impossible. The air-dried precipitate was greenish black and weighed 1.8 g, a yield of 55%.

Absorption Measurements.—The infrared spectra were recorded with a Perkin-Elmer Model 9 spectrophotometer using sodium chloride prisms. KBr disks were used.

Magnetic Moment Measurements.—Magnetic susceptibilities were measured at 27 ± 1° by the Gouy method. Solid $Hg[Co(NCS)_4]$ was used to calibrate the instrument. $[RuTu_6]_2[HgI_4]_3$ is paramagnetic and μ_{eff} (with diamagnetic correction of 1306×10^{-6} cgsu applied to χ_M of 296×10^{-6} cgsu) is 2.0 ± 0.1 BM.

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Dimerization Reactions and Monosubstituted Derivatives of Ruthenium Tetracarbonyl Dihalides

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Ruthenium tetracarbonyl dihalides, $Ru(CO)_4X_2$, were isolated by Calderazzo and L'Eplattenier by the reaction of ruthenium pentacarbonyl with halogens.[1] Corey, *et al.*, prepared the diiodide.[2] Cotton, *et al.*, isolated the dibromide and diiodide from the reaction of $H_2Ru(CO)_4$ with the appropriate halogen.[3] Johnson, *et al.*, have described an alternative route which involves the action of halogens on $Ru_3(CO)_{12}$.[4,5]

We have reconsidered the thermal decomposition of $Ru(CO)_4X_2$ (X = Br, I) whereby the corresponding ruthenium tricarbonyl dihalides, $[Ru(CO)_3X_2]_2$, are obtained

$$2Ru(CO)_4X_2 \longrightarrow [Ru(CO)_3X_2]_2 + 2CO \qquad (1)$$

In this paper we shall report a kinetic study of reaction 1 along with a detailed investigation of it under preparative conditions. We have now also found that under relatively mild conditions ruthenium tetracarbonyl halides give monosubstituted products by reaction with pyridine or pyridine derivatives (L)

$$Ru(CO)_4X_2 + L \longrightarrow Ru(CO)_3X_2L + CO \qquad (2)$$

These novel tricarbonyl derivatives will also be described in this paper.

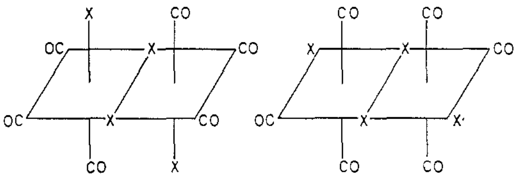
Results and Discussion

(A) Dimerization Reactions of $Ru(CO)_4X_2$.—Reaction 1 proceeds under relatively mild conditions, in such solvents as chloroform. The halogen-bridged complexes have been isolated in only one of the possible isomeric forms as yellow crystals which are stable in solution even in the presence of air. They are diamagnetic in the solid and nonconducting in nitrobenzene solution. These compounds are dimeric: their molecular weights were determined either by osmometric methods or by the appearance of the parent molecular ions in the mass spectra. These compounds have also been isolated by the reaction of $Ru_3(CO)_{12}$ and the halogens[4,5] or CHX_3.[6,7] The infrared spectra of our compounds in the carbonyl stretching region consist of two strong bands (Table I); the lower one is broader than the upper one and exhibits a shoulder. Such spectral features suggest a C_{2h} symmetry. It should be noted that such shoulder cannot be attributed to the presence of other isomers of these compounds since it would then be accompanied by additional bands, and, more important, it does not correspond to any of the bands observed by other authors and assigned to isomers.[4-7] We feel that this shoulder is probably due to a better resolution resulting from the greater purity of our samples. The infrared evidence does not allow one to distinguish between the two possible isomers, I and II (Figure 1).

