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TRIFLUOROPHOSPHINE SUBSTITUTION OF GROUP VII PENTACARBONYLHYDRIDO COMPOUNDS

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Summary

Trifluorophosphine substitutes carbon monoxide in pentacarbonylhydridorhenium, yielding each possible composition and all geometric isomers. Each octahedral isomer has been observed and identified by mass spectroscopy and infrared spectroscopy. The substitution reaction occurs under either UV or thermal-pressure conditions. The substitution compositions and geometric isomers for each are separated by GLC at 20—30°C. Isomer rearrangement without disproportionation occurs at higher column temperatures. This $HRe(PF_3)_x(CO)_{5-x}$ system contrasts with the analogous manganese system in the isomer separation characteristics, since the isomers in the latter are inseparable by the same techniques. Isomer rearrangement via an intermolecular hydrogen exchange mechanism is proposed for both systems, at very different rates, based on deuteration experiments. NMR data of initial substitution compositions of the manganese and rhenium systems are given.

Introduction

There has been considerable interest in transition metal hydride chemistry in recent years, in part due to their catalytic properties [1]. Further interest in these compounds is based on the complex stereochemical problems presented by them [2]. In this paper, we are concerned with the stereochemical aspects of trifluorophosphine substituted Group VII mononuclear metal carbonyl hydrides.

Six-coordinate octahedral metal carbonyls, metal carbonyl halides and metal carbonyl alkyls appear stereochemically rigid. Numerous PF_3 substitution complexes of these compounds exist which also appear rigid. For instance, in the $Mo(PF_3)_x(CO)_{6-x}$ system, all compositions exist and all individual isomers have been isolated [3]. A given isomer rearranges only by dissociative disproportiona-

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tion, involving substitution compositions of higher and lower PF_3 content.

$HMn(CO)_5$ has been conclusively shown to be a slightly distorted octahedral C_{4v} complex with the radial carbonyls bent toward the hydrogen atom [4]. The PF_3 substitution system, $HMn(PF_3)_x(CO)_{5-x}$ has been synthesized and the individual compositions isolated [5]. However, the individual octahedral isomers are not separable by GLC techniques, in contrast to other octahedral metal carbonyl derivatives of PF_3, such as the molybdenum system. Infrared evidence confirmed the presence of the possible isomers within each substitution composition $HMn(PF_3)_x(CO)_{5-x}$. Since the individual compositions appeared stable with respect to disproportionation, either a rapid intermolecular or intramolecular hydrogen rearrangement was assumed to be occurring. In the original manganese hydride work [5] it was only possible to establish that the rearrangement was rapid with respect to chromatographic isolation conditions. Stereochemical nonrigidity has been found to be present [6] in a number of six-coordinate hydrides of the type $H_2M(PR_3)_4$.

It was hoped that a chemical study of the rhenium system and an NMR study of both manganese and rhenium would elucidate the stereochemical problems in Group VII $HM(PF_3)_x(CO)_{5-x}$ systems. The preparation and characterization of these compounds are reported here.

Experimental

Pentacarbonylhydridorhenium was prepared by methods [5,7] previously reported for pentacarbonylhydridomanganese synthesis. However, certain modifications were necessary in order to obtain adequate yields due to the extreme sensitivity of the sodium salt to humidity and oxygen.

While under vacuum, 5 g of dirhenium decacarbonyl (Alfa Inorganics) was dissolved in 40 ml of dried tetrahydrofuran (distilled from $LiAlH_4$) and treated with fresh sodium amalgam to form the $NaRe(CO)_5$ salt. After removal of amalgam and evaporation of solvent, the residue was heated in vacuum to about 45°C for 5 h in order to remove the last traces of solvent. Degassed *ortho*-phosphoric acid was added dropwise to the salt under vacuum, while the resulting $HRe(CO)_5$ was recovered after vacuum distillation through Linde 4A molecular sieves. The activated sieves removed traces of water and trapped polymeric compounds, so that further purification was not necessary.

Substitution of trifluorophosphine for carbon monoxide was accomplished by both UV irradiation and thermal-pressure reaction techniques. In both procedures, a mixture of substitution products always resulted.

