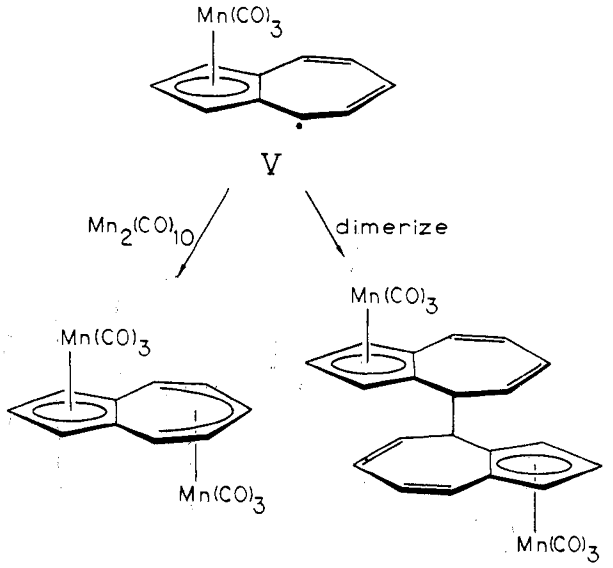
moieties for electron density.] In keeping with this proposal, it may be noted that the mean Mn–CO bond distance in other compounds (where there *is* competition for π-electron density) is greater, *viz.*, 1.823 Å in $Mn_2(CO)_{10}$,[50] 1.823 Å in $HRe_2Mn(CO)_{14}$,[51] and 1.836 Å in $HMn(CO)_5$.[52]

Discussion

The results of the present structural analysis would appear to strengthen our previously stated ideas[17] on the reaction of azulene with transition metal carbonyls. If the initial reaction produces an intermediate such as V, then the present complex *trans*-$C_{10}H_8Mn_2(CO)_6$ (VI) and the $[C_{10}H_8Mn(CO)_3]_2$ of Burton, *et al.*[3] (VII), are to be expected as products. The particular factors that favor the formation of one product rather than the other have yet to be determined, but it would seem likely that manganese-rich VI will be preferentially formed in solutions containing an excess of dimanganese decacarbonyl, while dimeric VII will form in solutions containing an excess of azulene. However, the limited stability of VII as compared to VI will complicate the over-all pattern.

Intermolecular Contacts

Figure 5 shows the packing of molecules within the crystal lattice. *Quantitative* data on intermolecular interactions are collected in Table VIII. There are no abnormally short contacts, thus confirming that the crystal consists of a discrete molecular unit of *trans*-$C_{10}H_8Mn_2(CO)_6$. Shortest contacts of each type are: carbon···hydrogen, 2.83 Å; carbon···oxygen, 3.21 Å; oxygen···oxygen, 3.07 Å; oxygen···hydrogen, 2.58 Å; hydrogen···hydrogen, 2.43 Å.



V

VI

VII

Acknowledgments.—This work has been generously supported by the National Science Foundation (Grant No. GP-8077) and the Advanced Research Projects Agency (Contract SD-88).

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Metal Carbonyl–Phosphorus Trifluoride Systems. VI. Manganese Pentacarbonyl Hydrides and Perfluoroalkyls

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Manganese pentacarbonyl hydride reacts with phosphorus trifluoride under the influence of uv irradiation to yield species of all possible compositions $HMn(PF_3)_x(CO)_{5-x}$. The mixtures which result can be separated by gas–liquid partition chromatography yielding moderately stable, volatile liquids having properties quite similar to those of the parent. Substitution of PF_3 is also found to occur in carbonyls of the type $R_fMn(CO)_5$ where R_f = HCF_2CF_2, CF_3, and CF_3CO. Geometric isomers are readily isolated for these alkylmanganese compounds but not for the hydride, even under highly efficient conditions. Very strong evidence is given for the presence of nonresolvable isomers in the various hydride compositions and the possible reasons for this nonresolvability are discussed.

Introduction

The remarkable similarity between the properties of metal carbonyl complexes and their phosphorus trifluoride substituents has been adequately demonstrated.[2] It was felt that a study of the substitution of phosphorus trifluoride into manganese pentacarbonyl hydride should be undertaken in order to complement both the studies that have already been done[2a] and a study of the $HCo(CO)_4$–PF_3 system that was then in progress.

