

is sufficient room for the slightly larger PF₃ ligand in the monometallic compounds. Yet replacement of CO by PF₃ in dimanganese decacarbonyl stops abruptly at four. Thus far, no compound with more than two trifluorophosphines in the equatorial positions are observed. Due to the short metal-metal bond length, the steric requirements are presumably more stringent for the polynuclear compounds than for the monometallic compounds. The equatorial ligands on one metal appear crowded by the equatorial ligands on the second metal.

There is little in this investigation or the following study that would allow us to determine any mechanistic details for the reactions. As a start, one would like to study the sequence of product formation.

Preliminary steric calculations have been done that indicate that the series of compounds Cr(PF₃)_x(CO)_{6-x} (x = 0-6) may not be a good model for the situation in the two halves of Mn₂(CO)₁₀. Several results appear from the calculations that we hope to confirm by more sophisticated calculations.

Thermal and Photolytic Substitution of Ditechnetium and Dirhenium Decacarbonyl with Trifluorophosphine

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The substitution reaction of Tc₂(CO)₁₀ and Re₂(CO)₁₀ with PF₃ has been studied under both thermal and photolytic conditions. Complete substitution was not observed for either system. Substitution of up to nine of the ten carbonyls by PF₃ results in the formation of at least 33 different species in the rhenium system. In the technetium system, substitution of up to eight of the carbonyls results in the formation of at least 24 different species. The disubstituted products 1,1'-M₂(CO)₈(PF₃)₂ and 2,2'-M₂(CO)₈(PF₃)₂ (M = Re or Tc) are readily formed, but formation of 1,2'-Re₂(CO)₈(PF₃)₂ was not observed.

Introduction

The substitution of the CO moiety within the group-7 dimetal decacarbonyls (M₂(CO)₁₀, M = Mn, Tc, and Re) with various ligands is, among other things, a way to investigate metal-metal bonding.¹ Large bulky ligands such as PPh₃ have, in general, been shown to preferentially substitute at the axial sites.²⁻⁵ (See Figure 1 for ligand nomenclature.) Less sterically demanding groups such as the isonitriles substitute preferentially at the equatorial sites.⁶⁻⁸ The weaker π overlap (relative to CO) of the isonitriles favors substitution opposite a CO group (the equatorial position) than in the axial position where a greater π electron density is present, resulting from the metal-metal bond trans to the site.

A small ligand with good π-acid properties should yield substitution in the favored axial sites. Trifluorophosphine (PF₃) is such a ligand. The π-acceptor and σ-donor properties of PF₃ have been shown to be similar to those of CO.^{9,10} In addition, PF₃ is a relatively small molecule possessing a cone angle of 104°. The predominant pattern of substitution in Mn₂(CO)₁₀ by trifluorophosphine is the replacement of the two axial groups, followed by subsequential substitution at the equatorial sites. However, under certain conditions equatorially substituted compounds with one nonsubstituted axial position were observed.¹² All observed products were substituted at least once in an axial position.

This paper reports the results of the PF₃ substitution of Tc₂(CO)₁₀ and Re₂(CO)₁₀. Compositional and structural assignments for the Re₂(PF₃)_x(CO)_{10-x} system are based upon GC-MS, and GC-IR, and ¹⁹F NMR data and also through comparisons with the dimanganese system. Assignments for the technetium system are based on GC-MS data and on comparisons with the dirhenium system.