For the initial PF_3 substitution into $HRe(CO)_5$, the following thermal-irradiation reaction was most efficient. About 14 mmol of PF_3 and 2 mmol of $HRe(CO)_5$ were vacuum distilled into a 500 ml roundbottom Pyrex flask at −196°C. This mixture was warmed to 70°C and irradiated with a Pyrex filtered 1000 W A-H6 mercury lamp. After short irradiation times of about 30 min, mixtures of predominantly mono- and di-substituted compositions resulted. With longer irradiation times, more extensive substitution occurs, with $HRe(PF_3)_5$ being the major product after 6 h of reaction. Unfortunately, decomposition of the monomeric rhenium carbonyl hydride to polymeric species occurs and approximately 30% is lost in initial stages of substitution. When the same reaction was carried out with Vycor filtered UV apparatus, more extensive decomposition occurred.

Trifluorophosphine substitution for carbon monoxide in $HRe(CO)_5$ occurred slowly at 90°C and 10 atm PF_3 pressure, but significant amounts of polymeric rhenium carbonyls were still formed. The reactions were carried out in 30 ml stainless steel Hoke cylinders. When the temperature was raised to 100°C, decomposition predominated. However, after the initial PF_3 substitution, the monomeric rhenium hydride derivatives become more thermally stable with respect to polymeric decomposition. Consequently, reaction for several days at 90°C, produced mixtures of $HRe(PF_3)_3(CO)_2$, $HRe(PF_3)_4(CO)$ and $HRe(PF_3)_5$.

Separation of reaction products was accomplished on a Varian—Aerograph A-100 gas liquid chromatograph, equipped with a 3 m column loaded with 30% DC 702 silicone oil on 80/100 mesh Kromat FB. Helium flow rates were approximately 55 cm^3/min, with column temperatures in the range of 25° to 60°C. Column temperatures had to be optimized for each reaction mixture.

The trifluorophosphine manganese compounds were made as before [5]. Alternatively, both the manganese and rhenium compounds could be made by treating $M_2(CO)_{10}$ with PF_3 at 20 atm pressure and H_2 at 70 atm additional presure with temperatures of 180—200°C for 24 h.

Hydrogen—deuterium exchange reactions were carried out by thawing layers of $DMn(CO)_5$ and $HRe(PF_3)_x(CO)_{5-x}$ or $HMn(PF_3)_x(CO)_{5-x}$ in an evacuated sealed NMR tube along with lock standard, and periodically examining the fluorine NMR spectrum.

Trifluorophosphine was obtained from Ozark—Mahoning Co. and purified as before by bubbling through a water column, followed by low temperature vacuum distillation [3].

The bulk of the NMR work was done on a Bruker HFX-90 spectrometer using $CF_3C_6H_5$ as internal fluorine lock or cyclopentane as internal proton lock. Chemical shift and coupling constant data were obtained from this instrument. A Varian HA-60 and a Bruker HX-270 were used for other frequencies. Cyclopentane was assumed to be 1.51 ppm downfield of TMS and data are reported relative to TMS.

Infrared spectra of the metal carbonyl derivatives were obtained as 1% solutions in n-hexane. The Perkin—Elmer 521 spectrometer was calibrated with gaseous DCl.

The chemical composition of each geometric isomer was determined with a Nuclide mass spectrometer after separation by gas chromatography. These complexes were introduced as gases since their vapor pressure is about 10 torr.

A Dupont Curve Resolver was used to estimate the relative abundances of the rhenium geometric isomers for each degree of substitution. Within a given composition, the various isomers should give quite similar responses on thermal conductivity detectors, and thus fairly accurate abundance data. In the case of $HRe(PF_3)_4(CO)$ the relative intensities of the infrared carbonyl stretches were used to approximate relative concentrations and must be considered rough values.

Results

Trifluorophosphine substitutes sequentially for carbon monoxide in $HRe(CO)_5$ yielding all of the related species $HRe(PF_3)_x(CO)_{5-x}$. The preferred reaction for producing the PF_3 substitution compositions is a combined thermal and low energy UV (Pyrex filtered) irradiation of a mixture of trifluorophosphine and pentacarbonylhydridorhenium. At ambient temperature, the low energy ultraviolet radiation does not result in significant substitution. Apparently heating the reaction mixture is necessary to volatilize sufficient $HRe(CO)_5$ for reaction in the homogeneous gas phase. Higher energy ultraviolet radiation from a Vycor filtered mercury lamp produces substitution, but this reaction is accompanied by excessive decomposition to yield polymeric rhenium complexes. Thermal-high pressure reaction of PF_3 and $HRe(CO)_5$ occurs, although it is also accompanied by decomposition to polynuclear species. Once PF_3 substitution has taken place by any procedure, the monomeric hydride complexes are considerably stabilized with respect to degradation to polynuclear species. The yields are always low during the first stages of substitution with 50% recovery of hydrides being about the maximum obtained. The yields are quite variable and we have been unable to control them precisely. Once initial substitution has occurred, the substitution reaction is dominant provided oxygen and water are excluded. Therefore high-energy ultraviolet radiation methods can be used for the later stages of substitution.

