved.

(b) **Dodecacarbonyltriruthenium.**—After separation of $Ru(CO)_5$ as described in section 1a, a yellow-orange crystalline residue was left in the autoclave. This was washed with heptane,

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(3) O. Ruffo and E. Vidic, *Z. Anorg. Allgem. Chem.*, **136**, 49 (1924).
(4) G. Braca, G. Sbrana, and P. Pino, *Chim. Ind.* (Milan), **46**, 206 (1964).
(5) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).
(6) R. J. Irving, *J. Chem. Soc.*, 2879 (1956).

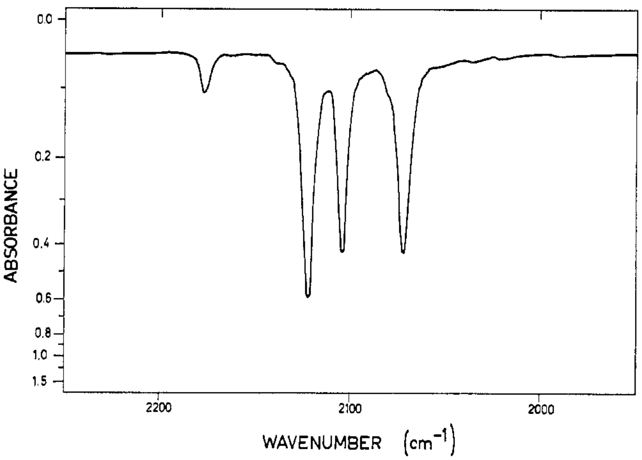

Figure 2.—Infrared spectrum of $RuBr_2(CO)_4$. Carbon tetrachloride solution; 1-mm cell.

filtered, and then sublimed at 90° (~10^{-3} mm). The sublimed product was found to be $Ru_3(CO)_{12}$ by infrared spectrum[7] (see also Table I) and elemental analysis.

By reaction with iodine in pyridine, the trimer was converted into $[RuI_2(CO)_2]_n$ with evolution of 2 moles of CO per ruthenium. The trimer does not absorb carbon monoxide at atmospheric pressure and room temperature.

(c) **Reactions of $Ru(CO)_5$ with Halogens.**—The heptane solutions of $Ru(CO)_5$ obtained as described in section 1a were treated with a slight excess of the halogen at about −40°. After a few minutes the reaction mixture was allowed to warm to room temperature, and the practically insoluble halogenocarbonyls were filtered and dried *in vacuo*. The conversions were practically quantitative, as inferred from the absence of carbonyl bands due to unreacted $Ru(CO)_5$ in the filtered solution.

The iodo derivative, $RuI_2(CO)_4$, was identified by its infrared spectrum, which was found to be identical with that published by Dahl and co-workers.[8]

The bromo derivative, $RuBr_2(CO)_4$, which had not been reported before, was characterized by analysis and infrared spectrum. For the latter, see Figure 2 and Table II. The yellowish compound sublimes unchanged at 80–90° (~10^{-3} mm) as shown by the invariance of the infrared spectrum after sublimation. *Anal.* Calcd for $C_4Br_2O_4Ru$: C, 12.88; H, 0.00; Ru, 27.10. Found: C, 12.60; H, 0.00; Ru, 26.85.

The chloro derivative could not be isolated in a pure state. The product obtained after treatment with chlorine was a yellowish microcrystalline powder, which sublimed at 80–90° (~10^{-3} mm). The infrared spectra of the product before and after sublimation were substantially identical and contained several bands in addition to the four expected for the C_{2v} symmetry of *cis*-$RuCl_2(CO)_4$.

The bromo- and iodotetracarbonyl derivatives of ruthenium did not appear to be oxidized rapidly by atmospheric oxygen, and they were not hydrolyzed rapidly by water; they behave as hydrophobic substances and are not attacked readily at room temperature by concentrated sulfuric acid.

