31. tert-Butyl Fluoro Phosphine Complexes 173

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31. tert-BUTYL FLUORO PHOSPHINES AND THEIR TRANSITION METAL COMPLEXES [cis-[Bis-(tertbutyldifluorophosphine)tetracarbonylmolybdenum(0)] and trans-Dibromobis(di-tert-butylfluorophosphine)Nickel(II)]

Submitted by O. STELZER and R. SCHMUTZLER* Checked by PATRICIA BLUM and DEVON W. MEEK †

Alkyl and aryl fluorophosphines, $R_n PF_{3-n}$ (R = hydrocarbon group; n = 1,2) are known to undergo spontaneous redox disproportionation^{1,2} in accord with

 $3R_2PF \longrightarrow R_2PPR_2 + R_2PF_3$ $2RPF_2 \longrightarrow \frac{1}{r}(RP)_x + RPF_4 \quad (usually \ x = 5)$

This facile disproportionation makes the study of the coordination chemistry of these valuable ligands difficult. Although fluorodimethylphosphine and difluoromethylphosphine are known to undergo disproportionation with ease, the presence of electronegative substituents on trivalent phosphorus is known to decrease the rate of disproportionation. A similar, even more pronounced, effect has been observed upon introduction of the bulky *tert*-butyl group as a substituent, and both *tert*-butyldifluorophosphine³ and di-*tert*-butylfluorophos-

^{*}Lehrstuhl B für Anorganische Chemie der Technischen Universität, Pockelsstrasse 4, 33 Braunschweig, Germany.

[†]Department of Chemistry, Ohio State University, Columbus, OH 43210.

phine³ are completely stable with regard to disproportionation. Both compounds are thus very useful fluorophosphine ligands.

The synthesis of the fluoro phosphines is accomplished using chlorine-fluorine exchange in the corresponding chloro phosphines with sodium fluoride in sulfolane (tetrahydrothiophene 1,1-dioxide). The preparation of representative fluoro phosphine complexes with both a zero-valent and bivalent transition metal, Mo(0) and Ni(II), respectively, is also described.

A. tert-BUTYLDIFLUOROPHOSPHINE

 $(CH_3)_3CPCl_2 + 2NaF \xrightarrow{sulfolane} (CH_3)_3CPF_2 + 2NaCl$

Procedure

• Caution. The toxicity of fluoro phosphines is not known, but careful handling of the compounds inside a well-ventilated hood is recommended at all times. tert-Butyldifluorophosphine is spontaneously flammable in air. Special care must be taken because of its high volatility.

The reaction is conducted in a 250-mL, three-necked flask, fitted with a mechanical stirrer, a thermometer reaching close to the bottom of the flask, and a 25-cm Vigreux column to which has been connected a distillation head with multiple receiver. *tert*-Butyldichlorophosphine⁴ (31.8 g, 0.2 mole) is added to a stirred suspension of NaF* (25.2 g, 0.6 mole) in 100 mL of sulfolane[†] over a period of 1 hour. A slow stream of nitrogen is passed through a T-tube connected to the outlet of the distillation apparatus. After the addition of the chlorophosphine, the reaction mixture is heated as follows: 45 minutes at 80°, 15 minutes at 100-180°, and 30 minutes at 180°. Distillation of the fluorophosphine commences at 80° and is complete at 180°. The product is collected in a receiver flask cooled in Dry Ice. *tert*-Butyldifluorophosphine is obtained as a colorless liquid of bp 41-44°; the yield is 20-23 g (79-91%, based on *tert*-butyl-dichlorophosphine[‡]). *Anal.* Calcd. for C₄H₉F₂P: P, 24.6; F, 30.2. Found: P, 24.1; F, 29.0.

tert-Butyldifluorophosphine may be stored for short periods in glass bottles at 0° ; metal cylinders are recommended for long-term storage.

*Merck reagent grade sodium fluoride employed in these preparations was dried at $100-120^\circ$ for 24 hours.

