process *may* involve an α-hydride elimination step.

Compound **2** reacts with a series of 2e ligands (L) at low temperature to produce a family of adducts having the formula $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)](PEt_3)_3L]^+O_3SCF_3^-$ (L = I^-, CO, NCMe, and $CNCMe_3$; compounds **4–7**, respectively). Reaction of **2** with PMe_3 also leads to adduct formation but is accompanied by phosphine exchange. The product in this case is $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (**8**). Treatment of **2** with lithium diisopropylamide (LDA) in acetone results in proton abstraction and production of the stable metallabenzene complex $(Ir\cdots CH\cdots C(Me)\cdots CH\cdots C(Me)\cdots CH)(PEt_3)_3$ (**9**).

The chemistry of metallacyclohexadienes and metallabenzenes continues to be investigated in our laboratories and will be described in future reports.

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Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compound **8** (7 pages); a listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

Thermal and Photolytic Substitution of Dimanganese Decacarbonyl with Trifluorophosphine

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Under thermal conditions, the PF_3 substitution of $Mn_2(CO)_{10}$ produces five different compounds: 1-$Mn_2(CO)_9(PF_3)$, 1,1′-$Mn_2(CO)_8(PF_3)_2$, 1,2-$Mn_2(CO)_8(PF_3)_2$, 1,1′,2-$Mn_2(CO)_7(PF_3)_3$, and 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$. Photolytic excitation results in the formation of four additional compounds. Substitution is rigorously limited to the replacement of four carbon monoxides, but that replacement is fairly readily achieved. Compounds are identified by using a combination of GC-MS, ^{19}F NMR, and IR. Back reaction of 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$ with ^{13}CO produces only the previously observed PF_3-substituted compounds having extensive label. Side products produced include the monometallic hydride series $HMn(CO)_{5-x}(PF_3)_x$ (x = 1–5), the hydrogen-bridged series $Mn_2(\mu\text{-}H)(\mu\text{-}PF_2)(CO)_{8-x}(PF_3)_x$ (x = 2–5), and the bisphosphido-bridged series $Mn_2(\mu\text{-}PF_2)_2(CO)_{8-x}(PF_3)_x$ (x = 2–7).

Introduction

With monometallic carbonyl complexes such as $Mo(CO)_6$ and $Fe(CO)_5$, PF_3 can sequentially replace CO and ultimately yield the compounds $Mo(PF_3)_6$ and $Fe(PF_3)_5$.[1,2] Trifluorophosphine has been shown to form σ and π bonds to metals with bonding characteristics similar to those of CO.[3] Numerous PF_3 analogues of mononuclear metal carbonyls have been prepared, and their intermediate species have been extensively studied.[4] However, little is known about the substitution reactions of PF_3 with simple polynuclear complexes such as $Mn_2(CO)_{10}$[5] $Fe_2(CO)_9$, and $Co_2(CO)_8$. The substitution chemistry of dimanganese decacarbonyl has been studied under both thermal and photolytic conditions by using various ligands.[5-10] With bulkier ligands, substitution stops with the replacement of two carbonyls, while with smaller ligands up to four ligands may be replaced. The mechanism of substitution was controversial for many years. It is now generally assumed that under thermal conditions, the substitution occurs through the dissociative loss of a CO to form an unsaturated enneacarbonyl complex with the metal–metal bond intact.[11] Under photolytic conditions, dissociative loss of a CO is observed, as well as a second mechanism involving the homolytic cleavage of the metal/metal bond.[9,12,13] The relative rates of the two mechanisms have been shown to be wavelength dependent with the ratio of the homolytic cleavage route to the dissociative CO loss increasing with increasing wavelengths.

The clear separation of a potentially large number of physically similar compounds and their definitive characterization are among the problems that stand in the way of an extensive study of PF_3 substitution into polynuclear

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compounds. The thermal stability of the manganese compounds in packed gas chromatography columns is marginal for their isolation by that technique.[5,14] However, increased thermal stability is observed when capillary columns are used. Thus these compounds are well suited for analysis by hyphenated techniques such as GC-MS and GC-FTIR.

