dichloromethane solutions using a silica gel column. A bright yellow band which separated was collected and saved. Further elution of the column with dichloromethane–acetone solutions resulted in the separation of a dark red band followed by a broad yellow band. An infrared spectrum taken of the material in the second yellow band indicated peaks characteristic of 1-*m*-FC_6H_4-(3)-1,2-$B_9C_2H_{11}^-$ compounds, together with a peak at 11.64 μ characteristic of $C_5H_5^-$ compounds. The red band appeared to be $(C_5H_5)_2$Co[1-*m*-FC_6H_4-(3)-1,2-$B_9C_2H_{10}]_2$Co and the yellow band to be $(C_5H_5)_2$Co(1-*m*-FC_6H_4-(3)-1,2-$B_9C_2H_{11}$]. The compound obtained from the first yellow band to separate was recrystallized once from benzene–heptane and twice from dichloromethane–heptane, washed with a few small portions of heptane, and dried *in vacuo* at 78° for 3 hr, to afford 1.03 g (0.0029 mol) of yellow-orange, crystalline [1-*m*-FC_6H_4-(3)-1,2-$B_9C_2H_{10}$]Co[C_5H_5], mp 229–230°. The yield was 28% based on initially employed carborane salt.

(b) [1-*p*-FC_6H_4-(3)-1,2-$B_9C_2H_{10}$]Co[C_5H_5]. Starting with 3.0 g of $(CH_3)_3NH$[1-*p*-FC_6H_4-(3)-1,2-$B_9C_2H_{11}$] and following the procedure described above afforded 0.86 g (0.0025 mol) of yellow, finely crystalline [1-*p*-FC_6H_4-(3)-1,2-$B_9C_2H_{10}$]Co[C_5H_5], mp 250–251.8°. The yield was 24% based on the starting carborane salt.

Preparation of 1-*m*- and 1-*p*-Fluorophenyl-(3)-1,7-dicarbollylcyclopentadienylcobalt(III). (a) [1-*m*-FC_6H_4-(3)-1,7-$B_9C_2H_{10}$]Co[C_5H_5]. Starting with 1.50 g (0.00522 mol) of $(CH_3)_3NH$[1-*m*-FC_6H_4-(3)-1,7-$B_9C_2H_{11}$], 2.42 g (0.0365 mol) of cyclopentadiene, and 6.10 g (0.0470 mol) of cobaltous chloride, the same general procedure was followed as was employed for the 1,2 isomers. The residue obtained upon removal of the THF from the filtered reaction solution was extracted with several portions of boiling benzene and the residue was chromatographed using the same solvent systems as described above. A series of colored bands was obtained, but only one (a dark yellow, broad band) afforded a crystalline solid upon solvent removal; solvent removal from the other fractions afforded only small amounts of oils. The yellow solid was recrystallized twice from dichloromethane–heptane and dried *in vacuo* at 78° for 2.5 hr to afford 0.19 g (0.54 mmol) of yellow crystalline [1-*m*-FC_6H_4-(3)-1,7-$B_9C_2H_{10}$]Co[C_5H_5], mp 186–186.5°. The yield was 10% based on the starting carborane salt.

(b) [1-*p*-FC_6H_4-(3)-1,7-$B_9C_2H_{10}$]Co[C_5H_5]. Starting with 0.90 g (0.0031 mol) of $(CH_3)_3NH$[1-*p*-FC_6H_4-(3)-1,7-$B_9C_2H_{11}$], 1.45 g (0.022 mol) of cyclopentadiene, and 3.65 g (0.028 mol) of cobaltous chloride, the same procedure employed in the meta compound preparation was used to afford 0.08 g (0.23 mmol) of yellow crystalline [1-*p*-FC_6H_4-(3)-1,7-$B_9C_2H_{10}$]Co[C_5H_5], mp 209–210°. The yield was 7% based on the starting carborane salt.

Acknowledgments. This research was supported in part by the Office of Naval Research and the Army Research Office (Durham). The authors wish to express their gratitude for the aid of Professor R. W. Taft and his coworkers in obtaining decoupled ^{19}F nmr spectra at the University of California, Irvine, and for a gift of *p*-fluorophenylboron dichloride.

