TABLE IV

CALCULATED DISSOCIATION ENERGIES FOR SEVERAL Cu_n MOLECULES

Molecule	Internuclear dist, Å	D_e, ev
Cu_3 (linear)	2.3	2.84
Cu_3 (triangular)	2.3	2.24
Cu_4 (square planar)	2.3 (adjacent atoms)	3.11
Cu_6 (octahedral)	2.4 (from center of inversion)	3.6

Clementi and Raimondi[16] or by Slater's[20] rules, were found to be inadequate.[21]

The traditional transition metal basis set of 3d, 4s, and 4p orbitals proved to be optimum for the description of the Cu_2 molecule. The lowest filled molecular orbitals, which are largely 3d in character, were important in accounting for the core repulsions at short distances and were extremely important for the calculation of the stretching frequency, ω_e. The inclusion of the higher lying 4p orbitals in the basis set was important for the calculation of the spectral transition, Δ, since the 4s–$4p_z$ mixing effectively lowers the energy of the σ^* orbital. The 4s orbitals were the most important ones since all molecular properties of Cu_2 are largely dependent upon them.

The energy and core repulsion in the Cusachs approximation varies as $S^2/(1 + S)$ at short internuclear distances. This dependence approximates the core repulsions of Cu_2 and gives the best reproduction of the potential energy curves in the bonding and repulsive regions. The solutions obtained by using other approximations are substantially poorer and a variation of parameters (H_{ii}, K, and orbital exponent), within reasonable limits, will not substantially improve the results.

The calculations of D_e, r_e, ω_e, Δ, and the ionization potential comprise all of the bonding parameters for Cu_2. These results are good and illustrate that the semiempirical extended Hückel theory may be used with adequate choice of parameters and basis set to calculate other such molecular properties. Unfortunately such data do not always exist for most problems of interest to inorganic chemists, but it should be required that calculations of this nature faithfully reproduce other properties in addition to the spectrum. Presently, calculations are in progress on other homonuclear diatomic molecules of the transition metals. It is hoped that the parameters which best describe these molecules can be extended to heteronuclear diatomic molecules and complexes of the transition metals.

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(20) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(21) We have found that calculations using double ζ valence orbital basis sets yield results that are nearly identical with those using single orbital exponents; hence, only the latter were used here.

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Metal Carbonyl–Phosphorus Trifluoride Systems. V. Decacarbonyldimanganese

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Decacarbonyldimanganese reacts with phosphorus trifluoride to yield a variety of substitution products. These products are formed either by thermal reaction or ultraviolet irradiation under several sets of conditions. The product of the ultraviolet reaction is usually a mixture of four major species having mono-, di-, and triphosphine substitution plus trace amounts of other minor species. The species from this uv reaction have both axial and equatorial substitution. They can be isolated by gas–liquid partition chromatography and identified by a variety of means. The thermal reaction gives a different product distribution from the ultraviolet reaction in that substitution here is almost exclusively on the axial positions. The $Mn_2(PF_3)_x(CO)_{10-x}$ species are yellow solids melting below 100°. They are moderately stable in air and some solvents, but react rapidly with solvents like alcohols yielding solvolysis products such as $Mn_2(CO)_9[P(OCH_3)_3]$.

Introduction

Dimanganese decacarbonyl contrasts strongly with most other metal carbonyls in that only a limited number of simple substitution derivatives have been prepared. By way of comparison, the group VI carbonyls form literally hundreds of simple substitution products.[2] The tendency of the parent carbonyl to undergo valence disproportionation instead of substitution and the intractability of substitution products once formed are among the most important factors in the sparsity of substitution products of dimanganese decacarbonyl.[3] Some simple substitution products do occur, particularly with ligands capable of some degree of π bonding.

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(1) Part of this research is included in the dissertation of H. Haas submitted to the Graduate School of Florida State University.