⁺Sulfolane was obtained from Shell Chemicals and distilled twice *in vacuo* over potassium hydroxide; bp 153-154° at 18 torr.

[‡]The checkers report a yield of 85%, on one-half of the above scale. The use of magnetic stirring, instead of mechanical stirring, was found satisfactory by the checkers in small-scale runs.

Properties

tert-Butyldifluorophosphine is sensitive to air and moisture and must be handled in, an atmosphere of nitrogen* or argon,* or in a vacuum line throughout; the latter technique is particularly appropriate.

Physical properties and spectroscopic data for *tert*-butyldifluorophosphine, $(CH_3)_3CPF_2$ are given below:

Boiling point 41-44° (reference 3)
40-41° (checkers)
NMR data
³¹P:
$$\delta_P$$
 -231.2 ppm (ext. H₃PO₄)³
226.1 ppm (checkers)
¹⁹F: δ_F , +111.5 ppm (int. CCl₃F)³
¹J_{PF}, 1219 Hz³; 1182 Hz (checkers)
¹H: δ_H , -0.96 ppm (int. SiMe₄)³
-1.00 ppm¹⁷
³J_{PH}, 12.3 Hz³; 12.9 Hz¹⁷; 12.5 Hz (checkers)
⁴J_{FH}, 1.8 Hz³; 2.0 Hz¹⁷; 1.5 Hz (checkers)

The simplicity of ¹H, ¹⁹F, and ³¹P NMR spectra of both free and coordinated *tert*-butylfluorophosphine ligands is particularly noteworthy, as valuable bonding information can be obtained from the NMR spectra.⁶

Because of its stability with regard to disproportionation, $t-C_4H_9PF_2$ can be employed as a useful P(III) ligand, and a variety of complexes with transition metals, both zerovalent⁶ and in positive oxidation states,^{7,8} as well as those with boron acceptors,^{9,18} have been prepared. The preparation of a representative complex is described below.

Oxidative fluorination of $t-C_4H_9PF_2$ with antimony trifluoride gives the tetrafluorophosphorane, $t-C_4H_9PF_4$, which may serve as a precursor to other *tert*butylphosphorane derivatives.³

The vibrational spectrum of $t-C_4H_9PF_2$ has been assigned.¹⁰

B. cis-[BIS(tert-BUTYLDIFLUOROPHOSPHINE)TETRACARBONYL-MOLYBDENUM(0)]

 $C_7H_8Mo(CO)_4 + 2t-C_4H_9PF_2 \longrightarrow cis(t-C_4H_9PF_2)_2Mo(CO)_4 + C_7H_8$

C₇H₈ =bicyclo[2.2.1] hepta-2,5-diene(bicycloheptadiene)

*Dried by passage over P₄O₁₀ dispersed on glass wool.

Procedure

The reaction is conducted in a 100-mL Schlenk tube.¹² tert-Butyldifluorophosphine (1.26 g, 0.01 mole), contained in a hypodermic syringe, is added to a solution of (bicycloheptadiene)tetracarbonylmolybdenum¹³ (1.5 g, 0.005 mole) in 20 mL of anhydrous pentane. There is an immediate reaction, indicated by a discharge of color. After a 5-hour stirring period the solvent and the bicycloheptadiene displaced by the fluorophosphine ligand are removed by pumping and the pressure gradually decreases from 10 to 1 torr. The oily residue thus left is distilled in a short-path distillation apparatus¹⁴ at 100° (10⁻⁴ torr). The complex [t-C₄H₉PF₂]₂Mo(CO)₄ is obtained as a colorless oil; yield 2.1-2.2 g (91-96%). Anal. Calcd. for C₁₂H₁₈F₄MoO₄P₂: C, 31.3; H, 3.9; F 16.5; P. 13.5. Found: C, 31.5; H, 4.0; F. 16.2; P. 13.4.

Properties

cis-[Bis(*tert*-butyldifluorophosphine)tetracarbonylmolybdenum(0)] is decomposed slowly upon prolonged exposure to moist air.

