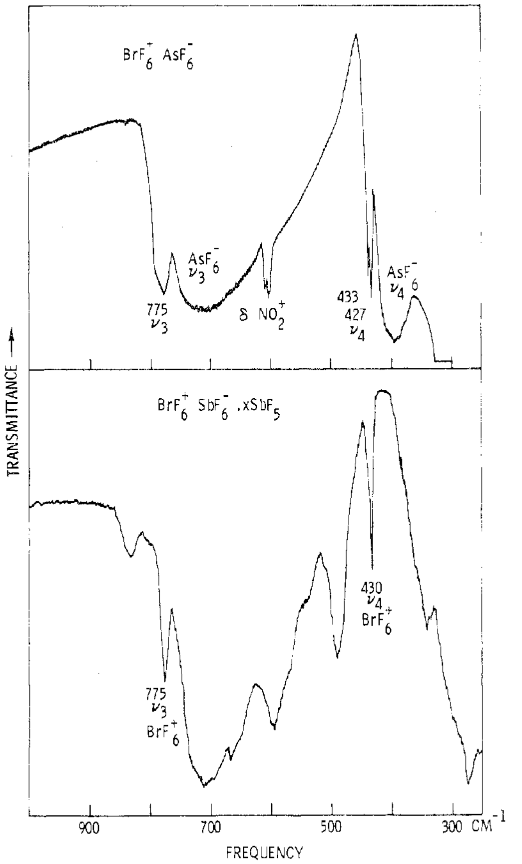

Figure 1. Infrared spectra of $BrF_6^+AsF_6^-$ recorded as a dry powder between AgCl plates at −196° and of $BrF_6^+SbF_6^- \cdot xSbF_5$ recorded as a AgBr disk at 25°. The increase in background at the low-frequency end of the spectra is due to absorption by the windows.

warm to ambient temperature or when the ir sample of the SbF_5 adduct was kept at ambient temperature for several hours. The remaining bands in the infrared spectra changed only little, thus supporting the assignment of the 775- and 430-cm^{-1} bands to ν_3 and ν_4, respectively, of the powerful oxidizing species BrF_6^+. The ready interaction between BrF_6^+ and the silver halide window material can also account for the weakening of the intensity of the BrF_6^+ infrared bands in the room-temperature spectrum of the SbF_5 adduct.

In $BrF_6^+AsF_6^-$, the 430-cm^{-1} band shows a splitting of 6 cm^{-1}. Since the two components are of similar intensity, splitting due to the $^{79}Br^{81}Br$ isotopes must be considered. The following arguments augur against the splitting being caused by the bromine isotopes and favor its attribution to crystal field or site symmetry effects. (i) The SbF_5 adduct does not show a comparable splitting. (ii) The observed splitting of 6 cm^{-1} is much larger than that (~2 cm^{-1}) predicted for the Br isotopes. (iii) The NO_2^+ deformation in the same spectrum shows a comparable splitting. (iv) The site symmetry of BrF_6^+ in space group *Pa*3 is only C_{3i}.

Force Constants. Since both the infrared- and the Raman-active fundamentals are now known, it was interesting to compute a force field for BrF_6^+. This allows a more quantitative comparison of the relative bond strength of BrF_6^+ with those of related species.

Except for the F_{1u} block, all the symmetry force constants of BrF_6^+ are unique. The F_{1u} block is undetermined since only two frequency values are available for the determination of three force constants. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants,[18] was tested for the isoelectronic series SF_6, SeF_6, and TeF_6, for which general valence force fields have been reported.[19-21] As can be seen from Table II, the condition F_{44} = minimum very closely duplicates the GVFF values for the two heavier molecules SeF_6 and TeF_6. Therefore, it is also expected to be a very good approximation for the force field of BrF_6^+. The values so obtained for BrF_6^+ are listed in Table II and correlate well with the remaining species of Table II. The modified valence force fields, listed for the lightest isoelectronic series, *i.e.*, PF_6^-, SF_6, and ClF_6^+, are less reliable since the lighter central atoms cause stronger coupling of the stretching and bending modes.

