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Methanol Solvolysis of Metal Trifluorophosphine Complexes

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Complexes of the type $Co(NO)(CO)_x(PF_3)_{3-x}$ readily undergo partial or complete solvolysis with methanol or, with greater facility react with sodium methoxide in methanol with replacement of –F by –OCH_3. The complexes with a lower degree of solvolysis are isolated by gas-liquid chromatography and identified. The volatility of the complexes decreases rapidly as the degree of solvolysis increases. The stretching frequencies of the characteristic carbonyl and nitrosyl bands shift to progressively lower values as the degree of solvolysis increases. This solvolysis reaction appears to be the simplest procedure to prepare complexes of the type $PF_2(OCH_3)$ and $PF(OCH_3)_2$. The end product of solvolysis are trimethylphosphite complexes.

Introduction

Work with phosphorus trifluoride as a ligand has shown that it resembles carbon monoxide in many respects.[1-2] As in the case of carbon monoxide, phosphorus trifluoride rarely forms complex compounds with pure sigma acceptors, but it readily forms complexes that are analogous to carbonyl complexes of lower valent transition metals. It also appears that carbon monoxide and phosphorus trifluoride can replace each other nearly randomly.[1]

In spite of these analogies, it is apparent that there must be some differences between carbonyl and trifluorophosphine complexes. Among these differences will be their behavior toward solvents. In the free state, phosphorus trifluoride will undergo slow solvolysis and other reactions with a number of solvents and bases.[3] It is also clear that the complexes are also subject to attack. Studies have shown that trifluorophosphine complexes do not survive a number of solvents such as alcohols, acetone and perhaps even ethers.[1-2]

This paper is a report of the first of a series of detailed studies into the reactivity of PF_3 complexes toward certain solvents and other selected reagents. Specifically it deals with the reaction of methanol or sodium methoxide with primarily the $Co(NO)(CO)_x(PF_3)_{3-x}$ series of compounds. Results concerning the various products formed by the solvolysis of P–F bonds to form $POCH_3$ groups are reported.

Experimental Section

The starting materials for the work were generally prepared by previously published procedures. The $Co(NO)(CO)_x(PF_3)_{3-x}$ complexes were prepared as described earlier[1] and were used immediately after GLC isolation. Sodium methoxide was produced by allowing sodium to react with an excess of absolute methanol.

The general approach to the production of complexes of the $Co(NO)(CO)_x(PF_3)_{3-x}$ species having a lower degree of solvolysis is illustrated in the following paragraphs.

$Co(NO)(PF_3)_2(PF_2OCH_3)$. Equal volumes of $Co(NO)(PF_3)_3$ and CH_3OH were mixed and allowed to stand for about 20 minutes. The excess methanol was removed by distilling the mixture through either 4A Molecular Sieves or granular P_4O_{10}. The liquid mixture of complexes was separated by gas-liquid chromatography on an Autoprep A-700. The conditions were as follows: A 4 m×1/4 in column of 15% DC-703 silicone oil on Kromat FB, flow 70 cc/min at 60°. Injection quantities of up to 50 μl could be used. The compound was trapped at –78° and dried by distilling it at room temperature under vacuum over freshly activated 4A Molecular Sieves.

$Co(NO)(PF_3)(PF_2OCH_3)_2$ and $Co(NO)(PF_2OCH_3)_3$. These species can be isolated in small quantities from the previous preparation, but large yields necessitate a change in conditions. To develop quantities of the species, their preparation requires at least a 2:1 volume ratio of methanol to complex and 8 and 18 hr respectively. Inert gas protection was desirable to prevent partial oxidation. A 2 m silicone column gave adequate resolution and shortened the retention time that would be required on the 4 m column. Considerably shorter reaction times resulted when $NaOCH_3$ solutions in methanol were used. Roughly stoichiometric quantities of methoxide were used.

$Co(NO)(CO)(PF_3)(PF_2OCH_3)$ and $Co(NO)(CO)(PF_2OCH_3)_2$. These two monocarbonyl complexes were prepared under approximately the same conditions as the corresponding products above using the 2 m column for separation.