A high pressure procedure for preparing the $HM(PF_3)_x(CO)_{5-x}$ species ($M =$ Mn and Re) was developed subsequent to the direct approach described above. It has the advantage that the yields can be high and in addition it avoids some very air and moisture sensitive steps. However, it does not readily yield the lower phosphines, particularly with rhenium. It appears that at least two to four of the carbonyl groups in $Mn_2(CO)_{10}$ must be replaced before the metal—metal bond is broken by hydrogen and the number must be higher for $Re_2(CO)_{10}$.

Gas—liquid chromatography at moderate temperatures is an adequate separation method of resolving the substitution compositions in the $HRe(PF_3)_x(CO)_{5-x}$ series. In addition, at column temperatures between 25 and 35°C, the geometric isomers of $HRe(PF_3)(CO)_4$, $HRe(PF_3)_2(CO)_3$ and $HRe(PF_3)_3(CO)_2$ can be resolved and collected for identification. Infrared analysis of $HRe(PF_3)_4(CO)$ confirms that both of the potential isomers exist although column conditions were not found for separation. Examination of head and tail cuts of the composite peak indicates some resolution of these isomers. Table 1 reports the relative retention volumes of the isomers in each composition. As had been observed for trifluorophosphine derivatives of pentacarbonylhydridomanganese [5] and many other substituted metal carbonyls [9], the elution order is a regular sequence based upon molecular weight or degree of PF_3 substitution. The derivatives with the highest degree of PF_3 substitution are eluted first, indicating that they interact the least with the silicone oil on the stationary phase.

Difficulties were experienced in isolating milligram quantities of the individual geometric isomers by gas chromatographic techniques owing to the low column separation efficiencies of the columns that had to be used. The column compositions were selected based on optimum resolution of other metal carbonyl—trifluorophosphine systems [9] at higher temperatures. Attempts to improve separation efficiency with new column compositions were not successful. Consequently, column injection quantities were restricted to microliter volumes in order to retain good resolution.

Because of the minimal quantities of the isolated rhenium isomers, mass spec-

TABLE 1. INFRARED SPECTRA AND RETENTION VOLUMES OF THE $HRe(PF_3)_x(CO)_{5-x}$ SUBSTITUTION SERIES

Composition	Symmetry	Relative retention volume	Relative [a] abundance	CO Region	MH Region	PF Region
$HRe(CO)_5$	C_{4v}	1.000	100	2131vw 2041vw 2016vs 2007s 1983vw [b] 1965vw [b]	1832vw	
$HRe(PF_3)(CO)_4$	C_s (I)	0.457	57	2112w 2040m 2016s 2008m		904w 896w 882m
	C_{4v} (II)	0.364	43	2119vw 2018vs 1986vw [b]	1850vw	870w 868m
$HRe(PF_3)_2(CO)_3$	C_s (III)	0.231	16	2085m 2031m 2006s	1855vw	915w 906 [c] 900m 892 [c] 867s [c] 855w
	C_{2v} (IV)	0.205	20	2096vw 2040vw 2014vs 1983vw [b] 1972vw [b]		907m 891w 868s
	C_s (V)	0.196	64	2101w 2041m 2016s 1986vw [b]	1852vw	900m 875m 856m
$HRe(PF_3)_3(CO)_2$	C_s (VI)	0.132	13	2063s 2012vs 1988vw [b] 1973vw [b]		928m 912w 903m 888w 866vs
	C_s (VII)	0.124	32	2072s 2035s 2000vw [b]	1856vw	924s 908m 896m 875m 867m 854m
	C_{2v} (VIII)	0.094	55	2087vw 2014vs 1985vw [b]	1859vw	922vw 908m 899m 876s 864m 853m
$HRe(PF_3)_4(CO)$	C_s (IX)	0.081	95	2053vs 2006vw [b]	1863w	944s 908vs 889m 873s 863s 852m
	C_{4v} (X)	0.081	5	2022vw		
$HRe(PF_3)_5$	C_{4v}	0.067	100		1871vw	967w 912vs 871m 864s 850w

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[a] The relative abundances refer only to the isomeric concentration within each individual composition. [b] These absorptions are assigned as ^{13}CO containing species. [c] These absorptions may be due to isomer IV which was a known impurity since complete separation was never achieved

troscopy was the only viable means of chemical analysis. Sufficient quantities of complexes for infrared analysis were prepared by rinsing trace quantities from chromatographic collection tubes with n-hexane.

