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Preparation and Characterization of Bis(trifluoromethyl)phosphanide Salts of Outstanding Stability

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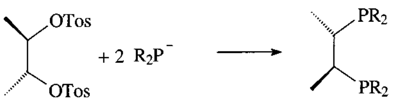
The stable compounds $[NEt_4][P(CF_3)_2]$ and $[18\text{-crown-6-K}][P(CF_3)_2]$ were synthesized in quantitative yields by treatment of $HP(CF_3)_2$ with ionic cyanides at low temperature. These novel salts were characterized by multinuclear NMR spectroscopy, elemental analysis, and vibrational spectroscopy. Excellent agreement of experimental and theoretical vibrational frequencies, calculated at the B3PW91 level of theory, clearly confirms the saltlike character of these compounds. Due to their ionic nature, these salts are excellent nucleophilic reagents for the transfer of $P(CF_3)_2$ groups, suitable for the synthesis of chiral bidentate bis(trifluoromethyl)phosphine containing compounds.

Introduction

Bidentate phosphine ligands play an important role in asymmetric catalysis.[1] The bidentate phosphine ligands are most frequently synthesized by reacting 1,2-di-tosylethane derivatives and diarylphosphide anions,



The extension of this procedure to the synthesis of bis(trifluoromethyl)phosphine chelate ligands requires nucleophilic $P(CF_3)_2$ group transfer reagents which so far have been unknown.

$Na[P(CF_3)_2]$ and $Cs[P(CF_3)_2]$ are thermally unstable. They were prepared by the reaction of $HP(CF_3)_2$ with the corresponding alkali metal in liquid ammonia.[2] At elevated temperature, the alkali metal salts eliminate $CF_3-P=CF_2$ and form the corresponding fluorides. The anion was characterized exclusively by its NMR spectra. Due to a fast side reaction of $HP(CF_3)_2$ with the solvent, no pure compound could be obtained.[3]

Burg et al. reacted $HP(CF_3)_2$ and $ZnMe_2$ to obtain bis(trifluoromethyl)phosphido zinc compounds. Due to the high Lewis acidity and fluorophilicity of the metal atom, the reaction resulted in the formation of Zn(Me)F and $(CF_3-PCF_2)_2$.[4]

To stabilize $[P(CF_3)_2]^-$ compounds, it is essential to reduce the fluorophilicity of the positive counterpart. A hint for a stable $[P(CF_3)_2]^-$ compound is found in the reaction of tetrakis(dimethylamino)ethylene (TDAE) and bis(trifluoromethyl)chlorophosphine. Treatment of this product with methyl triflate leads to the formation of $MeP(CF_3)_2$ and methyl chloride.[5]

Saltlike compounds containing the $[P(CF_3)_2]^-$ anion are suggested to be the most suitable $P(CF_3)_2$ group transfer reagents in S_N2 type reactions. On the basis of the good results in the synthesis of bis(trifluoromethyl)phosphanido complexes by reacting mercury cyanides with $HP(CF_3)_2$,[6,7] and the formation of $[Ge(CF_3)_3]^-$ by interaction of $HGe(CF_3)_3$ with cyanides,[8] we investigated the reactions of $HP(CF_3)_2$ and saltlike cyanides.

Experimental Section

Materials and Apparatus. Chemicals were obtained from commercial sources and used without further purification. Modified literature methods were used for the synthesis of $HP(CF_3)_2$.[9] Instead of Me_3SnH, the less volatile Bu_3SnH was used for the reduction of $(CF_3)_2PBr$. This allows separation by fractional condensation after reacting for 30 min at 0 °C. Bromobis(trifluoromethyl)phosphine was synthesized by treating neat $(CF_3)_2PNEt_2$[10] with gaseous HBr at −78 °C. ***CAUTION!*** The toxic compounds $(CF_3)_2PBr$ and $(CF_3)_2PH$ react violently with air. Solvents were purified by standard methods.[11] Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques.