Table I. Infrared Data on Dirhenium Compounds

compd	sym	abs, cm ⁻¹
parent	D _{4d}	2068 s, 2013 vs, 1976 s
II 1	C _{4v}	2108 w, 2052 m, 2013 vs, 1982 m, 1955 w
VI 1,1'	D _{4d}	2050 w, 2013 s
VII 2,2'	C _{2v}	2100 w, 2056 m, 2021 (sh), 2013 s, 1995 m, 1983 m
IX 1,1',2	C _s	2101 w, 2047 w, 2020 (sh), 2014 s, 1995 m
XV 1,1',2,2'	C ₂	2088 w, 2044 m, 2019 s, 2003 m, 1985 m, 1961 w

Experimental Section

Dirhenium decacarbonyl was purchased from Strem Chemical and used without further purification. Ditechnetium decacarbonyl was prepared from NH₄TcO₄, purchased from the Oak Ridge National Laboratory. Roughly 400 mg of NH₄TcO₄ was placed under 6200 psi of CO at 210 °C. After a minimum of 48 h, the Tc₂(CO)₁₀ was sublimed into a cold trap, giving yields between 80 and 90%. Appropriate precautions were taken in the handling of such quantities of technetium, which is a low-energy β and bremsstrahlung emitter. Analysis was done on a tracer scale.

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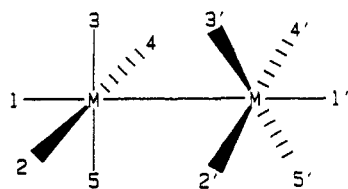


Figure 1. Two positions along the axis of the metal-metal bond referred to as axial sites and numbered 1 and 1', with the prime indicating the second metal. The eight positions orthogonal to the axis of the metal-metal bond are referred to as equatorial and numbered 2-5 and 2'-5'.

Trifluorophosphine was produced by reacting SbF_3 with PCl_3 in acetonitrile. Helium was bubbled through the solution to sweep out PF_3 , which was then collected in a -196°C trap. The apparatus and procedures employed for the synthesis of PF_3 have been described in detail.¹³ Reactions of dirhenium and dirhenium decacarbonyls were done using 50 mg (0.10 mmol) and 100 mg (0.15 mmol), respectively. Glass reaction flasks were fitted with metal-to-glass seals and metal valves that allowed for the heating and periodic removal of evolved CO and the replacement of PF_3 .

Thermal reactions were carried out neat at 110°C for $\text{Tc}_2(\text{CO})_{10}$ and 150°C for $\text{Re}_2(\text{CO})_{10}$. Photolytic reactions were carried out in hexane at room temperature using a 450-W, medium-pressure mercury lamp.

GC-MS, UV, and solution-phase IR spectra were obtained as described in the preceding paper.

Results

Composition and/or structural assignments are based upon mass spectral information, infrared data, and GC elution order. The total number of carbonyl groups replaced by PF_3 and their distribution between the two metals can be determined unambiguously for each compound from their mass spectra. Gas-phase infrared data has been obtained on the dirhenium compounds and compared with the solution spectra of the analogous $\text{Mn}_2(\text{CO})_{10-x}(\text{PF}_3)_x$ compounds where possible. A few of the dirhenium compounds have been isolated, and solution-phase IR spectra obtained as shown in Table I. The structural assignments of isomers when based upon GC elution orders are not definitive but can be partially justified based upon the established GC elution patterns of many compositions and structural isomers of PF_3 complexes studied in this lab. Each addition of a PF_3 up to a relative high number decreases the interaction of the analyte with the stationary phase and decreases the retention time. In addition the structural location of the PF_3 also affects the retention time. The patterns established for PF_3 substituted metal carbonyls are as follows:

(1) Upon successive substitutions with PF_3 , retention time decreases for monometallic species. For the bimetallic compounds the retention times decrease progressively through the first six substitutions. Then when the seventh CO has been replaced, the retention time increases with further substitutions.

(2) Trans isomers elute faster than cis isomers. Similarly, meridional compounds elute faster than facial. In bimetallic compounds, trans and cis refer to the equatorial substituents on the same metal.

(3) For bimetallic species, an isomer with PF_3 in an axial position elutes faster than a compound with the PF_3 in an equatorial site.

(4) For bimetallic compounds with a given number of PF_3 groups, their presence on one metal will result in longer retention times compared to when they are divided between two metals.