The Nature of So-Called Titanocene, $(C_{10}H_{10}Ti)_2$

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Abstract: Mass spectral and chemical evidence indicates that the compound $(C_{10}H_{10}Ti)_2$, sometimes referred to as "titanocene", is in fact the dimer of a cyclopentadienyltitanium hydride, containing one cyclopentadienylidene moiety (C_5H_4) per subunit: $((C_5H_5)(C_5H_4)TiH)_2$. Ir data are consistent with the presence of a double hydrogen bridge in the dimer. The instability of $(h^5\text{-}C_5H_5)_2Ti$ toward rearrangement to this metal hydride structure is in accord with the view that the reaction intermediate $(h^5\text{-}C_5H_5)_2Ti$ has a carbene-like reactivity.

The compound $(C_{10}H_{10}Ti)_2$ is prepared by reaction of $(h^5\text{-}C_5H_5)_2Ti(CH_3)_2$ with H_2 gas in hexane[1] or by reduction of $(h^5\text{-}C_5H_5)_2TiCl_2$ with sodium naphthalide[2] or sodium sand.[3] Initially thought of as a dimer of titanocene, $(h_5\text{-}C_5H_5)_2Ti$, the compound was recently shown to exhibit ir and nmr spectra far too complex for such a structure.[3] Although $(C_{10}H_{10}Ti)_2$ is of considerable interest because of its participation in various catalytic reactions[4–7] and in the reduction of nitrogen,[8] an acceptable structure has not been proposed yet. We want to report evidence that $(C_{10}H_{10}Ti)_2$ is a titanium hydride complex and contains two of its four ring ligands in form of C_5H_4 units.

Reaction to $((C_5H_5)(C_5H_4)TiCl)_2$

When solutions of $(C_{10}H_{10}Ti)_2$ in ether are treated with HCl gas, formation of a purple chloride is observed, which differs from either $(h^5\text{-}C_5H_5)_2TiCl$ or $(h^5\text{-}C_5H_5)_2TiCl_2$.[3] We find that formation of the purple chloride from $(C_{10}H_{10}Ti)_2$ occurs under evolution of exactly 1 mol of H_2 gas per mol of titanium. This establishes the stoichiometry of the reaction product as $C_{10}H_9TiCl$ or a multiple thereof. Mass spectra (see below) confirm this formulation and show that the compound is in fact the dimer $(C_{10}H_9TiCl)_2$. The exchange of chlorine for one hydrogen in each $C_{10}H_{10}Ti$ unit by HCl gas indicates the presence of a hydride moiety in this unit. This suspicion is confirmed by reaction of $(C_{10}H_{10}Ti)_2$ with DCl. The evolved hydrogen is now essentially pure HD and must therefore originate from interaction of a hydride with DCl. To judge from this reaction, "titanocene" should therefore be formulated as $(C_{10}H_9TiH)_2$.

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Table I. Mass Spectra of $(C_{10}H_9TiH)_2$ and Comparison Compounds[a]

$(C_{10}H_9TiH)_2$[b]			$(C_{10}H_9TiCl)_2$[b]			$(C_{10}H_{10}Ti(CH_3)_2$[c]		
m/e	Rel intensity	Assignment	*m/e*	Rel intensity	Assignment	*m/e*	Rel intensity	Assignment
356	55	M	424	100	M	372	1	$(C_{10}H_{10}TiCH_3)_2^+$
354	100	$M - H_2$	359	16	$M - C_5H_5$	209	2	$M + H$
352	100	$M - 2H_2$	241	72	$M - C_5H_5TiCl$	193	100	$M - CH_3$
350	5	$M - 3H_2$	213	14	$C_{10}H_{10}TiCl$	178	95	$C_{10}H_{10}Ti^+$
128	19	$C_{10}H_8^+$	128	10	$C_{10}H_8^+$			
66	30	$C_5H_6^+$	66	24	$C_5H_6^+$	66	27	$C_5H_6^+$
65	11	$C_5H_5^+$	65	6	$C_5H_5^+$			

[a] Given in the table are the monisotopic species with ^{12}C, ^{35}Cl, and ^{48}Ti; assignments are based on the polyistopic distribution patterns for each of the ions. [b] Ionizing voltage, 18 ev. [c] Ionizing voltage, 15 eV.