The force constant of greatest interest is the stretching force constant f_r. For BrF_6^+ its value of 4.9 mdyn/Å is the highest found to date for any BrF bond.[23-25] This is not surprising since the covalency and therefore also the force constant of such a bond tend to increase with increasing oxidation state of the central atom and a formal positive charge.[22] Since the Br–F bonds in BrF_6^+ are stronger than those in other bromine fluorides, the reactivity of these salts must be due to the high oxidizing power of BrF_6^+.

Acknowledgment. We are indebted to Drs. C. J. Schack and L. R. Grant for helpful discussions. This work was supported by the Office of Naval Research, Power Branch.

Registry No. $BrF_6^+AsF_6^-$, 51063-29-7; $BrF_6^+SbF_6^-$, 53432-26-1; PF_6^-, 16919-18-9; AsF_6^-, 16973-45-8; SbF_6^-, 17111-95-4; SF_6, 2551-62-4; SeF_6, 7783-79-1; TeF_6, 7783-80-4; ClF_6^+, 38217-33-3; IF_6^+, 21303-14-0; BrF_6^+, 51063-27-5.

References and Notes

(1) R. J. Gillespie and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 90 (1974).
(2) R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, **13**, 1230 (1974).
(3) K. O. Christe, *Inorg. Chem.*, **12**, 1580 (1973).
(4) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 1783 (1967).
(5) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **7**, 1685 (1968).
(6) K. O. Christe, *Inorg. Chem.*, **9**, 2801 (1970).
(7) K. R. Loos, V. A. Campanile, and C. T. Goetschel, *Spectrochim. Acta, Part A*, **26**, 365 (1970).
(8) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 841 (1960).
(9) H. H. Claassen, H. Selig, and J. Shamir, *Appl. Spectrosc.*, **23**, 8 (1969).
(10) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, **24**, 291 (1970).
(11) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **12**, 2879 (1973).
(12) F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Amer. Chem. Soc.*, **87**, 25 (1965).
(13) A. B. Ray, *Inorg. Chem.*, **6**, 110 (1967).
(14) D. Moy and A. R. Young, *J. Amer. Chem. Soc.*, **87**, 1889 (1965).
(15) S. P. Beaton, Ph.D. Thesis, University of British Columbia, 1966.
(16) W. H. Zachariasen, *J. Amer. Chem. Soc.*, **70**, 2147 (1948).
(17) F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).
(18) W. Sawodny, *J. Mol. Spectrosc.*, **30**, 56 (1969).
(19) A. Ruoff, *J. Mol. Struct.*, **4**, 332 (1969).
(20) S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **44**, 3353 (1966).
(21) S. Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967).
(22) K. O. Christe, *Int. Congr. Pure Appl. Chem., 24th*, **4**, 115 (1974).
(23) K. O. Christe and C. J. Schack, *Inorg. Chem.*, **9**, 2296 (1970).
(24) K. O. Christe, E. C. Curtis, and D. Pilipovich, *Spectrochim. Acta, Part A*, **27**, 931 (1971).
(25) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 1679 (1972).

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Carbon-13 Nuclear Magnetic Resonance Studies of Borane Adducts of Trimethylamine

R. A. Geanangel

Received June 14, 1974 AIC403859

A recent study of ether–boron trihalide adducts by ^{13}C nmr (cmr) has shown[1] that the chemical shifts of the α-carbon atoms of several ethers gave downfield displacements when the ethers were coordinated with BF_3 or BCl_3. The magnitudes of the shifts for adducts of BF_3 increased with increasing proton basicities of the ethers. Furthermore when BCl_3, which is known to be a stronger acceptor, replaced BF_3, the α-carbon resonance shifted downfield. These observations were taken to indicate that cmr shifts for α-carbon atoms on coordinated ethers probably reflect electron density shifts associated with adduct formation.