Table II. Substitution Products of $\text{M}_2(\text{CO})_{10}$ and PF_3 ($\text{M} = \text{Re}$ and Tc)

compd	isomers possible	Re_2L_{10} isomers	
		obsd	Tc_2L_{10} Isomers obsd
$\text{M}_2(\text{CO})_9(\text{PF}_3)$	2	2	2
$\text{M}_2(\text{CO})_8(\text{PF}_3)_2$	6	5	5
$\text{M}_2(\text{CO})_7(\text{PF}_3)_3$	9	6	6
$\text{M}_2(\text{CO})_6(\text{PF}_3)_4$	14	8	4
$\text{M}_2(\text{CO})_5(\text{PF}_3)_5$	14	6	(3)
$\text{M}_2(\text{CO})_4(\text{PF}_3)_6$	14	3	3
$\text{M}_2(\text{CO})_3(\text{PF}_3)_7$	9	3	1
$\text{M}_2(\text{CO})_2(\text{PF}_3)_8$	6	2	1
$\text{M}_2(\text{CO})(\text{PF}_3)_9$	2	1	
$\text{M}_2(\text{PF}_3)_{10}$	1		

Extensive substitution occurs under both photolytic and thermal conditions. The total number of isomers possible for each composition are listed, along with the number of different isomers observed, in Table II. We are ignoring the optical isomers that could occur for certain structures and further assume that there is free rotation about the metal-metal bond. With increasing substitution, the actual number of isomers found compared to the number possible decreases as a result of a preference for axial substitution. As with the dimanganese compound thermal reaction rates are slower than the photolytic ones. Substitution of seven or more carbon monoxides is observed only under photolytic conditions. The ratio of side products such as monometallic hydrides relative to the simple metal-metal substituted compounds increases with the time the reaction mixture is exposed to UV irradiation. Although the more highly substituted compounds are formed in yields of only a few percent, at least nine of the carbon monoxides and possibly ten could be replaced by PF_3 under photolytic conditions. A trace component possessing $\text{Re}(\text{PF}_3)_5^-$ fragments and eluting after the ennea-substituted species could possibly be the fully substituted compound. Kruck has reported the synthesis of $\text{Re}_2(\text{PF}_3)_{10}$ by another method although the compound has not been fully characterized.⁹

The number of trifluorophosphines substituted on each dimetal complex and its distribution can be readily obtained from the GC-MS data. The assignment of a particular structure to a composition is based on its GC retention time as discussed earlier and the assumption that the axial positions will be occupied preferentially by PF_3 . As the number of substitutions increases to more than three per metal, the possibility that carbon monoxide will occupy an axial position is remote. In addition, it is always possible that a particular GC species may consist of a mixture of structural isomers rather than be a single compound. Table III lists, in order, the rhenium compounds as they eluted from the GC. Tentative structural assignments have been made for each isomer. The more highly substituted species were not isolated, and assignments become somewhat tenuous. Structures for which we have a low degree of confidence are marked with an asterisk.

The relative concentration of the equatorial monosubstituted isomer to the axial isomer is always less than 1 and decreases rapidly as the reaction proceeded. Whether the entering PF_3 ligand adds partially in the equatorial site and then rapidly undergoes some kind of isomerization or whether the equatorial monophosphine reacts with PF_3 faster than the axial isomer is not certain.