Infrared spectra were recorded on a Nicolet-5PC-FT-IR spectrometer as KBr pellets. Raman spectra were measured on a Bruker FRA-106/s spectrometer with a Nd:YAG laser operating at $\lambda = 1064$ nm.

The NMR spectra were recorded on Bruker model AMX 300 (^{13}C, 75.47 MHz; ^{31}P, 121.50 MHz; ^{19}F, 282.35 MHz) and Bruker model AC200 spectrometers (^{31}P, 81.01 MHz; ^{19}F, 188.31 MHz; ^{13}C, 50.32 MHz; ^{1}H, 200.13 MHz), with positive shifts being downfield from the external standards 85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F), and TMS (^{13}C and ^{1}H). Higher order NMR spectra were calculated with the program gNMR.[12]

Preparation of Tetraethylammonium Bis(trifluoromethyl)phosphanide. $[NEt_4]CN$ (860 mg, 5.50 mmol) was dissolved in 5 mL of CH_2Cl_2, and 20 mL THF was added. $HP(CF_3)_2$ (1.05 g, 6.20 mmol) was condensed at −196 °C onto the suspension. The reaction mixture

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was stirred for 1 h in the temperature range from −78 to −50 °C. After removing excess $HP(CF_3)_2$ in vacuo, 20 mL of Et_2O was condensed at −78 °C onto the well-stirred colorless solution from which $[NEt_4][P(CF_3)_2]$ began to precipitate. After precipitation was completed, the solvents were taken off via a syringe and the solid residue was washed several times with Et_2O. After drying the solid in vacuo, the temperature was raised to ambient over a period of 2 h. $[NEt_4][P(CF_3)_2]$ (1.64 g, 5.48 mmol, 100%) was obtained as an extremely hygroscopic white powder which starts to decompose above 140 °C (DTA/TG). Elemental analysis (calc. for $C_{10}H_{20}F_6NP$): P 11.0 (10.3); F 40.5 (38.1); N 5.8 (4.6); C 41.5 (40.1). Infrared spectrum (cm^{-1}, KBr pellet): 2992 m, 2956 vw, 2358 vw, 1614 vw, 1493 s, 1479 w, 1463 w, 1442 w, 1398 m, 1375 w, 1311 w, 1231 w, 1212 w, 1188 m, 1174 m, 1136 vs, 1087 vs, 1072 s(br), 999 sh, 897 w, 798 s, 790 s, 721 vw, 582 w, 561 w, 505 vw, 481 vw, 465 w, 450 w, 423 vw. Raman (cm^{-1}): 2992 (100), 2953 (95), 2897 (35), 2053 (15), 1461 (40), 1303 (15), 1136 (24), 1120 (20), 1069 (22), 1004 (22), 893 (17), 732 sh, 720 (49), 661 (25), 555 (13), 465 (26), 450 (18), 418 (22), 388 (20), 296 (23), 268 (19), 124 (17). NMR data (acetone-d_6, 243 K) of the $[NEt_4]^+$ counterion: $\delta(^1H)$ 3.0 ppm (2H); $\delta(^1H)$ 0.9 ppm (3H); $^3J(HH)$ 7.5 Hz; $\delta(^{13}C)$ 52.2 ppm (CH_2); $\delta(^{13}C)$ 52.2 ppm (CH_3). The NMR spectroscopic data of the $[P(CF_3)_2]^-$ anion are uneffected by the counterion: $\delta(^{31}P)$ −1.9 ppm; $\delta(^{19}F)$ −31.4 ppm; $\delta(^{13}C)$ 146.5 ppm; $^1J(CF)$ −315.6 Hz; $^1J(PC)$ 92.5 Hz; $^2J(PF)$ 47.2 Hz; $^3J(CF)$ −12.1 Hz; $^4J(FF)$ 9.0 Hz.