$Co(NO)(CO)_2(PF_2OCH_3)$. This compound can be obtained as nearly pure product when equal volumes of the pure monophosphine and methanol are mixed and allowed to stand for about 20 minutes. The methanol is removed by the use of 4A Molecular Sieves or P_4O_{10}. The parent is completely solvolyzed and little

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(1) R. J. Clark, *Inorg. Chem.*, 6, 299 (1967) and earlier references in series.

(2) Th. Kruck, *Angew. Chem. Intern. Ed. Engl.*, 6, 53 (1967). A good review showing the scope of the similarity between the ligands CO and PF_3.

(3) A. B. Burg in "Fluorine Chemistry", J. H. Simons, Ed., Academic Press, New York, N. Y., vol. 1, p. 98 (1950).

of the second stage of solvolysis has begun under these conditions. However, since the starting material $Co(NO)(CO)_2(PF_3)$ can disproportionate into $Co(NO)(CO)(PF_3)_2$ and $Co(NO)(CO)_3$ quite readily, a GLC check for purity is advisable. After solvolysis takes place, the tendency for disproportionation to occur drops markedly.

Elution chromatography on either silica or alumina was not particularly successful in separating these species. It seemed to lead to considerable decomposition of some sort.

All of the P—F bonds in a trifluorophosphine complex can be solvolyzed to yield the corresponding trimethylphosphite compounds as illustrated in the following example. About 30 ml of 1.5 *M* $NaOCH_3$ in methanol and 0.3 ml $Co(NO)(PF_3)_3$ were mixed at room temperature in a inert atmosphere and allowed to stand several hours. Most of the methanol was then removed by high vacuum at room temperature. To the residue was added 50 ml of hexane followed by about 5-10 grams of P_4O_{10} in 1 g portions (with cooling) to remove the base and methanol. Finally the filtered hexane solution was evaporated and the product crystallized. It was frequently necessary to pass the hexane solution through a short column of alumina in order to obtain a crystalline product.

In order to obtain infrared data in the carbonyl and nitrosyl regions on the solvolysis products of intermediate to higher degrees of substitution, a series of reactions were run using various sodium methoxide to complex ratios. Known quantities of complex were added to hexane, and various volumes of sodium methoxide in methanol were added. After a few hours of equilibration, the infrared spectra of the hexane solutions were taken. Since the methanol and hexane solutions have limited miscibilities, the spectra were almost as dependent upon the degree of agitation as on the relative concentrations. Still, it is readily possible to sort out the carbonyl and nitrosyl frequencies that result from successively higher degrees of solvolysis.

Infrared data were obtained on a P-E 521 in hexane or in CCl_4 when checking for C—H stretching frequencies. The data reported here were in hexane. NMR data were obtained on a Varian A-60 using TMS as an internal reference. Limited analytical data (used as confirmation of other methods of assignment) were obtained by either Galbraith Microanalytical Laboratories or Pascher Microanalytisches Laboratorium, Bonn, Germany.

Anal. Calcd. for $Co(NO)(PF_3)_2(PF_2OCH_3)$: C, 3.29; H, 0.83; P, 25.47; F, 41.65. Found: C, 3.39; H, 1.07; P, 23.31; F, 39.96. Calcd. for $Co(NO)(PF_3)(PF_2OCH_3)_2$: C, 6.37; H, 1.61; P, 24.65. Found: C, 6.91; H, 1.79; P, 23.65. Calcd. for $Co(NO)(PF_2OCH_3)_3$: C, 9.26; H, 2.34; P, 23.89. Found: C, 10.40; H, 2.64; P, 22.70.

Results

It is quite evident that phosphorus trifluoride complexes of cobalt nitrosyl carbonyl of the type $Co(NO)(CO)_x(PF_3)_{3-x}$ undergo extensive reaction with methanol. The vapor-phase chromatograph peaks of the parent trifluorophosphine complexes rapidly disappear when they are dissolved in methanol. There is no sign of gas evolution which rules out the already unlikely possibility of methanol behaving as a ligand capable of replacing CO or PF_3 in the coordination sphere. Instead, the weight of evidence points to a general solvolysis reaction of the P—F bonds with the formation of $POCH_3$ groups and HF. The solvolysis products can be identified by several different approaches, all giving the same results. These are discussed in the following paragraphs.