Structural Assignments for Dirhenium Compounds. There are two possible monoligated species with substitution in either an axial site or an equatorial site. Both of the monosubstituted products are observed, and identical mass spectral data are obtained on each. The

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Table III. Re₂(CO)_{10-x}(PF₃)_x Compounds in GC Elution Order

compd type	isomer	MW	tentative struct assignt
3-3	*	1012	1,1',2,2',4,4'
3-3	*	1012	1,1',2,2',3,4'
4-3	*	1072	1,1',2,2',3,4,4'
4-3	*	1072	1,1',2,2',3,3',4
3-2	*	952	1,1',2,2',4
3-2	*	952	1,1',2,2',4
4-2	*	1012	1,1',2,2',3,4
3-2	*	952	1,1',2,2',3
4-4	*	1132	1,1',2,2',3,3',4,4'
2-2	XV	892	1,1',2,2'
5-3	*	1132	1,1',2,2',3,4,4',5
4-1	*	952	1,1',2,3,4
3-1	XVIII	892	1,1',2,4
3-1	XIX	892	1,1',2,3
5-2	*	1072	1,2,2',3,4,4',5
5-4	*	1192	1,1',2,2',3,3',4,4',5
2-1	IX	832	1,1',2
3-2	*	952	1,2,2',3,4'
2-2	XVI	892	1,2,2',4'
2-2	XVII	892	1,2,2',3'
1-1	VI	772	1,1'
2-1	X	832	1,2',4'
2-1	XI	832	1,2',3'
2-1	XII	832	1,2,2'
1-1	VII	772	2,2'
3-1	XX	892	1,2,2',4
3-1	XXI	892	1,2,2',3
2-1	XIII	832	2,2',4
2-1	XIV	832	2,2',3'
2-0	III	772	1,2
1-0	II	712	1
2-0	IV	772	2,4
2-0	V	772	2,3
1-0	I	712	2
0-0		652	

rhodium pentacarbonyl cation and the rhodium tetracarbonyl trifluorophosphine cation were observed at *m/z* 327 and 387, respectively (major Re isotope 187). To assign the correct structure, the earlier eluting monophosphine in major concentration was isolated, and its IR spectrum obtained. The spectrum is similar to that of the axially substituted Mn₂(CO)₉(PF₃) compound. As observed with the manganese compounds, substitution in the axial position tends to interfere with the interaction of the carbonyl with the stationary phase more than substitution in an equatorial site. Thus, the compound with the longer elution time is assigned as 2-Re₂(CO)₉(PF₃) (structure I, Chart I). The earlier eluting compound has been assigned as 1-Re₂(CO)₉(PF₃) (structure II).

There are six possible disubstituted isomers, five of which are seen. These may be broken into two groups each containing three potential members: (1) both substituents on the same metal; (2) the substituents on different metals. Three of the compounds have monometallic fragments corresponding to [Re(CO)₅]⁺ and [Re(CO)₃(PF₃)₂]⁺, indicating that both substituents are on the same metal. The species of this set eluting first is indicated to have a PF₃ in an axial position. This species has been assigned as 1,2-Re₂(CO)₈(PF₃)₂ (structure III).

To assign the remaining two structures, we need to note the chromatographic behavior of *cis*- and *trans*-Mo(CO)₄(PF₃)₂.¹⁴ The *trans* trifluorophosphines on *trans*-Mo(CO)₄(PF₃)₂ hinder the interaction of the remaining carbon monoxides with the stationary phase, and this isomer elutes earlier than the *cis* isomer. Because the chromatographic behavior of the group-7 dimetal decarbonyl systems is similar to those of the group-6 hexa-