In both the chloride and the hydride we are then left with one C_5H_4 ligand per titanium, in addition to a normal C_5H_5 unit, and the structure of both compounds can be symbolized by $((C_5H_5)(C_5H_4)TiX)_2$, X being either H or Cl.[9] For the dimer we can therefore envision several structures, depending on which of the ligands serve as bridging groups between the two subunits. In the following we shall present evidence that the presence of a double hydrogen bridge in the dimer describes the properties of titanocene most appropriately.

Mass Spectra

The mass spectrum of $(C_{10}H_{10}Ti)_2$ differs from those of other metallocenes most strikingly, not only in that the parent peak corresponds to a dimer, but also in its fragmentation patterns (see Table I). The ion $C_{10}H_{10}M^+$ (M = metal), which is the most abundant one for practically all metallocenes,[10] is virtually absent with titanocene. Instead, doubly ionized species begin to appear at higher ionizing voltages in the *m/e* 178 region. Dominant among the low-mass fragments is the ion $C_5H_6^+$, which has not been observed with any of the other metallocenes nor, for instance, with $(h^5\text{-}C_5H_5)_2TiCl_2$.[11] Most surprising, however, is the observation, next to the parent peak, of a series of ions which correspond to the loss of one or more H_2 molecules from the dimer. At 15-eV ionization voltage the ions with mass 354 and 352, generated by loss of one and two H_2 molecules, respectively, are quite intense. At higher voltages ions with even lower masses, corresponding to the loss of up to four H_2 molecules, are observable. To the best of our knowledge, such a behavior has not been reported for organometallic compounds yet.[12] We propose that these observations are all consistent with the occurrence of a double hydrogen bridge. The presence of two closely adjacent H ligands in the dimer could obviously provide a suitable pathway for the facile H_2 elimination observed. This view is borne out, for example, by the very facile thermal loss of H_2 from the related dimeric hydride $((C_5H_5)_2TiH)_2$, for which the presence of a double hydrogen bridge has been established otherwise.[13] Just as the intermediate $((C_5H_5)_2Ti)_2$ which would originate from such an elimination rearranges to $((C_5H_5)(C_5H_4)TiH)_2$, so, apparently, is the H_2 elimination from $((C_5H_5)(C_5H_4)TiH)_2$ followed in turn by a further hydride transfer step from the ring ligands to the metal atoms, leading to the subsequent loss of a second H_2 molecule.

The high intensity of the ion $C_5H_6^+$ is a puzzling observation. While one is tempted to speculate on the presence of C_5H_6 ligands in titanocene, the high abundance of $C_5H_6^+$ in the mass spectrum of $(C_{10}H_9TiCl)_2$ seems to rule this out. If a C_5H_6 moiety were present in each unit, the remaining ligand would have to be C_5H_3:$((C_5H_6)(C_5H_3)TiCl)_2$. Such a species does not appear acceptable, however, for the normal structure of the molecule. In an energetically excited state of the molecule on the other hand, such a hydrogen transfer between the C_5H_5 and C_5H_4 rings might be possible. At any rate, the appearance of the ion $C_5H_6^+$ seems to be an empirical observation associated with the presence of a C_5H_4 moiety. Interestingly, in both the hydride and the chloride, an ion $C_{10}H_8^+$ is observed with moderate intensity.

Otherwise the mass spectrum of $(C_{10}H_9TiCl)_2$ is quite normal and the identity of the parent ion is confirmed by its isotope distribution. As one might expect from the replacement of the double hydrogen bridge by two μ-Cl ligands, no loss of H_2 from the parent ion is observed here. Monometallic fragments are quite abundant for the chloride, in contrast to their almost complete absence in the hydride. In analogy to similar observations with other dinuclear organometallic compounds,[14] we take this as an indication of the presence of a fairly strong titanium–titanium bond in $((C_5H_5)(C_5H_4)TiH)_2$.