In this paper, we are reporting a study of the substitution of PF_3 into $Mn_2(CO)_{10}$ using GC-MS as the primary tool. In the following paper, the results of a study of the corresponding technetium and rhenium compounds will be presented.[15] It is the purpose of this investigation to determine what compounds can be formed and, if possible, to determine their structures. In subsequent work, we will attempt to explore the mechanism of reaction.

Experimental Section

Dimanganese decacarbonyl was obtained frm Strem Chemical or as a gift from F. G. A. Stone. It was purified before use by sublimation at 40 °C and 10^{-2} Torr. 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 followed by further purification. The apparatus and procedures employed have been described in detail.[16]

Reactions were typically carried out by using 200-mg (0.50 mmol) quantities of dimanganese decacarbonyl with 1 atm of trifluorophosphine. Glass flasks were fitted with metal-to-glass seals plus metal valves that allowed for the heating, periodic removal of evolved CO, and the replacement of PF_3. Thermal reactions were carried out neat at 110 °C. Photolytic reactions were carried out in hexane at room temperature using a 450-W, medium-pressure mercury lamp.

A Finnigan 4500 GC-MS was used to obtain 70-eV electron impact data as well as positive and negative chemical ionization data. For positive ion analysis (EI and PCI), the samples were dissolved in hexane to give an approximate 500 ng/μL solution of the sample mixture. For analysis by negative chemical ionization (NCI), samples were further diluted by a factor of 100. A 0.32 mm × 30 m DB-5 capillary column (B & W) with helium as the carrier gas was used. Injections of 1 μL were made on an on-column injector. Short 3 m × $^1/_4$ in. 30% DC 702 silicone oil packed columns were used at 90 °C for the isolation of the individual species. The peaks isolated on packed column were often checked for purity by reinjection on the capillary columns.

Infrared spectra were obtained on a Perkin-Elmer 983 spectrophotometer. Spectrophotometric-grade hexane from Mallinckrodt was used as the solvent. The UV spectra were obtained on a Perkin-Elmer Lambda 3, double-beam spectrophotometer by using matched quartz cells having 1-cm path lengths. The solvent was UV grade hexane from B & J Solvents.

The ^{19}F NMR spectra were obtained on a 3.55-T (150 MHz) in-house-constructed "Seminole" NMR. Trichlorofluoromethane, $CFCl_3$, was used as the external standard. Initially, NMR samples were freeze–pump–thawed and sealed with a torch to eliminate problems caused by dissolved oxygen. This procedure was found unnecessary, and satisfactory spectra could be obtained by placing several milligrams of the compound directly into a 5-mm NMR tube with 0.5 mL of hexane. To prevent oxidation products from forming, samples were kept in a freezer until they were run. Generally, 200 scans were acquired and averaged to increase the S/N ratio.

Results

Thermal substitution of $Mn_2(CO)_{10}$ under a PF_3 atmosphere results in the formation of five substitution products (I–V). Photolytic excitation produces all of the thermal products and, in addition, at least four new compounds. In the combined cases, only four CO ligands are replaced by PF_3 ligands. More severe conditions result in the disruption of the metal–metal-bonded compound, yielding monometallic hydrides, several polymeric species, and inorganic material. In the nomenclature being used, 1 (or 1′) refers to axial position(s) and 2–5 (or 2′-5′) refers to the equatorial sites (see Figure 1).

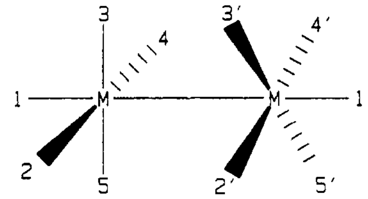

Figure 1. Two positions along the axis of the metal–metal bond, referred to as axial sites and numbered 1 and 1′ with the prime indicating the second metal. The eight positions orthogonal to the axis of the metal–metal bond are referred to as equatorial and numbered 2–5 and 2′–5′.

