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METAL CARBONYL-TRIFLUOROPHOSPHINE SYSTEMS
IX*. TETRACARBONYLNITROSYLMANGANESE SUBSTITUTION

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SUMMARY

The compound $Mn(NO)(CO)_4$ reacts with PF_3 under thermal-high pressure conditions to yield all compositions of the type $Mn(NO)(PF_3)_x(CO)_{4-x}$ except $x=4$. These compounds are separable by gas-liquid partition chromatography. The infrared spectra show clear evidence for more than one isomer within each composition. Solvolysis studies show that isomerization occurs among the compositional species and the chemistry of this system clearly indicates it to be an intramolecular process. Fluorine NMR gives time average spectra at room temperature showing that the intramolecular process is an extremely fast one.

INTRODUCTION

Recently, several examples of stereochemical non-rigidity[1a,2,3] have been studied in metal carbonyl systems by the examination of phosphorus trifluoride substituents of five-coordinate metal carbonyls. The non-rigidity apparently can occur in these compounds because of the remarkable similarity between CO and PF_3. Earlier work[1] has shown that PF_3 substitutes readily into metal carbonyls, replacing carbonyl groups over the entire composition and isomer ranges while at the same time, causing little change in the physical properties or bonding in the various species.

The earlier studies have shown very clear evidence that five-coordinate systems like $Fe(PF_3)_x(CO)_{5-x}$[2] and $CF_3Co(PF_3)_x(CO)_{4-x}$[3] undergo some form of intramolecular inversion perhaps utilizing the mechanism proposed by Berry[4] that has been suggested frequently in recent literature. The cobalt system was studied by variable temperature NMR, but the inversion process in the iron system could not be slowed to within NMR times even at the lowest temperatures (−120°) that we have thus far been able to reach. The inversion process in the iron system was studied more indirectly through methanol solvolysis reactions.

The reaction products of phosphorus trifluoride with tetracarbonylnitrosylmanganese have been studied in an effort to obtain a somewhat different series of stereochemically non-rigid molecules, hopefully compounds undergoing inversion

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* For Part VIII, see ref. 1a.

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within the NMR time scale. This paper is a report on the synthesis and characterization of the various $Mn(NO)(PF_3)_x(CO)_{4-x}$ species that could be produced.

EXPERIMENTAL

The compound $Mn(NO)(CO)_4$ was prepared by the nitrosation of $HMn(CO)_5$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) according to the method of King[5].

The PF_3 substitution products were prepared by a thermal-high pressure method. Samples of $Mn(NO)(CO)_4$ were vacuum distilled into a small (30 or 150 ml) high pressure reaction vessel at −196° and sufficient PF_3 was added to yield pressures of 300 to 3000 psi at working temperatures. The pressure vessel was then subjected to a series of heating and −196° pump-down cycles. The evacuation removed the evolved CO to help prevent the reverse substitution. The vessel was first subjected to three 12 h heating-evacuation cycles at 40°, then three more at 75°, and finally three more at 110°. It was discovered through experience that if the higher temperatures were approached before at least one stage of substitution was completed at lower temperatures, excessive decomposition would occur. The actual pressure used seemed to have only a minor influence on the extent of reaction.

Attempts were made to carry out a photochemical substitution of PF_3 into the manganese compounds. Unfortunately, either $Mn(NO)(CO)_4$ itself or the intermediate $Mn(NO)(PF_3)_x(CO)_{4-x}$ species underwent extensive photochemical degradation and very little of the desired material was produced. The decomposition product contained dimers of the type $Mn_2(PF_3)_x(CO)_{10-x}$ which were identified by comparison of their infrared carbonyl frequencies with those reported by Clark *et al.*[6].

The intermediate species were separated by gas-liquid partition chromatography. The separation conditions were basically those used with the iron[2] system, a 7.5 m × 0.25 in. 40% DC-702 silicone column on Chromosorb at about 50° using a Varian Aerograph A-700 chromatograph. These conditions readily yielded components corresponding to the individual compositions. Various columns and conditions and even head and tail cutting were tried without success in an attempt to separate the compositions into isomers.

Solvolysis reactions were carried out on the isolated species under the same conditions as used for the iron system[2].

NMR data for ^1H and ^{19}F were obtained at 60.0 and 56.4 MHz on a flux stabilized Varian HR-60 spectrometer. Reference compounds were TMS and $CFCl_3$. Infrared data were obtained on a Perkin–Elmer 521 spectrometer calibrated with gaseous DCl[7]. The spectra were obtained in hexane solution. Mass spectral data were obtained at 70 eV on a Nuclide 12 90-G1.5 instrument.