In an attempt to observe the ion $C_{10}H_{10}Ti^+$ as a major species we have finally investigated the mass spectrum of $(h^5\text{-}C_5H_5)_2Ti(CH_3)_2$. As expected from analogy with other metal alkyl compounds,[15] loss of the methyl groups occurs very easily and the ion $C_{10}H_{10}Ti^+$ is in fact a dominant species in the mass spectrum. The occurrence of $C_5H_6^+$ appears to point again to the presence of a C_5H_4 ligand, that is, to a rapid rearrangement of any primarily generated $(h^5\text{-}C_5H_5)_2Ti$ to $(C_5H_5)(C_5H_4)TiH$. Loss of hydrogen, however, is much less prominent than with $(C_{10}H_9TiH)_2$. Even at 70 eV loss of

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[9] An analogous zirconium compound $((C_5H_5)(C_5H_4)ZrCl)$ or a multiple thereof has been reported to form when $(C_5H_5)_2ZrCl_2$ is treated with amines: E. Samuel and R. Setton, *C. R. Acad. Sci.*, **256**, 443 (1963). This would indicate that the $(C_5H_4)Zr$ unit forms even more readily than the corresponding titanium moiety and that what is said here about the structure of $(C_{10}H_{10}Ti)_2$ holds *a forteriori* for the apparently isostructural compound $(C_{10}H_{10}Zr)_2$: G. W. Watt and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 5926 (1966).

[10] J. Müller and L. D'Or, *J. Organometal. Chem.*, **10**, 313 (1967).

[11] J. G. Dillard and R. W. Kiser, *ibid.*, **16**, 265 (1969).

[12] A similar phenomenon is observed in the mass spectra of polyhedral, hydrogen-bridged boranes: J. J. Kaufman, W. S. Koski, L. J. Kuhns, and R. W. Law, *J. Amer. Chem. Soc.*, **84**, 4198 (1962); T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 581 (1964).

[13] J. E. Bercaw and H. H. Brintzinger, *ibid.*, **91**, 7301 (1969).

[14] See also J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, **1**, 245 (1968).

[15] See, for example, J. Tanaka and S. R. Smith, *Inorg. Chem.*, **8**, 265 (1969).

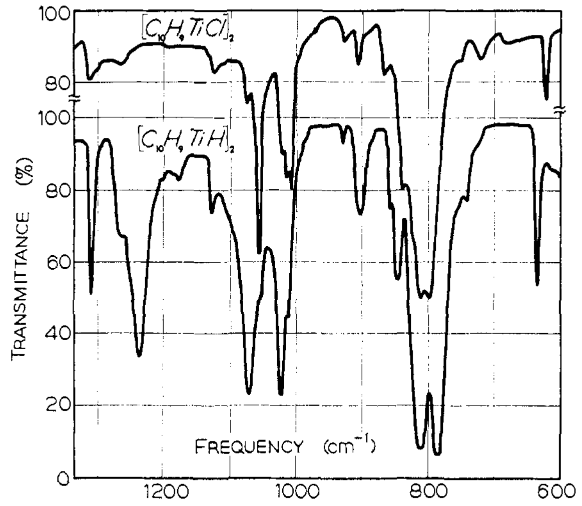


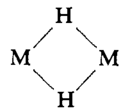
Figure 1. Infrared spectra of $(C_{10}H_9TiCl)_2$ (top) and $(C_{10}H_9TiH)_2$ (bottom), both in Nujol mull.

C_2H_2 or C_5H_5 units is the preferred fragmentation process. This would substantiate our hypothesis that the presence of two closely adjacent hydride ligands in $((C_5H_5)(C_5H_4)TiH)_2$ is responsible for the observed ease of H_2 elimination.[14]

Ir Spectra

While our previous evidence clearly shows that $(C_{10}H_{10}Ti)_2$ reacts, in solution and in the gas phase, *as though* it were $((C_5H_5)(C_5H_4)TiH)_2$, the question remains whether this is the normal structure of this compound or only an easily available reactive configuration. We have obtained ir data which indicate that titanocene as a solid is in fact $((C_5H_5)(C_5H_4)TiH)_2$, containing a double hydrogen bridge.

As observed before,[2,3] titanocene has a very complex ir spectrum with a large number of bands not present in normal $(h^5\text{-}C_5H_5)_2Ti$ derivatives. We find that the ir spectrum of the chloride $(C_{10}H_9TiCl)_2$ is almost identical with that of $(C_{10}H_9TiH)_2$ (Figure 1). The only and striking exception to this is the presence of a strong band at 1230 cm^{-1} in $(C_{10}H_9TiH)_2$ and its absence in $(C_{10}H_9TiCl)_2$. This observation identifies the band at 1230 cm^{-1} as due to a vibrational mode of the hydride ligands. We and others have observed earlier, however, that this is in fact in the frequency range of an antisymmetric



stretching mode.[13,16] These data are clearly consistent, therefore, with the presence of a double hydrogen bridge in titanocene and would thus indicate that this substance is in fact $((C_5H_5)(C_5H_4)TiH)_2$ even as a crystalline solid.