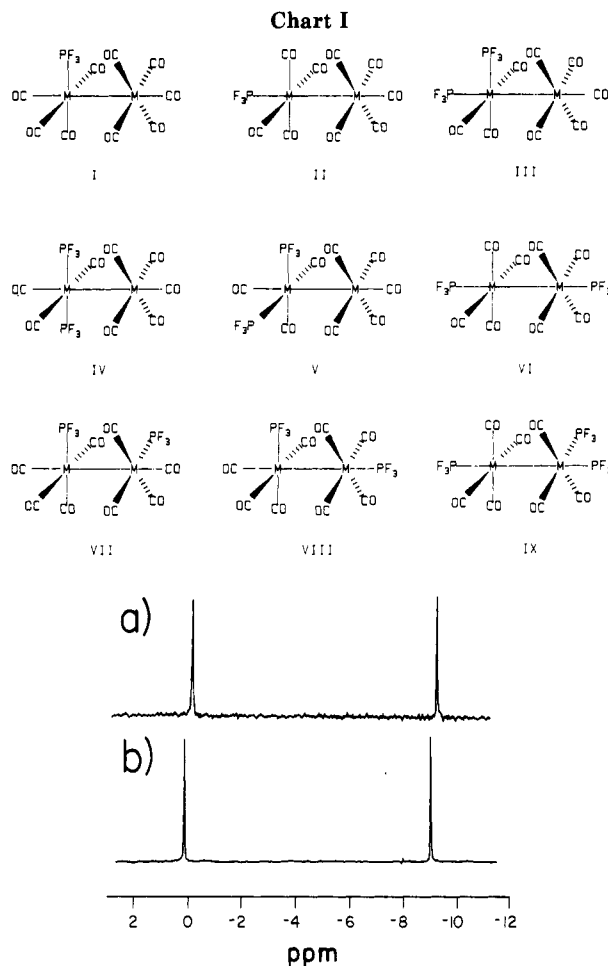


Figure 2. ¹⁹F NMR spectra of (a) 1,1'-Re₂(CO)₈(PF₃)₂ and (b) 2,2'-Re₂(CO)₈(PF₃)₂.

carbonyls, *cis* and *trans* isomers can be tentatively identified by their relative GC retention times. Thus the *trans*-equatorial compound 2,4-Re₂(CO)₈(PF₃)₂ should elute prior to the *cis*-equatorial compound 2,3-Re₂(CO)₈(PF₃)₂, and the compounds are assigned structures IV and V, respectively.

The remaining two observed disubstituted products yield only the [Re(CO)₄PF₃]⁺ ion, indicative of a single substituent on each metal. Both are major species among the diphosphines. There are three possible structural assignment for these two 1-1 isomers. Both compounds were isolated, and their IR spectra obtained. The compound with the shorter retention time has a spectrum similar to that of the diaxial dimanganese compound¹² and similar to that found by Reiman and Singleton.¹⁵ It has been assigned structure VI. A structure determination for the second compound was not possible on the basis of IR and MS data alone. The ¹⁹F NMR spectra for both of the disubstituted compounds were obtained and are shown in Figure 2. Each yields a single doublet. The doublet results from the characteristic splitting of ¹⁹F by ³¹P of about 1300 Hz. Both 1,1'-Re₂(CO)₈(PF₃)₂ (VI) and 2,2'-Re₂(CO)₈(PF₃)₂ (VII) have the substituents in symmetrical positions, which would result in a single doublet.

Structure VIII should give a pair of doublets if the axial and equatorial chemical shifts are not accidentally degenerate. Comparison of the spectra in Figure 2 shows that the signals are separated by 0.1 ppm (14 Hz), indicating

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Chart II

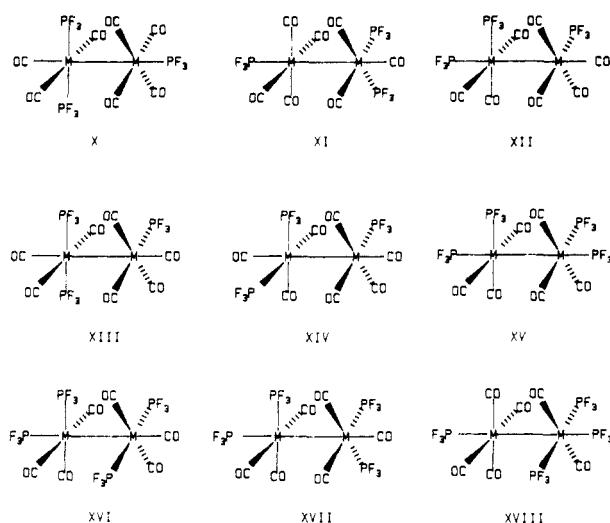
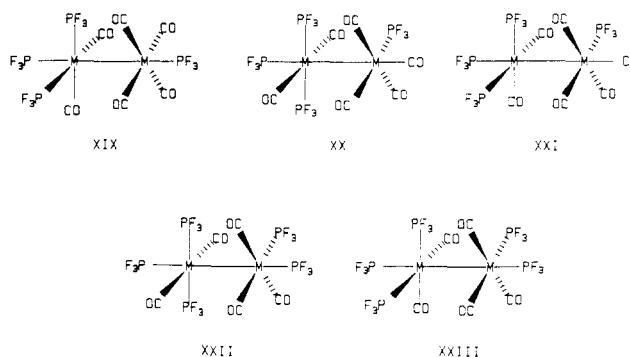


