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METAL CARBONYL–TRIFLUOROPHOSPHINE SYSTEMS
X*. MONO- AND TRIRUTHENIUM CARBONYLS

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SUMMARY

Triruthenium dodecacarbonyl reacts with high pressure PF_3 or with PF_3/CO mixtures to yield two series of compounds. At high PF_3 pressures, the mononuclear species $Ru(PF_3)_x(CO)_{5-x}$ ($x=5$, 4 and 3) are the main products with only traces of $Ru(PF_3)_2(CO)_3$ and $Ru(PF_3)(CO)_4$ being found. With high carbon monoxide pressure and less PF_3, the species $Ru_3(PF_3)_y(CO)_{12-y}$ ($y=0$–6) are the main products. It is seen that $Ru_3(CO)_{12}$ can have up to six CO groups replaced sequentially before the cluster is broken followed by the formation of the mononuclear species. The evidence shows that the $Ru(PF_3)_x(CO)_{5-x}$ species are stereochemically non-rigid.

INTRODUCTION

Extensive studies have been done in these laboratories on five-coordinate metal carbonyl–phosphorus trifluoride complexes. The central purpose has been to examine the stereochemical non-rigidity among isomers of the various $M(PF_3)_x(CO)_{5-x}$ compositions. In general, IR studies clearly show that all possible isomers exist for a compound[1,2] and further studies have shown that the isomers are undergoing rapid intramolecular exchange among themselves. The exchange process has been demonstrated by both NMR[3] and methanol solvolysis reactions[4,5]. This work has been particularly extensive with the iron compounds[1,4].

It is logical that these studies should be extended to ruthenium which, as a member of the iron group, should be capable of yielding species analogous to the $Fe(PF_3)_x(CO)_{5-x}$ compounds[1]. However, the direct analogy between the iron and ruthenium systems presents both problems and fascinating new challenges.

Iron pentacarbonyl is a stable, commercially available compound. However, $Ru(CO)_5$ which was first reported by Manchot and Manchot[6] in 1936, was not seriously studied until Calderazzo[7] did so in 1967. It is clear that $Ru(CO)_5$ is quite unstable and readily transforms into $Ru_3(CO)_{12}$. However, past experience has shown that PF_3 almost invariably stabilizes the trifluorophosphine intermediate species relative to the parent carbonyl. Therefore, there was a good chance that the inter-

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mediate $Ru(PF_3)_x(CO)_{5-x}$ species would be moderately stable and thus be able to be studied in terms of their stereochemical non-rigidity. Kruck[8] has prepared the compound $Ru(PF_3)_5$ and found it to be fairly tractable.

The existence of $Ru_3(CO)_{12}$ which presents a problem relative to the formation of the five-coordinate mononuclear species presents an opportunity to study the PF_3 polynuclear species of the type $Ru_3(PF_3)_y(CO)_{12-y}$. There are a number of examples of phosphine or phosphite complexes of the general formula $Ru_3(CO)_9(PR_3)_3$, but other compositions are rare[9]. A study of the inter-relationship between the mononuclear compound and the trinuclear compounds would be quite valuable.

EXPERIMENTAL

Triruthenium dodecacarbonyl was made by the procedure of Stone and Bruce[10]. This reaction between ruthenium trichloride and carbon monoxide was run at 65° and 200 psi in a 1-l Magnedrive Autoclave yielding both $Ru_3(CO)_{12}$ and $[Ru(CO)_3Cl_2]_2$. The former could be separated from the latter on the basis of the size of the crystals formed under the conditions we used, but frequently they were used together since the chloro complex did not interfere with the reaction of $Ru_3(CO)_{12}$.