Chromatographic separation of geometric isomers of each composition is temperature dependent in an unusual way. The $HRe(PF_3)(CO)_4$ composition with its *cis* and *trans* isomers best illustrates this phenomenon since it yields the simplest set of resolved isomers. At room temperature, isomer resolution is complete with a 3 m column of 30% DC 702 silicone oil on Kromat fire brick. Essentially pure isomers may be collected and then characterized by infrared and mass spectroscopy. As the column temperature is increased above 50°C, a new peak appears between the two isomers. Mass spectroscopy of this new peak and of fore and tail cuts of it, indicates that only $HRe(PF_3)(CO)_4$ is present. Infrared analysis identified the presence of both the *cis* and *trans* isomers in the new peak. The *cis* isomer appears to increase at the expense of the *trans* isomer. Figure 1 illustrates the temperature dependence of the composite isomer peak and the resolved *cis* and *trans* isomers of $HRe(PF_3)(CO)_4$.

Mass spectroscopy provides definitive chemical analysis of the isolated geometric isomers of each substitution composition. The parent ion is observed and all of the cracking products resulting from sequential loss of H, CO, or PF_3 are seen. Fragments containing rhenium are readily identified by the isotope ratios of ^{185}Re and ^{187}Re.

Assignment of geometries to the individual octahedral isomer can be carried out by means of group theoretical arguments applied to the carbonyl absorptions in the infrared spectrum. The infrared data shown in Table 1 are discussed later.

The proton and fluorine NMR spectra confirm the isomeric assignments for the lower phosphine species which are separable with the rhenium system. Also the NMR data show that more than one isomer is present in the various GLC peaks of the manganese compounds. These sharp GLC manganese peaks are associated with various $HMn(PF_3)_x(CO)_{5-x}$ compositions rather than individual isomers. In addition, one can obtain information concerning the isomerization of the various species of a given composition. However, the acquisition or inter-

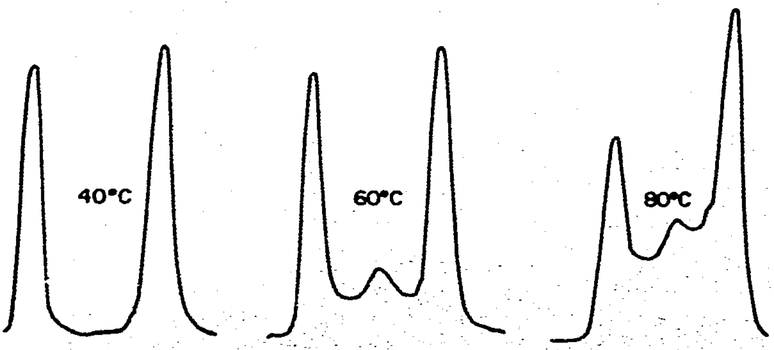

Fig. 1. Gas chromatographic traces of the $HRe(PF_3)(CO)_4$ composition at various temperatures with time increasing to the right. The peak on the left is the *cis* isomer, the one on the right the *trans*, and the middle peak contains both isomers.

pretation of NMR data is complicated by three factors. With increasing numbers of PF_3 groups, there is an increasing amount of both first and second order coupling causing bad band overlap. The inseparability of the individual manganese isomers, also causes overlap problems. Finally, although the rhenium isomers are separable, the difficulty of doing so in quantity for the higher phosphines makes it difficult to circumvent the previous problem.

The proton and fluorine NMR spectra for the monophosphine isomers of manganese and rhenium yield qualitatively similar data. The fluorine spectrum of each isomer is a doublet of doublets as expected. The proton spectrum of the *cis* isomer is a doublet of quartets whereas the *trans* isomer has a slightly broadened single quartet in which the $^2J(HP)$ value is small. The *cis* and *trans* isomers of rhenium are isolable and their structures are readily assigned on the basis of the infrared spectra (four strong stretches versus one). The inseparable manganese isomers are assigned on the basis of the similarity of their NMR parameters to those of the rhenium species. The results are shown in Table 2. It is seen that for each metal, the value of $^2J(HP_{cis})$ is much larger than $^2J(HP_{trans})$, in contrast to most known examples.