(2) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

(3) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

The lack of substitution products is particularly regrettable in view of the tremendous variety of stereochemistries that can occur—a veritable delight (or nightmare). If one assumes free rotation about the metal–metal bond, substitution by a monodentate ligand produces 2, 6, 9, 17, 14, 17, 9, 6, 2, and 1 isomers for mono, di, tri, etc., substitution for a total of 84 species of 11 compositions including the parent carbonyl. If free rotation about the metal–metal bond is restricted giving the staggered conformation, the numbers of geometric isomers become 2, 7, 12, 21, 23, 21, 12, 7, 2, and 1 for mono through deca substitution for a total of 109 species. Of these, 43 have optical isomers. Thus the very magnitude of the stereochemical possibilities has complicated the search for these compounds because of the difficulty in separating the species. For a given ligand, the substituted products should be quite similar to one another and their high molecular weights would tend to make them rather intractable.

Of the species thus far reported, most are disubstituted and have been shown fairly conclusively to be diaxial.[4a] Some monosubstituted species have been reported,[4b] N donors substituting equatorially and $P(C_6H_5)_3$ axially. A few bidentate ligands have been found to form complexes of the type $Mn_2(CO)_8L$. In these cases it is not known whether the ligands act as an additional bridge between the two metal atoms or whether they replace two carbonyls on a single metal atom.[5]

Of all the substitution ligands for $Mn_2(CO)_{10}$, phosphorus trifluoride would seem to have the greatest chance of freely replacing the carbonyl groups. It has been shown to be clearly capable of substituting more or less randomly to almost any extent into metal carbonyls. For instance, molybdenum hexacarbonyl reacts with PF_3 yielding substitution in all possible positions. Seven compositions are produced, three of which have *cis* and *trans* isomers, for a total of 10 species including the parent carbonyl.[6] Manganese carbonyl has a related structure to the octahedral molybdenum hexacarbonyl. In the solid state, it consists of essentially two octahedra joined at a corner and having a staggered conformation.[7]

This paper describes some of the results obtained in a study of the $Mn_2(CO)_{10}$–PF_3 system. The preparation, separation, characterization, and properties of some of the species will be discussed. The only other previous work on this system is the report of the disubstituted axial isomer $Mn_2(CO)_8(PF_3)_2$ of Kasenally, *et al.*[8]

Experimental Section

There are several approaches to the production of $Mn_2(PF_3)_x(CO)_{10-x}$ species. These include high-pressure–high-temperature reactions and various forms of ultraviolet irradiation used in earlier systems.[6,9]

The approach that was largely used in this work was high-temperature ultraviolet irradiation. In this application, a 200-ml Pyrex flask was used. A 7-mm tube was sealed to the bottom and a Kovar seal to the upper neck of this flask. A brass needle valve was attached to the Kovar tube by means of a Swagelok connector. A quantity of finely ground $Mn_2(CO)_{10}$ (usually 0.50 g, 1.28 mmol) was placed in the flask before the valve was attached. The vessel was evacuated at room temperature and a volume of PF_3—usually 100 ml, 4.06 mmol—was condensed in the flask at $-195°$. The vessel was placed in a box containing heaters and a 1000-w high-pressure AH-6 mercury lamp. The material was allowed to react at 100–120° under irradiation for 2–3 hr. This resulted in a fairly general mixture of mono-, di-, and trisubstituted species. Higher concentrations of the mono species were obtained by either shortening the reaction time or lowering the amount of PF_3 added. Higher concentrations of the trisubstituted species were obtained by adding more PF_3, irradiating for a longer period, and occasionally cooling the flask to $-195°$ and pumping off the evolved CO.

The reaction was carried out with the flask in a horizontal position with the lamp above, but the product was recovered by placing the flask in a vertical position during the last 5–10 min so that the liquid reaction product would collect in the bottom extension tube. There was no sign of decomposition products.

The other ultraviolet method that was used early in the experiments involved dissolving $Mn_2(CO)_{10}$ (0.5 g) in *n*-hexane and irradiating the flask at room temperature while either bubbling PF_3 through the solution or allowing the PF_3 to react in a closed, stirred system. The $Mn_2(PF_3)_x(CO)_{10-x}$ species were recovered by evaporating the solvent under vacuum.