It became important to study the $HMn(PF_3)_x(CO)_{5-x}$ compounds in an attempt to shed further light on the

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[1] This work was submitted to the Graduate School of Florida State University for partial fulfillment of the requirements for the degree of Master of Science.

[2] (a) R. J. Clark, J. P. Hargaden, H. Haas, and R. K. Sheline, *Inorg. Chem.*, **7**, 673 (1968), and earlier references in the series; (b) Th. Kruck, *Angew. Chem. Intern. Ed. Engl.*, **6**, 53 (1967); this is an excellent review of totally substituted trifluorophosphine complexes.

stereochemistry of these species. After the discovery of $HMn(CO)_5$, Hieber and Wagner[3] pointed out the remarkable similarity between it and $Fe(CO)_5$ and suggested that this manganese compound was a pseudoiron carbonyl with the hydrogen atom plus the manganese atom acting together as an iron atom. For some time, the high-field proton shift was cited in support of this hypothesis, but it is now believed that the nmr data do not necessarily need to be so interpreted.[4]

Several recent studies have shown that the structure of $HMn(CO)_5$ should be interpreted in terms of six-coordination rather than five-coordination. Notably, the infrared spectrum of $HMn(CO)_5$ has recently been shown to be readily interpretable on the basis of C_{4v} symmetry.[5] This is in agreement with the earlier X-ray structure of the solid[6] which shows carbonyl groups essentially occupying five of the six corners of an octahedron with the sixth site presumably being occupied by a hydrogen atom.

If manganese pentacarbonyl hydride is a rigid six-coordinate structure, then substituents of the type $HMn(PF_3)_x(CO)_{5-x}$ should be isolable into geometric isomers. There can exist two, three, three, two, and one isomers for mono-, di-, tri-, tetra-, and pentasubstitution, respectively. A reduction in the number of isomers could be attributed to a number of causes such as nonrandom substitution or stereochemical nonrigidity.

A study of the $HMn(CO)_5$–PF_3 as well as some R_f-$Mn(CO)_5$–PF_3 systems was undertaken to shed some light on these and other questions. It was felt that, even if the hydrides were not stereochemically rigid, the perfluoroalkyl-substituted manganese compounds would be.

Experimental Section

Manganese pentacarbonyl hydride was prepared by the acidification of manganese pentacarbonyl anion with phosphoric acid using the procedure of King[7] with only slight modification. The contamination by tetrahydrofuran was kept low by heating the flask containing the "dry" $NaMn(CO)_5$ to 80° for 1 hr under high vacuum. The final hydride was freed from water by vacuum distillation over 4A molecular sieves.

The material $HC_2F_4Mn(CO)_5$ was prepared by the procedure of Treichel, Pitcher, and Stone.[8]

Trifluoroacetylmanganese pentacarbonyl was formed from the reaction of the $Mn(CO)_5^-$ anion with trifluoroacetic anhydride.[9]

Phosphorus trifluoride from Ozark Mahoning Co. was freed from its impurities first by water scrubbing and then by a series of trap-to-trap distillations from −115° baths.

The reaction of $HMn(CO)_5$ was induced by ultraviolet irradiation using a 1000-W A-H6 mercury lamp. In a typical reaction, 0.4 g (2 mmol) of hydride was distilled through vacuum manipulation into a 500-ml flask which was equipped with a high-vacuum stopcock. Addition of 15 mmol of PF_3 resulted in a pressure of about 0.75 atm at room temperature. The vessel was irradiated and periodically the amount of evolved CO was determined by pressure–volume measurements with the flask immersed in liquid nitrogen. This evolved CO was also pumped off periodically at these temperatures. For the preparation of up to the first four stages of substitution, Pyrex flasks and Pyrex velocity tubes on the uv lamp were used. Mixtures of hydride species were always obtained. Since the substitution is sequential, the general over-all composition was controlled by the time of irradiation. However, for the final stage of substitution, Vycor or quartz apparatus was found to yield much faster substitution. Nearly pure $HMn(PF_3)_5$ was obtained when the CO was removed regularly.

The excess ligand gas was separated from the reaction product by vacuum distillation at −78°, and then the hydrides were separated from a low-volatility yellow residue by vacuum distillation at room temperature using a limited time of about 10 min.