Two different types of experiments were done to show that the single quartet of the minor manganese isomer of $HMn(PF_3)(CO)_4$ does not have a second component, perhaps hidden under a major quartet. First, the proton spectrum was run at both 60 and 90 MHz. The separation between the middle of the minor quartet and the mid point between the two major quartets increases proportionate to the increasing field strength. Then an INDOR experiment was run by a "tickling" study which generated the proton spectra indirectly from the fluorine spectrum. It is found that the value of $^2J(HP_{trans})$, is 2 Hz. This small value is observed in the direct spectrum only as the extra broadness in the components of the minor quartet.

The NMR spectra of the diphosphine compound of manganese show clearly the presence of three species, presumably the three $HM(PF_3)_2(CO)_3$ isomers of Fig. 2. The proton pattern of the three isomers is badly overlapping, but by running the spectra on 60, 90, and 270 MHz instruments, the various first order patterns can be sorted out with the data being given in Table 3. Species A and B yield well resolved spectra and represent isomers with equivalent PF_3 groups and must be assigned to isomers III and IV of Fig. 2, but not necessarily in that order. The third species C must be assigned to isomer V. Its pattern consists of two broad, ill-resolved doublets separated by about 60 Hz. This splitting is presum-

TABLE 2

NMR DATA FOR THE $HM(PF_3)(CO)_4$ SPECIES

M	$\delta(H)$[a]	$\delta(F)$[b]	$^1J(PF)$	$^2J(HP)$	$^3J(HF)$	Rel[c] area
Mn_{cis}	−8.78	58.6	1309.8	70.3	12.8	13
Mn_{trans}	−7.06	62.2	1306.8	2	12.8	1
Re_{cis}	−6.37	52.8	1282	34	12.0	1.3[c]
Re_{trans}	−5.33	58.3	1293	~0	20.6	1[c]

[a] Chemical shift in ppm upfield of TMS. [b] Chemical shift in ppm downfield of $CF_3C_6H_5C$. [c] Determined from the gas-chromatographic traces.

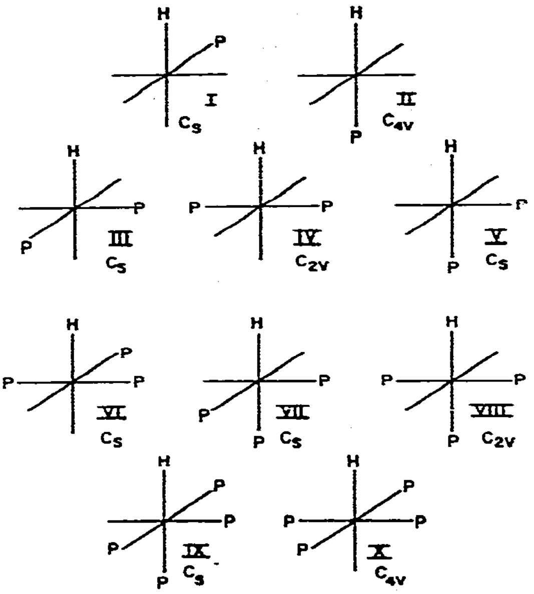

Fig. 2. The isomers of the $HRe(PF_3)_x(CO)_{5-x}$ system based on octahedral geometry.

ably caused by $^2J(HP_{cis})$ coupling. The small *trans* coupling plus two different kinds of fluorine coupling are no doubt responsible for the broadness. In addition the proton resonance occurs well downfield from the resonance of the other isomers and this is expected for a *trans* isomer as found in the assignment of the monophosphine isomer.

The fluorine spectrum also clearly shows that three species are present in the single GLC peak of composition $HMn(PF_3)_2(CO)_3$. The appearance of the pattern [10] shows that two of them have equivalent PF_3 groups. The relative intensities allow one to match these two species to A and B of the proton spectra. The third isomer has a first order pattern and is assignable to isomer V. The data are collected in Table 3. A tentative assignment of the patterns of A and B to isomers III and IV can be made of the basis of the $^3J(PF')$ values. No $^3J(PF')$ coup-

TABLE 3

NMR DATA FOR THE $HMn(PF_3)_2(CO)_3$ ISOMERS

Species	Rel. area	δ(H) [a]	δ(F) [b]	$^1J(PF)$	$^2J(PP')$	$^2J(HP)$	$^3J(PF')$	$^3J(HF)$
A	3	−9.66	60.08	1302 [e]	154	61	18 [e]	12
B	1	−9.40	61.19	1302	123	62	~0	10
C	1	−8.47	63.39 [c]	1298	d	65	~0	11
			60.31	1292	d	~0	~0	13