In the high-pressure–high-temperature method, 1.0 g of $Mn_2(CO)_{10}$ was placed in a 50-ml stainless steel pressure vessel and various volumes of PF_3 were added. The vessel was heated to 120° for 48–72 hr. A reaction was also run at atmospheric pressures under conditions that approximated the ultraviolet reaction without actually irradiating the sample.

A mixture of species always resulted from these procedures and an efficient method had to be developed for their separation. Elution chromatography was fairly successful when carefully applied. The crucial feature involved having the solid phase properly prepared. Alumina could not be used as its basic character caused rapid decomposition presumably through attack of the P–F bonds. Silica gel as received also caused extensive decomposition. However, it was found that decomposition could be kept to a minimum by the following procedure. Activated silica gel (Davison Chemical, Grades 922, 923), approximately 200 mesh, was washed on a large column with 0.5 *N* sulfuric acid and then with distilled water until the washings were of pH 3 or slightly higher. It was then dried and heated at 110° for 1 hr and kept in sealed jars until use. For chromatography, a silica gel column 50 cm long and 2 cm in diameter was packed in *n*-hexane, and a saturated *n*-hexane solution (10 ml) of the $Mn_2(PF_3)_x(CO)_{10-x}$ species was adsorbed on it. On elution with *n*-hexane, a clean separation of the yellow compounds into separate bands was never obtained, but examination of successive 10-ml fractions by infrared spectroscopy showed that extensive separation did occur. In general, the higher substitution products came off the column first and the parent carbonyl last.

A second method of separating the species was gas–liquid partition chromatography which proved to be capable of giving much cleaner separation, but in rather small quantities. The best column that has been found was a 1.3 m × 6 mm 40% diisodecyl phthalate column on Chromosorb P. The temperature of operation was 90–105° with the injector and detectors at about the

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[4] (a) See, for example: A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 634 (1964); D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc., Sect. A*, 695 (1966); J. Lewis, A. R. Manning, and J. R. Miller, *ibid.*, 845 (1966); (b) M. L. Ziegler, H. Haas, and R. K. Sheline, *Chem. Ber.*, **98**, 2454 (1965).

[5] W. Hieber and W. Schropp, Jr., *Z. Naturforsch.*, **15b**, 273 (1960).

[6] R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965). For a recent review of PF_3 chemistry, see Th. Kruck, *Angew. Chem. Intern. Ed. Engl.*, **6**, 53 (1967).

[7] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

[8] A. S. Kasenally, R. S. Nyholm, D. J. Parker, and M. H. B. Stiddard, *Chem. Ind.* (London), 2097 (1965).

[9] R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964); **6**, 299 (1967); R. J. Clark and E. O. Brimm, *ibid.*, **4**, 651 (1965); and unpublished work.

same temperature. Rather high helium flows of 70-100 ml/min were used. Collection was done at 0°. Injections of mixtures containing 20 mg of complexes were always separated cleanly. The separation of considerably larger quantities was possible for certain mixtures. Mixtures that melted at low temperatures were dissolved in hexane, and these solutions were used for separation. The higher melting mixtures required too large a volume of hexane so tetrahydrofuran was used. The THF solutions had to be handled with unusual care because the PF_3 complexes are quite sensitive to water and perhaps oxygen in this solvent. The solid was placed in a convenient vessel containing only a needle-sized opening. Dry nitrogen was purged through the flask and dry THF was injected into the container. Using these simple precautions, little decomposition took place in 24 hr. The base line was too unstable with the manganese carbonyl system to allow automated collection on the Autoprep A700 which was used.

Species I and III as well as the minor species can be concentrated well above their naturally produced abundance by treating the reaction mixture with a quantity of hexane such that 50% or less of the product is taken into solution.

The diisodecyl phthalate column is far from ideal. It gave far better separation than a variety of other columns that have been tried (particularly silicone columns), but the system is still somewhat unstable under the conditions used. Some decomposition (but apparently not disproportionation) takes place on the column at 100°. Doubling the length of the column does not improve the resolution and results in much more decomposition.

In order to characterize the compositions of the species, systematic "order of formation" studies were made using the various preparative techniques. The relative heights of the glpc peaks for the various substituted species were determined for widely varying conditions of temperature, reaction time, and mole ratio of reactants

The general stabilities of the various species toward solvents were studied by dissolving mixtures in a solvent, allowing them to stand for 30–60 min, and checking for the presence or absence of the various species by glpc.