Preparation of 18-Crown-6-potassium Bis(trifluoromethyl)phosphanide. [18-crown-6-K][CN] (880 mg, 2.67 mmol) was dissolved in 5 mL CH_2Cl_2. After adding 20 mL THF, $HP(CF_3)_2$ (585 mg, 3.50 mmol) was condensed onto the white suspension at −196 °C. Stirring for 1 h at −78 to −50 °C gave a clear colorless solution. After distilling 20 mL diethyl ether onto the well-stirred solution at −78 °C, the product precipitated as a white powder. After removing the solvent, washing the solid with diethyl ether for several times, and drying in vacuo, the temperature was raised to room temperature. $[18\text{-crown-6-K}][P(CF_3)_2]$ (1.26 g, 2.67 mmol, 100%) was obtained as a white powder. The neat substance decomposes at 145 °C (DTA/DT). Elemental analysis (calc. for $C_{14}H_{24}F_6KO_6P$): P 7.1 (6.6); F 25.8 (24.1); C 35.4 (35.6); H 4.9 (5.1). Infrared spectrum (cm^{-1}, KBr pellet): 2906 s, 2831 w, 2802 vw, 2751 w, 2717 vw, 2696 vw, 1977 vw, 1509 vw, 1474 w, 1458 w, 1435 vw, 1354 m, 1329 vw, 1286 w, 1253 m, 1242 w, 1211 vw, 1135 s, 1109 vs, 1071 m, 1057 m, 998 m, 963 s, 840 m, 733 vw, 580 w, 556 w, 525 w, 503 vw, 462 w, 448 w, 419 vw. Raman (cm^{-1}): 2956 (36), 2895 (100), 2847 (90), 2810 (50), 2786 (16), 2730 (14), 2710 (10), 1479 (55), 1456 (10), 1410 (9), 1274 (40), 1247 (10), 1136 sh, 1081 (8), 1067 sh, 999 (7), 947 (6), 867 (40), 832 (20), 731 (5), 719 (26), 549 (12), 462 (8), 447 (8), 292 (26), 269 (26), 102 (8), 78 (10). NMR data (acetone-d_6, 243 K) of the $[18\text{-crown-6-K}]^+$ counterion: $\delta(^1H)$ 3.5 ppm; $\delta(^{13}C)$ 70.8 ppm. The NMR spectroscopic data of the $[P(CF_3)_2]^-$ anion are unaffected by the counterion, see above.

Reaction of $[NEt_4][P(CF_3)_2]$ with 1,2-Ethanediol Bis(4-methylbenzenesulfonate). To a well stirred solution of 730 mg (2.44 mmol) $[NEt_4][P(CF_3)_2]$ in 15 mL THF, 370 mg (1.10 mmol) 1,2-ethanediol bis(4-methylbenzenesulfonate) dissolved in 3 mL THF was added. During a period of 20 h, the reaction temperature was raised from −70 °C to room temperature. The yield of 80% was determined by integrating the ^{19}F NMR spectrum after addition of 2.00 mmol 1,3-bis(trifluoromethyl)benzene. The product, $(CF_3)_2PCH_2CH_2P(CF_3)_2$, was identified on the basis of its characteristic ^{19}F and ^{31}P NMR spectrum ($\delta(^{31}P)$ −3.2 ppm; $\delta(^{19}F)$ −54.9 ppm; $^1J(PP)$ 44.0 Hz; $^2J(PF)$ 71.4 Hz; $^5J(PF)$ 2.0 Hz).[13]

