4420 *Inorg. Chem.* **1992,** *31,* 4420–4421

Notes

Synthesis of Difluorophosphoranes from Phosphines and Mercuric Fluoride

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Received April 23, 1992

Introduction

Although the mercuric chloride complexes of many tertiary phosphines (e.g., Me_3P,[1] Et_3P,[1] *n*-Bu_3P,[2] and Ph_3P[2]) have been prepared and crystallographically characterized, there are no literature reports of the corresponding mercuric fluoride complexes. Our attempts to prepare the complexes of these phosphines with mercuric fluoride have instead yielded the corresponding difluorophosphoranes (**1**–**4**). Although the oxidative transfer of fluorine from mercuric fluoride to dimethyl sulfide has been reported,[3] this transfer is unprecedented for phosphines.

$$R_3P + HgF_2 \longrightarrow R_3PF_2 + Hg^0$$

1 R = Me
2 R = Et
3 R = n-Bu
4 R = Ph

The apicophilicity and NMR visibility of fluorine have led to many studies of fluorophosphoranes as probes of pentavalent phosphorus geometry and configurational stability.[4] However, despite an initial report of the conversion of alcohols to alkyl fluorides,[5] fluorophosphoranes have not played a significant role in organic synthesis. This may in part be due to the volatility, toxicity, and/or high cost of the reagents typically used for their preparation (e.g., SF_4,[6] R_2NSF_3,[7] COF_2,[8] F_2,[9] and AsF_3[10]). Antimony tri-[10,11] and pentafluoride[12] have been used for the preparation of heteroatom-substituted fluorophosphoranes from phosphines, but to our knowledge, the latter reagents have not been used for the preparation of difluorotriorganophosphoranes. The electrochemical fluorination of phosphines by ammonium fluoride has been reported,[13] and recently, Wang and Mallouk[14] prepared **4** photochemically, using AgF as a fluoride source. Alternatively, difluorophosphoranes have been obtained from reactions of other phosphorus(V) compounds, including the reactions of sodium fluoride with bromophosphoranes[15] and antimony trifluoride[16] or sulfuryl chloride fluoride[17] with phosphine sulfides.

Herein we report a simple preparation of difluorotriorganophosphoranes through the previously unreported redox reaction between phosphines and mercuric fluoride.

Experimental Section

All manipulations were performed under an atmosphere of purified dry nitrogen or argon. Benzene and benzene-d_6 were distilled from sodium/benzophenone ketyl prior to use. Mercuric fluoride and trimethyl-, triethyl-, and tri-*n*-butylphosphine were used as received (Aldrich Chemical Co.). Triphenylphosphine was dried in vacuo at room temperature prior to use. *Caution*! Mercuric fluoride and mercury byproducts must be treated with appropriate safety precautions, avoiding skin contact and exposure to dust or vapor and working in a well-ventilated fume hood.

Difluorotrimethylphosphorane (1).[4d,18–20] Trimethylphosphine (0.030 mL, 0.29 mmol) was added to a suspension of mercuric fluoride (0.146 g, 0.612 mmol) in benzene-d_6 (0.5 mL, including 0.10 mmol of toluene as an internal standard). Upon mixing, the solid immediately became charcoal-gray. After the solid settled, the supernatant solution was decanted and assayed by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR (Table I). The yield of Me_3PF_2, by integration against the toluene internal standard, was 66% (based on PMe_3).

Difluorotriethylphosphorane (2).[4d] Triethylphosphine (0.025 mL, 0.10 mmol) was added to a suspension of mercuric fluoride (0.024 g, 0.10 mmol) in benzene-d_6 (0.5 mL, including 0.060 mmol of toluene as an internal standard). Upon mixing, the solid immediately became black, and metallic mercury separated. After the solid settled, the supernatant solution was decanted and assayed by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR (Table I). The yield of Et_3PF_2, by integration against the toluene internal standard, was 78% (based on HgF_2).

Difluorotri-*n*-butylphosphorane (3).[4d,20,21] Tri-*n*-butylphosphine (0.030 mL, 0.12 mmol) was added to a suspension of mercuric fluoride (0.023 g, 0.096 mmol) in benzene-d_6 (0.5 mL, including 0.050 mmol of toluene as an internal standard). Within 10 min, the solid began to darken. After overnight stirring at room temperature, metallic mercury was evident. The colorless solution was decanted and assayed by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR (Table I). The yield of *n*-Bu_3PF_2, by integration against the toluene internal standard, was 62% (based on HgF_2).

Difluorotriphenylphosphorane (4).[4d,20] Triphenylphosphine (0.262 g, 1.00 mmol) and mercuric fluoride (0.238 g, 1.00 mmol) were combined in ca. 20 mL of benzene. The resulting suspension was heated under reflux for 42 h, resulting in a dense gray precipitate containing metallic mercury. The solution was transferred via cannula to a Schlenk flask, and the solvent was removed in vacuo, affording a white solid. This material was washed with two 5-mL aliquots of diethyl ether and dried in vacuo, giving **4** in 71% yield (0.21 g, 0.71 mmol); mp 140–158 °C. Anal. Calcd for $C_{18}H_{15}PF_2$: C, 72.00; H, 5.03; P, 10.31. Found: C, 71.82; H, 5.10; P, 10.26. For ^1H, ^{13}C, ^{19}F, and ^{31}P NMR data, see Table I.