The solvolysis reaction with alcohols was studied for several of the species in order to help elucidate some of the stereochemistries and compositions. The infrared spectra of the trifluorophosphine complexes were determined as a function of the degree of solvolysis which was controlled by regulating the nature of the solvent—either methanol or sodium methoxide solution in methanol—and the time of reaction. For example, practially pure mono-, di-, and trisolvolysis products of IV could be obtained in 0.005 *m* $NaOCH_3$ after 5 sec, 0.05 *m* $NaOCH_3$ after 10 sec, and 0.5 *m* $NaOCH_3$ after 30 min, respectively. Other $Mn_2(PF_3)_x(CO)_{10-x}$ species were studied in a similar fashion.

Infrared spectra in this study were run in spectroscopic grade hexane on a PE 521. The spectra were run at several concentrations to show the weak peaks. The instrument was calibrated by gaseous DCl for the carbonyl region and gaseous NH_3 for the PF region.[10] Band positions are felt to be accurate to slightly better than ± 1 cm^{-1}. Spectra were run on an expanded scale (10 cm^{-1}/cm) and the chart speed was about 11 cm^{-1}/min. The spectral slit width was calculated to be 1.22 cm^{-1}.

Microchemical analyses were done by Pascher Microchemisches Laboratorium, Bonn, Germany, and Schwarzkopf Laboratories, Woodside, N. Y. Manganese carbonyl was obtained from Alfa Inorganics and either used as received or sublimed once under high vacuum. Phosphorus trifluoride was obtained from Ozark Mahoning and was purified by water washing and low-temperature distillation before use.

Anal. Calcd for $Mn_2(CO)_9(PF_3)$: C, 24.03; F, 12.67. Found: C, 24.73; F, 13.00. Calcd for $Mn_2(CO)_8(PF_3)_2$: C, 18.84; F, 22.36. Found: (III) C, 19.43; (II) C, 19.07; F, 22.22. Calcd for $Mn_2(CO)_7(PF_3)_3$: C, 14.75; F, 30.00. Found: C, 15.45; F, 30.40.

Results

Four new major species are seen in the gas–liquid partition chromatogram of a general reaction product of $Mn_2(CO)_{10}$ and PF_3 under the influence of ultraviolet light at elevated temperatures. These are listed as species I–IV in Table I along with their relative retention times. Species V is the parent carbonyl. Other weak peaks are seen, but under the conditions thus far used, they have been produced in quantities too low for characterization. They are also listed in Table I.

TABLE I

SPECIES IDENTIFICATION

Species	Rel ret time[a]	Mp, °C	Probable identity
		Major Components	
I	0.22	38	$Mn_2(CO)_7(PF_3)_3$
II	0.26	81	$Mn_2(CO)_8(PF_3)_2$ (diaxial)
III	0.43	45	$Mn_2(CO)_8(PF_3)_2$
IV	0.51	90	$Mn_2(CO)_9(PF_3)$ (axial)
V	1.00	...	$Mn_2(CO)_{10}$
		Minor Components	
VI	0.15	...	...
VII	0.20	...	...
VIII[b]	0.34	...	...
IX[b]	0.71	...	...[c]

[a] Slightly variable, depending upon the exact conditions. [b] These two species appear only in a few preparations and it has not yet been possible to prepare them at will. [c] The relative retention time of this species strongly suggests that it is the other monosubstituted species—the equatorial.

Several types of evidence can be brought to bear on the determination of the composition and stereochemistry of the four major species. The first is the order of compound formation as a function of reaction conditions. It is reasonable to assume that the carbonyl groups will be replaced sequentially. Thus by progressively increasing the degree of substitution, one can observe the appearance and disappearance of the species and fairly accurately assign their compositions.