(2) **Osmium Carbonyls.**—The pentacarbonyl was prepared by allowing OsO_4 (0.5–1 g) to react with CO at 160° and 100–200 atm according to the method described by Hieber and Stallmann.[2] The reaction was run either in heptane (50 ml) or without solvents.

In the first case at the end of the reaction (usually 7 hr) the autoclave was cooled and the gases were vented. The solvent and the volatile osmium compounds were then condensed *in vacuo* into a trap cooled to Dry Ice temperature. The infrared

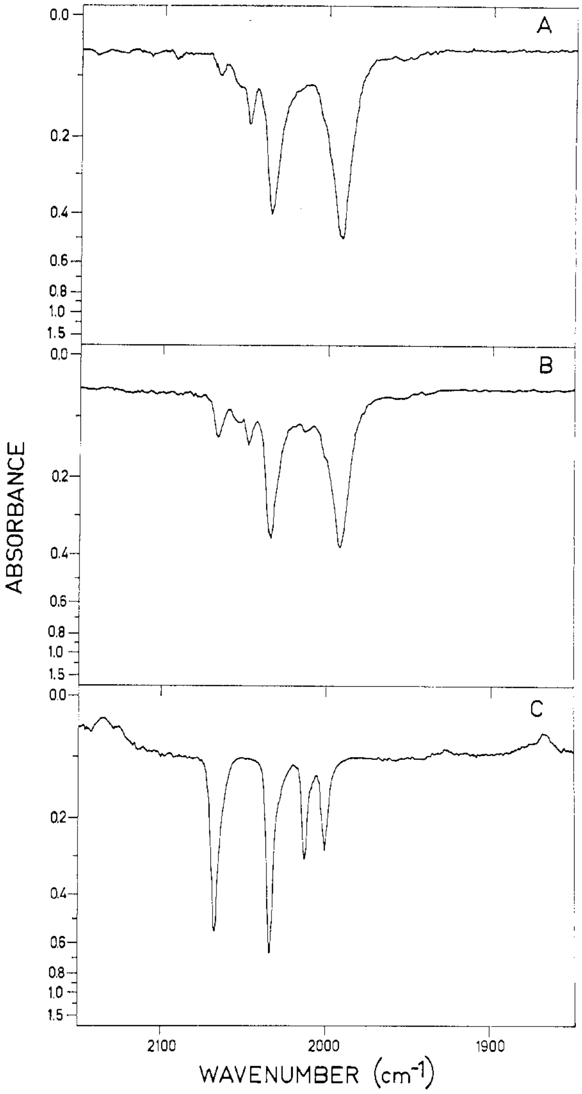

Figure 3.—A. Infrared spectrum of a volatile fraction containing pentacarbonylosmium predominantly. Heptane solution; 0.1-mm cell. The band at 2046 cm^{-1} is due to an unknown species (see text); small amounts of $Os_3(CO)_{12}$ are indicated by the band at 2068 cm^{-1}. B. The same solution as A after 30-min exposure at sunlight. The band at 2068 cm^{-1} and the shoulders at 2014 and 2002 cm^{-1} indicate conversion of the monomer to the trimer. The band at 2034 cm^{-1} appears practically unaffected because it is replaced by the 2035-cm^{-1} band of the trimer (see Table I). C. Infrared spectrum of $Os_3(CO)_{12}$. Cyclohexane solution; 1-mm cell. The bands are at 2068, 2035, 2014, and 2002 cm^{-1} (see also ref 9).

spectrum of this heptane solution was immediately measured under exclusion of air and light. Three bands were observed at 2046, 2034, and 1992 cm^{-1} (see spectrum in Figure 3A). Only the 2034- and 1992-cm^{-1} bands are, however, due to $Os(CO)_5$, as discussed later. On exposure to sunlight the infrared spectrum changes to that of $Os_3(CO)_{12}$ (spectra in Figure 3B and C).