Discussion

A first sight, the abstraction of one of the ring hydrogens and its shift to the titanium center in $(C_5H_5)(C_5H_4)TiH$ might appear surprising. Such a rearrangement is perfectly understandable, however, if we bear in mind that $(h^5\text{-}C_5H_5)_2Ti$ can be predicted to be an unstable species with a carbene-like reactivity.[17] It is well known that a carbene rearranges most frequently by abstraction of an α hydrogen and formation of an olefin.[18] Analogously, the titanium center in $(h^5\text{-}C_5H_5)_2Ti$ is prone to abstract—possibly *via* a $(h^1\text{-}C_5H_5)$ derivative—one of the ring hydrogens to form the titanafulvene structure indicated in Figure 2. The fact that titanocene is unique among the third-row metallocenes in this rearrangement is yet another manifestation of the unusual tendency for spontaneous distortions predicted for this d^2 system by second-order perturbation theory.[17]

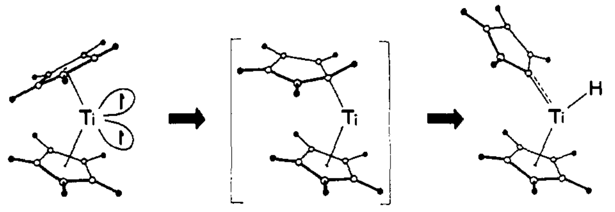
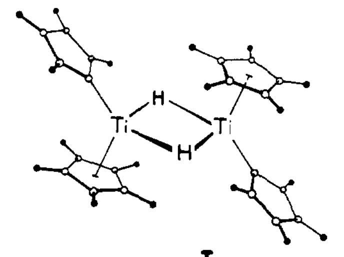


Figure 2. Postulated rearrangement of di-h^5-cyclopentadienyltitanium to h^5-cyclopentadienyl-h^1-cyclopentadienylidenetitanium hydride. For an MO analysis of spontaneous distortions in $(h^5\text{-}C_5H_5)_2Ti$, see ref 17.



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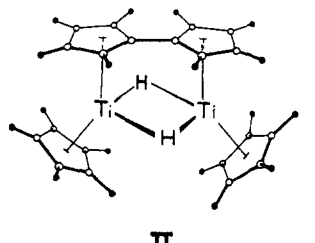

II

For the way in which the C_5H_4 units are bonded in the dimer, two alternative structures can be envisioned. In one (I) the two $(C_5H_5)(C_5H_4)TiH$ subunits would be bridged by the hydride ligands only; each unit would then contain a single cyclopentadienylidene ligand, C_5H_4. It is interesting to note that quite recently very stable complexes have been obtained with the carbene cyclopropenylidene as a π-acceptor ligand.[19] In analogy to this case, structure I would appear quite reasonable. The tendency of titanium(II) complexes to coordinate π-acceptor ligands, demonstrated by the stability of the carbonyl complex $(h^5\text{-}C_5H_5)_2Ti(CO)_2$, and the capability of a carbene ligand C_5H_4 to act as such a π acceptor might in fact provide the driving force for the rearrangement pictured in Figure 2.

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(16) See, *e.g.*, V. N. Kapshtal and L. M. Sverdlov, *Zh. Fiz. Khim.*, 40, 2818 (1966), and earlier references quoted there.

(17) H. H. Brintzinger and L. S. Bartell, *J. Amer. Chem. Soc.*, 92, 1105 (1970).

(18) See, *e.g.*, W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(19) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, 8, 916 (1969).

On the other hand, the two C_5H_4 moieties could also be present in the form of a $C_{10}H_8$ ligand in the dimer (structure II). This structure would be perfectly in accord with the occurrence of the ion $C_{10}H_8^+$ in the mass spectra of both the hydride and the chloride, and of the ion $M - C_5H_5TiCl$ in the spectrum of the chloride. Since there is little hope of distinguishing structures I and II by ir, nmr, or other spectral techniques, this particular problem might have to be settled by a crystal structure determination of the dimer.