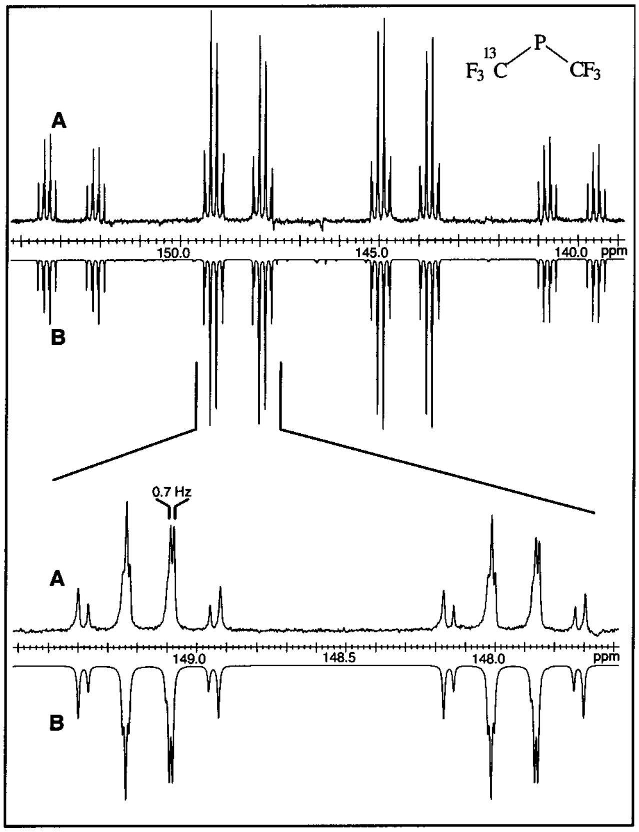

Figure 1. Experimental ^{13}C NMR spectrum (**A**) of the $[P(CF_3)_2]^-$ anion compared with the calculated spectrum (**B**). The spectrum was recorded at 263 K by means of DEPT polarization transfer from ^{19}F (6956 scans, 16 K data points, spectra with 2645 Hz, relaxation delay 2 s, variable pulse length 45°, no decoupling).

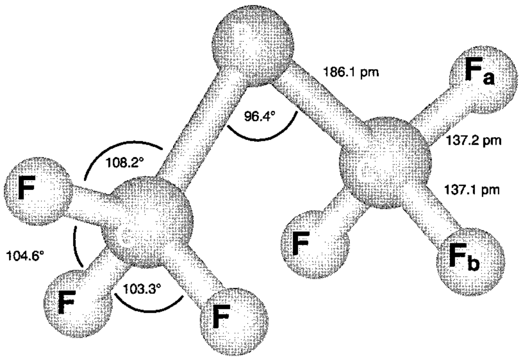

Figure 2. Geometry of the $[P(CF_3)_2]^-$ anion optimized at the B3PW91/6-311G** level. The F−C(P)C−F dihedral angle has a value of 3.7°.

Results and Discussion

The displacement of a weaker acid by a stronger acid during the reaction of $HP(CF_3)_2$ with KCN in DMF at −50 °C leads to the formation of the $[P(CF_3)_2]^-$ anion, which is detected in low-temperature NMR experiments and is trapped by adding EtI, giving $EtP(CF_3)_2$.[14] Reaction mixtures containing $K[P(CF_3)_2]$ decompose rapidly above −50 °C. To increase the stability of the $[P(CF_3)_2]^-$ salts, a cation of lower Lewis acidity is needed to avoid fluoride elimination. If the less fluorophilic cations $[NEt_4]^+$ or $[18\text{-crown-6-K}]^+$ are used, decomposition of the reaction mixtures begins above −30 °C. Attempts to isolate the compounds $[NEt_4][P(CF_3)_2]$ or $[18\text{-crown-6-K}][P(CF_3)_2]$, respectively, by pumping of solvent, HCN, and excess of $HP(CF_3)_2$ at low temperature give oily products which decompose upon warming.