The reaction of OsO_4 with CO was also carried out without solvent in the course of experiments aimed at measuring the infrared spectrum of the pentacarbonyl in the gas phase. In this case, after reaction, the gases were vented through 20 ml of heptane maintained at Dry Ice temperature. The infrared spectrum of the heptane solution showed an intense band at 2046 cm^{-1}, together with weak bands at 2034 and 1992 cm^{-1} due to $Os(CO)_5$. The autoclave was then cooled to Dry Ice temperature and evacuated at about 12 mm; it was then warmed again to

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[7] W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

[8] E. R. Corey, M. V. Evans, and L. F. Dahl, *J. Inorg. Nucl. Chem.*, **24**, 926 (1962).

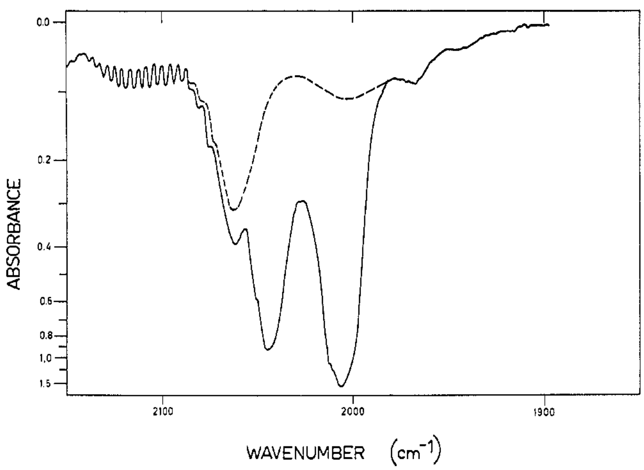

Figure 4.—Solid curve: gas-phase infrared spectrum of a volatile fraction containing pentacarbonylosmium predominantly in a 10-cm cell. The weak bands at high energies are due to carbon monoxide. The band at 2062 cm^{-1} is due to an unknown species. Dotted curve: the same after 2-hr exposure to ultraviolet irradiation.

room temperature and connected to a gas cell maintained *in vacuo*. The spectrum of the vapors was then immediately measured (see Figure 4 and Table I). Three bands at 2062, 2047, and 2006 cm^{-1} were observed. The two latter bands which rapidly disappeared under ultraviolet irradiation are attributed to $Os(CO)_5$. The band at 2062 cm^{-1} was more slowly affected by ultraviolet light (see spectra in Figure 4). The comparison of the heptane and vapor spectra suggests that the band at 2062 cm^{-1} is shifted to 2046 cm^{-1} in heptane and is due to another compound different from and probably more volatile than $Os(CO)_5$. We could also show that the extra band is not due to tetracarbonylnickel. The species responsible for the 2062-cm^{-1} band appears to be a minor component of the reaction mixture. Vapor-phase spectra measured on successive volatile fractions from the same run showed drastically decreasing intensities of this band relative to the bands of $Os(CO)_5$.

The yields of $Os(CO)_5$ varied from 20 to 50%, based on initial OsO_4, depending on the reaction conditions, in particular the presence of the solvent and the amount of starting material. Either in the dry reaction of OsO_4 with CO or in that in the presence of heptane, considerable amounts of solid osmium carbonyls were found (50–80%) in the autoclave after elimination of the volatile fractions. This solid residue was sublimed fractionally at 100–200° (~10^{-3} mm) and was shown by infrared spectra to consist mainly of $Os_3(CO)_{12}$[9] and another carbonyl which was not identified but which could possibly be the tetroxododecacarbonyl $Os_4O_4(CO)_{12}$ recently described by Lewis and co-workers.[10]