Species IV is the first to appear in the reaction between $Mn_2(CO)_{10}$ and PF_3 and thus should be a monophosphine. Compounds III and II appear next as a pair and should be assigned as diphosphines. The single compound I appears next at the expense of III and II, more from the latter than the former, and should therefore be a triphosphine. By the time I becomes predominant, IV and V have almost completely disappeared. The other species are in too low a concentration to have any accurate assessment made of their composition.

The relative retention times can be cited as somewhat indirect evidence in favor of this assignment. In all metal carbonyl–trifluorophosphine systems that have been studied thus far,[6,9] the lower substitution compositions have fallen into a pattern. It is always found that the higher the PF_3 content, the shorter

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(10) IUPAC Commission on Molecular Structure and Spectroscopy, *Pure Appl. Chem.*, **1**, 537 (1961).

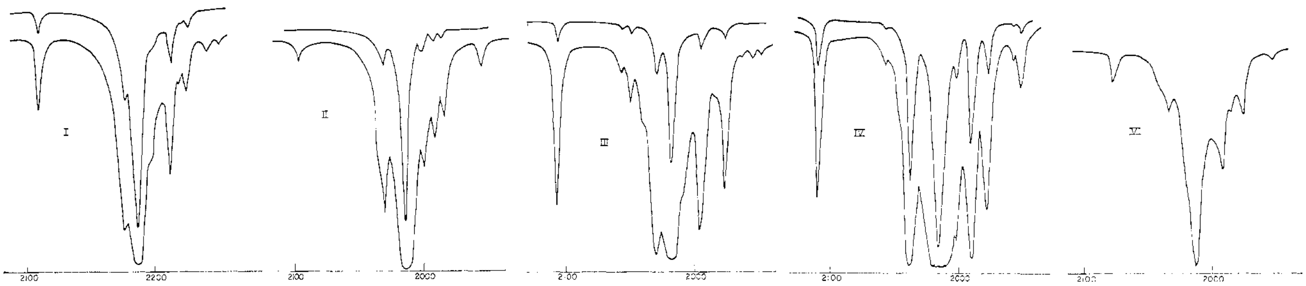

Figure 1.—Infrared spectra of $Mn_2(PF_3)_x(CO)_{10-x}$ species in the carbonyl region: I, $Mn_2(CO)_7(PF_3)_3$; II, $Mn_2(CO)_8(PF_3)_2$, diaxial; III, $Mn_2(CO)_8(PF_3)_2$; IV, $Mn_2(CO)_9(PF_3)$, axial; VI, tri- or tetrasubstituted isomer.

the retention time. This has been true whether the volatility increases or decreases upon substitution and is independent of the nature of the column. Thus, the retention times are entirely consistent with the assignments made from the order of formation. Of course, nothing can be said about the nature of the isomers by either approach.

The limited analytical data shown in the Experimental Section offer complete support for the compositional assignment made by previous methods.

The nature of the stereochemistry of these species is less easy to determine. The melting points listed in Table I offer the first tentative clue. Species I and III have noticeably lower melting points than II and IV. The trend in melting point is also reflected in the much greater solubility of the former pair in hexane than the latter. A reasonable explanation is to assume that compounds II and IV involve only axial substitution while compounds I and III involve some equatorial. Compounds with axial substitution should disrupt the lattice much less and result in correspondingly higher melting points and lower solubilities than compounds with equatorial substitution. Thus compounds I and III would be tri- and diphosphine derivatives, respectively, with some equatorial substitution, whereas compounds II and IV would be the di- and monoaxial derivatives, respectively.

Infrared spectra of the carbonyl region combined with simple group theory have proven to be an important aid in assigning composition and/or isomer geometries for simpler mononuclear species. In this dinuclear system, group theory is of much more limited application owing to the number of species, their lack of symmetry, the complexity of the species, and the number of possible isomers. With few exceptions, most isomers are of very low symmetry and thus simple group theory loses its diagnostic power. For compounds IV and II, however, arguments will be made later in this paper to give strong support for their assignment as the mono- and diaxial substituted compounds previously assigned on theoretical grounds by Haas and Sheline.[11] The spectra of the various species in the carbonyl stretching region are shown in Figure 1 and the values of the CO and PF stretching frequencies are given in Table II.