NMR data

¹ H:	δ _H , ~1.01 ppm (int. TMS)
	${}^{3}\tilde{J}_{\rm PH}$, 16.6 Hz; ${}^{4}J_{\rm FH}$, 1.2 Hz

- ¹⁹F: $\delta_{\rm F}$ +65.4 ppm (int. CCl₃F) |¹J_{PF} + ³J_{PF}| 1104 Hz
- ³¹P: δ_{P} -263.4 ppm (ext. H₃PO₄)

IR⁶: ν_{CO} 2035 (m), 1980 (m), 1957 (s), 1951 (s) (cm⁻¹)

C. DI-tert-BUTYLFLUOROPHOSPHINE

$$[CH_3)_3C]_2PCl + NaF \xrightarrow{sulfolane} [(CH_3)_3C]_2PF + NaCl$$

Procedure

• Caution. The toxicity of $(t-C_4H_9)_2PF$ is unknown. It is recommended that the compound be handled inside a well-ventilated hood. The compound may be flammable upon exposure to air.

Using the same apparatus as in Section A, 36.1 g (0.2 mole) of di-*tert*-butylchlorophosphine^{4,5} is added by means of a hypodermic syringe to a suspension of 12.6 g (0.3 mole) of NaF in 100 mL of sulfolane. The temperature of the reaction mixture, which gradually turns brown, is raised to $150-180^{\circ}$ and stirring is continued for another 12 hours. The fluorophosphine is recovered from the reaction mixture by distillation under reduced pressure and is obtained as a colorless liquid of bp 70-72° (55 torr); yield 28-30 g (85-91%,* based on di-*tert*-butylchlorophosphine). Anal. Calcd. for $C_8H_{18}FP$: C, 58.5; H, 11.0; F, 11.6; P, 18.9. Found: C, 57.4; H, 10.7; F, 10.3; P. 18.1.

The fluorophosphine may be stored in glass bottles at 0° for short periods; storage in metal containers is recommended for longer periods.

Properties

Di-tert-butylfluorophosphine is a colorless, volatile liquid. The compound is sensitive to air and moisture and should be handled in a nitrogen^{\dagger} or argon^{\dagger} atmosphere, or in a vacuum line.

Physical properties and spectroscopic data for $(t-C_4H_9)_2PF$ are as follows:

Boiling point 72° (55 torr) or 67-70° (48 torr³)

NMR data

¹ H:	δ _H , -1.03 ppm (int. TMS)
	${}^{3}J_{\rm PH}$, 11.9 Hz ³ ; 11.3 Hz ¹⁶ ; 11.5 Hz (checkers)
	${}^{4}J_{\rm FH}^{11}$, 2.1 Hz ³ ; 1.7 Hz ¹⁶ ; 1.5 Hz (checkers)
¹⁹ F:	$\delta_{\rm F}^{1}$, +223.5 ppm ³ (int. CCl ₃ F)
	$^{1}\dot{J}_{\rm PF}$, 848 Hz ³ ; -873.6 ± 0.02 Hz ¹⁶
³¹ P:	$\delta_{\rm P}, -210.4 \rm ppm^3$

The infrared spectrum of $(t-C_4H_9)_2$ PF has been assigned.¹¹

D. trans-[DIBROMOBIS(DI-tert-BUTYLFLUOROPHOSPHINE)NICKEL(II)]

 $NiBr_2 + 2(t-C_4H_9)_2PF \longrightarrow Br_2Ni[(t-C_4H_9)_2PF]_2$

Procedure

The reaction is conducted in a 100-mL Schlenk tube.¹² Di-*tert*-butylfluorophosphine (1.64 g, 0.01 mole) is added from a pressure-equalizing dropping funnel to a suspension of anhydrous $NiBr_2^{15}$ in 50 mL of solvent, either acetone (dried over P_4O_{10}) or benzene (dried by distillation over sodium) saturated with argon or nitrogen. After stirring for 48 hours at room temperature, excess $NiBr_2$ is

*The checkers report a yield of 85%, on one-half of the above scale. The use of magnetic stirring, instead of mechanical stirring, was found satisfactory by the checkers in small-scale runs.