[a] Chemical shift in ppm upfield of TMS. [b] Chemical shift in ppm downfield of $CF_3C_6H_5$. [c] Presumably the axial PF_3 of isomer V of Fig. 2. [d] Cannot be obtained from the first order pattern of this isomer. [e] These values are of opposite sign. $^4J(FF') \cong 2$ Hz.

ling is seen in the first order spectrum of isomer V (C) (assuming the ^3J(HF) coupling has been correctly assigned). The ^3J(PF′) in the second order spectrum of species B is also approximately zero and therefore one can tentatively assign it to isomer III since it also has *cis*-PF_3 groups.

The fluorine and proton spectra of $HMn(PF_3)_3(CO)_2$ show clearly that more than one isomer is present. However, the extensive overlap does not allow one to sort out the separate spectra even, for instance, when the proton pattern is determined at 270 MHz.

Phosphorus spectra could not be obtained on the manganese compounds presumably owing to quadrapolar broadening.

NMR studies also give further information concerning the isomerization process within the $HM(PF_3)_x(CO)_{5-x}$ species. In the case of manganese, the isomers can not be isolated by GLC, but they are seen by IR and NMR as discussed earlier. To support the hypothesis of rapid isomerization, and disprove the possibility that GLC simply failed to resolve the isomers, the following experiment was performed. $HMn(PF_3)(CO)_4$ and $DMn(CO)_5$ were separately condensed and frozen in an NMR tube containing an internal lock standard. With the 90 MHz spectrometer already tuned and locked on a related sample the fluorine spectrum of the previously frozen sample was obtained as rapidly as possible. A 1 : 1 : 1 triplet, arising from coupling of the deuterium with an I of 1, is resolved within the 12 Hz ^3J(HF) doublet. Repeated recording of the spectrum of the sample showed no change, indicating that equilibrium was achieved in the approximately two minutes required to obtain the initial spectrum.

On the other hand, similar experiments between $DMn(CO)_5$ and $HRe(PF_3)_x(CO)_{5-x}$ show very slow deuterium exchange. The 1 : 1 : 1 triplet appears in the proton spectrum of the rhenium species as it does with the manganese compounds, but it develops over a period of hours rather than seconds. The rate of appearance is of a comparable magnitude to the rate of isomerization of the isolated rhenium species as followed by gas chromatography. However, no effort has thus far been made to obtain accurate data in order to compare the exchange process and the isomerization process owing to the very different media involved.

The spectra of $HMn(PF_3)(CO)_4$ run in CH_3Cl, CH_2Cl_2, and CH_3CN all appear quite similar. There appears to be little sign of broadening or little difference in the ratio of major to minor isomer caused by these three solvents of different polarity.

Discussion

Sequential replacement of carbon monoxide by trifluorophosphine occurs with $HRe(CO)_5$ under either thermal-pressure or thermal-ultraviolet radiation conditions. The compound, $HRe(PF_3)_5$ has been reported previously by Kruck [10]. The substitution complexes reported here are liquids or solids with melting points close to room temperature. The ability of PF_3 to substitute, partly or completely, for CO in transition metal carbonyls and hydrides is attributable to its π bonding capacity, since primarily σ bonding phosphines seldom replace more than two carbonyls in analogous systems [11]. Also its small cone angle [12] when compared to most organic phosphines must play a role. The σ bonding tertiary phosphine derivatives show drastically reduced volatility that is not seen with the PF_3 complexes.

The trifluorophosphine derivatives of $HRe(CO)_5$ are separable by gas—liquid chromatography. In contrast to the $HMn(CO)_5$ derivatives, the individual isomers of each rhenium composition can be resolved. The number of species found for each composition corresponds to the number of geometric isomers possible for octahedral coordination as seen in Fig. 2. A group theoretical prediction of the number of carbonyl stretches and their approximate intensity is in agreement with the observed spectra of the isolated components when these assignments are based on octahedral coordination. The weak M—H stretches were not observed for every isomer in each rhenium composition, but the presence of the hydride is clearly demonstrated by mass spectroscopy in each case. NMR spectra showing hydride protons and fluorine spectra of the phosphines of a low degree of substitution showing coupling with hydrogen is additional confirmation. The ^{19}F NMR spectra of the mono-, di-, and tri-phosphine compositions also show definite changes upon deuteration with $DMn(CO)_5$, further confirming the presence of hydrogen in these species. All evidence indicates that the basic octahedral geometry of $HRe(CO)_5$ is preserved upon the substitution of trifluorophosphine for carbon monoxide.