However, isolation of the compounds is successful if the cyanide is first dissolved in CH_2Cl_2 and precipitated by adding THF, to give a fine suspension. The precipitate dissolves after

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Table 1. Calculated (B3PW91/6-311G**) Vibrational Frequencies and Observed Infrared and Raman Spectra of $[P(CF_3)_2]^-$ and $S(CF_3)_2$

assignments and approx. mode descript in point group C_2		[18-C-6-K][$P(CF_3)_2$]		[NEt_4][$P(CF_3)_2$]		$[F_3C-P-CF_3]^-$	$F_3C-S-CF_3$[a]		
		IR	Raman	IR	Raman	calc'd [IR] (Ra)	IR (gas)	Raman	calc'd [IR] (Ra)
ν_1(A)	$\nu(CF_3)$	1135 vs	1136 sh	1136 vs	1136 (51)	1141.3 [46] (97)	1222 vs	1220 (1)	1241.2 [82] (7)
ν_{12}(B)		1071 vs	1067 sh	1072 vs	1069 (44)	1082.9[100](33)	1197 vs	1190 (1.5)	1217.7 [98] (9)
ν_2(A)		1057 vs				1079.3 [31] (11)			1186.7 [0] (0)
ν_{13}(B)						1036.5 [67] (20)	1161 s	1160 (1.5)	1176.8 [40] (8)
ν_3(A)						1020.4 [0] (2)			1161.3 [15] (9)
ν_{14}(B)		998 s	999 (22)	999 sh		1006.1 [0] (100)	1078 vs	1070 (1)	1069.9 [100](9)
ν_{15}(B)	$\delta_s(CF_3)$	733 vw	731 (5)		732 (6)	725.8 [0] (0)	775 wm	775 (7)	768.7 [7] (0)
ν_4(A)			719 (100)		720 (100)	722.8 [0] (75)	768 wm	768 (100)	771.1 [1](100)
ν_5(A)	$\delta_{as}(CF_3)$	556 w		561 w	555 (15)	556.8 [2] (26)	589 m	593 (2)	590.7 [0] (18)
ν_{16}(B)						524.9 [0] (0)			546.0 [0] (3)
ν_6(A)						522.7 [0] (0)		545 (2)	545.3 [0] (26)
ν_{17}(B)						516.5 [0] (41)	545 m		545.5 [2] (4)
ν_7(A)	$\nu_s(PC_2)$	462 w	462 (22)	465 w	465 (53)	465.1 [2] (59)	480 wm	475 (40)	477.4 [0] (60)
ν_{18}(B)	$\nu_{as}(PC_2)$	448 w	447 (17)	450 w	450 (31)	446.7 [1] (24)	475 sh		474.3 [0] (40)
ν_{19}(B)						338.9 [0] (27)		358 (1)	361.2 [0] (11)
ν_8(A)			292 (89)		296 (50)	292.6 [0] (29)		304 (73)	300.7 [0] (43)
ν_{20}(B)						264.0 [0] (12)			280.0 [0] (10)
ν_9(A)			269 (39)		268 (27)	262.4 [0] (29)	281 vw	286 (13)	281.4 [0] (19)
ν_{10}(A)						114.0 [0] (3)	126 m	130 (4)	126.0 [0] (2)
ν_{21}(B)	$\tau(CF_3)$					67.5 [0] (3)	77 vw	75 (3)	75.3 [0] (1)
ν_{11}(A)						25.7 [0] (0)	63 vvw		13.7 [0] (0)

[a] See refs 18 and 20.

Table 2. Experimental Geometric Parameters of $O(CF_3)_2$ and $S(CF_3)_2$ vs the Calculated Data at the B3PW91/6-311G** Level of Theory[a]

	CF_3-O-CF_3		CF_3-S-CF_3		$[CF_3-P-CF_3]^-$
	exp.[b]	B3PW91	exp.[c]	B3PW91	B3PW91
E−C	136.9(4)	137.5	181.9	182.7	186.1
C−F$_a$	132.7(2)	132.1[d]	133.0	133.5[d]	137.2[d]
C−F$_b$		133.0[d]		133.1[d]	137.1[d]
∠C-E-C	119.1(8)°	120.7°	97.3°	100.1°	96.4°

[a] Bond length in pm. [b] See ref 19. [c] See ref 20. [d] See Figure 2.