TABLE I
CARBONYL STRETCHING FREQUENCIES OF RUTHENIUM CARBONYL DERIVATIVES IN $CHCl_3$ SOLUTION[a]

Compound	ν_{CO}, cm^{-1}				
$Ru(CO)_4Br_2$[b]	2177 m	2123 vs	2105 s	2073 s	
$Ru(CO)_4I_2$[b]	2160 m	2119 vw	2105 vs	2095 s	2066 s
$[Ru(CO)_3Br_2]_2$		2131 vs	2065 vs	2059 sh	
$[Ru(CO)_3I_2]_2$		2122 vs	2064 vs	2050 sh	
$Ru(CO)_3Br_2(C_5H_5N)$		2128 vs	2069 vs	2045 vs	
$Ru(CO)_3Br_2$(3-pic)		2138 vs	2078 vs	2052 vs	
$Ru(CO)_3Br_2$(3,4-lut)		2138 vs	2078 vs	2052 vs	
$Ru(CO)_3I_2(C_5H_5N)$		2119 vs	2063 vs	2043 s	

[a] All spectra recorded on a Perkin-Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium; vw, very weak; sh, shoulder. [b] From ref 1.



I II

Figure 1.

Thus, we are inclined to assume structure I for our halogen-bridged complexes, similar to that of the compound $[Ru(CO)_3Br_2]_2$ recently investigated.[8]

(B) Monosubstituted Derivatives of Ruthenium Tetracarbonyl Dihalides, $Ru(CO)_3X_2L$ (X = Br, I).—Disubstituted derivatives of ruthenium tetracarbonyl dihalides, $Ru(CO)_2X_2L_2$, are well known and can be

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obtained by various methods.[9-12] We have now found that the reaction of ruthenium tetracarbonyl dihalides with pyridine or a pyridine derivative leads to the replacement of one carbon monoxide molecule. The resulting dihalotricarbonylruthenium(II) complexes, $\mathrm{Ru(CO)_3X_2L}$, were isolated as crystalline solids which appeared to be diamagnetic in the solid, nonelectrolytic in acetone solution, and monomeric in chloroform. Their ir spectra (Table I) indicate that their most probable structure is like that given in Figure 2. The C_i symmetry of this molecule requires in fact three infrared-active C–O stretching vibrations, in agreement with those observed experimentally. No evidence was found for the presence of other isomeric species. It has been reported that a related derivative, $\mathrm{Ru(CO)_3Cl_2L}$ (L = THF), was formed from a solution later postulated to contain $\mathrm{Ru(CO)_4Cl_2}$.[9]

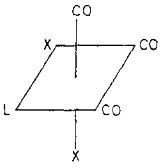

Figure 2.

(C) **Kinetic Studies.**—Kinetic data for reaction 1 in different solvents are presented in Table II.

Table II

Rate Constants for the Reaction

$$2\mathrm{Ru(CO)_4X_2} \longrightarrow [\mathrm{Ru(CO)_3X_2}]_2 + 2\mathrm{CO}$$

in Different Solvents

Solvent	Temp, °C	10^5k_{obsd}, $\mathrm{sec^{-1}}$
	X = I	
Nitromethane	60	6.82
Nitromethane	65	13.1
Nitromethane	75	45.9
1,2-Dichloroethane	50	3.15
1,2-Dichloroethane	60	11.4
1,2-Dichloroethane	65	21.4
	X = Br	
Nitromethane	40	2.85
Nitromethane	50	12.7
Nitromethane	60	46.1
1,2-Dichloroethane	40	4.57
1,2-Dichloroethane	50	21.8
1,2-Dichloroethane	60	88.7
Chloroform	30	6.27
Chloroform	40	22.5
Chloroform	45	31.3
Nitrobenzene	60	26.7
Dioxane	60	57.9
Methyl isobutyl ketone	60	76.4

$\mathrm{Ru(CO)_4X_2}$ undergoes dimerization according to a first-order rate law. This behavior was observed in all of the solvents studied. The first-order rate constants given in Table II are averages of at least three but usually five different rate determinations. The kinetic results suggest that the species that is responsible for the dimerization is the labile, five-coordinated $\mathrm{Ru(CO)_3X_2}$ formed by loss of one CO group in a dissociative path

$$\mathrm{Ru(CO)_4X_2} \xrightarrow[\text{slow}]{-\mathrm{CO}} \mathrm{Ru(CO)_3X_2}$$