Isomer rearrangement has been shown to occur on the chromatography column and to be a function of temperature. The lack of gas chromatographic, mass spectroscopic or infrared evidence for disproportionation to other compositions illustrates that dissociation of CO and PF_3 are not involved in the rearrangement mechanism. (It seems quite unlikely that one ligand would dissociate to the exclusion of the others.) When chromatographic separation of isomers is carried out close to room temperature (40°C) virtually no rearrangement occurs, indicating that the rearrangement rate is slower than the column retention time of about one hour. Isomer rearrangement is apparent above 60° C for all compositions.

The gas chromatographic behavior of $HRe(PF_3)(CO)_4$ at various column temperatures shown in Fig. 1 appears somewhat analogous to what one finds in the NMR pattern of a dynamic system. In this case, it is a system in which the two species have unequal populations and populations that probably change with temperature. At low temperature, one sees the two species. At high temperature where rapid rearrangement should be occurring, one should see only a single composite peak as is found with the manganese compounds [5]. The three peaks seen at 60 and 80°C must represent some form of an intermediate behavior. Stability problems prevent us from taking the compound to high enough temperatures to reduce the chromatogram to a single peak.

The separate isomers for each trifluorophosphine substitution composition of rhenium pentacarbonyl hydride can be assigned to the various structures of Fig. 2 based on their infrared spectra. These spectra are reported in Table 1.

For the $HRe(PF_3)(CO)_4$ composition, two isomers are expected, with substitution in the radial plane or at an axial position. On axial substitution (PF_3 *trans* to H, isomer II), the molecule retains the C_{4v} symmetry of $HRe(CO)_5$ and its spectrum should show only the asymmetric E stretch and the weak higher frequency A_1 radial stretch. The radial substituted isomer I has C_s symmetry so that all four possible vibrations are allowed. The isomer with the longer retention time shows four relatively intense vibrations and is assigned to the *cis* structure, while the other species, assigned as *trans*, shows the very intense E stretch with almost no shift from $HRe(CO)_5$ and the very weak A_1 radial vibration. The A_1 vibration is shifted 12 cm^{-1} to lower energy since the A_1 axial vibration is no longer present for coupling.

In the $HRe(PF_3)_2(CO)_3$ composition, the *cis*-diradial isomer III (two PF_3 *cis* to each other in the radial plane) should have three strong vibrations since it has C_s symmetry. The *trans*-diradial isomer IV has C_{2v} symmetry and is expected to have an intense B_1 asymmetric vibration of the *trans* carbon monoxides. The A_1 symmetric stretch for these *trans* carbonyls and the A_1 axial stretch are expected to be much weaker. The *cis*—*trans* isomer V has C_s symmetry and the asymmetric stretch of the *trans* carbonyls is expected to be the strongest vibration while their symmetric stretch should be the weakest. Since the three predicted spectra are observed in three isolated $HRe(PF_3)_2(CO)_3$ species, the assignments are made as shown in Table 1.

In the $HRe(PF_3)_3(CO)_2$ composition, the *trans*-radial isomer VIII (the two remaining carbon monoxides *trans* to each other in the radial plane), has C_{2v} symmetry and the B_1 asymmetric stretch should be much more intense than the A_1 symmetric stretch (which should occur at higher energy). The *cis*-radial species VII with C_s symmetry should show two strong vibrations with one ^{13}C vibration per stretch. The *cis*—*trans* isomer VI should also have two strong fundamental vibrations. However, as there are two possible non-degenerate ^{13}CO substitution sites, each of these contributes one associated peak for each vibration of the most abundant isotope species.

The *trans*-radial isomer was easily identified by the difference in intensity of its two absorptions. The *cis*—*trans* isomer was identified by the two ^{13}C satellites of the low energy asymmetric vibration. The two satellites for the other peak were hidden and not detected since a vibration from a small amount of *cis*-radial isomer present obscured the region. The third isomer was then assigned as the *cis*-radial species.