Separation of the reaction mixture was accomplished by gas–liquid partition chromatography. For most species, a 7.5-m column of 40% DC-702 silicone oil on Kromat FB (30–60 mesh) was used in an Aerograph A-700 Autoprep. The column temperature was 60° and the injector and detector temperatures were not more than 30° hotter. Helium was the carrier gas with a flow of 50 cm³/min. These components were eluted in order of decreasing molecular weight and were collected in traps immersed in a Dry Ice–acetone mixture. Manual injection and automatic collection were usually employed. The purity of the separated components was tested by injecting a sample back into the chromatograph under analytical conditions. Water was removed from the isolated species by vacuum distillation through activated 4A molecular sieves. Shorter columns of 4–5 m were used profitably when only the monophosphine was being collected. For the separation of tetra- and pentaphosphine, a 7.5-m 40% diisodecyl phthalate column on Chromosorb P was used. The tetraphosphine could be obtained pure on the longer silicone column only when the concentration of the pentaphosphine was low. The retention times of the species with lower substitution became unmanageably long on the phthalate column.

It was not found convenient to separate all components from one reaction mixture. Usually only three components were present in sufficient quantity to make trapping practical. Several preparations could be mixed and all five phosphine species trapped during each cycle. Injection quantities varied from 12 to 80 μl. The lower quantities were necessary to get clean separation of the highly substituted species, while the larger quantities could be used with the species of lower PF_3 content. Table I contains representative irradiation times necessary to yield the various components as major constituents (up to 50%).

TABLE I

Species	Rel retention times	Irradiation time, min[a]	Melting range, °C
$HMn(CO)_5$	1.00	. . .	−25
$HMn(CO)_4(PF_3)$	0.61	105	−56 to −52
$HMn(CO)_3(PF_3)_2$	0.36	300	−73 to −51
$HMn(CO)_2(PF_3)_3$	0.25	520	≤−108
$HMn(CO)(PF_3)_4$	0.20	790	−56 to −24
$HMn(PF_3)_5$	0.18	1400	+18.5

[a] Approximate time needed to produce a mixture having the listed over-all species composition under the typical experimental conditions: 2 mmol of $HMn(CO)_5$, 15 mmol of PF_3, A-H6 lamp, Pyrex flask, and frequent CO removal.

Attempts to separate the possible geometric isomers for each composition of the hydride species were not successful. Nine different columns and various temperatures and flow rates were tried. Attempts were even made to look for differences in head and tail cuts of some compositions.

Since the hydride species possess a vapor pressure of about 20 torr, their molecular weights were determined by the vapor density method.

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[3] W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 339 (1958).

[4] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 389 (1965). A historic review is presented concerning the problem of the structure of $HMn(CO)_5$.

[5] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).

[6] S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *ibid.*, **86**, 2289 (1964); *Inorg. Chem.*, **3**, 1491 (1964).

[7] R. B King, *Organometal. Syn.*, **1**, 158 (1965).

[8] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

[9] See ref 7, p 148.

The manganese content was determined by the use of atomic absorption. Known amounts of hydride samples and standard manganese solutions were diluted in 95% ethanol and used directly from this medium. The hydride was treated with a small amount of base and allowed to stand for 24 hr and then acidified before the analysis.

The di- and trisubstituted species were sent to the Mikroanalytisches Laboratorium in Bonn, Germany, for carbon and fluorine analyses.

Geometric isomers of the species $HC_2F_4Mn(CO)_4(PF_3)$ were produced in two ways. In the first, 0.3 g (1.0 mmol) of $HC_2F_4Mn(CO)_5$ was distilled into the reaction vessel described for the hydride work and then 15 mmol of PF_3 was added to the flask. The flask was irradiated by the full intensity of a Pyrex-filtered A-H6 lamp for 17 hr at room temperature with the evolved CO being removed periodically at −196°. The ligand gas was removed and the products were separated by gas–liquid partition chromatography. For this separation, a 3-m column of 30% DC-702 on Chromosorb P was used. The temperature was 68° and the flow was 70 cm^3/min. The products of prime interest were the two major peaks in the chromatogram just preceding the peak of the parent compound $HC_2F_4Mn(CO)_5$. The retention times relative to the parent under these conditions were 0.61 and 0.44. Other peaks at yet earlier times were present in the chromatogram and these belonged to more highly substituted species and species of the series $HMn(PF_3)_x(CO)_{5-x}$. The latter were identified by the comparison of their retention times with those of known hydride species.