$Ru(PF_3)_x(CO)_{5-x}$ *species*

Pure $Ru_3(CO)_{12}$ (0.8 g) was allowed to react with sufficient PF_3 in a 150 ml autoclave to yield a pressure of 500 psi at room temperature. The vessel was heated to 160° for 12 h and then the products recovered by vacuum manipulation. The PF_3 was removed at −78° leaving about 0.15 g of a light yellow solid. This solid, dissolved in a minimum of hexane, was separated on an 8 m × 0.25 inch copper GLC column containing 40% dibutyl phthalate on Chromosorb FB. The column was at room temperature with a He flow of 60 ml/min. A Varian–Aerograph Autoprep A-700 was used, with the compounds being trapped at −78°. The product contained three peaks, 95% of which was $Ru(PF_3)_5$ (identified by its IR[8]). Two minor peaks having progressively longer retention times were also seen.

Mixtures containing higher proportions of the intermediates were prepared most simply by reacting a crude mixture of $Ru_3(CO)_{12}$ and $[Ru(CO)_3Cl_2]_2$ (and possibly left over zinc) with a gas mixture of CO and PF_3. Neither $[Ru(CO)_3Cl_2]_2$ nor the zinc seem to interfere or get involved in the reaction. In a typical preparation, one gram of the crude carbonyl was placed in a 150 ml autoclave which was evacuated and cooled to −196°. Sufficient PF_3 was added to yield a pressure of 300 psi at room temperature and then enough CO was added to give a total pressure of 1100 psi. The vessel was then heated to 150° for 18 h. The PF_3 and CO were removed at −78°, and a light yellow liquid distilled out rapidly at room temperature leaving behind small quantities of a viscous low-volatility oil that required prolonged pumping to remove.

The light yellow liquid was separated on the 8 m DBP column. Five peaks were seen, the first three matching the three components found when no CO was added. Runs were made with various CO to PF_3 ratios in an effort to alter the relative amounts of the five compounds.

Photochemical reactions on the $Ru(PF_3)_x(CO)_{5-x}$ mixtures with CO were carried out by irradiating 0.1 ml samples in a 500 ml flask using an AH-6 General

Electric UV lamp. Various times from minutes to hours were tried. The flask was kept at ambient temperatures.

Attempts were made to react $[Ru(CO)_3Cl_2]_2$ with PF_3. Pressures of up to 350 psi and temperatures of up to 160° were used. Reducing agents such as Cu, Zn or H_2 were tried. Trace quantities of light yellow oils were recovered by vacuum manipulation.

$Ru_3(PF_3)_y(CO)_{12-y}$ species

When the preparation of the $Ru(PF_3)_x(CO)_{5-x}$ species was carried out in a pressure vessel such that the head was considerably cooler than the body, then quantities of a red, sublimable solid were isolated. The quantity increased as the proportion of CO in the CO/PF_3 reaction mixture increased. This material was chromatographed through short GLC columns such as 2 m, 15% DC-702 columns, but individual components were not seen. Various cuts on the broad ill-defined peak were taken and examined by IR.

Solvolysis studies on $Ru(PF_3)_4(CO)$ and $Ru(PF_3)_3(CO)_2$ were run as with the iron system[4]. IR spectra were run in hexane on a PE 521 calibrated against gaseous DCl. Mass spectra were run on a Nucleide 1290-Gl.5 instrument. Fluorine NMR spectra were run on a Varian HA-60 spectrometer at 54.66 MHz. Phosphorus trifluoride was obtained from Ozark Mahoning and purified as before[12].

RESULTS

Ruthenium compounds of the general formula $Ru(PF_3)_x(CO)_{5-x}$ are produced by the reaction of $Ru_3(CO)_{12}$ with CO/PF_3 mixtures under pressure. When pure PF_3 is added to the pressure vessel and carbon monoxide comes only from the $Ru_3(CO)_{12}$, the product is 95% pure $Ru(PF_3)_5$. This compound is identified by comparing its IR spectrum and other properties with those reported by Kruck[8]. Its spectrum shows only strong P–F absorptions at 920, 897 and 846 cm^{-1}.

The various $Ru(PF_3)_x(CO)_{5-x}$ compounds ($x=5$ through 1) are identified by a variety of means. For $x=2$ and 1, the evidence is limited.