TABLE II

INFRARED FREQUENCIES OF $Mn_2(PF_3)_x(CO)_{10-x}$ SPECIES

		Freq, cm^{-1}			
Species	Formula	CO region		PF region	
I	$Mn_2(CO)_7(PF_3)_3$	2089	1989	898 s	
		2022 sh	1981	881 m	
		2012	1975	867 vs	
		2000	1959	852 mw	
			1950		
II	$Mn_2(CO)_8(PF_3)_2$	2096	1999	895 vw	
		2034 sh	1993	880 m	
		2029	1985	866 s	
		2012	1955		
III	$Mn_2(CO)_8(PF_3)_2$	2104	2004 sh	894 s	
		2053	1995	879 w	
		2046	1976	868 m	
		2037 sh	1963	850 mw	
		2027	1955		
		2015	1948		
IV	$Mn_2(CO)_9(PF_3)$	2110	1992	871 s	
		2038	1980	877 sh	
		2015	1960		
		2002	1954		
VI	. . .	2078	1977 w	908 sh	872 s
		2034 w	1953 vw	901 m	854 m
		2012 vs		891 ms	
		1994 m		880 m	

The solvolysis studies provide further clues to the stoichiometry of II and IV and additional information on their stereochemistry. In IV, there are three and only three stages of solvolysis, showing again that it is a monotrifluorophosphine complex. The ir data for this solvolysis series are shown in Figure 2. There is a linear shift of frequency with the degree of solvolysis indicating that the final product is probably of the same gross symmetry as the starting trifluorophosphine complex. Since the spectrum of the resulting solvolysis product $Mn_2(CO)_9P(OCH_3)_3$ is similar to that of the known axial $Mn(CO)_9P(C_6H_5)_3$,[4] then $Mn_2(CO)_9P(OCH_3)_3$ and hence IV are almost certainly axial.

The infrared spectra of II and its final solvolysis product $Mn_2(CO)_8[P(OCH_3)_3]_2$ both support the conclusion that the former is diaxial $Mn_2(CO)_8(PF_3)_2$. This species which has D_{4d} symmetry is the most symmetric of any species, and group theory predicts only two bands, an E_1 and a B. Only two bands are observed except at high concentration. It is to be particularly noted that the high-frequency band, which is probably an A_1 symmetry, is found only very weakly in concentrated solution—much weaker than in any of the other species where it is allowed. Finally, the

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[11] H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967).

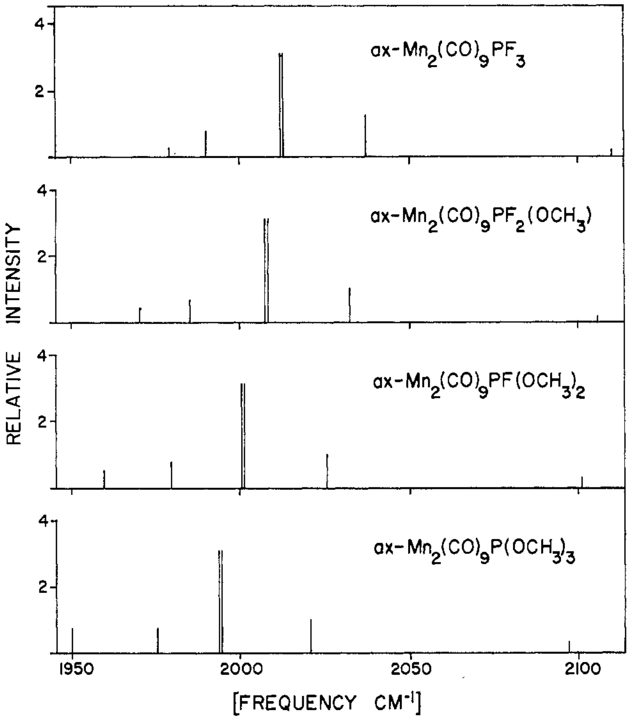

Figure 2.—Spectra of solvolysis products of $Mn_2(CO)_9(PF_3)$.

infrared spectrum of the total solvolysis product is similar to that of known diaxial substitution products,[3] having only two bands at 1996 (w) and 1968 (vs) cm^{-1}.