A second method for the formation of the geometric isomers of $HC_2F_4Mn(CO)_4(PF_3)$ involved the reaction of C_2F_4 with purified $HMn(CO)_4(PF_3)$. About 0.5 g (2 mmol) of $HMn(CO)_4(PF_3)$ was distilled into a 50-ml stainless steel pressure vessel *in vacuo*. Then 11 ml of *n*-pentane was distilled into the reaction vessel followed by 6 mmol of tetrafluoroethylene. When the reaction vessel reached 34°, the internal pressure of the reactants was about 5 atm. After 22 hr at this temperature, the unreacted C_2F_4 was vented into a hood. The pentane solution was decanted and the reaction vessel was thoroughly rinsed to remove the product. The solvent was vacuum distilled from the isomers at −50°. The two monosubstituted geometric isomers were separated and collected under the same conditions as in the preceding preparation of $HC_2F_4Mn(PF_3)_{5-x}(CO)_x$.

Species of the two systems $CF_3COMn(CO)_5$–PF_3 and $CF_3Mn(CO)_5$–PF_3 were produced by the reaction of the trifluoroacetyl compound with PF_3. Trace amounts of substituents were produced when the acetyl compound was irradiated in the presence of PF_3 by the procedure described earlier. Most of the material decomposed to nonvolatile products, but a 7.5-m 40% DC-702 column at 95° showed the presence of 18 components in the remaining volatile fraction. These species have not yet been isolated.

The following approach which resulted in much less decomposition did not use irradiation. Trifluoroacetylmanganese pentacarbonyl (1 mmol) was placed in the reaction vessel used for hydride substitution. After the vessel was evacuated, 10 mmol of PF_3 was added. A thermal reaction of PF_3 with $CF_3COMn(CO)_5$ was allowed to take place for 17 hr at 80°. Carbon monoxide and phosphorus trifluoride were removed in the same manner as described for the hydride substitution. The reaction mixture was separated by a 2-m column of 30% DC-703 on Chromosorb P. The column temperature was 50° and the flow rate was 60 cm^3/min. Trace amounts of $CF_3COMn(CO)_5$ were present. The major products were the two geometric isomers of $CF_3COMn(CO)_4(PF_3)$. Unfortunately, one geometric isomer was contaminated with $CF_3Mn(CO)_5$ which could not be cleanly separated from it on this short column. The $CF_3Mn(CO)_5$ was identified by its characteristic C–F absorptions in the infrared spectrum which differs from the C–F absorptions of the trifluoroacetyl derivatives. About 25% of the reaction mixture was shown to be higher substituted acetyl derivatives and substituted $CF_3Mn(CO)_5$ derivatives.

The infrared spectra of the various manganese compounds were obtained on a Perkin-Elmer 521, calibrated by gaseous DCl and NH_3.[10] Solutions of approximately 1 μl of compound to 200 μl of *n*-hexane were generally used for determining the liquid spectra. A 10-cm gas cell at a pressure of 1 torr was used for the gas-phase spectra.

Anal. Calcd for $HMn(CO)_4(PF_3)$: Mn, 21.5; mol wt, 256. Found: Mn, 21.6; mol wt, 257. Calcd for $HMn(CO)_3(PF_3)_2$: Mn, 17.4; C, 11.39; F, 36.2; H, 0.32; mol wt, 316. Found: Mn, 17.5; C, 11.38; F, 37.0; H, 0.67; mol wt, 316. Calcd for $HMn(CO)_2(PF_3)_3$: Mn, 14.6; C, 6.39; F, 45.5; H, 0.27; mol wt, 376. Found: Mn, 14.6; C, 6.42; F, 46.0; H, 0.34; mol wt, 373. Calcd for $HMn(CO)(PF_3)_4$: Mn, 12.6; mol wt, 436. Found: Mn, 12.6; mol wt, 433. Calcd for $HMn(PF_3)_5$: Mn, 11.1; mol wt, 496. Found: Mn, 11.6; mol wt, 493.