Order of elution

Five peaks are found in the gas chromatograms of the mixtures. Six compositions are possible. The known instability of $Ru(CO)_5$[7,9] makes it seem quite likely that even if it were present in the mixtures, it would not survive the time in a column. Past results have shown that as the degree of PF_3 substitution increases, the retention time progressively decreases[5]. The parent carbonyl is normally used as the reference point from which the mono-, di- and higher phosphines are identified. In this case, the known compound $Ru(PF_3)_5$ is the reference point. Thus the five compounds are assumed to be $Ru(PF_3)_5$, $Ru(PF_3)_4(CO)$, $Ru(PF_3)_3(CO)_2$, $Ru(PF_3)_2(CO)_3$ and $Ru(PF_3)(CO)_4$ in order of increasing retention time.

Sequence of formation

Various ratios of PF_3/CO were used to form various $Ru(PF_3)_x(CO)_{5-x}$ mixtures. Using pure PF_3, nearly pure $Ru(PF_3)_5$ is found. As the PF_3/CO ratio changes, the relative heights of the peaks should vary in a manner that is dependent upon the gas mixture composition. This is found for the first three components which helps confirm their earlier identification, but it does not occur for the last two. Neither this high pressure procedure nor the UV irradiation method produces more than trace quantities of the fourth and fifth components that are seen in the gas chromatograms. Thus this procedure is of no help in the identification of the last two components which are assumed to be $Ru(PF_3)_2(CO)_3$ and $Ru(PF_3)(CO)_4$.

Mass spectroscopy

The first three compounds are readily isolated for examination by mass spectroscopy. The parent ion molecular weights for the compounds assigned the formulas $Ru(PF_3)_5$, $Ru(PF_3)_4$ (CO), and $Ru(PF_3)_3(CO)_2$ are as expected. The main cracking fractions correspond to the loss of PF_3 and/or CO groups.

IR spectroscopy

The IR data for the various isolated peaks are shown in Table 1. It is clear that there are more carbonyl stretching frequencies present than are possible on the basis of group theory for any given isomer. However, these extra bands are to be expected on the basis of the results from the $Fe(PF_3)_x(CO)_{5-x}$ system[1,4]. A comparison of the two systems shows a close agreement in the number of bands implying that the iron and ruthenium systems are quite similar particularly with regard to the occurrence of isomers. However, the exact band positions and intensities vary enough so that one

TABLE 1

IR SPECTRA (cm^{-1}) OF THE $Ru(PF_3)_x(CO)_{5-x}$ COMPOUNDS

Compound	Carbonyl region	P–F region
$Ru(PF_3)(CO)_4$	2106 w	900 mw
	2087 w	887 ms
	2041 s	862 w
	2027 w	846 ms
	2008 w	
$Ru(PF_3)_2(CO)_3$	2084 vw	900 mw
	2071 mw	892 mw
	2041 s	873 mw
	2026 w	862 m
	2008 w	848 s
$Ru(PF_3)_3(CO)_2$	2078 w	922 w
	2038 s	893 s
	2026 w	873 s
	2007 vw	859 vw
		848 vs
$Ru(PF_3)_4(CO)$	2070 s	941 w
	2026 w	914 m
		891 m
		878 vw
		847 m
$Ru(PF_3)_5$		920 s
		897 s
		847 s

would not be safe in assuming that the relative amounts of the various isomers are the same.

Fluorine NMR

The fluorine spectra of $Ru(PF_3)_3(CO)_2$ and $Ru(PF_3)_4(CO)$ are typical of what has been seen for the spectra of three[13] and four equivalent PF_3 groups. The spectrum of each has two complex mirror-imaged halves separated by about 1300 Hz. The triphosphine spectrum is more complex, owing to second order coupling, than a typical readily recognizable diphosphine spectrum and the tetraphosphine is more complex than the triphosphine spectrum. It was not possible to obtain spectra of the mono- and diphosphines. They would have been easily identifiable and readily analyzed.