The infrared spectra of the other species and their solvolysis products are quite complicated and were not particularly helpful in structural determinations. However, there is an interesting trend in the infrared spectra involving the band of highest frequency. The value for this band as seen in Table I shows a steady, small decrease as one goes from species V to I. This change also parallels the decrease in retention time and somewhat reflects the degree of substitution.

It should be noted at this juncture that the species obtained by glpc and those obtained by elution chromatography have totally comparable infrared spectra. Fraction cutting produced clear evidence for each of the species trapped by glpc. The order of elution was I, II, III, IV, and V. These materials were never completely free from one another, but the main features of the ir spectra for each species could be sorted out and agreed completely with the spectra obtained for the isolated species. No other fractions or infrared features were found in addition to those species isolated by glpc except a very small first cut that had ir bands attributable to VI.

The observations mentioned above are quite important in that they seem to eliminate the possibility that the species trapped from the glpc were created by the relatively high temperature of the column itself. They further indicate that the species being trapped are pure and not disproportionating or decomposing.

Other species are clearly indicated in the gas–liquid partition chromatograms, but thus far they have been found in too low a quantity to really characterize them. Species VI and VII are produced in larger amounts when lower glpc temperatures are used. They decompose almost completely at the higher column temperatures that are normally used. Enough of VI has been isolated to obtain its ir spectrum, but the spectrum is too complicated to be of much value in its identification. Other species such as VIII and IX are frequently found in trace amounts in hexane extracts of the general ultraviolet preparation. Their production is not consistently reproducible.

Sealed evacuated tubes of II, IV, and V mixtures irradiated at 120° for 1 hr did not show any appreciable sign of the species being rescrambled. It appears that ligand gas is necessary for the reaction. Temperatures above 200° lead to complete decomposition in these tubes yielding an unidentified amorphous black powder.

There is a fundamental difference in the nature of the mixture produced by the two basic types of reaction procedures—ultraviolet and thermal. By the thermal route, at either low or high pressures, the mixtures consisted of species II, IV, and V. There was no more than 1 or 2% of I and III. The ultraviolet reaction produced a mixture of all five species I–V plus trace quantities of others. The same general mixture was produced by irradiation at either room temperature in solution or at elevated temperatures in the absence of solvent. In both of the two basic procedures, the longer reaction times, high PF_3:Mn ratios, higher pressures, and higher temperatures pushed the mixtures toward higher substitution.

All of the species isolated are yellow solids moderately stable to most conditions with relatively low vapor pressures. They sublime slowly under vacuum at room temperature, but quite easily at slightly elevated temperatures. They can be handled for short periods in air and seem to be indefinitely stable in the solid state in sealed, evacuated ampoules.

These species have the same stability characteristics toward solvents as other PF_3 species,[6,9] *i.e.*, instability in solvents like alcohols and acetone where solvolysis can take place and general stability in dry solvents like ether, benzene, and hexane. Traces of water in solvents like THF in which the complexes are soluble lead to rapid reaction. However, the complexes are sufficiently hydrophobic that they react only slowly with pure water.

One unexpected phenomenon is a slow change in the ir spectrum of I in hexane. In 1 hr, two new peaks that are clearly attributable to IV appear in the ir spectrum of a hexane solution of I. No other new bands appear, nor do the total spectral intensities significantly decrease to indicate that general decomposition is taking place. Thus far, it has not been possible to detect peaks attributable to II and III or peaks attributable to species higher than trisubstitution. There does not appear to be any clear way to explain this reaction as decomposition, disproportionation, or radical recombination. No other principal species shows evidence for comparable change in solution.

Discussion

Phosphorus trifluoride is clearly the most versatile of any ligand that has yet been found to substitute into dimanganese decacarbonyl. In the present study, four substitution products have been examined in detail, and at least four others have been clearly identified as being present. It seems clear that many more can be isolated and characterized and such a study is planned for the near future.