Results

Manganese pentacarbonyl hydride and phosphorus trifluoride have been shown to react extensively in the presence of Pyrex-filtered uv light resulting primarily in the substitution products of the type $HMn(PF_3)_x(CO)_{5-x}$ where x ranges from 1 to 5. The final stage of substitution becomes quite slow with Pyrex apparatus, but in Vycor or quartz, it is much faster. There is also formed a small amount of a yellow residue of low volatility which has been tentatively identified primarily as species of the dimanganese series $Mn_2(PF_3)_x(CO)_{10-x}$.

The volatile hydride species have been identified by several techniques. Since all of the species from the pentacarbonyl to the pentaphosphine are readily separable by gas–liquid partition chromatography, a study of the peaks as a function of the degree of reaction allows a rapid compositional assignment. It requires only the assumption of the sequential replacement of carbonyl groups. The lowest molecular weight compound $HMn(CO)_5$ is the last to be eluted and the highest molecular weight species $HMn(PF_3)_5$ is the first. The species with a relative retention time of 0.61 is the first to be formed from the pentacarbonyl and should be the tetracarbonyl. Its formation is followed *in turn* by those with progressively shorter retention times and higher degrees of substitution. The retention times can be seen to change systematically through the series as shown by the data of Table I. This general pattern of retention and formation has been observed in all other metal carbonyl–trifluorophosphine systems studied thus far. The approximate time required to cause each stage of reaction to take place in Pyrex apparatus is also shown in Table I.

Gas chromatography which allows the tentative identification of the species is also useful for their isolation. Each composition yields one sharp, symmetrical peak, and on the 7.5-m DC 702 column, an efficiency of 3500 theoretical plates was obtained. Each compound is stable to general vacuum manipulation, molecular sieve drying, etc., and reinjection shows them to be chromatographically pure.

The analytical data shown in the Experimental Section on the isolated fractions give good agreement with the predicted compositions for each of the species. They are monomeric as shown by the vapor density measurements.

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

The trifluorophosphine substitution species of manganese pentacarbonyl hydride are all colorless liquids which have vapor pressures of the order of 20 torr at ambient conditions. The approximate melting ranges are shown in Table I. Since these materials appear to become glassy solids rather than crystalline, it is not certain what significance can be connected with these ranges. As the degree of PF_3 substitution increases, the stability of the intermediates with respect to air oxidation increases. The parent $HMn(CO)_5$ reacts rapidly with air at $-78°$ and becomes dark red. The monosubstituted intermediate colors more slowly than the parent at $-78°$. The disubstituted complex slowly turns yellow in air at room temperature while the higher substituted species show no evidence of air oxidation. The complete series of hydrides is thermally stable under ambient conditions when they are sealed in evacuated ampoules.

Attempts to resolve the expected geometric isomers for the intermediate species (assuming either a pentacoordinate or octahedral structure) did not succeed. Nine columns were tried in an attempt to bring about separation of the isomers. Forecuts and tailcuts of each chromatographic peak showed the same infrared patterns. This implies that the peak is composed of only one compound. If two components were in one peak, there would probably be some degree of separation even though the peak may appear symmetrical. The probability that geometric isomers will have exactly identical retention volumes, so that they appear homogeneous, is extremely small.

In contrast to what is normally encountered with substituted metal carbonyls, the infrared spectra are of little value in giving definitive identification of the individual species. Frequently, when simple substitution takes place in mononuclear metal carbonyls, group theory will not only allow one to distinguish between various isomeric possibilities, but it will give the first experimental clues as to the actual degree of substitution. However, this is not found in the present case.

The infrared spectra are shown in Table II. The hydride bands of the various species occur in the 1780–1850-cm^{-1} region, are weak and broad (about 20 cm^{-1} at half-height), and shift progressively about 9–12 cm^{-1} to higher frequency for every degree of substitution. This band shows more clearly than the hydrogen analysis that the species are indeed hydrides. The gas spectrum of a typical hydride mixture in a DCl atmosphere showed a slow weakening in intensity of the 1800-cm^{-1} hydride band and the appearance of the deuteride stretch at about 1290 cm^{-1}. This reconfirms the fact that the stretch at about 1800 cm^{-1} belongs to a hydride atom.

The only absorptions in the ir region of 4000–700 cm^{-1} other than hydride bands are found in the 2125–1950- and 800–950-cm^{-1} regions characteristic of terminal carbonyls and PF_3 groups, respectively. Spectra of $HMn(CO)_3(PF_3)_2$ which are characteristic of the whole series are shown in Figure 1.