The investigators reported a shift in the opposite direction for the β and γ carbons which was attributed to the influence of the paramagnetic term on the ^{13}C chemical shift. This effect was also believed to be operative at the α-carbon positions but to be overshadowed by the change in the diamagnetic term resulting from the substantial charge withdrawal associated with adduct formation. We have investigated this phenomenon further as it applies to the cmr spectra of trimethylamine–borane adducts of the forms $(CH_3)_3N{\cdot}BH_nF_{3-n}$ ($n = 1$–3) and $(CH_3)_3N{\cdot}BX_3$ (X = F, Cl, Br).

The cmr spectra of the adducts were obtained in either $CDCl_3$ or $CDCl_3$–CH_3CN solution using the Fourier transform technique with a Varian CFT-20 instrument. Broad-band proton decoupling was employed in all spectra producing symmetrical singlets in all cases except those for the adducts $(CH_3)_3N{\cdot}BH_2F$, $(CH_3)_3N{\cdot}BHF_2$, and $(CH_3)_3N{\cdot}BF_3$. The signal for the monofluorinated adduct (Figure 1) appeared as a doublet ($J \simeq 2.0$ Hz) apparently due to long-range coupling with the fluorine atom. The resonance for the methyl carbons in the difluorinated adduct was an ill-resolved triplet ($J \simeq 2.4$ Hz), again presumably due to spin coupling with the two fluorine atoms on boron (Figure 1). The cmr signal of trimethylamine–trifluoroborane appeared as an unresolved multiplet which we cannot confidently analyze. Heitsch[2] has reported spin coupling between the methyl protons in $(CH_3)_3N{\cdot}BF_3$ and the fluorines, but the splitting was further complicated by coupling with the ^{11}B nucleus. Such coupling could be complicating the cmr spectra of $(CH_3)_3N{\cdot}BF_3$.

The chemical shifts of the adducts studied are listed in Table I; cmr shifts are given in ppm downfield from tetramethylsilane. In light of the ether adduct studies described in the foregoing, it is of interest to determine whether the cmr shifts of the methyl carbons bear any relationship to adduct strength. The shifts for the three boron trihalide adducts can be used qualitatively to test this idea. A considerable body of evidence[4] exists which supports the order of acceptor strength as $BF_3 < BCl_3 < BBr_3$. If cmr shifts mirror acceptor strength, the shifts of the trimethylamine adducts should increase in the same order. Although the measured shift differences are not large, the data are consistent with this expectation. (Reproducibility of cmr shifts in the same solvent was found to be about ±0.1 ppm.) A considerable solvent shift was observed between $CDCl_3$ and $CDCl_3$–CH_3CN (1:2, v/v) solutions of the same compound, so comparisons were only made between shifts in the same solvent.

Further examination of the cmr shifts of these adducts uncovered no direct correlation whatever between ^{13}C and ^{11}B shifts in the same molecules. This is not really surprising since the boron environment in a series of adducts varies in a major way owing to primary changes in substituents whereas the carbon environment changes only in a secondary manner. There is little evidence that ^{11}B chemical shifts directly reflect acceptor or adduct strengths except in isolated instances.[5,6] Spielvogel[7,8] has shown that there is a correlation between ^{11}B and ^{13}C shifts in many isoelectronic compounds. Also Noeth[9] recently reported a similar correlation between ^{11}B and ^{14}N chemical shifts.

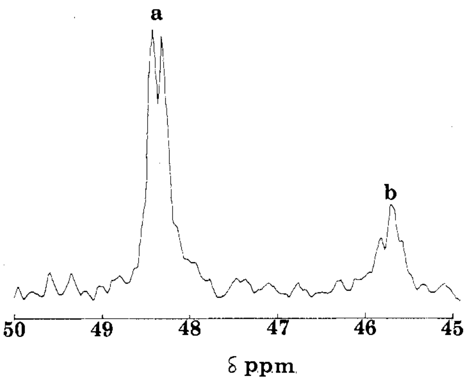

Figure 1. ^{13}C nmr spectra of $(CH_3)_3N{\cdot}BH_2F$ (a) and $(CH_3)_3N{\cdot}BHF_2$ (b).