RESULTS

The thermal-high pressure reaction between $Mn(NO)(CO)_4$ and PF_3 produces all of the individual compositions of the general formula $Mn(NO)(PF_3)_x(CO)_{4-x}$ except $x=4$. The compounds are isolated chromatographically pure by GLC. They are orange to red, slightly air sensitive liquids at room temperature. They have rather low melting points, generally not freezing at dry ice temperatures. The general stability increases as the PF_3 content increases.

The individual species that are trapped chromatographically are identified by a variety of techniques. These include the following:

1. *Order of formation.* Since the substitution of the carbonyl groups can be expected to occur sequentially, the new chromatographic peaks can be readily identified by studying the reaction as a function of time.

2. *Order of elution.* The retention times of the $Mn(NO)(PF_3)_x(CO)_{4-x}$ species decrease as x increases. This is the order of elution that has inevitably been found to occur in metal carbonyl-trifluorophosphine systems.

3. *Mass spectra.* Parent ion molecular weights agree with the expected values. In addition, the cracking pattern was qualitatively as expected. Carbonyl and trifluorophosphine groups were lost stepwise in addition to some loss of the nitrosyl group. Only small amounts of ligand cracking fragments were found.

4. *NMR spectra.* The ^{19}F pattern was as expected for one, two or three equivalent PF_3 groups.

5. *Infrared spectra.* The infrared spectra contain strong absorptions in the 2000, 1800, and 900 cm^{-1} region as expected of carbonyl, nitrosyl, and P–F stretches, respectively. No other major absorptions are present. The infrared data for the various compounds are shown in Table 1. It becomes immediately obvious that more than one species is present for each composition. There are more carbonyl and nitrosyl stretching frequencies than can be accounted for on the basis of any single isomer.

TABLE 1

INFRARED SPECTRA (cm^{-1}) OF $Mn(NO)(PF_3)_x(CO)_{4-x}$ COMPOUNDS AND ISOMER ASSIGNMENT[a]

Compound	Carbonyl region	Nitrosyl region	P–F region
$Mn(NO)(CO)_3(PF_3)$	2074 m[b]	1775 (sh)	899 w
	2035 vw[c]	1767 s	883 m
	2018 m[b]		866 w
	2004 w[c]		858 (sh)
	1972 s[b]		
	1943 vw[i]		
$Mn(NO)(CO)_2(PF_3)_2$	2056 w[f]	1783 (sh)	904 m
	2034 w[d]	1774 (sh)	892 (sh)
	2013 w[e]	1768 s	872 m
	1995 w[f]		853 w
	1967 vs[d]		846 vw
	1938 vw[i]		
$Mn(NO)(CO)(PF_3)_3$	2043 m[h]	1773 s[h]	919 s
	1995 s[g]	1781 (sh)[g]	907 s
			874 s
			863 w
			847 s

[a] Probable isomer assignment: trigonal bipyramid, NO group always equatorial, designation based on phosphine group. [b] C_s (axial). [c] C_s (equatorial). [d] C_{2v} (axial). [e] C_{2v} (equatorial). [f] C_1. [g] C_s (diaxial). [h] C_s (monoaxial). [i] ^{13}CO absorption.

The important question is whether we have simply failed to separate the isomers or whether there is some rapid isomerization occurring which would make such a separation impossible.

The room temperature ^{19}F spectra for the mono-, di-, and triphosphines appear as spectra of compounds containing equivalent PF_3 groups. The spectrum of the monophosphine consists of a simple doublet [$J(PF) = 1337$ Hz; $\delta = 6.53$ ppm] and the di-, and triphosphines have more complex second order spectra containing mirror image patterns of upfield and low field peaks. This mirror imaging is characteristic of equivalent PF_3 groups[8]. Although the NMR spectra appear as if only a single isomer is present, it is obvious from the IR data that one is seeing time average spectra.

Low temperature spectra were obtained which do not particularly clarify the situation. The spectrum of $Mn(NO)(CO)_3(PF_3)$ remains essentially unchanged as the temperature is lowered. The second order spectrum of $Mn(NO)(CO)_2(PF_3)_2$ broadens considerably at temperatures around −20°. The relative separation between the minor peaks changes somewhat when the spectrum resharpens at lower temperature, but the qualitative nature remains the same.