Table II

Infrared Spectra of the Hydride-Substitution Series (cm^{-1})

HMn-$(CO)_5$	HMn-$(CO)_4(PF_3)$	HMn-$(CO)_3(PF_3)_2$	HMn-$(CO)_2(PF_3)_3$	HMn-$(CO)(PF_3)_4$	HMn-$(PF_3)_5$
2118 vw	2101 w	2086 m	2071 vvw	2038 vs	
2113 sh	2045 sh	2076 m	2058 w	2011 m	
2046 w	2035 m	2031 m	2052 w	1989 vw^{a}	
2017 vvs	2016 vs	2027 m	2023 w		
2008 sh	2009 sh	2011 vvs	2007 vs		
1982 w^{a}	1985 vw^{a}	1976 w^{a}	1975 vw^{a}		
1967 vw^{a}	1968 vw^{a}	1969 vw^{a}	1964 vw^{a}		
1780 vw	1790 vw	1806 vw	1823 vw	1835 vw	1845 vw
	897 m	911 m	921 m	941 m	962 vw
	888 s	899 s	902 s	908 s	914 vs
	875 s	884 sh	890 s	902 sh	906 vs
	867 sh	882 m	873 s	882 m	901 sh
		873 m	858 s	869 w	880 vw
		863 s	852 sh	858 s	868 sh
		855 sh		851 m	857 s
					849 m

[a] Probable C^{13} stretches.

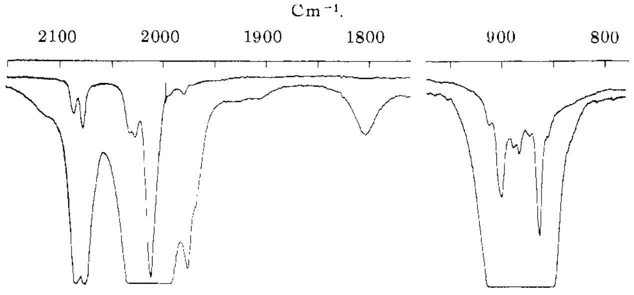

Figure 1.—Infrared spectra of $HMn(CO)_3(PF_3)_2$ in hexane. Concentrations: 7 and 0.7 µl/200 µl of hexane.

However, close examination of the carbonyl region shows that the spectra are not characteristic of any single species that might be expected. As an example, the material clearly shown to be monomeric and of a composition $HMn(CO)(PF_3)_4$ has three carbonyl stretching frequencies: 2038 (vs), 2011 (m), and 1989 (vw) cm^{-1}. The 1989-cm^{-1} vibration can be attributed to a C^{13} mode, but the medium-strong 2011-cm^{-1} vibration is too intense to be so assigned. For one single monomeric monocarbonyl, there can obviously be only one fundamental stretching vibration. Thus one is forced to conclude that there is either an extra source for absorption in this region or that there is more than one isomer present. This general pattern of excess absorptions is observed with all of the intermediate species.

In order to shed some light on these questions, phosphorus trifluoride substitution into other related manganese compounds has been studied.

The geometric isomers of $HC_2F_4Mn(CO)_4(PF_3)$ have been produced by two reaction procedures. In the first, the two species are just two of several products in the uv reaction between $HC_2F_4Mn(CO)_5$ and PF_3 which are isolable by glpc. In the second, they were the sole products of the reaction between $HMn(CO)_4(PF_3)$ and C_2F_4. The identity of the two products produced by the two routes in itself essentially proves the composition of the species. The fact that these two compounds are produced simultaneously and are the first reaction products from the interaction between

$HC_2F_4Mn(CO)_5$ and PF_3 further confirms the composition. Thus in this system as in the molybdenum species,[11] geometric isomers are readily isolated.

The infrared spectra of the $HC_2F_4Mn(CO)_4(PF_3)$ species shown in Table III add further confirmation to the identification of the compounds. Strong absorption occurs only in regions attributable to P–F, C–F, and C–O groups. In the carbonyl region, four and only four major absorptions occur for these two carbonyl compounds.