Table I. Carbon-13 and Boron-11 Chemical Shifts of Some Trimethylamine–Borane Adducts

	$\delta(^{13}C)$,[a]			
	$CDCl_3$ solvent	$CDCl_3$–CH_3CN solvent[b]	Adduct $\delta(^{11}B)$[c]	$\Delta\delta(^{11}B)$[d]
$(CH_3)_3N{\cdot}BH_3$	54.14	52.68	26.2	78.6[g]
$(CH_3)_3N{\cdot}BH_2F$	48.27[e]		13.2	
$(CH_3)_3N{\cdot}BHF_2$	45.71[f]		14.2	
$(CH_3)_3N{\cdot}BF_3$	46.97, 47.09	45.67	17.5[h]	8.8[h]
$(CH_3)_3N{\cdot}BCl_3$		48.33	7.9[h]	36.3[h]
$(CH_3)_3N{\cdot}BBr_3$		48.97	22.6[h]	43.9[h]

[a] Ppm downfield from TMS. Spectra run on a Varian CFT-20 ^{13}C nmr instrument in FT mode with broad-band proton decoupling. [b] Because of solubility limitations, spectra of these adducts were taken in $CDCl_3$–CH_3CN (1:2 v/v). [c] Ppm upfield from external trimethyl borate reference. [d] $\Delta\delta(^{11}B) = \delta((CH_3)_3NBX_3) - \delta(BX_3)$. [e] Doublet ($J \simeq 2.0$ Hz). [f] Triplet ($J \simeq 2.4$ Hz). [g] $\delta(^{11}B[BH_3])$ −70.5 ppm from ref 9. [h] $\delta(^{11}B)$ values taken from ref 3. Adducts in $CHCl_3$ solution; boranes in free state except as noted in g.

Some investigators have used the $\Delta\delta(^{11}B)$ parameter[10] in considering adduct strengths; this is the difference in ^{11}B chemical shift between free BX_3 and coordinated BX_3. Noeth,[11] however, viewed this skeptically citing calorimetric data for trimethylamine–fluoromethylborane adducts which do not show a correlation to $\Delta\delta(^{11}B)$ values. In that case, however, the influence of steric factors cannot presently be fully assessed so it seems justified to study this question somewhat further.

A comparison between cmr shifts and $\Delta\delta(^{11}B)$ values[10] (Table I) for the boron trihalide and parent borane adducts from this study reveals a rather striking correlation, a plot of which is shown in Figure 2 ($r = 0.999$). In the absence of more data to test the correlation, conclusions must be tentative; however, it seems justified to consider cmr shifts as a possible new source of information on adducts. It is generally held[12] that cmr spectra are principally controlled by the electronic environment within the molecule containing the carbon; a linear relationship has been shown to exist between cmr shifts and substituent electronegativities in a series of CH_3X compounds, provided methyl halides (which show their own correlation) are excluded.[13] Thus there is some justification for considering that cmr shifts in closely defined systems might vary closely with charge drift caused by adduct formation.

If this criterion is applied to the cmr shifts of the trimethylamine–fluoroboranes, it suggests an order of adduct strengths similar to that indicated by proton nmr shifts.[14] The order derived from the methyl proton shifts is $(CH_3)_3N{\cdot}BH_3 \simeq (CH_3)_3N{\cdot}BF_3 > (CH_3)_3N{\cdot}BH_2F > (CH_3)_3N{\cdot}BHF_2$, while cmr shifts (Table I) indicate that trimethylamine–trifluoroborane lies between the mono- and difluoro adducts: $(CH_3)_3N{\cdot}BH_3 > (CH_3)_3N{\cdot}BH_2F > (CH_3)_3N{\cdot}BF_3 > (CH_3)_3N{\cdot}BHF_2$. Caution is indicated in the interpretation