Chart III



that the signal produced by axial PF_3 should be distinguishable from the signal produced by the equatorial PF_3 . Thus the second disubstituted product with a substituent on each metal can be tentatively assigned structure VII. Interestingly, one of the 1-1 compounds was not observed, presumably $1,2'\text{-Re}_2(\text{CO})_8(\text{PF}_3)_2$ (VIII). We searched for evidence for an extra compound lost in another GC peak, but it was not found by either MS or IR. Some preliminary GC-IR work has been done, but none of the likely GC peaks in which it should be found has the extra IR peaks expected for two compounds. Since there are significant quantities of the two observed compounds, it is surprising that there is no evidence for the related third, regardless of the correctness of our assignment.

There are nine possible isomers that could result when three CO moieties have been replaced by PF_3 . These are broken down into two groups, one having all three substituents on the same metal, 3-0, and the second having two substituents on one metal and a third substituent on the second metal, 2-1. Trace amounts of the 3-0 compounds may have been formed, but the amounts are insufficient to obtain a reliable mass spectrum. There are six possible 2-1 isomers, and six chromatographic peaks displaying 2-1 fragmentation in the mass spectrum are observed. The $1,1',2\text{-Re}_2(\text{CO})_7(\text{PF}_3)_3$ species should be the first to elute, and through a comparison of its IR with that of the analogous dimanganese compound we can assign it structure IX.

The remaining isomers in this series are assigned by using retention times. The second and third 2-1 isomers to elute are separated by a few seconds, indicative of a trans-cis pair. There are two possible trans-cis pairs of the 2-1 isomers (structures X and XI and structures XIII and XIV, Chart II). The earlier eluting pair would presumably have the lone substituent in an axial position (X and XI), with the trans isomer eluting prior to the cis.

The fourth 2-1 isomer to elute has the lone substituent in an equatorial position while the two substituents on the second metal occupy an axial and an equatorial position and is assigned as $1,2,2'\text{-Re}_2(\text{CO})_7(\text{PF}_3)_3$ (XII). The fifth and sixth 2-1 isomers are the second trans-cis pair. The first compound to elute would have the two substituents on the same metal trans and is assigned $2,2',4\text{-Re}_2(\text{CO})_7(\text{PF}_3)_3$ (XIII). The second compound of the pair would have the two substituents cis and is assigned $2,2',3\text{-Re}_2(\text{CO})_7(\text{PF}_3)_3$ (XIV).

There are 14 possible tetrasubstituted isomers. These can be broken down into three groups depending upon the

number of PF_3 ligands on each metal: two 4-0 isomers, six 3-1 isomers, and six 2-2 isomers. None of the 4-0 isomers are observed, while four of the 3-1 isomers and three of the 2-2 isomers are seen. The first of the 2-2 isomers to elute has been assigned as $1,1',2,2'\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (structure XV). It has been isolated, and its IR spectrum is similar to that of the dimanganese compound. It is the major species among the tetraphosphines.