TABLE III

INFRARED SPECTRA OF THE GEOMETRIC ISOMERS OF $HC_2F_4Mn(CO)_4(PF_3)$ (CM^{-1})

	$HC_2F_4Mn(CO)_4(PF_3)$	
Infrared region	Isomer a	Isomer b
C–O str	2116 m	2071 vvw
	2106 sh[a]	2065 vvw
	2061 s	2040 vs
	2038 vs	2009 vw
	2013 vs	
	1982 vw[a]	
	1970 vw[a]	
C–F	1352 w	1352 w
	1173 vw	1097 m
	1097 m	1083 m
	1081 w	1013 m
	1013 m	997 m
	986 w	
P–F str	915 m	887 s
	903 m	877 s
	882 s	

[a] Probable C^{13} stretches.

Thus these fluoroalkyl species contrast strongly with the hydrides in that the isomers of the former system are readily isolable and extra bands do not appear in the carbonyl region.

In the reaction between $CF_3COMn(CO)_5$ and PF_3, enough work has been done so that a similar statement can be made about the isolability of the isomers. This applies to both the acetyl compounds and the decarbonylated trifluoromethyl series. Greater detail will be reported later concerning these $R_fMn(CO)_5$–PF_3 systems.

A considerable amount of effort has been expended in order to eliminate sources for the extra bands in the carbonyl region of the hydride species other than nonseparable isomers. This was done to show that these bands are not due to volatile or nonvolatile impurities caused by such reactions as disproportionation, polymerization, partial oxidation, etc., during the handling of the species. Analytical chromatograms of solutions from which spectra have been obtained show the presence of only solvent plus the original compound. No other volatile species are seen. The gas-phase spectra are essentially identical with those of the liquid phase except for a small frequency shift. This shows that nonvolatile species have not made any contribution. Since vacuum manipulation can be air free, this eliminates partial oxidation products.

Some of the extra, weak bands at low frequency can be attributed to C^{13} modes, but the weak bands at the higher frequency cannot be assigned in that fashion. It does not seem too reasonable that these are combinations or overtones arising from P–F absorptions. Since the P–F stretching modes occur below 950 cm^{-1}, the combinations or overtones should not appear as high as the carbonyl region. In addition, such values have never been observed in other PF_3 systems.[1,2]

Discussion

Experimental evidence which has been presented in the preceding sections shows that the hydrogen atom has a very unusual role in manganese pentacarbonyl hydride and its trifluorophosphine derivatives. Contrary to the theory that the hydride is buried in the manganese electron cloud and therefore regarded as a pseudo-iron complex, the hydride certainly must influence the stereochemistry of the complex.[4] However, the present work also shows that these complexes probably should not be represented as rigid geometric entities. The evidence implies that the properties of the hydride may be a compromise of the contrasting theories concerning its stereochemistry.

It has been shown that the manganese carbonyl hydride substitution compositions are isolated in very high purity. However, *each* derivative possesses more fundamental carbonyl vibrations than are allowed by group theoretical considerations. These extra bands cannot readily be attributed to any type of coupling or mixing phenomenon. Disproportionation or decomposition does not occur while the infrared spectrum of each compound is being determined. It must, therefore, be assumed that all of the carbonyl vibrations arise from only the trifluorophosphine-substitution compositions. It is concluded that these extra bands must indicate the presence of nonseparable geometric isomers in each composition.

Phosphorus trifluoride derivatives of other metal carbonyls do not consistently exhibit rigid geometric properties. Geometric isomers are found for each PF_3-substituted composition of the octahedral complexes of molybdenum,[11] chromium,[12] and tungsten hexacarbonyls.[12] Substitution products of five-coordinated complexes, however, such as iron pentacarbonyl[13] and cobalt tetracarbonyl hydride[14] do not contain separable geometric isomers. These intermediates also have more carbonyl vibrations in their infrared spectra than group theory arguments predict. The existence of too many bands in the PF_3 substitution series of $Fe(CO)_5$ has been interpreted to be a result of a mixture of nonseparable geometric isomers.[13] It is suggested that the geometric isomers are undergoing rapid internal inversion so that physical separation is impossible.

It is now postulated that manganese pentacarbonyl hydride and its PF_3-substitution products may also undergo a rapid internal inversion so that the geometric isomers of each composition would not be separable.

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(11) P. I. Hoberman and R. J. Clark, *Inorg. Chem.*, **4**, 1771 (1965).

(12) R. J. Clark and A. Kamhawi, unpublished work.

(13) R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).