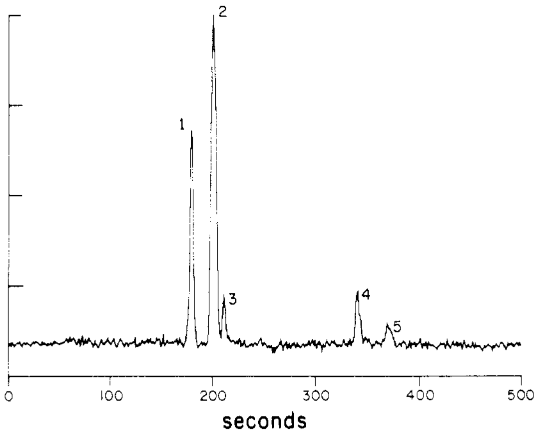

Figure 2. Gas chromatographic trace of the thermal products of $Mn_2(CO)_{10}$ and PF_3: 1, $Mn_2(CO)_6(PF_3)_4$; 2, $Mn_2(CO)_7(PF_3)_3$; 3, $Mn_2(CO)_8(PF_3)_2$; 4, $Mn_2(CO)_8(PF_3)_2$; 5, $Mn_2(CO)_9(PF_3)$.

Table I. UV and Fluorine NMR[a]

compd	struct	λ, nm	ax	ax′	eq	eq′
parent		336				
V	1	338	1.1			
IV	1,2	345	0.3		2.3	
III	1,1′	339	1.3	1.3		
II	1,1′,2	345	0.2	1.0	2.7	
I	1,1′,2,2′	350	0.1	0.1	2.4	2.4

[a] The centered values in ppm from $CFCl_3$. Coupling between ^{31}P and ^{19}F results in a doublet separated by 9.2 ppm.

Removal of evolved CO under thermal conditions pushes the reaction toward the tetrasubstituted species, but even after 2 weeks of heating with daily removal of released CO, less than one-third of the remaining dimanganese compounds is tetrasubstituted containing no trace of higher substituted compounds. Frequent removal of evolved CO under photolytic conditions pushes the product to a 95% mixture of the tetra- and 5% trisubstituted compounds within 6 h. No sign of the pentasubstituted species could be found even among the trace peaks. In general, the higher the substitution the earlier the elution,[4] so if any $Mn_2(CO)_5(PF_3)_5$ compounds were formed they should be readily observable. In addition, the main GC peaks were examined carefully for pentasubstituted products hidden within them.

Compounds I–V were isolated by preparative gas chromatography, and their IR, ^{19}F NMR, and UV spectra obtained. Figure 2 shows a typical chromatogram produced

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under thermal conditions. The IR and ^{19}F NMR spectra of some of these compounds were available from an earlier study in this lab.[14] The UV spectra showed a trend in which the absorption maximum of the σ to σ^* transition increased in wavelength with increasing PF_3 substitution, from 336 nm for the parent to 350 nm for the tetrasubstituted species (Table I).

The ^{19}F NMR spectra of the substituted dimanganese compounds show remarkably little coupling. Two chemically equivalent PF_3 groups when coupled are expected to yield a second-order spectrum since they are magnetically inequivalent, which results in splittings that should be described as an $AA'X_3X'_3$ pattern. Generally, this results in two spikes (separated by a characteristic 1300-Hz P–F splitting) containing half of the area. The other half is found as a mirror-imaged pattern of peaks around the spikes spread over 50–200 Hz.[17] A third equivalent PF_3 generally causes so much second-order splitting that the spectrum can be quite broad and almost uninterpretable.[18] If the PF_3 groups are not equivalent, first-order coupling of one PF_3 to another should be seen. These expected patterns are found in most metal carbonyl–trifluorophosphine complexes. A small amount of the coupling could be lost in the line widths, but the lines are moderately sharp, so the coupling must be unusually small. We have no explanation for this. This situation (the absence of coupling) is consistent throughout the series even when the phosphines are on only one atom. Stereochemical nonrigidity would not explain it, nor would metal–metal bond rotation. The presence of a quadrupolar manganese seems not to be the explanation. For instance, in the compounds $HMn(PF_3)_x(CO)_{5-x}$ hydrogen couples through the manganese to phosphorus and fluorine and vice versa.[19]

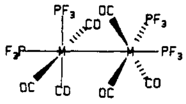
The lack of coupling has simplified the use of NMR in the characterization of the samples. Significant chemical shift is still present. The ^{19}F NMR data for compounds I–V are given in Table I. The spectrum of an axial PF_3 is a doublet centered 0–2 ppm relative to the standard, and the equatorial is found between 2 and 3 ppm. The number and type of phosphines can generally be counted and used to aid in structural assignments.