The other 2-2 compounds elute close together, suggesting a trans-cis pair such as $1,2,2',4'\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (XVI) and $1,2,2',3'\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (XVII). The general tendency for axial substitution favors this assignment. The remaining three possible 2-2 isomers are unlikely to occur as they have all four substituents in equatorial positions in various mixed trans and cis structures. However, given the apparent formation of only the $1,1'$ (VI) and $2,2'$ (VII) disubstituted compounds, the assignment of this pair of compounds to structures XVI and XVII is open to question.

Of the six possible 3-1 isomers, two can be dismissed as highly improbable because they have the three substituents on the same metal in equatorial positions. The first pair of 3-1 isomers to elute has both axial positions filled. These are the $1,1',2,4\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (XVIII) and $1,1',2,3\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (XIX, Chart III). The next pair of 3-1 isomers to elute has the axial position on the metal with the lone PF_3 occupied by CO. The first of these to elute is assigned as $1,2,2',4\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (XX) and the second as $1,2,2',3\text{-Re}_2(\text{CO})_6(\text{PF}_3)_4$ (XXI). All of these isomers are minor relative to the 2-2, with the first pair above slightly more abundant than the second pair.

There are two types of pentasubstituted compounds observed, two 3-2 isomers and one 4-1 isomer. No sign of the 5-0 isomer was seen. There are insufficient data to make even tentative structural assignments for these. Only the number of substitutions and their distributions are certain. There is a strong possibility that similar structures such as $1,1',2,2',4\text{-Re}_2(\text{CO})_5(\text{PF}_3)_5$ (XXII) and $1,1',2,2',3\text{-Re}_2(\text{CO})_5(\text{PF}_3)_5$ (XXIII) may coelute, as the addition of a second and third PF_3 have less effect on the interaction of the compound with the stationary phase.

There are three hexasubstituted compounds (two 3-3 and one 4-2 isomers), three heptasubstituted compounds (two 4-3 and one 5-2 isomers), two octasubstituted isomers (one 4-4 and one 5-3 isomer), and one ennea-substituted isomer (5-4). We have assigned tentative structures to these compounds on the basis of the assumption that both axial positions are occupied by a PF_3 group.

Technetium. Thermal reactions run at 130°C result in the decomposition of the metal-metal bond and produce only monometallic species. The decomposition is due to a combination of the faster substitution reactions and to the presence of unavoidable contaminants such as traces of oxygen and water and probable reaction with solvent.

Table IV. GC Elution Order of Tc₂(CO)_{10-x}(PF₃)_x Compounds

composition	MW	struct assgnt
3-3	838	1,1',2,2',4,4'
3-3	838	1,1',2,2',3,4'
4-3	898	1,1',2,2',3,4,4'
3-2	778	1,1',2,2',3
4-2	838	1,1',2,2',3,4
2-2	718	1,1',2,2'
3-1	718	1,1',2,4
4-4	958	1,1',2,2',3,3',4,4'
4-1	778	1,1',2,3,4
2-1	658	1,1',2
3-1	718	1,1',2,3
2-2	718	1,2,2',4'
1-1	598	1,1'
2-1	658	1,2,2'
2-1	658	1,2',4'
2-1	658	1,2',3'
1-1	598	2,2'
3-0	658	1,2,4
2-0	598	1,2
3-0	658	1,2,3
1-0	538	1
2-0	598	2,4
2-0	598	2,3
1-0	538	2
0-0	478	

The PF₃ stabilizes monometallic species such as the hydrides. The presence of these trace contaminants is not as critical in the substitution reactions of the dimanganese or dirhenium decacarbonyls where the larger available quantities of starting material swamp such effects.

Thermal reactions run at 110 °C produce the metal-metal bonded compounds with up to six of the carbonyls replaced by trifluorophosphines. Photolytic reactions produce products in which up to eight of the carbonyl groups have been replaced by PF₃. Table IV lists the combined thermal and photolytic products observed in order of the elution. More highly substituted products may have been formed, but their concentrations were insufficient to produce a reliable mass spectrum. As in the case with the substitution of dirhenium decacarbonyl, the higher substituted dimetal products (>7 PF₃ groups) are produced in yields of less than 2%.