Results and Discussion

Pentacarbonyls of Ruthenium and Osmium.—The two pentacarbonyls of ruthenium and osmium were obtained by carbonylation[4] of tris(acetylacetonato)-ruthenium(III) and OsO_4,[2] respectively. We could confirm also that the reaction of tris(acetylacetonato)-ruthenium(III) with CO and H_2 in methanol gives high yields of $Ru_3(CO)_{12}$. However, the same reaction in heptane as solvent leads to the formation of considerable amounts of $Ru(CO)_5$—about 50% based on starting ruthenium—provided light is excluded during the manipulations of the reaction mixtures. We did not attempt to isolate the pure $Ru(CO)_5$, which was described as a volatile liquid by Manchot and Manchot.[1] We were interested in obtaining heptane solutions of the pentacarbonyl since that solvent is known to give the best resolution in the carbonyl stretching region. The organic by-products of the reaction, namely, acetylacetone and possibly other compounds derived from it, did not interfere with our measurements in the terminal CO stretching region. The presence of hydrogen during the carbonylation of tris(acetylacetonato)ruthenium(III) would have suggested the possible formation in the reaction conditions of a hydridocarbonyl, for example, the still unknown $RuH_2(CO)_4$. However, we did not find any evidence of its presence in the final reaction mixture. Only one compound appears to be present among the volatile fractions; that this compound is $Ru(CO)_5$ is shown by the analytical data and by the fact that its infrared spectrum in the CO stretching region is identical with that of $Fe(CO)_5$, apart from a wavenumber shift of one of the two bands due to the change of metal. No other bands were observed in the region 2100–1750 cm^{-1} except the three bands of $Ru_3(CO)_{12}$ formed by light-induced decomposition during the measurement of the spectrum.

In the case of the reaction of OsO_4 with CO, on the other hand, infrared evidence exists for the presence of another compound, in addition to $Os(CO)_5$. The latter was identified in this reaction mixture by Hieber and Stallmann[2] and is undoubtedly the major component. The evidence for the additional compound is the presence of a band at 2046 cm^{-1} in heptane solution (see Figure 3A) shifted to 2062 cm^{-1} in the gas phase (see Figure 4). Further investigation is now under way aimed at clarifying the nature of the species responsible for the extra infrared band.

A very important consideration which arises from our infrared data on the two pentacarbonyls and from their comparison with the infrared data known for $Fe(CO)_5$[11] (see Table I) is that the pentacarbonyls of the iron subgroup all have a trigonal-bipyramidal configuration of D_{3h} symmetry for which two infrared-active CO stretching vibrations are expected. By X-ray diffraction studies[12] on the solid compound and by an electron diffraction investigation[13] of the vapor, $Fe(CO)_5$ has been shown to have a trigonal-bipyramidal configuration. A tetragonal pyramidal configuration of C_{4v} symmetry could also be a possibility for a monomeric pentacarbonyl. The selection rules, however, predict three infrared-active CO stretching vibrations for this symmetry, which is therefore regarded as unlikely for $Ru(CO)_5$ and $Os(CO)_5$ in view of the lower number of bands observed. The failure to assume a tetragonal-pyramidal configuration is quite common for compounds of transition elements of formula ML_5—*i.e.*, with five identical ligands.[14] In terms of the elec-

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[9] D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, **4**, 166 (1965).

[10] B. F. G. Johnson, J. Lewis, I. G. Williams, and J. Wilson, *Chem. Commun.*, 391 (1966).

[11] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962), and references therein.

[12] J. Donohue and A. Caron, *Acta Cryst.*, **17**, 663 (1964); *J. Phys. Chem.*, **70**, 603 (1966).

[13] M. I. Davis and H. P. Hanson, *ibid.*, **69**, 3405 (1965).

[14] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

TABLE I

INFRARED CO STRETCHING VIBRATIONS OF CARBONYL COMPOUNDS OF IRON SUBGROUP METALS

Compound	ν_{CO}, cm^{-1}	Phase
$Fe(CO)_5$	2022 s, 2000 vs	Heptane[a]
	2034, 2014	Gas[b]
$Ru(CO)_5$	2035 s, 1999 vs	Heptane
$Os(CO)_5$	2034 s, 1991 vs	Heptane
	2047 s, 2006 vs	Gas
$Ru_3(CO)_{12}$	2060 vs, 2029 s, 2010 m	Heptane[c]

[a] From ref 11. [b] W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963). [c] Bands at 2061, 2032, and 2015 cm^{-1} are reported in ref 7 for a carbon tetrachloride solution.

tron-pair repulsion theory this is explained by the repulsion among five ligands being the least when they are placed at the vertices of a trigonal bipyramid.[15]

Dihalogenotetracarbonyls of Ruthenium.—Pentacarbonyliron is known to react readily with halogens to give the dihalogenotetracarbonyl derivatives $FeX_2(CO)_4$.[11] The chloro compound, $FeCl_2(CO)_4$, is, however, thermally rather unstable and decomposes to $FeCl_2$ at about 10°. The thermal stabilities of the bromo and iodo derivatives are considerably higher.