The composition of the products is readily determined by mass spectrometry. In addition to the parent ion, cleavage of the metal–metal bond produces characteristic pentaligated monometallic fragments such as $[Mn(CO)_5]^+$ and $[Mn(CO)_3(PF_3)_2]^-$. The fragments with a lower degree of substitution are readily observed in the positive ion mass spectra. With increasing substitution by the more electronegative PF_3 group, the relative formation of the pentaligated monometallic fragments decreases in the positive mass spectrum but increases in the negative ion mass spectra. By use of a combination of the positive and negative ion spectra, the PF_3 distribution between the two metals is determined unambiguously. Under electron impact ionization the parent molecular ion was observed for each compound. Under negative chemical ionization the molecular ion is not observed; however, the highest mass peak in each spectrum corresponds to the loss of a CO to give the $[M - 28]^-$ anion (where M is the molecular ion). Infrared data are given in Table II.

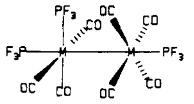
Thermal Products. The first compound to elute from the GC has a molecular ion of weight 630, indicative of a tetrasubstituted compound. The appearance of only the $[Mn(CO)_3(PF_3)_2]^+$ (315 m/z) monometallic fragment indicates 2–2 distribution. The ^{19}F NMR shows two doublets. The doublets result from coupling with the ^{31}P, which has a characteristic J value of about 1300 Hz. The pair of doublets indicates only two chemically different environments. For the 2–2 type isomers only the diaxial, diequatorial compound would produce this spectrum. This compound had been assigned as 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$ (structure I).

Table II. Infrared Data on Dimanganese Compounds

	compd	sym	abs, cm^{-1}
	parent	D_{4d}	2043 s, 2012 vs, 1981 s
I	1,1′,2,2′	C_2	2074 w, 2030 w, 2009 s, 1991 m, 1974 w, 1952 w
II	1,1′,2	C_s	2087 w, 2034 w, 2019 (sh), 2009 s, 1986 m, 1973 w
III	1,1′	D_{4d}	2026 w, 2009 s
IV	1,2	C_s	2099 w, 2044 m, 2024 (sh), 2012 s, 1982 m, 1809 w
V	1	C_{4v}	2106 w, 2034 m, 2012 vs, 1989 m, 1977 w



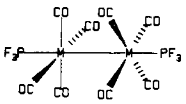
I



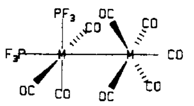
II

The second peak to elute from the GC has a molecular weight of 570, indicative of a trisubstituted compound. Characteristic monometallic fragments in the mass spectra at m/z 255 and 315 indicate a 2–1 type of distribution. The ^{19}F NMR of peak 2 shows three doublets. Only two of the six 2–1 isomers, the 1,1′,2 isomer and the 1,2,2′, would produce three doublets. Peak 2 has been assigned as 1,1′,2-$Mn_2(CO)_8(PF_3)_3$, structure II, on the basis of the chemical shifts in the fluorine NMR, the general tendency to form axial species by the thermal route, and its elution order.

The third compound to elute has a molecular weight of 510, and only the $[Mn(CO)_4(PF_3)]^+$ fragment is observed in the mass spectrum. This is consistent with the substitution of a PF_3 on each metal. The ^{19}F NMR shows only one doublet, limiting the structure to either the diaxial or diequatorial isomer. The diaxial isomer has D_{4d} symmetry while the diequatorial isomer is C_2. Group theory predicts two active CO stretches for the diaxial isomer and eight for the diequatorial isomer. The infrared spectrum shows only two peaks, indicative of the diaxial disubstituted compound. In addition a partially refined X-ray crystal structure of $Mn_2(CO)_8(PF_3)_2$, synthesized under similar conditions, placed both PF_3 ligands in the axial positions.[20] Chromatography peak 3 has been assigned as 1,1′-$Mn_2(CO)_8(PF_3)_2$ (structure III).