addition of $HP(CF_3)_2$ to give a colorless solution at −50 °C. The phosphanide is precipitated by addition of diethyl ether. After decanting the solvent, extracting the precipitate several times with Et_2O, and drying it in vacuo, it is possible to handle the salt at higher temperature.

$$[\mathrm{Cat}]\mathrm{CN} + \mathrm{HP(CF_3)_2} \xrightarrow[-50\ ^\circ\mathrm{C}]{} \mathrm{HCN} + \underset{100\%}{[\mathrm{Cat}]^+\,[\mathrm{P(CF_3)_2}]^-}$$

$$[\mathrm{Cat}] = [\mathrm{NEt_4}],\ [\text{18-C-6-K}]$$

The neat phosphanides [NEt_4][$P(CF_3)_2$] and [18-crown-6-K]-[$P(CF_3)_2$] obtained by this procedure are stable up to 140 °C and characterized by an exact mass balance of the reaction, elemental analysis, vibrational spectroscopy, and multinuclear NMR spectroscopy.

The ^{13}C NMR spectrum clearly displays high order effects (Figure 1). In the isotopomer $[F_3{}^{13}C-P-CF_3]^-$, the ^{13}C isotope shift of the ^{19}F resonance $\Delta\delta(F^{12}C-F^{13}C) = \delta_A-\delta_B = -0.136$ ppm causes a chemical nonequivalence of the two trifluoromethyl groups. This results in a high order A_3B_3MX spin system with $A = F_3{}^{12}C$, $B = F_3{}^{13}C$, $M = {}^{13}C$ and $X = P$. The experimental spectrum is in excellent agreement with the simulated spectrum shown in the lower trace of Figure 1.

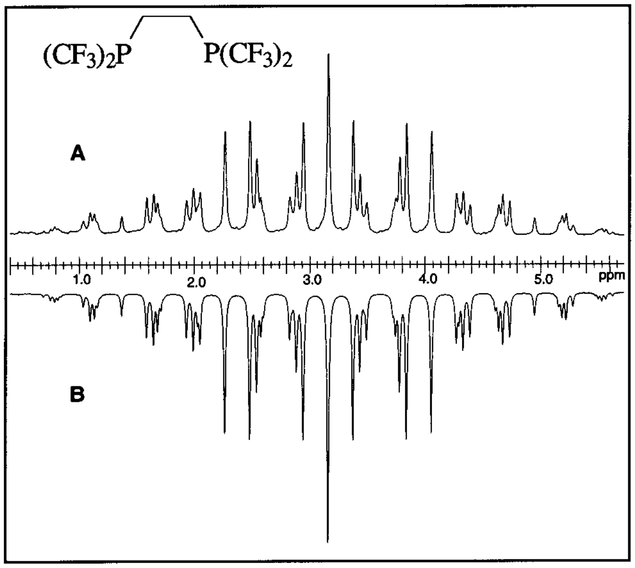

Figure 3. Proton decoupled $^{31}P\{^1H\}$ NMR spectrum of $(CF_3)_2PCH_2CH_2P(CF_3)_2$. **A** experimental spectrum, **B** simulation.

Ab initio structure and frequency calculations for the $[P(CF_3)_2]^-$ anion were carried out at the Hartree−Fock (HF) and Møller−Plesset (MP2) levels of theory using a standard 6−311 G basis set. The hybrid DFT calculations were carried out at the B3LYP and B3PW91 levels of theory with the 6-311G** basis set. The Gaussian G98 program was used for all structure and frequency calculations.[15] For better comparison, we also calculated the isoelectronic molecules $O(CF_3)_2$ and $S(CF_3)_2$. The suggestions of either staggered conformations of the CF_3 groups (C_s symmetry) or eclipsed conformations (C_{2v} symmetry) as starting geometries led in all cases of geometry optimization to structures with a W-type arrangement of the F−C(E)C−F unit (Figure 2). Geometries with an eclipsed conformation of the two CF_3 groups result, at different levels of theory, in negative values for the ν_{11} torsion mode, indicating a first-order saddle point.[16] The imaginary frequency corresponds to a torsion mode with