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X-Ray diffraction, proton resonance, and infrared evidence indicate that the hydrogen occupies a coordination site in its octahedral complexes.[4-6] Because of the small size of the hydride ligand, it may be possible for it to slip between two of the bulkier ligands without producing much steric strain. If the activation energy for this inversion process were small, then the reaction would be extremely rapid.

However, also plausible at this juncture is an exchange mechanism in which the hydrogen ionizes as a proton, leaving behind the five-coordinate $Mn(PF_3)_x(CO)_{5-x}^-$ anion which undergoes an inversion by the re-formation of the hydride, or, alternately, it could be attributed to the random attack of the proton at various positions of the anion to give all possible hydride isomers. By this approach, one need not postulate that the hydride atom is small enough to allow the other groups to pass by it, only that it be able to ionize. The p*K* of the $HMn(CO)_x(PF_3)_{5-x}$ species can be estimated to be 7—the same as that of the parent carbonyl.[3]

The substitution of bulky preferentially σ-bonding organic phosphines into manganese pentacarbonyl hydride results in the formation of geometric isomers.[15] These ligands place a greater electron density on the central metal atom which results in an increase in the metal–hydrogen bond strength leading to a decrease in acidic properties. If the inversion takes place by a proton ionization path, then the isolability of geometric isomers is perhaps explicable.

However, it cannot necessarily be concluded that this is the only explanation for the occurrence of isomers in species such as $HMn(CO)_4(PR_3)$. In the first place, all acidic properties are probably not lost. We could not find any data for the p*K* of any organic-phosphine-substituted manganese hydrides. However, the p*K* of $HCo(CO)_4$ changes from 1 to 7 on going to $HCo(CO)_3P(C_6H_5)_3$.[16] A similar change with $HMn(CO)_4P(C_6H_5)_3$ would yield a p*K* of 12–14 which might still allow for rapid exchange. The increase in size of the ligand and the effect of its steric hindrance would probably make inversion much slower and would be a far more important factor than p*K* decrease.

The relative behavior of manganese pentacarbonyl hydride toward fluoro and organic phosphines is paralleled by a similar relationship in iron carbonyls. In the iron carbonyls, no ionization is possible. The $Fe(PF_3)_x(CO)_{5-x}$ species show every sign of undergoing internal inversion, whereas compounds of the types $Fe(CO)_4(PR_3)$ and $Fe(CO)_3(PR_3)_2$ do not.[17] Experiments in progress[18] show clearly that very little change in the $Fe(PF_3)_x(CO)_{5-x}$ species needs to be made to change the isomer mixture. The change to which we refer is solvolysis of the P–F bond to P–OR groups.

The existence of a rapid inversion mechanism for manganese pentacarbonyl hydride is consistent with $C^{13}O$-exchange experiments performed by Kaesz, *et al.*[5] In a rigid octahedral structure, the hydride should exert a *trans* effect on the axial carbon monoxide so that $C^{13}O$ enrichment at this position would occur at a different rate than for the radial positions. Their results showed that enrichment occurs at the same rate for substitution at both positions. This equivalence of the carbonyls to exchange could be brought about by a rapid internal inversion.

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The Reactions of Lewis Bases with Methylmanganese Pentacarbonyl

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The reactions of a variety of Lewis bases with $CH_3Mn(CO)_5$ were examined as a function of time by H^1 nmr and infrared spectral methods. Triphenylphosphine, triphenylarsine, and trimethyl phosphite react with $CH_3Mn(CO)_5$ to yield a mixture of *cis*- and *trans*-$CH_3COMn(CO)_4L$ complexes. Other phosphorus donor ligands, triphenylstibine, and various amines yield exclusively *cis*-$CH_3COMn(CO)_4L$ derivatives. All acetylmanganese complexes, except those with L = amine, were shown to decarbonylate upon heating to yield exclusively *cis*-$CH_3Mn(CO)_4L$. The reaction equilibria are affected by variations in the nucleophilicities and steric requirements of the ligands. A modified methyl-migration mechanism is able to explain the stereochemistry of the products of the decarbonylation reaction.

Introduction

The reactions of methylmanganese pentacarbonyl, $CH_3Mn(CO)_5$, with amines[2] and a number of phosphine and arsine derivatives[3,4] to produce monoligated acetylmanganese tetracarbonyl complexes, $CH_3COMn(CO)_4L$, have been known for some time. More

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