III



IV

The fourth compound to elute has a molecular weight of 510 with monometallic fragments at 195 and 315, indicating 2–0 substitution. The ^{19}F NMR shows two doublets, one centered at 0.3 ppm as found in compound II and the other at 2.3 ppm. Substitution in two equatorial sites should produce a distinctive $AA'X_3X_3$ second-order pattern if resolved or a single doublet if not resolved regardless of whether the trifluorophosphines are cis or trans

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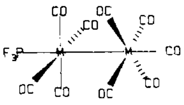
to one another. The compound must therefore have one PF_3 in the axial position and the second PF_3 in an equatorial position. Peak four has been assigned as 1,2-$Mn_2(CO)_8(PF_3)_2$ (structure IV).

The fifth compound to elute from the GC has a molecular ion of weight 450, indicative of a monosubstituted product. Mass spectral fragments at m/z 195 and 255 correspond to $[Mn(CO)_5]^+$ and $[Mn(CO)_4(PF_3)]^+$, respectively, a 1–0 type distribution. The axially substituted species has C_{4v} symmetry, while the equatorially substituted species has C_s symmetry. Group theory predicts that the axial species would have five active CO stretches in the IR region, while the equatorial species should have nine active CO stretches. The infrared data in Table II show only four active CO stretches, indicating axial substitution. In addition, the spectral pattern is quite similar to those of the monoaxial compounds[21] whose structures are known. The ^{19}F NMR shows a single doublet centered at 1.1 ppm, as expected for a single PF_3 group being assigned an axial position. GC peak five has thus been assigned the 1-$Mn_2(CO)_9(PF_3)$ (structure V).



V

Photolytic Products. In addition to the compounds just assigned, substitution under photolytic excitation produces three additional products in trace amounts. These could not be isolated for further identification. Their minor amounts plus marginal stability on packed columns makes their isolation in purity quite difficult. A second tetrasubstituted compound having a 3–1 distribution is formed that coelutes with species II. A second trisubstituted compound of 2–1 type distribution is formed and elutes between compounds III and IV. In addition, a third disubstituted compound of 2–0 distribution is formed that elutes after the monosubstitued compound V. It is possible that the additional products produced by photolysis consist of two or more structural isomers that are unresolved by the GC.

The photolysis of an eqimolar mixture of 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$ and $Mn_2(CO)_{10}$ in hexane under an inert atmosphere produces an additional product. The resulting solution contains a mixture of the aforementioned products and a new product that elutes between compounds IV and V. The mass spectrum gives a molecular weight of 570 for a trisubstituted species. The presence of fragments of $[Mn(CO)_5]^+$ and $[Mn(CO)_2(PF_3)_3]^+$ indicates 3–0 substitution. The exact structure is uncertain and may consist of a mixture of two or all three of the possible isomers. These results concerning the reaction of two compounds are intriguing and will be pursued further.

All efforts to push the reaction beyond tetrasubstitution failed. One possibility is that the ligands in $Mn_2(CO)_6(PF_3)_4$ (CO in particular) are inert to exchange or substitution. However, reactions of the 1,1′2,2′ compound with ^{13}CO shows that the ligands in the tetrasubstituted compound are quite labile. Under both thermal and photolytic conditions ^{13}CO rapidly exchanges with bound ^{12}CO, resulting in extensive isotopic labeling. The replacement of bound trifluorophosphines is significantly slower than the ^{12}CO exchange. When it occurs, it produces a mixture of PF_3-substituted compounds all extensively labeled. These compounds exhibited almost complete ^{13}CO incorporation, with the bulk of the ^{12}CO present resulting from the 10% unlabeled CO used in the experiment. This shows clearly that 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$ is still subject to ligand exchange and is not inert to substitution by carbon monoxide.