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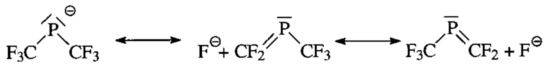
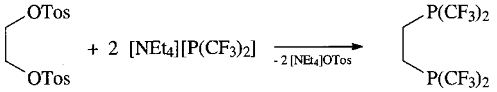
the two CF_3 groups twisting in opposite direction, indicating a more stable structure with twisted CF_3 groups. If starting geometries with C_2 symmetry are used for the optimizations, structures with C_2 symmetry with positive Eigenvalues for all 21 vibration modes are obtained. The F−C(E)C−F dihedral angles, with values of 3.7° for $[P(CF_3)_2]^-$ and 3.8° for $S(CF_3)_2$, do not significantly influence the remaining calculated frequencies except for the torsion modes, with values of 25.7 and 13.7 cm^{-1}, respectively. According to these results, infrared and Raman spectra were interpreted assuming C_2 symmetry. The frequencies calculated by ab initio methods deviate significantly from the experimental IR and Raman frequencies especially for the ν(CF) valence modes. Best results were obtained by DFT methods. As outlined in Table 1 , the calculated frequencies at the B3PW91 level of theory are in excellent agreement with the experimental frequencies for the $[P(CF_3)_2]^-$ anion and the molecules $O(CF_3)_2$[17] and $S(CF_3)_2$.[18] In addition, the calculated atomic distances and the C−E−C angle (E = O,[19] S[20]) are in good agreement with experimental results (Table 2). The optimized geometry for the $[P(CF_3)_2]^-$ anion is shown in Figure 2. In comparison to solid or gaseous tetrakis(trifluoromethyl)diphosphine, $(CF_3)_2P{-}P(CF_3)_2$,[21] the P−C bond distance of 186.1 pm is shortened by 2.2 and 3.9 pm, respectively, whereas the C−F bond distances are elongated by 5.4 and 3.1 pm, respectively. These results may be attributed to the resonance structures



which also explain the tendency of $[P(CF_3)_2]^-$ to eliminate a fluoride ion. As expected, the C−F stretching modes of the $[P(CF_3)_2]^-$ anion are shifted to lower frequencies with respect to those of $HP(CF_3)_2$[22] and $S(CF_3)_2$ (Table 1). Comparable observations have been published for the $[OCF_3]^-$ anion[23] and CF_3EX derivatives (E = Se, Te; X = H, halogen, CN, CF_3, ECF_3).[24]

The reactivity of the bis(trifluoromethyl)phosphanide was tested by reacting 1,2-ethanediol bis(4-methylbenzenesulfonate) and $[NEt_4][P(CF_3)_2]$, which gives 1,2-bis[bis(trifluoromethyl)phosphino]ethane[13] in 80% yield.



The NMR spectra exhibit characteristic high-order patterns. Due to a long range ^5J(PF) coupling of 2.0 Hz, the $P(CF_3)_2$ units are magnetically nonequivalent, resulting in an $[AX_6]_2$ spin system with A = P and X = F. The experimental ^{31}P NMR spectrum (upper trace of Figure 3) is in excellent agreement with the simulated spectrum in the lower trace.

In this work, a new, convenient synthesis for salts with the anion $[P(CF_3)_2]^-$ is described. In comparison with known compounds,[2] the new derivatives $[Cat][P(CF_3)_2]$ ([Cat] = $[NEt_4]$, [18-C-6-K]) show that low coordinating cations are essential in stabilizing salts with this anion, making them to suitable tools for nucleophilic substitutions. Investigations into the synthesis of chiral bidentate bis(trifluoromethyl)phosphine containing ligands for the use in asymmetric catalysis are in progress.

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