This may be followed by a rapid reaction of the labile intermediate with $\mathrm{Ru(CO)_4X_2}$ involving displacement of CO and formation of the halogen bridge

$$\mathrm{Ru(CO)_3X_2} + \mathrm{Ru(CO)_4X_2} \xrightarrow{\text{fast}} [\mathrm{Ru(CO)_3X_2}]_2 + \mathrm{CO}$$

The data in Table II indicate that the rate of dimerization decreases with the nature of coordinated halide in the order Br > I. This has been explained by the different electronegativity of the halide ligands: the more electronegative bromide causes a lower electron density on ruthenium which in turn means less back-donation of d electrons, lower metal–CO bond strength, and hence faster reaction.[13]

The nature of the solvent appears to have little effect on the rate of reaction 1. Indeed there is no suggestion that the dielectric constant[14] and/or the coordination ability[15] of the solvent are significant factors in determining rates.

Recorded in Table III are the activation parameters calculated from the rate constants at three different temperatures. The positive values of activation entropy are in agreement with a dissociative process where some degrees of freedom are gained in the transition state. It can be seen that the rate-increasing effect of the lower ΔH^* for iodide relative to bromide is offset by the less favorable ΔS^*. The net effect is that the observed rates vary in the order Br > I.

Table III

Activation Parameters for the Reaction

$$2\mathrm{Ru(CO)_4X_2} \longrightarrow [\mathrm{Ru(CO)_3X_2}]_2 + 2\mathrm{CO}$$

in Nitromethane and 1,2-Dichloroethane Solution

Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
	X = Br	
Nitromethane	28.2	10.7
1,2-Dichloroethane	30.1	17.6
	X = I	
Nitromethane	28.5	7.8
1,2-Dichloroethane	27.2	5.0

Experimental Section

Compounds and Solvents.—The compounds $\mathrm{Ru(CO)_4Br_2}$ and $\mathrm{Ru(CO)_4I_2}$ were prepared according to the procedure of the literature.[1] The complexes were identified by carbon, oxygen, and halogen analyses and by their infrared spectra.

The solvents 1,2-dichloroethane, chloroform, nitrobenzene (Analar, British Drug Houses Ltd.), and nitromethane (Schuchardt, Munich) were distilled before use and stored under nitrogen. Dioxane was refluxed over sodium wire and then

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TABLE IV

Complex	Color	Mp, °C[a]		Mol wt	Analyses, %				
					C	H	N	O	Halogen
$[Ru(CO)_3Br_2]_2$	Yellow	. . .	Calcd	691	10.43	. . .	. . .	13.89	46.25
			Found	691[b]	10.45	. . .	. . .	13.93	45.78
$[Ru(CO)_3I_2]_2$	Yellow	. . .	Calcd	879	8.20	. . .	. . .	10.92	57.74
			Found	890[c]	8.40	. . .	. . .	10.85	56.91
$Ru(CO)_3Br_2(C_5H_5N)$	Ivory yellow	180	Calcd	424	22.67	1.19	3.30	11.32	37.70
			Found	445	22.57	1.17	3.29	11.13	36.90
$Ru(CO)_3Br_2$(3-pic)	Ivory yellow	149	Calcd	438	24.67	1.61	3.20	10.96	36.48
			Found	446	24.65	1.78	3.39	10.71	36.40
$Ru(CO)_3Br_2$(3,4-lut)	Ivory yellow	164	Calcd	452	26.57	2.00	3.10	10.62	35.35
			Found	483	26.56	2.12	3.17	10.84	35.90
$Ru(CO)_3I_2(C_5H_5N)$	Ivory yellow	143	Calcd	518	18.55	0.97	2.70	9.27	49.00
			Found	532	18.71	1.05	2.66	9.51	49.50

[a] Uncorrected values determined in evacuated tubes. [b] Determined by mass spectra. [c] Determined in $CHCl_3$ solution using a Mechrolab osmometer, Model 301 A.

distilled. Methyl isobutyl ketone was dried over anhydrous calcium sulfate and then distilled.