Monometallic hydride formation accompanies both thermal and photolytic PF_3 substitution into $Mn_2(CO)_{10}$. Extensive photolytic reaction results in the hydrides as the major product sometimes even when a hydrogen source is not obvious. The hydrides themselves are extensively PF_3 substituted,[19] and the higher PF_3 substituted products predominate. $HMn(CO)_5$ is not observed when PF_3 is present but could be formed under either a H_2 or CO atmosphere. The compound $HMn(CO)_5$ is a clear liquid at 0 °C, and at room temperature it decomposes to $Mn_2(CO)_{10}$, giving off H_2. This reaction can be observed by eye, as the re-formation of the metal–metal bond produces a light yellow compound. The recombination of the PF_3-substituted metal hydrides to give substituted compounds having a metal–metal bond has not been observed.

A series of polynuclear compounds having both a H and a PF_2 bridge between the metals is also observed under both thermal and photolytic conditions. The use of unpurified PF_3 tends to increase the yield of these compounds relative to the normal substituted compounds. However, efforts to stop these side reactions using reagents of high purity and well-dried vessels have not been successful. Reactions run in the presence of traces of D_2O, although decreasing the overall yield, show incorporation of the D in place of the H. Similar bridged compounds have been produced by other workers using $HPPh_2$ in which the PR_2 group is inserted into the metal–metal bond.[22] Under extensive reaction using either photolytic or a combination of photolytic and thermal conditions, a series of di-PF_2-bridged compounds is produced in trace quantities having the general formula $Mn_2(\mu\text{-}PF_2)_2(CO)_{8-x}(PF_3)_x$. These compounds contain a minimum of two trifluorophosphines.

The formation of all of these side products is slow relative to the rate of production of the main products. It does not seem to us that their formation should be invoked as an explanation for the lack of the formation the penta- and higher phosphines in compounds with metal–metal bonds intact.

Discussion

Replacement of up to four carbon monoxides by PF_3 produces nine new products having a manganese–manganese bond. Photolysis produces products more rapidly than thermal reactions. It results in all nine of the products observed between $Mn_2(CO)_{10}$ and PF_3, whereas thermal substitution produces only five of the observed products. Reaction of the tetrasubstituted compound with ^{13}CO showed rapid exchange of CO and gradual substitution of PF_3.

Forcing reaction conditions result in the formation of several other types of organometallic species that are produced through a variety of transformations. These include the monometallic hydrides, the $L_4Mn(\mu\text{-}H)(\mu\text{-}PF_2)MnL$ compounds, and the $L_4Mn(\mu\text{-}PF_2)_2MnL_4$ compounds. Deuterium can be incorporated into the hydrogen bridged compounds and is shown by a mass spectrum with fragments increased by 1 amu.

The complete substitution of the manganese pentacarbonyl hydride[19] with trifluorophosphine and the preparation of $Cr(PF_3)_6$[23] are convincing evidence that there

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is sufficient room for the slightly larger PF_3 ligand in the monometallic compounds. Yet replacement of CO by PF_3 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 $Cr(PF_3)_x(CO)_{6-x}$ (x = 0–6) may not be a good model for the situation in the two halves of $Mn_2(CO)_{10}$. 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 $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ with PF_3 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 PF_3 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 $1,1'$-$M_2(CO)_8(PF_3)_2$ and $2,2'$-$M_2(CO)_8(PF_3)_2$ (M = Re or Tc) are readily formed, but formation of $1,2'$-$Re_2(CO)_8(PF_3)_2$ was not observed.

Introduction

The substitution of the CO moiety within the group-7 dimetal decacarbonyls ($M_2(CO)_{10}$, 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 PPh_3 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 (PF_3) is such a ligand. The π-acceptor and σ-donor properties of PF_3 have been shown to be similar to those of CO.[9,10] In addition, PF_3 is a relatively small molecule possessing a cone angle of 104°.[11] The predominant pattern of substitution in $Mn_2(CO)_{10}$ 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 PF_3 substitution of $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$. Compositional and structural assignments for the $Re_2(PF_3)_x(CO)_{10-x}$ system are based upon GC-MS, and GC-IR, and ^{19}F 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 NH_4TcO_4, purchased from the Oak Ridge National Laboratory. Roughly 400 mg of NH_4TcO_4 was placed under 6200 psi of CO at 210 °C. After a minimum of 48 h, the $Tc_2(CO)_{10}$ 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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