The substituted ditechneium compounds have not been isolated, and the assignment of structures is based primarily on their mass spectra, relative GC retention times, and comparison with the analogous dirhenium compounds (Table III). The ¹⁹F NMR of reaction mixtures produced broad peaks as a result of the combination of the ⁹⁹Tc quadrupolar moment and coupling not found for the rhenium and manganese compounds.¹⁶

The substitution products of ditechneium decacarbonyl resemble those of dirhenium decacarbonyl more closely than the substitution products of dimanganese decacarbonyl. Under photolytic conditions, both axial and equatorial monosubstituted isomers are formed, whereas under thermal conditions only the axial isomer is observed. Two isomers of 1-1 substitution are observed for the dirhenium and ditechneium products, while only the diaxial manganese product was observed. These have been assigned as 1,1'-Tc₂(CO)₈(PF₃)₂ and 2,2'-Tc₂(CO)₈(PF₃)₂ on the basis of the observed rhenium products.

Discussion and Conclusions

Under the photolytic conditions employed, the rate of dissociative loss of CO should be similar for all three systems, while homolytic cleavage should be more prominent in the dimanganese decacarbonyl.¹⁷ The substitution of carbon monoxide by PF₃ occurs faster on the technetium atom than for either manganese or rhenium, at least in the temperature range 110–130 °C. This relatively faster rate of technetium substitution is observed under both thermal and photolytic conditions. The faster rate of substitution or exchange of second-row metal carbonyls is common.¹⁸

Both the axial and equatorial monosubstituted isomers are observed for the ditechneium and dirhenium compounds under photolytic conditions, whereas under thermal conditions the ditechneium equatorial monosubstituted product is not observed. The relative concentration of the two isomers is dependent upon the reaction time. Short reaction periods (UV, less than 30 min; thermal for rhenium only, less than 2 h) result in a higher relative concentration of the equatorial isomer. There are four equatorial ligands for each axial ligand, and the relative amount may be an initial statistical phenomenon. However, the equatorial carbonyl ligand may be lost preferentially to the axial. As the reaction proceeds, the concentration of the axial isomer increase relative to the equatorial isomer. The conversion occurs more rapidly in the technetium system. The equatorial isomer is not observed at all in the manganese system.

What is of particular interest are the compounds that are not observed in this study. In particular, the fully substituted compounds and the 1,2' axial-equatorial disubstituted compound have not been seen. The latter compound could have the same retention time as some other compound, but our preliminary GC-IR work has not shown a peak with an unusual number of carbonyl stretching vibrations. We can predict rather well where any compound should elute if present, which provides a guide to the search. The absence of Re₂(PF₃)₁₀ is probably due to a lack of room for the eighth equatorial PF₃. In the technetium system the metal-metal bond is a little shorter as are the metal-phosphorus bonds; consequently there is apparently room for only six of the equatorial CO groups to be replaced. In the manganese system only two of the equatorial positions could be substituted by PF₃ and yet maintain the metal-metal bond intact.

The absence of 1,2'-Re₂(CO)₈(PF₃)₂ suggests the possibility of a substitution mechanism common to both the thermal and photolytic processes that favors the formation of 1,1'-Re₂(CO)₈(PF₃)₂ and to a lesser extent 2,2'-Re₂(CO)₈(PF₃)₂. Photochemical reactions between Re₂(CO)₁₀ and triphenylphosphine seem to show similar structural preferences.¹⁹ The authors assign two tetrasubstituted species diaxial-diequatorial and tetraequatorial geometries, while the monoaxial-triequatorial species was not observed. It is interesting to note that the steric bulk of PF₃ and PPh₃ are quite different, and hence electronic factors dominate the site of ligand substitution.

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