The solvolysis studies are more informative about the isomerization process. In these studies, the fluorine atoms are replaced stepwise by $-OCH_3$ groups through the reaction with methanol or sodium methoxide[2]. The infrared spectra of the solvolysis products can be sorted out at each stage. The data for the solvolysis of $Mn(NO)(CO)_3(PF_3)$, $Mn(NO)(CO)_2(PF_3)_2$ and $Mn(NO)(CO)(PF_3)_3$ are shown in Figs. 1, 2 and 3, respectively. It can be seen that two main effects occur. First, as the fluorine atoms are replaced by methoxide groups, there is a general shift of the carbonyl frequencies to lower values. This is to be expected on the basis of the changing bonding properties of the phosphine. Secondly, certain frequencies disappear as the various stages of solvolysis occur. This can be attributed to the selective formation of one isomer from the mixture of isomers.

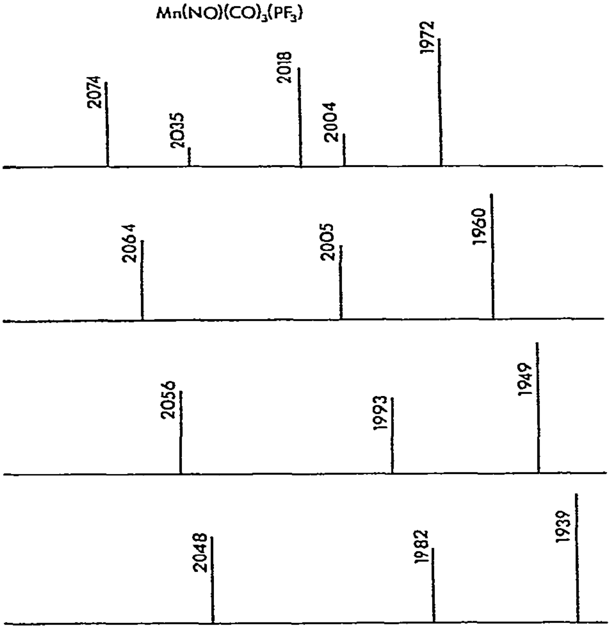

Fig. 1. Schematic representation of the infrared spectra in carbonyl region of $Mn(NO)(CO)_3(PF_3)$ (top) and the successive methanol solvolysis products. Top spectra in hexane, others in methanol/hexane.

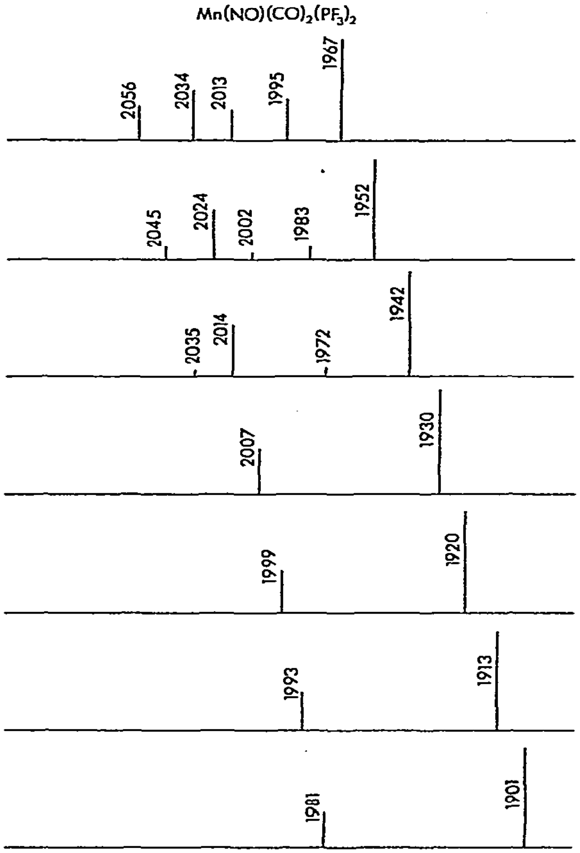

Fig. 2. Schematic representation of the infrared spectra in carbonyl region of $Mn(NO)(CO)_2(PF_3)_2$ (top) and six successive stages of solvolysis. Top spectra in hexane, others in methanol/hexane.