Methanol solvolysis studies have clearly shown a shifting equilibrium among the isomers for compositions in the $Fe(PF_3)_x(CO)_{5-x}$ system[4]. These solvolysis studies work most simply for the mono- and diphosphines. With the ruthenium system, only the tri- and tetraphosphine are available in sufficient quantity for the approach to be tried. The solvolysis is more rapid with pure methanol than with iron yet less extensive. As with the iron compounds, each vibrational band shifts about 9 to 10 cm^{-1} to lower frequency for each stage of solvolysis. In addition, the relative intensities change among the various bands. The data are shown in Table 2. For the monocarbonyl, the low frequency band gains in intensity relative to the high frequency band. This is the same type of change that is seen with $Fe(PF_3)_4(CO)$, which is interpreted in terms of a shifting of the isomer composition toward the species with the carbonyl group in the equatorial position of a trigonal bipyramid. For the dicarbonyl, $Ru(PF_3)_3(CO)_2$, the relative intensities are again seen to change. This is seen most clearly with the more intense high frequency bands, but the two weaker low frequency bands are sufficiently obscure in the composite spectra that one can not be sure what is happening to them and it is certainly not safe to try to assign bands to specific isomers.

The reaction of $Ru_3(CO)_{12}$ with PF_3/CO mixtures yields a low volatility residue. In a pressure bomb in which the head is cooler than the main body of the vessel, this residue appears as red sublimable crystals. These crystals can be slowly eluted

TABLE 2

METHANOL SOLVOLYSIS DATA ON $Ru(PF_3)_x(CO)_{5-x}$ SPECIES

Parent compound	Stage of solvolysis	Band positions (cm^{-1})			
$Ru(PF_3)_4(CO)$	0	2070(10)[a]	2026(3)		
	1	2061(10)	2016(4)		
	2	2053(10)	2007(5)		
	3	2046(10)	1999(6)		
$Ru(PF_3)_3(CO)_2$	0	2078(2)	2038(10)	2026[b]	2007[b]
	1	2068(3)	2027(10)	2013[b]	1993[b]
	2	2059(3)	2018(10)	?	1980[b]
	3	2049(4)	2008(10)	?	1965[b]

[a] Numbers in parenthesis are relative intensities, most intense equals 10. [b] The relative intensities of these bands are obscure in the composite spectra. Both are weak.

through short 1 to 2 m GLC columns, but a broad band appears rather than a series of sharp peaks. This band is obviously a collection of partially resolved components. When various cuts are taken of the broad band, the IR spectra of these cuts change quite markedly indicating that a series of compounds is being partially resolved.

The components of this residue are identified as members of the system $Ru_3(PF_3)_y(CO)_{12-y}$ ($y=1$ to 6) by mass spectroscopy. The various parent molecular ion peaks are all seen along with the cracking peaks corresponding to the loss of CO and PF_3. Samples obtained from reactions with varying PF_3 to CO ratios were examined. The relative intensities of the parent ions for $y=0$ through 6 change in the general way one would expect on the basis of the ratios of the ligand gases. At higher PF_3/CO ratios, the distribution favors the higher degree of substitution and at lower ratios, the lower degree of substitution predominates. Always, however, a run gives products containing no fewer than four identifiable components.

Reactions of $[Ru(CO)_3Cl_2]_2$ with PF_3 and/or CO and various reducing agents yield only trace quantities of the mono- or trinuclear species. Of course, the conditions we used are rather mild as compared to those of Kruck[14] who has successfully carried out similar reactions.

DISCUSSION

Either pure PF_3 or mixtures of PF_3 and CO react with $Ru_3(CO)_{12}$ to give species of the type $Ru(PF_3)_x(CO)_{5-x}$ ($x=5$ through 1) and $Ru_3(PF_3)_y(CO)_{12-y}$ ($y=0$ through 6). The relative proportion of the monoruthenium to the triruthenium compounds is determined primarily by the relative amounts of PF_3 and CO. High PF_3/CO ratios yield predominately the mononuclear compounds and low ratios yield more of the trinuclear ones.