As the interaction between any given PF_3 complex and methanol or methoxide proceeds, the volatility of the cobalt species decreases quite significantly. This is readily reflected in their behavior in vacuum. The PF_3 complexes themselves and methanol have similar volatilities, so it is quite difficult to separate them by simple vacuum distillation. However, after a short reaction period, products are formed that are not readily vaporized at −10 to −30° under high vacuum. At these temperatures, methanol can be volatilized in a short time. More extensive reaction yields products that are only slowly volatilized by vacuum at room temperature, and finally after very extensive reaction, reddish oils result that appear to be non-volatile under these conditions. This decrease in volatility would be expected for a series of complexes with an increasing degree of solvolysis.

This general behavior is repeated throughout the monophosphine series, $Co(NO)(CO)_2(PF_x(OCH_3)_{3-x})$; the diphosphine series, $Co(NO)(CO)(PF_x(OCH_3)_{3-x})(PF_y(OCH_3)_{3-y})$; and the triphosphine series, $Co(NO)(PF_x(OCH_3)_{3-x})(PF_y(OCH_3)_{3-y})(PF_z(OCH_3)_{3-z})$. For the sake of simplicity in referring to these compounds, a very specific set of notation has been used in this paper. Thus, the mono-, di-, and triphosphine complexes are referred to as the A, B, and C series and the degree of solvolysis is indicated by a number. Thus, the disolvolysis product of the diphosphine that can have the formula $Co(NO)(CO)(PF_2OCH_3)_2$ is B-2. The parent phosphines are A—O, B—O, and C—O with the latter being the totally substituted complex $Co(NO)(PF_3)_3$. No attempt is made to distinguish between the various potential isomers for a given composition.

Gas-liquid chromatography gives a much better assessment of the species formed. Retention times are usually roughly related to the volatility of related species and if significant differences in volatilities should exist between species, no inversions in retention times are to be expected. As mentioned earlier, one can expect the volatility to drop considerably as each stage of solvolysis takes place.

New species are seen in the gas-liquid chromatograms, which are much less volatile than the parent phosphine. For instance the peak for C—O, $Co(NO)(PF_3)_3$, almost completely disappears after about ten minutes in methanol. In the chromatogram, a new peak appears at a retention time of almost 4 times that of the parent. Presumably this should be assigned to the first solvolysis product C-1. After considerably longer reaction time, or after use of $NaOCH_3$ solution, still another peak appears in the gas chromatogram at still longer retention times. On the basis of the method of formation and the further decrease in volatility, it seems quite rational to assign this species to the disolvolysis product C-2. By the use of this approach, several of the lower solvolysis products of the A, B, and C series were assigned.

For practical isolation of these new compounds from mixtures several approaches can be taken, but preparative-scale gas-liquid chromatography is generally the best procedure. The separation of the parent compounds of the series $Co(NO)(CO)_x(PF_3)_{3-x}$ is done on a 15 m column. However, the solvolysis compounds have an unmanageably long retention time on this column particularly under isothermal operation. Shorter columns of one to four meters are usually employed. The badly tailing methanol is removed by using either P_4O_{10} or 4A Molecular Sieves prior to separation to avoid contamination by the solvent. The species C-1, C-2, C-3, B-1, B-2 and A-1 are readily isolated chromatographically pure.

Limited analytical data were obtained on the isolated species which are in agreement with the above GLC assignments and the assignments that can be made from infrared data.

The infrared spectra for these species are fairly simple in hexane. The bands in the carbonyl region and in the nitrosyl region are intense and sharp. The P—F stretching frequency region of 1000-800 cm^{-1} is considerably more complicated and frequently is not well resolved. Absorption occurs in the 1100-1050 and 800-650 cm^{-1} region in the solvolysis complexes but not in the parents. These are assigned as being due to various modes associated with the $P—O—CH_3$ grouping. Also, the C—H stretching frequencies can be seen when a solvent such as CCl_4 is used.

The bands in the carbonyl and nitrosyl region are the most informative. The 1800 cm^{-1} frequencies immediately confirm that the products are still nitrosyl complexes and the 2000 cm^{-1} region determines whether they are mono-, di-, or triphosphine complexes. The resemblance of the spectra of the isolated complexes to the spectra of the compounds from which they arose makes it apparent that only small changes have taken place during reaction. This again indicates that the reaction is certain to be stepwise solvolysis.