The only known dihalogenotetracarbonyl compound of ruthenium was $RuI_2(CO)_4$ described some years ago by Dahl and co-workers.[8] It had been obtained from the reaction of anhydrous RuI_3 with CO in the presence of copper. According to X-ray work, diiodotetracarbonylruthenium(II) has an octahedral configuration with the two halogens in *cis* position.[16]

Very little was known in the literature concerning the reactions of $Ru(CO)_5$ with halogens. Manchot and Manchot[1] reported the failure to isolate any iodocarbonyl from the reaction of iodine with $Ru(CO)_5$, whereas the latter was found to react with bromine but the composition of the products obtained was not established. We have now found that $Ru(CO)_5$ reacts very rapidly with halogens to give the species $RuX_2(CO)_4$, with X being Br and I. No pure product could be obtained from the reaction with chlorine. The infrared data suggest that the compounds have the *cis* configuration of C_{2v} symmetry for which four infrared CO stretching vibrations are expected. We did not find any evidence for the conversion of the *cis*-dihalogeno compounds to the *trans* isomers, even on prolonged exposure to the light beam of the infrared spectrophotometer. The corresponding iodo derivative of iron, $FeI_2(CO)_4$, is known to be present in solution as the *cis* isomer, although Pankowski and Bigorgne[17] have recently found some evidence for its conversion to the *trans* isomer upon irradiation with ultraviolet light. We did not investigate a similar conversion of our dihalogeno compounds.

As shown in Table II, the agreement between the bands of $RuX_2(CO)_4$ and those of the corresponding iron complexes is excellent as far as number and relative intensities are concerned. As expected, there is a wavenumber decrease from the bromo to the iodo derivative. This is due to a higher degree of d_π–p_π bonding from the metal to the carbon monoxide groups induced by the lower electronegativity of iodine compared with bromine.

TABLE II

INFRARED CO STRETCHING VIBRATIONS OF HALOTETRACARBONYL COMPOUNDS OF IRON AND RUTHENIUM

Compound	ν_{CO}, cm^{-1}	
	X = Br	X = I
cis-$FeX_2(CO)_4$	2150 m[a,b]	2131 s[a,c]
	2108 vs	2086 vs
	2098.5 vs–s	2062 s
	2074 s	2047 w
cis-$RuX_2(CO)_4$	2177 m[d]	2160 m[c,e]
		2119 vw
	2123 vs	2105 vs
	2105 s	2095 s
	2073 s	2066 s

[a] From ref 11. [b] Tetrachloroethylene solution. [c] Heptane solution. [d] Carbon tetrachloride solution. [e] In ref 8 the following bands are reported: 2161 m, 2119 w, 2106 vs, 2097 s, 2068 s cm^{-1}.

The reactions of $Os(CO)_5$ with halogens were also examined. There is infrared evidence that *cis*-dihalogenotetracarbonyl derivatives are also obtained, but the reactions appear considerably more complicated than in the previously described case of ruthenium. A detailed account of these reactions will be reported in a forthcoming publication.

Acknowledgment.—The authors wish to thank Dr. K. Noack for helpful discussions and help in measuring the infrared spectra and Mr. U. Schaerer for technical assistance.

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(15) R. J. Gillespie, *J. Chem. Soc.*, 4679 (1963).

(16) L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 946 (1962).

(17) M. Pankowski and M. Bigorgne, *Compt. Rend.*, **263**, 239 (1966).