The value of x and y within each of the general formulations is likewise controlled by the PF_3/CO ratio. When only PF_3 is added to the pressure vessel such that CO comes only from the $Ru_3(CO)_{12}$, the product contains 95% $Ru(PF_3)_5$ with only trace amounts of $Ru(PF_3)_4(CO)$ and $Ru(PF_3)_3(CO)_2$. Increasing CO pressures increase the amount of the mono and dicarbonyls. However, higher proportions of CO fail to increase the amounts of $Ru(PF_3)_2(CO)_3$ and $Ru(PF_3)(CO)_4$ above the trace level. Instead of increasing their relative concentrations, the proportions of the $Ru_3(PF_3)_y(CO)_{12-y}$ species is increased. The relative species distribution among the trinuclear compounds changes as expected depending upon the relative amounts of CO and PF_3.

Attempts to enrich the CO content of the $Ru(PF_3)_x(CO)_{5-x}$ mixture so as to have higher concentrations of $Ru(PF_3)_2(CO)_3$ and $Ru(PF_3)(CO)_4$ by room temperature UV irradiation yields only increasing amounts of the trinuclear species. Sometimes irradiation techniques are more selective and less violent than thermal reactions for producing unstable species[15]. This may also apply to these ruthenium compounds if low enough temperatures are used.

Most of the various species mentioned for the mono- and trinuclear compounds are firmly identified by the various techniques discussed earlier. However, the identification of $Ru(PF_3)_2(CO)_3$ and $Ru(PF_3)(CO)_4$ rests primarily on their relative retention times and must be considered only tentative. The IR spectra of these two compounds are similar in both the carbonyl and P–F stretching regions to the corresponding iron compounds. However, the comparison is not sufficiently tight that it can be thought to add too much strength to the assignment.

All evidence points to the fact that the $Ru(PF_3)_x(CO)_{5-x}$ species are stereochemically non-rigid like their iron counterparts[1,4]. The individual isolated components contain too many carbonyl stretching frequencies for any single isomer. Highly efficient GLC shows no sign of isomer separation even when taking head and tail cuts. The ^{19}F NMR spectra are recognizable as being due to equivalent PF_3 groups, presumably because of a time-averaging process. Finally, the solvolysis reaction appears to shift the isomer distribution from an essentially random arrangement of CO and PF_3 groups to one in which there are decided site preferences implying that there is a path for rearrangement.

One possible explanation for the general product distribution of the mono- and trinuclear species is to assume the following reaction,

$$3\,Ru(PF_3)_x(CO)_{5-x} \rightarrow Ru_3(PF_3)_y(CO)_{12-y} + n\,CO + (3-n)\,PF_3$$

When the reaction starts from $Ru_3(CO)_{12}$, simple substitution could occur from $y=0$ to 6. When the seventh is added, then the metal–metal bonds break yielding the mononuclear species with x starting at 3 going to 5. However, other reactions and intermediates are certainly not excluded.

Bruce and Stone[9] have pointed out in their review that the $Ru_3(CO)_{12}$ cluster is more stable than the $Fe_3(CO)_{12}$ cluster. The ruthenium complex can have three carbonyls replaced by phosphines to yield $Ru_3(CO)_9(PR_3)_3$ whereas $Fe_3(CO)_{12}$ yields only $Fe(CO)_4(PR_3)$ under comparable conditions. The relative behaviour of PF_3 with iron and ruthenium substantiates this view. We have never seen any evidence for polynuclear carbonyl(trifluorophosphine)iron complexes whereas in $Ru_3(CO)_{12}$ half of the carbonyl groups can be replaced by PF_3.

This substitution of PF_3 into $Ru_3(CO)_{12}$ is the most extensive yet seen for this ruthenium compound. Some phosphine ligands will yield identifiable complexes with three carbonyls replaced[9]. The lower substituents are generally not found and when an attempt is made to obtain a higher degree of substitution the cluster generally breaks down.

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