Thermal Decomposition of Ruthenium Tetracarbonyl Dihalides.—About 0.2 g (0.0005 mol) of the compounds $Ru(CO)_4X_2$ (X = Br, I), dissolved in 100 ml of chloroform or benzene, was allowed to react at 50°. The progress of the reaction was monitored by infrared spectroscopy. When no more $Ru(CO)_4X_2$ could be detected, the solution was cooled to room temperature and evaporated under reduced pressure. The products were precipitated by adding *n*-pentane, filtered, washed with *n*-pentane, and dried under high vacuum. The yields were practically quantitative. A further purification was effected by sublimation under high vacuum (120° and 10^{-3} mm). The yellow crystalline compounds $[Ru(CO)_3I_2]_2$ and $[Ru(CO)_3Br_2]_2$ have a different solubility in common organic solvents such as chloroform, 1,2-dichloroethane, benzene, toluene, nitromethane, nitrobenzene: $[Ru(CO)_3I_2]_2$ is very soluble in these solvents, whereas the analogous $[Ru(CO)_3Br_2]_2$ is only slightly soluble. They are insoluble in aliphatic hydrocarbons and decompose on being heated without melting. Infrared spectra, elemental analyses, and other data are given in Tables I and IV.

General Procedure for the Synthesis of $Ru(CO)_3X_2L$ (X = Br, I; L = Pyridine, 3-Picoline, 3,4-Lutidine).—$Ru(CO)_4X_2$ (0.0004 mol) and *ca.* 0.0005 mol of ligand dissolved in 50 ml of chloroform were allowed to react at room temperature. The conversion of $Ru(CO)_4X_2$ to $Ru(CO)_3X_2L$ was followed either spectroscopically or gas volumetrically. The conversion was practically complete within 20 min. The solution was then concentrated under reduced pressure and the product was precipitated by adding *n*-pentane. The ivory yellow crystalline compound was collected on a filter, washed with *n*-pentane, and dried under high vacuum. Purification was effected by recrystallization from chloroform–pentane (1:5). All the compounds are soluble in organic solvents such as chloroform, carbonte trachloride, benzene, and toluene and insoluble in aliphatic hydrocarbons. Infrared spectra, elemental analyses, and other data are given in Tables I and IV.

Kinetic Studies.—The rates of reaction 1 were followed by recording the decrease in intensity of the high-frequency CO stretching absorption of the $Ru(CO)_4X_2$ complexes at about 2170 cm^{-1}. The reactions were carried out under nitrogen in an aluminum-wrapped vessel fitted with a serum cap. A constant-temperature bath was used to maintain the temperature within 0.1°. The concentration of $Ru(CO)_4X_2$ was in the range 3.2×10^{-3}–12×10^{-3} *M*. At appropriate time intervals aliquots were withdrawn from the reaction vessel with a syringe and transferred into a 1-mm infrared cell, and their infrared spectra were measured against a reference containing only the solvent. Anywhere between 15 and 20 measurements were made during a period of 3 or 4 half-lives. All reactions proceeded to completion and the spectra at infinite time were in good agreement with those of the known products independently prepared. The pseudo-first-order rate constants were reproducible to 5% or better. More details about this method have been given previously.[16] Measurements were performed on a Perkin-Elmer Model 621 spectrophotometer. A general nonlinear least-squares program was used to calculate the activation parameters.

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The Metal–Metal Bond in Binuclear Rhodium(II) Acetate Monohydrate[1]

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Rhodium(II) acetate monohydrate is isostructural with binuclear copper(II) acetate monohydrate[2] and the published[2] Rh–Rh separation of 2.45 Å suggests significant Rh–Rh bonding [Rh–Rh = 2.69 Å in rhodium metal]. Many adducts of the type $Rh(CH_3CO_2)_2L$ have been prepared.[3-5] In most cases it is probable that these adducts are binuclear with the addends L terminally coordinated to rhodium atoms bridged by the acetate cage. This is consistent with the analytical data, diamagnetism, and electronic spectra.[3-5] The visible spectra of Rh(II) acetate and of some of its adducts have been reported but not interpreted.[3]

The visible spectra usually consist of two main absorptions: band I at ~600 mμ and band II at ~450 mμ (*cf.* Figure 1). Band II is relatively insensitive to terminal ligands while band I is particularly sensitive

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