It is readily evident that there is a systematic small shift to lower values in the carbonyl and nitrosyl stretching frequencies as one proceeds through the various solvolysis products. This observation can be used in order to obtain data for complexes that can not be isolated. Thus when $NaOCH_3$ and a trifluorophosphine complex react at various mole ratios, complex spectra are obtained, but spectra which have certain recognizable patterns. From these spectra, data for individual compounds can be assigned. This has been done for the mono- and dicarbonyl series.

In the monophosphine series, two sets of four carbonyl peaks and one set of four nitrosyl peaks can be sorted out of the spectra of the solvolysis mixtures of various reaction compositions. The peaks are assigned successfully to the various solvolysis products by assuming either that there will be a progressive shift in the frequencies or that the compounds are formed sequentially. Both approaches give the same results. The results can be seen clearly in Table I. The A-1 frequencies match those found for the complex that was actually isolated and the spectra for the compound assigned as A-3 matches that reported for the monotrimethylphosphite complex $Co(NO)(CO)_2P(OCH_3)_3$ by Thorsteinson and Basolo.[4] Their compound was prepared by the direct reaction between $P(OCH_3)_3$ and $Co(NO)(CO)_3$. The A-2 assignment as disolvolysis must almost certainly be correct.

The same procedure applied to the spectra of the diphosphine B series gives somewhat similar results. The species B-1 and B-2 are readily assigned and are identical with compounds actually isolated. The bands for the complexes B-3 to B-6 are not completely resolved. However, two new bands (15-20 cm^{-1} half width with indication of substructure) do appear that seem to belong to combinations of B-3 and B-4 and

Table I. Infrared Spectra of Solvolysis Products of $Co(NO)(NO)_x(PF)_{3-x}$ Species

Species	Composition [a]	CO region cm^{-1}	NO region cm^{-1}
A-0	$Co(NO)(CO)_2(PF_3)$	2083, 2037	1817
A-1	$Co(NO)(CO)_2(PF_2OCH_3)$	2071, 2019	1798
A-2	$Co(NO)(CO)_2(PF(OCH_3)_2)$	2062, 2011	1780
A-3	$Co(NO)(CO)_2(P(OCH_3)_3)$ [b]	2050, 1996	1764
B-0	$Co(NO)(CO)(PF_3)_2$	2059	1822
B-1	$Co(NO)(CO)(PF_3)(PF_2OCH_3)$	2047	1810
B-2	$Co(NO)(CO)(PF_2OCH_3)_2$	2035	1798
B-3	$Co(NO)(CO)(PF_2OCH_3)(PF(OCH_3)_2)$	2010 [c]	1760 [c]
B-4	$Co(NO)(CO)(PF(OCH_3)_2)_2$		
B-5	$Co(NO)(CO)(PF(OCH_3)_2)(P(OCH_3)_3)$	1980 [c]	1738 [c]
B-6	$Co(NO)(CO)(P(OCH_3)_3)_2$		
C-0	$Co(NO)(PF_3)_3$	—	1832
C-1	$Co(NO)(PF_3)_2(PF_2OCH_3)$	—	1821
C-2	$Co(NO)(PF_3)(PF_2OCH_3)_2$	—	1809
C-3	$Co(NO)(PF_2OCH_3)_3$	—	1795
C-9	$Co(NO)(P(OCH_3)_3)_3$	—	1708

[a] Where isomers are possible, the most symmetric solvolysis product is given. [b] Values reported by Basolo, reference 4. [c] These bands have a 15-20 cm^{-1} half width and appear to consist of several unresolved bands.

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[4] E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966).

B-5 and B-6. These two bands (in both the carbonyl and nitrosyl regions) appear at progressively lower frequencies from the earlier species. The separation between these broad bands is about twice that between corresponding bands in lower individual complexes such as B-1 and B-2. On extensive reaction, the bands at the lowest frequency in both the carbonyl and nitrosyl regions become sharp again indicating that they belong to the totally substituted complex $Co(NO)(CO)(P(OCH_3)_3)_2$. The data obtained for this latter complex matches well the value reported by Thorsteinson and Basolo.[5] Again, their complex was made by the direct reaction between $Co(NO)(CO)_3$ and $P(OCH_3)_3$.

No effort was made to untangle the nature of the tristrifluorophosphine series beyond C-3. This series has nine solvolysis products and many isomers.