Species IV has clearly been identified as the axial, monosubstituted phosphine $Mn_2(CO)_9(PF_3)$ and II as the diaxial diphosphine $Mn_2(CO)_8(PF_3)_2$. Species III and I have the composition of the di- and triphosphines, $Mn_2(CO)_8(PF_3)_2$ and $Mn_2(CO)_7(PF_3)_3$, respectively. Other than the certainty that they must have some equatorial substitution, it is not clear which exact isomer has been synthesized. Since the species seem to have a rather strong proclivity to form axial isomers, it is likely that III has an axial and an equatorial substituent on separate manganese atoms and I has an axial and an equatorial on one manganese and an axial on the other. Mass spectroscopy studies will be done on these species to determine the distribution of the ligands between the two metal atoms. It is hoped that crystallographic studies can also be done.

A number of white compounds in the $Re_2(PF_3)_x(CO)_{10-x}$ series corresponding to the manganese compounds have been obtained. These species are totally analogous to the manganese compounds. They will be discussed in detail in a later paper.

The existence of equatorial substitution in I, III, and the other species VI–IX certainly points out that there is no basic stereochemical restriction on this form of substitution in $Mn_2(CO)_{10}$—at least with phosphorus trifluoride.

The distribution of the different species produced by the two basic reaction procedures is certainly of considerable interest. Thermal reaction under a variety of conditions leads nearly exclusively to axial substitution whereas uv reaction leads to both axial and equatorial replacement. Although these results imply that a different mechanism operates in each case, elucidation of the exact nature of the mechanisms involved must await detailed kinetic studies of these substitution reactions. At the present stage there would seem to be two ways of explaining the observed behavior. One is to assume that ultraviolet light is sufficiently energetic to break both equatorial and axial M–CO bonds whereas thermal reaction can break only the axial bonds. In each case, the rate-determining step would involve dissociation of CO.

A different approach is to postulate the cleavage of the metal–metal bond by the ultraviolet irradiation. Hopgood and Poe[12] have presented kinetic evidence for a mechanism of substitution which utilizes in its first step the homolytic cleavage of the Mn–Mn bond. The $\cdot Mn(CO)_5$ radical can then react by substitution followed by recombination. The substitution on the square-pyramidal $\cdot Mn(CO)_5$ radical would probably be random. Even if the substitution is directed, there is precedence for the subsequent randomization of related species that are not felt to be stereochemically rigid.[13] The recombining fragments would give a variety of equatorial and axial isomers. In this general approach, it is necessary to postulate that the metal–metal bond is not broken under the conditions of our thermal reaction, but only in our uv reaction. Basolo[14] felt that metal–metal bond breaking did not occur in the reaction of $Mn_2(CO)_{10}$ with $P(C_6H_5)_3$ up to temperatures of 200°. Hopgood and Poe,[12] however, feel that even under thermal conditions metal–metal bond breaking occurs.

It should be pointed out that we have not yet found evidence for any monomeric species in our final products. These monomers would be analogous to the species $Mn(CO)_4P(C_6H_5)_3$ reported by Hieber[15] and refuted by Basolo.[14] Our reaction mixtures are essentially diamagnetic and there are no peaks in the gas–liquid partition chromatograms indicative of species having volatility expected for a monomer. It has not been possible to measure the susceptibility of the individual species because of the small amounts of materials available.

Some comment is in order concerning the work of Kasenally, *et al.*[8] Considering the number of species present in the system, it is surprising at first that they were able to obtain only the one reported product. Their procedure has not been reported in detail, but it is clear that a high-pressure thermal reaction was used. This would probably eliminate all of the equatorial substitution products, but in our hands this reaction has always led to mixtures of mono- and diaxial substituents as well as parent. The infrared spectra of their product showed two major bands at 2036.7 and 2013.8 cm^{-1} whereas we find the strongest absorptions for $Mn_2(CO)_8(PF_3)_2$ at 2029 and 2012 cm^{-1}. This difference in the values for the high-frequency band is clearly greater than our combined experimental errors. The 2037-cm^{-1} frequency reported by them is very close to one of the major bands for the monoaxial isomer (species IV). It seems probable, therefore, that their ir spectra may have been taken on a mixture. From a solution of such a mixture it is conceivable, however, that a relatively pure single crystal of diphosphine could have been obtained for their X-ray study.

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