For the mono- and diphosphine compounds, the third and sixth stages of solvolysis yield the complexes $Mn(NO)(CO)_3[P(OCH_3)_3]$ and $Mn(NO)(CO)_2[P(OCH_3)_3]_2$, respectively. The spectra at these terminal stages are very similar to the spectra of the triphenylphosphite complexes prepared and characterized by Wawersik and Basolo[9] (an X-ray crystal structure on the analogous triphenylphosphine complexes has been determined by Enemark and Ibers[10]). Thus it appears that at the limit of solvolysis, and generally many stages before this limit, those isomers with the phosphites axial and the nitrosyl equatorial become the preferred product. The other isomers have been quantitatively converted into this preferred isomer product.

Since solvolysis produces one isomer from a group of isomers, it is necessary to determine whether this was merely selective solvolysis of one isomer of the mixture, or whether it resulted from a shift of equilibrium upon solvolysis. The quantitative conversion certainly suggests the latter possibility. In addition, a solvolysis reaction was allowed to progress about half way to the first stage and then the unreacted parent recovered and reexamined by infrared. If the first alternative above is correct, the spectra will be radically changed owing to the enrichment of the recovered material in the unsolvolyzed isomers. In the later case, the infrared spectra will be completely

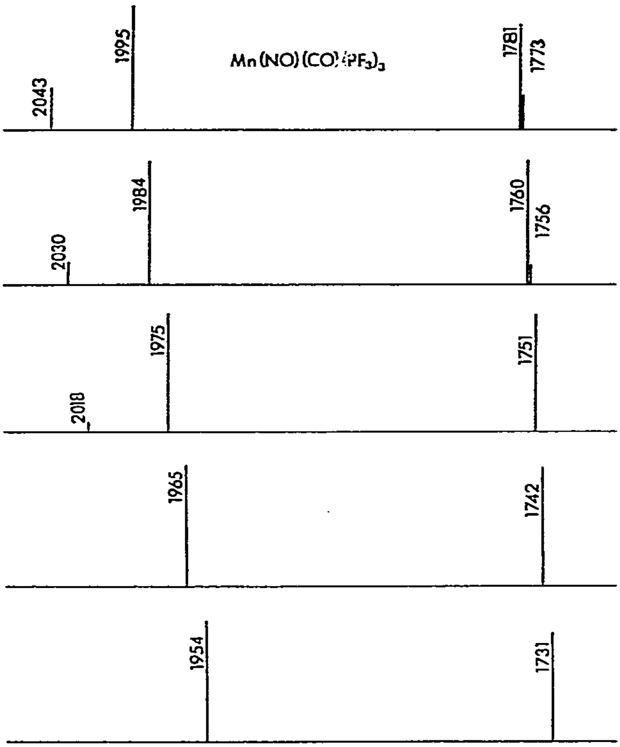

Fig. 3. Schematic representation of the infrared spectra in the carbonyl and nitrosyl regions of Mn(NO)(CO)(PF_3)$_3$ (top) and four successive stages of solvolysis. Top spectra in hexane and others in methanol/hexane.

unchanged since no matter what path the solvolysis follows, the parent isomers will readjust their concentration through isomerization to return to the original equilibrium point. The infrared spectra of the recovered parent in this experiment was always identical to that of the original mixture clearly indicating rapid isomerization. This was true for the mono-, di-, and triphosphines.

DISCUSSION

The reaction of Mn(NO)(CO)$_4$ with PF_3 under thermal-high pressure conditions yields all of the compounds of the general formula Mn(NO)(PF_3)$_x$(CO)$_{4-x}$ except Mn(NO)(PF_3)$_4$.

Gas-liquid partition chromatography of these compounds shows evidence for only one species even under highly efficient conditions. If the structure is based on a trigonal bipyramid, there can exist four, five, and four geometric isomers for the mono-, di-, and triphosphines or two, three, and two if the nitrosyl group is restricted to the equatorial plane.

The presence of several isomers in each composition is certain, based on an examination of the infrared spectra. This is most clearly shown in the nitrosyl stretches. There are two, three, and two vibrations for the three phosphines. As noted above, these are the number of isomers expected when the nitrosyl group is equatorial. The number of bands present in the carbonyl region is also consistent with the presence of the restricted number of isomers.