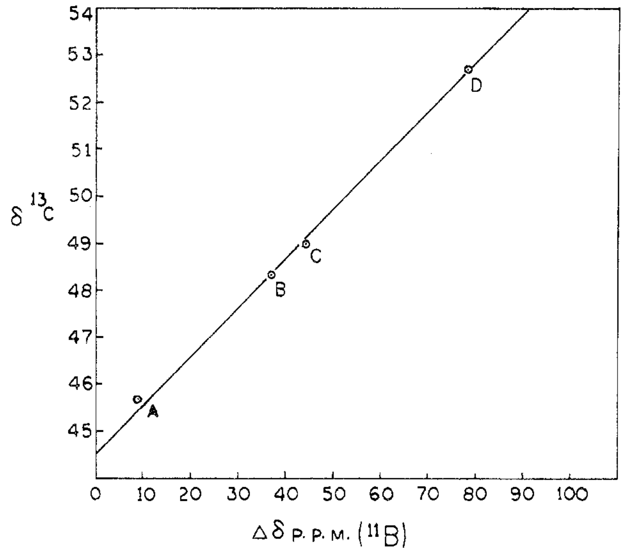

Figure 2. Plot of ^{13}C chemical shifts *vs.* $\Delta\delta(^{11}B)$ values for trimethylamine-borane adducts: A, $(CH_3)_3N{\cdot}BF_3$; B, $(CH_3)_3N{\cdot}BCl_3$; C, $(CH_3)_3N{\cdot}BBr_3$; D, $(CH_3)_3N{\cdot}BH_3$.

of such data especially when comparing adjacent members of the series, but there is nevertheless a clear suggestion the BH_3 adduct is significantly stronger than the fluoroborane adducts. Other workers[15,16] have accounted for the apparent weakening effect of substituting fluorine on borane Lewis acids by considering a competition between π lone pairs on fluorine and the σ-electron pair of the Lewis base for the boron acceptor orbital tending to weaken fluoroborane acceptors. If this effect is operative here, it might weaken the fluoroborane adducts relative to $(CH_3)_3N{\cdot}BH_3$, but alone, it does not account for the ordering of the entire series.

Acknowledgment. The support of this work by the Robert A. Welch Foundation (Grant E-439) is sincerely appreciated.

Registry No. $(CH_3)_3N{\cdot}BH_3$, 75-22-9; $(CH_3)_3N{\cdot}BH_2F$, 35449-24-2; $(CH_3)_3N{\cdot}BHF_2$, 35237-72-0; $(CH_3)_3N{\cdot}BF_3$, 420-20-2; $(CH_3)_3N{\cdot}BCl_3$, 1516-55-8; $(CH_3)_3N{\cdot}BBr_3$, 1516-54-7; ^{13}C, 14762-74-4; ^{11}B, 14798-13-1.

References and Notes

(1) A. F. Fratiello, G. A. Vidulich, and R. E. Schuster, *J. Inorg. Nucl. Chem.*, **36**, 93 (1974).
(2) C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).
(3) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N.Y., 1969.
(4) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).
(5) P. N. Gates, E. J. McLaughlan, and E. F. Mooney, *Spectrochim. Acta*, **21**, 1445 (1965).
(6) P. G. Davies and E. F. Mooney, *Spectrochim. Acta*, **22**, 953 (1966).
(7) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, **89**, 5294 (1967).
(8) B. F. Spielvogel, Abstracts, Second International Meeting on Boron Chemistry, Leeds, England, 1974, No. 76.
(9) H. Noeth and B. Wrackmeyer, *Chem. Ber.*, **106**, 1145 (1973); B. Wrackmeyer, Abstracts, Second International Meeting on Boron Chemistry, Leeds, England, 1974, No. 80.
(10) P. J. Clippard and R. C. Taylor, *Inorg. Chem.*, **8**, 2802 (1969).
(11) H. Noeth, *Progr. Boron Chem.*, **3**, 233 (1970).
(12) J. W. Emsley, J. Feemey, and L. H. Sutliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N.Y., 1966, p 992.
(13) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
(14) J. M. VanPaasschen and R. A. Geanangel, *J. Amer. Chem. Soc.*, **94**, 2680 (1972).
(15) D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).
(16) G. F. Lanthier and J. M. Miller, *J. Chem. Soc. A*, 346 (1971).