[†]Dried by passage over P_4O_{10} , dispersed on glass wool.

removed by filtration under nitrogen through a sintered-glass funnel, and the solvent is evaporated *in vacuo* $(0^{\circ}/10 \text{ torr})$. A 2.1-2.3 g (77-82%) yield of *trans*-[NiBr₂[$(tC_4H_9)_2PF$]₂] is obtained. The product may be recrystallized from dichloromethane or toluene at -50° using a Schlenk tube. *Anal.* Calcd. for C₁₆H₃₆Br₂F₂NiP₂: C, 35.1; H, 6.6; F. 6.9; P. 11.3; MW, 546.9. Found: C, 34.9; H, 6.8; F. 7.0; P. 11.3, MW (cryoscopic in benzene), 550.

Properties

trans-[Dibromobis(di-*tert*-butylfluorophosphine)nickel(II)] is a red-brown, crystalline compound that is stable upon brief exposure to air.

The trans structure is established from an x-ray crystal structure determination. 7

Spectral data⁷ for the complexes are as follows (all spectra recorded in CH_2Cl_2):

NMR⁷

¹H: broad peak at +3.5 ppm (int. CH₂Cl₂)

¹⁹F: broad doublet: δ_{F} , -12.3 ±0.2 ppm (int. C₆F₆); +175 ppm (int. CCl₃F)

³¹P: $\delta_{\rm P}$, -175 ppm (ext. H₃PO₄)

UV spectrum⁷

250 (>10.000), 315 (sh, 20,000), 407 (5900), and 485 nm (1200) (ϵ in parentheses)

Hydrolysis of NiBr₂ [$(t-C_4H_9)_2$ PF]₂ affords the paramagnetic, pseudotetrahedral complex, NiBr₂ [$t-C_4H_9$)₂ HPO]₂.⁸

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32. (DIALKYLAMINO) FLUORO PHOSPHORANES

 $PF_5 + (R_2N)Si(CH_3)_3 \longrightarrow (R_2N)PF_4 + (CH_3)_3SiF$

 $(R_2N)PF_4 + (R_2N)Si(CH_3)_3 \longrightarrow (R_2N)_2PF_3 + (CH_3)_3SiF$

Submitted by MICHAEL J. C. HEWSON* and REINHARD SCHMUTZLER* Checked by JOSEPH G. MORSE[†] and JAMES J. MIELCAREK[†]

(Dialkylamino) fluoro phosphoranes can be prepared by the direct aminolysis of fluoro phosphoranes with secondary amines.¹⁻⁴ However, besides the desired product, large quantities of ionic species are often formed, making isolation of the covalent species difficult. This class of compounds also can be prepared by the oxidation with halogen (chlorine or bromine) of the three-coordinate dialkylamino chloro or fluoro phosphines⁵ to give mixed halo phosphoranes^{4,5} followed by simple halogen-fluorine exchange on the latter using Group V fluorides such as arsenic trifluoride or antimony trifluoride.⁵ In some cases spontaneous exchange of ligands in the halo fluoro phosphoranes occurs to give the desired fluoro phosphorane, among other products.^{6,7} This is, however, a long and involved procedure. (Dimethylamino)tetrafluorophosphorane has been prepared from the reaction of bis(dimethylamino)sulfide⁸ (tetramethylsulfoxylic diamide) or tris(dimethylamino)phosphine⁹ (hexamethylphosphorus triamide) with phosphorus pentafluoride; however, the scope and utility of this type of reaction are limited. A clean and convenient method of synthesis of dialkylamino fluoro phosphoranes involves the cleavage reaction of the silicon-

^{*}Lehrstuhl B für Anorganische Chemie der Technischen Universität, Pockelsstrasse 4, 33 Braunschweig, Germany.

[†]Department of Chemistry, Utah State University, Logan, UT 84321.