Results and Discussion

Addition of 1 equiv, or a slight excess, of Et_3P or *n*-Bu_3P to a suspension of mercuric fluoride in dry benzene results in the

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Table I. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR Chemical Shifts and Coupling Constants for Fluorophosphoranes **1–4**[a]

	^1H	$^{13}C\{^1H\}$					
R_pF_2	H–C–P	C–P	C–C–P	C–C–C–P	C–C–C–C–P	^{19}F	^{31}P
1	δ 1.42, dt[b,c] J_{PH} = 17.3 Hz J_{FH} = 12.3 Hz	δ 19.7, dt $^1J_{PC}$ = 127 Hz $^2J_{FC}$ = 30 Hz				δ 73.4[d,e] $^1J_{PF}$ = 544 Hz $^3J_{HF}$ = 12.4 Hz	δ −15.9[b,e] $^1J_{PF}$ = 544 Hz
2	δ 1.81, m	δ 26.2 dt $^1J_{PC}$ = 123 Hz $^2J_{FC}$ = 28 Hz	δ 7.82, d $^2J_{PC}$ = 6.2 Hz			δ 39.8[d] $^1J_{PF}$ = 586 Hz $^3J_{HF}$ = 9.8 Hz	δ −12.0 $^1J_{PF}$ = 586 Hz
3	δ 1.89, m	δ 33.6, dt $^1J_{PC}$ = 120 Hz $^2J_{FC}$ = 26 Hz	δ 25.9, "q" $^2J_{PC}$ = 5.2 Hz $^3J_{FC}$ = 5.2 Hz	δ 24.5, d $^3J_{PC}$ = 20 Hz	δ 13.8, s	δ 44.6[d,e] $^1J_{PF}$ = 581 Hz $^3J_{HF}$ = 11.5 Hz	δ −14.0[e,f] $^1J_{PF}$ = 583 Hz
4	δ 8.13, m (ortho H)	δ 137.4, br d $^1J_{PC}$ = 180 Hz $^2J_{FC}$ unresolved	δ 134.3, dt $^2J_{PC}$ = 12.5 Hz $^3J_{FC}$ = 8.8 Hz	δ 128.5, d $^3J_{PC}$ = 21 Hz	δ 131.4, d $^4J_{PC}$ = 3.2 Hz	δ 40.0[d,e] $^1J_{PF}$ = 664 Hz $^2J_{FC}$ = 28 Hz	δ −54.4 $^1J_{PF}$ = 665 Hz

[a] ^1H spectra recorded at 300 MHz; chemical shifts in δ units relative to C_6D_5H at δ 7.15. ^{13}C spectra recorded at 75.5 MHz; chemical shifts in δ units relative to C_6D_6 at δ 128. ^{19}F spectra recorded at 282 MHz; chemical shifts in δ units relative to CF_3CO_2H at δ 0.0. ^{31}P spectra recorded at 162 MHz; chemical shifts in δ units relative to 85% H_3PO_4 at δ 0.0. [b] Reference 18. [c] Reference 19. [d] Reference 4d. [e] Reference 20. [f] Reference 21.

rapid precipitation of metallic mercury and the formation of the corresponding difluorophosphoranes, **2** and **3**. Although Me_3P also reacts instantly with mercuric fluoride under these conditions, the reduction of mercuric fluoride by the phosphine appears to be incomplete in that no metallic mercury is formed. Accordingly, preparation of the trimethyl derivative, **1**, was carried out using an excess of mercuric fluoride. Triphenylphosphine reacts smoothly with 1 equiv of mercuric fluoride in dry benzene to form **4** and metallic mercury; however, heating at reflux is required to effect this reaction.

Rather surprisingly, full multinuclear NMR spectral characterizations of the difluorophosphoranes have not been reported. We present ^1H, ^{13}C, ^{19}F, and ^{31}P NMR data for difluorophosphoranes **1–4** in Table I. The trialkylphosphoranes, **1–3**, exhibit $^1J_{PC}$ values of ca. 120 Hz; similar values have been reported for equatorial substituents in other trigonal bipyramidal phosphorus derivatives.[22] The triphenyl derivative, **4**, displays a larger $^1J_{PC}$ (180 Hz), consistent with the increased s-character of the carbon-centered bonding orbitals in this derivative.[23] To confirm the structure of difluorotriphenylphosphorane (**4**), we carried out an X-ray crystallographic analysis.[24] Crystallography confirms that, in the solid state, **4** has a trigonal bipyramidal geometry about phosphorus, with the fluorines occupying the axial positions. The structure is similar to that of difluorotris(pentafluorophenyl)phosphorane,[25] with the most significant differences being the increased twist of the phenyl groups in **4** from the equatorial plane and the opposition of one of the phenyl rings in **4** to the propeller-like arrangement found in the perfluoro derivative. We are continuing to examine the generality of this procedure and the use of difluorophosphoranes for the fluorination of organic substrates.

Acknowledgment. This work was supported by the National Institutes of Health, Institute of General Medical Sciences, Bethesda, MD.

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