An interesting question is whether the species $(h^5\text{-}C_5H_5)_2Ti$ can be regenerated from $(C_{10}H_9TiH)_2$. It has been observed that $(h^5\text{-}C_5H_5)_2Ti(CO)_2$ can be obtained, although inefficiently, from titanocene and CO.[20] This would indicate that—given a sufficient driving force and the absence of efficient competing reactions—regeneration of $(h^5\text{-}C_5H_5)_2Ti$ as a transient species is a marginal possibility. We plan to investigate further into the characteristics and possible modes of stabilization of the hypothetical reaction intermediate $(h^5\text{-}C_5H_5)_2Ti$ and of related compounds.

Experimental Section

Procedures for the handling of the air-sensitive materials and gases used were as outlined in an earlier publication.[13] Mass spectra were obtained on an AEI SP902 mass spectrometer with direct inlet system.

Preparation of $(C_{10}H_9TiCl)_2$. $(C_{10}H_9TiH)_2$ (538 mg, 1.51 mmol), obtained according to ref 3, is suspended in 15 ml of ether in a reaction vessel attached to a vacuum assembly. HCl gas (5 mmol) is condensed into the reaction vessel at liquid nitrogen temperatures. After warming to room temperature and stirring for about 1 hr, the initially green material is completely converted to a purple slurry and the initially vigorous hydrogen evolution ceases. The reaction mixture is then freed from H_2 gas and filtered on the vacuum line. The precipitate is washed with a little ether and dried *in vacuo*. The purple product, which is obtained in essentially quantitative yields—520 mg after purification—is moderately air-sensitive, especially in the presence of solvents; it can be stored indefinitely under Ar. The compound thus obtained has the correct elemental composition and spectral properties identical with those described by Salzmann and Mosimann.[3] On the other hand, differences are to be noted between this preparation and titanocene samples described by Watt, Baye, and Drummond.[2] In particular, Dr. Watt has drawn our attention to the observation that his samples are much more reactive toward air than ours, and to noticeable differences in the ir spectrum, such as a substantially lower intensity of the band at 1230 mμ, in his preparations. The causes for these differences are not clear at present.

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[20] F. Calderazzo, J. J. Salzmann, and P. Mosimann, *Inorg. Chim. Acta*, **1**, 65 (1967).

Synthesis and Characterization of Aminodifluorophosphine

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Abstract: The reaction of NH_3 and PF_2Cl or PF_2Br results in the formation of aminodifluorophosphine, H_2NPF_2. The deuterium derivative D_2NPF_2 was prepared by an analogous reaction between ND_3 and PF_2Cl. A similar reaction between CH_3NH_2 and PF_2Cl yields methylaminodifluorophosphine, $(CH_3NH)PF_2$. These compounds were characterized by mass, infrared, and nmr spectral studies.

Although aminophosphine dihalides of the type R_2NPX_2 (where X = F, Cl, Br, or I, and R is an alkyl or aryl group) have been known for almost 100 years, the fundamental member of the series, H_2NPX_2, has never been prepared. We wish to report the synthesis and characterization of H_2NPF_2, which is obtained from the reaction of NH_3 with difluorohalophosphines. A similar reaction occurs with CH_3NH_2. Specifically, when PF_2Br or PF_2Cl is allowed to interact with NH_3 or CH_3NH_2 at 23° the reaction proceeds according to

$$2RNH_2 + PF_2X \longrightarrow RHNPF_2 + NH_3RBr \qquad (1)$$

where X = Cl or Br and R = H or CH_3.

The reaction of NH_3 and PF_2Br to give H_2NPF_2 may be contrasted with the reaction of PH_3 and PF_2I. The latter reaction has been shown to yield only PF_2I and PF_2H as products, although it was postulated that the initial product was H_2PPF_2.[1] The interactions of PF_2X and NH_3 or RNH_2 are analogous to both the reaction between bis(trifluoromethyl)chlorophosphine and ammonia[2] and the reaction between trichloromethyldifluorophosphine and methylamine.[3]

Experimental Section

Synthesis. The work was carried out in Pyrex systems by using standard vacuum techniques. All gaseous reactants and products were measured by means of a calibrated volume. Spectral data were obtained as previously described.[4]

Chlorodifluorophosphine and bromodifluorophosphine were prepared by using previously described procedures.[5] Ammonia was dried over sodium before use. Methylamine (Matheson) was used as obtained.

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