Contribution from the Department of Chemistry,
University of Southern California,
Los Angeles, California 90007

The New Compound Silylbis(trifluoromethyl)phosphine and Some Phosphorus-Silicon Bond Cleavage Reactions

Leon Maya and Anton B. Burg*

Received July 18, 1974 AIC40490I

Compounds of the type $(CF_3)_2PSiR_3$ might be expected to serve as useful reagents for making other new $(CF_3)_2P$– and R_3Si– compounds, because the P–Si bond is relatively easy to cleave. The first work on this subject concerned $(CF_3)_2PSi(CH_3)_3$, which was found to react easily with HBr to make $(CF_3)_2PH$ and $(CH_3)_3SiBr$ or with CH_3I to make $(CF_3)_2PCH_3$ and $(CH_3)_3SiI$.[1]

We now have made $(CF_3)_2PSi(CH_3)_3$ and the new compound $(CF_3)_2PSiH_3$ by a relatively direct and highly efficient method:

$$(CF_3)_2PI + ISiH_3 + 2Hg \rightarrow (CF_3)_2PSiH_3 + Hg_2I_2 \qquad (1)$$

$$(CF_3)_2PI + ISi(CH_3)_3 + 2Hg \rightarrow (CF_3)_2PSi(CH_3)_3 + Hg_2I_2 \qquad (2)$$

However, our explorations of their P–Si bond cleavage reactions have been aimed at producing unusual and unstable new $(CF_3)_2PX$ compounds, so that the usual result was a variety of more stable products, often to be ascribed to decomposition of the desired cleavage products. Especially interesting and relatively well studied was a BF_3 cleavage, the first stage of which probably was

$$(CF_3)_2PSiH_3 + BF_3 \rightarrow SiH_3F + (CF_3)_2PBF_2 \qquad (3)$$

However, no $(CF_3)_2PBF_2$ could be isolated; indeed, this unknown compound was sought in vain some years ago in many experiments by our erstwhile colleague Dr. Andrew P. Lane, who concluded that its only possible synthesis would be at low temperatures, such that its decomposition might not be inevitable.

Instead of $(CF_3)_2PBF_2$, then, the reaction gave a 47% yield of the interesting ring compound $(CF_3PCF_2)_2$,[2] along with much H_2SiF_2, nonvolatiles, and traces of H_2, B_2H_6, $HSiF_3$, $(CF_3)_2PH$, and $P_2(CF_3)_4$. It is suggested that much bond energy will be gained if $(CF_3)_2PBF_2$ transfers one F from C to form BF_3, with dimerization of the resulting CF_3PCF_2 unit; indeed, something similar must have happened when $(CF_3PCF_2)_2$ was discovered in an attempt to make an $RZnP(CF_3)_2$ compound.[2] On this basis, BF_3 should act as a catalyst for converting $(CF_3)_2PSiH_3$ to $(CF_3PCF_2)_2$; and indeed it seems to do so.

Silylbis(trifluoromethyl)phosphine

Synthesis. Iodosilane was made from $C_6H_5SiH_3$ by action of hydrogen iodide[3] and shaken with mercury and $(CF_3)_2PI$ at 25°. The container was a vacuum-baked vertical stopcocked tube or tubulated bulb, with a side arm into which the volatiles could be condensed at −196°; then a fresh mercury surface could be restored by vacuum sublimation of the mercury iodides. The process was regarded as complete when the typical infrared pattern of $ISiH_3$ at 903 cm^{-1} (a doublet with side fine structure) had disappeared. A typical experiment employed 3 mmol of $ISiH_3$ with $(CF_3)_2PI$ added in 0.5-mmol portions up to a total of 7 mmol and yielded 2.85 mmol of $(CF_3)_2PSiH_3$ (95%). The surplus $(CF_3)_2PI$ was represented mostly by $P_2(CF_3)_4$, which implied no loss because its reconversion to $(CF_3)_2PI$ is very easy.

When $BrSiF_3$ was used instead of $ISiH_3$, it failed to react;