It is interesting to further consider the structures of the isomers. Several arguments can be invoked to suggest that the compounds are trigonal bipyramidal with the nitrosyl group equatorial. The number of isomers present as indicated by the number of nitrosyl and carbonyl bands is in agreement with this assignment as noted. In addition, the X-ray structure of related triphenylphosphine compounds shows them to be trigonal bipyramidal with the nitrosyl equatorial and the organic phosphines axial[10]. Extrapolation through the solvolysis series shows that one of the isomers in each of the $Mn(NO)(CO)_3(PF_3)$ and $Mn(NO)(CO)_2(PF_3)_2$ series has the same structure as the phosphite complexes of reference 10. Finally, arguments based on earlier work[2] show that ligands have definite site preferences in the trigonal bipyramid structure. The poorer π-bonding groups favor axial sites and groups like $PF_x(CF_3)_{3-x}$, which are slightly better at π-bonding than CO, prefer the equatorial sites. The nitrosyl group is generally thought to be a slightly better π-bonder than either CO or PF_3[11].

That the species are undergoing rapid isomerization is shown by the solvolysis studies. From the data of Figs. 1, 2 and 3 the isomer composition can be seen to be shifting as the degree of solvolysis changes. This is further confirmed by the recovery of unchanged parent following partial solvolysis.

The chemistry of these systems shows that the exchange and substitution of CO and PF_3 is much too slow to allow the isomerization to proceed by any mechanism other than an intramolecular process.

Our data provides no information relative to the actual mechanism of isomerization. However, the Berry model[4] seems quite plausible. The equatorial nitrosyl group could be the fifth unmoving group during the axial and equatorial exchange of the other four groups. However, for the diphosphine, such a simple one-step process would not allow for the direct exchange between all three isomers. It is necessary that at least a low concentration of an intermediate be formed in which the nitrosyl is axial. This intermediate would be in too low a concentration to be seen by infrared.

The variable temperature ^{19}F NMR data are somewhat unclear as to whether the intramolecular inversion can be brought within NMR times at low temperatures. For the monophosphine, the basic doublet remains fairly sharp over the 30° to −120° temperature interval implying no slowing of the equilibrium. For the diphosphine, the second order spectrum consists of two main spikes ($N = 1319$ Hz). Three sets of weaker peaks (apparently unresolved multiplets) surround each of the principle spikes in a mirror image pattern. The spectrum is similar to that shown in other papers[12,13]. On cooling, definite spectral broadening occurs and finally a new spectrum reappears which is qualitatively similar to the room temperature spectrum, yet which has definite changes in the relative separation of the lines. The separation of the main spikes has remained essentially unchanged but the $J(PP)$ coupling has changed from 87 to 137 Hz in the low temperature spectrum. Certainly these changes do not appear like usual cases of variable temperature phenomena in which as the temperature is lowered, the spectra are broadened, then lost almost altogether, and finally totally new spectra appear at yet lower temperatures.

In the normal variable temperature spectral example, the two species involved are chemically identical, have the same energies and are therefore present in the same concentration. With these manganese compounds, the isomers are not identical, they do not necessarily have exactly the same energy and therefore will not be present in the same amount. There can be, in addition to a tendency to slow down an exchange, a tendency to change the isomer concentration. With the diphosphines, it seems possible that at low temperatures, only one isomer is left. This isomer would be one of the C_{2v} isomers having equivalent PF_3 groups, thus a spectrum similar to, yet not identical to, the time average spectra.

The infrared frequencies in the carbonyl and nitrosyl regions can be tentatively assigned to the various isomers using the solvolysis data. The disappearance of all but the isomer in which the phosphites are axial allows the assignment of that PF_3 isomer to be made through an extrapolation procedure. For the monophosphine and triphosphine, the remaining bands are clearly assigned to the second isomer. For the diphosphine where three isomers are present, the assignment is based on the assumption that the C_{2v} (equatorial) isomer will disappear more rapidly than the C_s isomer which will in turn be lost leaving the C_{2v} (axial) isomer as the surviving species. This assignment is shown in Table 1.

The difficulty experienced in preparing the tetraphosphine does not indicate to us any inherent instability. To the contrary it has inevitably been found in metal carbonyl-trifluorophosphine systems that increasing PF_3 content means increased thermal and general handling stability. The stability of the compounds increases through the first three stages of PF_3 substitution and should continue to the fourth. However, it is also true that the rate of substitution decreases, frequently markedly, as the degree of substitution increases. This slowness necessitates more vigorous reaction conditions which we feel in this nitrosyl system has overtaken the enhanced stability under the thermal and photochemical preparative conditions thus far tried. Apparently, Kruck has thus far been unable to prepare $Mn(NO)(PF_3)_4$ by his direct synthesis approach that has yielded so many trifluorophosphine compounds[14].

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