The totally solvolyzed material can be made readily by reacting the complexes with an excess of 1,2 *M* $NaOCH_3$ solution. This was done for the cobalt nitrosyl trifluorophosphine complexes and also for a number of other examples of PF_3 compounds.

The spectra of the cobalt compounds are as would be expected on the basis of data obtained from earlier work on these species. The nitrosyl stretching frequencies occur at the proper extrapolated value. Also the carbonyl absorption, if present, occurs at the value to be expected. In the compounds assigned formulas of $Co(NO)(CO)(P(OCH_3)_3)_2$ and $Co(NO)(P(OCH_3)_3)_3$, no absorption occurs in the 800-1000 cm^{-1} P—F region. There is absorption in the 1000-1200 and 700-800 region as has been observed for species containing $POCH_3$ groups. These compounds are red solids, but they tend to be oils if not purified properly.

The proton NMR spectra were recorded for a few of the cobalt species (A-1, B-1, C-1, C-2, and C-9). All spectra consist of a fairly sharp doublet centered somewhere in the $\sigma = 3.5$ to 3.9 region relative to tetramethylsilane. There is no sign of splitting due to nonequivalent protons or to fluorine coupling. The splitting of the doublet is always about 12 cps. The center of the doublet shifts fairly smoothly from 3.90 for C-1 to 3.72 for A-1 and from 3.90 for C-1 to 3.50 for C-9.

Discussion

It is clear that for many complexes, the fluorines in various trifluorophosphine complexes can be removed sequentially by solvolysis. The properties of the resulting species such as infrared spectra, volatilities and the proton resonance change smoothly with the varying degree of solvolysis.

For some of these cobalt complexes, a number of isomers can exist. However, there is no real information as to which isomers are present or whether there is indeed any isomerization at all. For instance, in the trisolvolysis compound of the triphosphine, three positional isomers could be formed having compositions of $Co(NO)(PF_3)_2(P(OCH_3)_3)$, $Co(NO)(PF_2OCH_3)_3$, and $Co(NO)(PF_3)(PF_2OCH_3)(PF(OCH_3)_2)$. The gas chromatographic peak for C-3 is a single sharp peak. There is no indication of other peaks for C-3 species or any indication that the one peak observed belongs to more than one species. Still it is not certain that the various isomers would be sufficiently different to distinguish on the short columns that must be used for this work.* Also, the sharpness of the CO and NO stretching frequency peaks in the various isolated compounds gives no indication of isomers being present.

The only data that might be attributed to isomerization is found in the CO and NO spectral region of the B-3 to B-6 species. Two broad bands in each region were found for these four compounds and the expected four sharp peaks were not seen. Since the total separation is adequate to have all four peaks clearly resolved by a P-E 521, the broadening could be attributed to several related isomers being present. The compounds B-3 and higher are not sufficiently volatile to be tested by GLC.

The fact that no detectable fluorine coupling takes place makes it impossible to use proton NMR to determine specifically which isomers are formed. Fluorine NMR combined with phosphorus decoupling would probably do the job readily. However, it is felt that the prime form of the solvolysis reaction would cause the replacement of one fluorine from each phosphorus trifluoride ligand before a second is replaced.

Reactions of this sort in which P—F bonds are broken and replaced by other groups may prove quite useful as a procedure for preparing species that are otherwise not accessible. A perusal of recent reviews on Lewis base substitution into metal carbonyls[7,8] shows that although many phosphite complexes are known, only about half of the carbonyl groups can usually be replaced. Further, the substitution is stereoselective yielding only a limited number of the possible isomers. By contrast, PF_3 substitutes almost randomly into all positions, and the various isomers of the various compositions can be isolated. Thus methods such as those discussed in this paper which are capable of converting the PF_3 complexes into phosphites and perhaps other phosphines *in situ* by mild conditions will yield products that will not be readily prepared by other means. However, this method would not be a preferred one. The difficulty in isolating the initial PF_3 complexes in adequate quantity followed by the subsequent loss in recovering pure phosphite solvolysis product would be a serious drawback.

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(5) E. M. Thorsteinson and F. Basolo, *Inorg. Chem.*, *5*, 1691 (1966).

(*) Isomers have been separated in the $Mo(CO)_x(PF_3)_{6-x}$ system.[6]

(6) R. J. Clark and P. I. Hoberman, *ibid.*, *4*, 1771 (1965).

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

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