In the $HRe(PF_3)_4(CO)$ composition, the CO absorption of the *trans* isomer (CO trans to H) should occur at lower energy than the absorption of the *cis* isomer since the hydrogen cannot compete for the π bonding as well as PF_3. When a head-cut of the composite $HRe(PF_3)_4(CO)$ peak is taken, the intensity of the 2022 cm^{-1} peak increases relative to the 2053 cm^{-1} peak indicating that the *trans* isomer is partially resolved in the fore portion of the peak.

The relative abundance values of the various species as reported in Table 1 only show geometric isomer distribution within each individual degree of substitution. These values do not relate to the equilibrium conditions for various degrees of PF_3 substitution for CO; however, current work is in progress to define the equilibrium constants for the related $HMn(PF_3)_x(CO)_{5-x}$ and $Fe(PF_3)_x$-$(CO)_{5-x}$ systems.

The hydride stretching frequency is observed for most of the isolated complexes. The frequency of the M—H stretch increases with PF_3 substitution. This trend is also seen with the analogous manganese [5] and cobalt carbonyl hydrides [13]. The M—H absorptions are quite weak compared to carbonyl absorptions, but when the hydrogen is *trans* to PF_3, it seems somewhat more intense than when *trans* to CO. Extremely limited quantities have prohibited concentrations which would allow detection of some of these weak M—H stretches.

The hydrides of rhenium discussed above contrast in an interesting way with the corresponding hydrides of manganese. For the manganese species $HMn(PF_3)_x(CO)_{5-x}$, the six possible compositions are isolated by GLC; however, the individual isomers have not been resolved but are seen by IR and NMR. In the rhenium system, as now shown, the individual isomers can be isolated at low column temperatures and on short columns. It is tempting to speculate that the difference in acidity between $HMn(CO)_5$ and $HRe(CO)_5$ (a difference which is probably also carried to the corresponding PF_3 compounds) is responsible. The manganese hydrides have a reported pK of about 7.1 whereas the value for rhenium hydrides is not measurable by the same technique and therefore much larger [14]. Thus if the isomerization is occurring via some intermolecular hydrogen exchange process, the more acidic manganese hydrides should isomerize more rapidly.

NMR evidence shows that the $HMn(PF_3)_x(CO)_{5-x}$ compounds undergo rapid hydrogen—deuterium exchange but the rhenium compounds undergo the corresponding exchange much more slowly. The rate of hydrogen—deuterium exchange as measured by NMR for the rhenium compounds is roughly comparable to the rate of isomerization as seen by GLC. The evidence strongly suggests that the dynamic process is primarily an intermolecular one involving hydrogen, but we cannot exclude the occurrence of some intramolecular contribution such as is found for species [6] of the type $H_2Fe(PR_3)_4$. While an intermolecular hydrogen exchange is occurring, it is slow enough that spin correlation between the hydrogen and phosphorus or fluorine is maintained even for the more facile manganese compounds [8]. Thus neither sets of compounds are fluxional on the NMR time scale at reasonable temperatures, at least in a low polarity medium.

References

1 J.P. McCue, Coord. Chem. Rev., 10 (1975) 265.
2 J.P. Jesson in E.L. Muetterties (Ed.), Transition Metal Hydride, Vol. 1, Marcel Dekker, Inc., New York, 1971, Ch. 4.
3 R.J. Clark and P.I. Hoberman, Inorg. Chem., 4 (1965) 1771.
4 B.A. Frenz and J.A. Ibers, in E.L. Muetterties (Ed.), Transition Metal Hydride, Vol. 1, Marcel Dekker, Inc., New York, 1971, p. 33.
5 W.J. Miles and R.J. Clark, Inorg. Chem., 7 (1968) 1801.
6 E.L. Muetterties in L.M. Jackman and F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Chapter 8., Academic Press, Inc., New York, 1975.
7 R.B. King, Organometallic Syntheses: Transition-Metal Compounds, p. 158, Academic Press, New York, 1965.
8 W.J. Miles, Jr. and R.J. Clark, to be published.
9 R.J. Clark and M.A. Busch, Accts. Chem. Res., 6 (1973) 246.
10 T. Kruck and A. Engelmann, Angew. Chem., Int. Ed. Engl., 5 (1966) 836.
11 N. Flitcroft, J.M. Leach and F.J. Hopton, J. Inorg. Nucl. Chem., 32 (1970) 137.
12 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956.
13 C.A. Udovich and R.J. Clark, Inorg. Chem., 8 (1969) 938.
14 E.L. Muetterties (Ed.), Transition Metal Hydride, Vol. 1, Marcel Dekker, Inc., New York, 1971, p. 239.