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Article

Stabilization of the P(CF₃)₂⁻ Ion as a Reversible CS₂ Adduct, [P(CF₃)₂CS₂]⁻, and Its Potential Use as a Nucleophilic P(CF₃)₂⁻ Source: Synthesis and Structure of [18-Crown-6-K][P(C₆F₅)₂CS₂][†]

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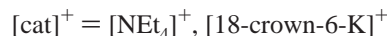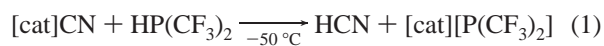*Institut für Anorganische Chemie, Universität zu Köln, D-50939 Köln, Germany*

The bis(trifluoromethyl)phosphanide ion, P(CF₃)₂⁻, decomposes slowly above −30 °C in CH₂Cl₂ and THF solution. An increase of the thermal stability of the P(CF₃)₂⁻ moiety is observed if excess CS₂ is added. The P(CF₃)₂⁻ moiety is stabilized because of the formation of the bis(trifluoromethyl)phosphanodithioformate anion. Solutions of a [P(CF₃)₂CS₂]⁻ salt still act as a source of P(CF₃)₂⁻, even in the presence of excess of CS₂. The stable compound [18-crown-6-K][P(CF₃)₂CS₂] was characterized by multinuclear NMR spectroscopy, elemental analysis, and vibrational spectroscopy in combination with quantum chemical calculations. The thermally unstable P(C₆F₅)₂⁻ ion decomposes even at −78 °C in solution giving polymeric material. The intermediate formation of the bis(pentafluorophenyl)-phosphanide anion in the presence of excess of CS₂ allows the isolation of [18-crown-6-K][P(C₆F₅)₂CS₂]. The novel compound crystallizes with one solvent molecule CH₂Cl₂ in the monoclinic space group $P2_1/n$ with $a = 1151.8(1)$ pm, $b = 1498.1(2)$ pm, $c = 2018.2(2)$ pm, $\beta = 102.58(1)°$, and $Z = 4$. Optimized geometric parameters of the [P(C₆F₅)₂CS₂]⁻ ion at the B3PW91/6-311G(d) level of theory are in excellent agreement with the experimental values.

Introduction

Nucleophilic bis(perfluoroorganyl)phosphanide sources are important intermediates in the synthesis of chiral bidentate bis(perfluoroorganyl)phosphanes. Because of their weak σ-basicity and strong π-acidity,[1] these compounds are desirable for the formation of chiral Lewis-acids.[2]

Transition metal complexes with terminal P(CF₃)₂[3] as well as P(C₆F₅)₂[4] groups are potential P(R_F)₂⁻ sources. But because of their to some extent tedious synthesis and low reactivity, the use of more reactive salts such as bis-(perfluoroorganyl)phosphanides is preferred. Bis(trifluoro-methyl)phosphanides are synthesized in quantitative yield through the reactions of HP(CF₃)₂ with [NEt₄]CN or [18-crown-6-K]CN under formation of HCN.[5]

$$[\text{cat}]\text{CN} + \text{HP}(\text{CF}_3)_2 \xrightarrow{-50\ °C} \text{HCN} + [\text{cat}][\text{P}(\text{CF}_3)_2] \quad (1)$$

$$[\text{cat}]^+ = [\text{NEt}_4]^+, [\text{18-crown-6-K}]^+$$

The analysis of the vibrational spectra in combination with quantum theoretical calculations predicts elongated C−F and shortened P−C bonds for the P(CF₃)₂⁻ ion in comparison with those of neutral trifluoromethylphosphanes. This effect, which was confirmed by X-ray crystallography,[6] may be attributed to negative hyperconjugation, which has been established for the trifluoromethoxide anion.[7] In terms of

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† Dedicated to Professor Dr. Hans Bürger on the occasion of his 65th birthday.

(1) Apel, J.; Grobe, J. *Z. Anorg. Allg. Chem.* **1979**, *453*, 53−67.

(2) At the present time, only bis(pentafluorophenyl)phosphinite ligands have been tested in asymmetric catalysis. For example: Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1219−1223.
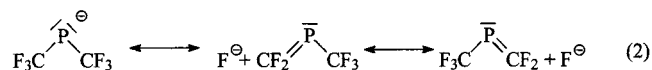
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$$F_3C \overset{\underset{\displaystyle \ominus}{\parallel}}{\underset{CF_3}{P}} \longleftrightarrow F^\ominus + CF_2 \overset{\parallel}{\underset{CF_3}{\overline{P}}} \longleftrightarrow F_3C \overset{\parallel}{\underset{CF_2}{\overline{P}}} + F^\ominus \qquad (2)$$

molecular orbital theory, this effect can be described as an electron donation from the phosphorus lone pair orbitals to σ^*-orbitals of C$-$F bonds. This activation of the C$-$F bonds favors decay of the dissolved compound, whereas in the solid-state bis(trifluoromethyl)phosphanide salts exhibit a remarkable thermal stability.

The goal of this work is the stabilization of the P(CF$_3$)$_2^-$ ion in solution. This should enhance its capability to be used in nucleophilic displacement reactions. In addition, we are searching for a P(C$_6$F$_5$)$_2^-$ source, which, on the first view, should offer comparable characteristic features. However, less is known about the bis(pentafluorophenyl)phosphanide anion, P(C$_6$F$_5$)$_2^-$. To our knowledge, the unsuccessful attempt to capture LiP(C$_6$F$_5$)$_2$ by reaction with chloro transition metal complexes[4] is the only work dealing with the bis(pentafluorophenyl)phosphanide moiety.

Experimental Section

Materials and Apparatus. All chemicals were obtained from commercial sources and used without further purification. A modified literature method[8] was used for the synthesis of HP(CF$_3$)$_2$. Instead of Me$_3$SnH, the less volatile Bu$_3$SnH was used for the reduction of P(CF$_3$)$_2$Br. This allows a convenient separation by fractional condensation after a reaction time of 30 min at 0 °C. Bromobis(trifluoromethyl)phosphane was synthesized treating neat (CF$_3$)$_2$PNEt$_2$[9] with gaseous HBr at -78 °C. **Caution!** The toxic compounds P(CF$_3$)$_2$Br as well as HP(CF$_3$)$_2$ violently react with air. Literature methods were used for the synthesis of [18-crown-6-K]P(CF$_3$)$_2$.[5] Bis(pentafluorophenyl)phosphane[4,10,11] was synthesized from P(C$_6$F$_5$)$_2$Br[10] and Me$_3$SnH.[12] Solvents were purified by standard methods.[13] Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N$_2$ atmosphere by using Schlenk techniques.

Differential thermal analysis was carried out on a Netzsch Model STA 409-Skimmer instrument. Infrared spectra were recorded on a Nicolet-5PC$-$FT-IR spectrometer as KBr pellets. Raman spectra were obtained with 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 AC 200 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$_3$F (^{19}F), and TMS (^{13}C and ^{1}H).

Preparation of 18-Crown-6-potassium Bis(trifluoromethyl)-phosphanodithioformate. A 0.517 g (6.790 mmol) portion of CS$_2$ was condensed onto a solution of 0.748 g (1.583 mmol) of [18-

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crown-6-K]P(CF$_3$)$_2$ in 10 mL of acetone. The intensive red solution was stirred for 30 min at -78 °C. Removal of all volatile compounds in vacuo was performed during the warming up to room temperature and yielded 0.867 g (1.581 mmol, 99.9%) of [18-crown-6-K][P(CF$_3$)$_2$CS$_2$] as a red powder. The neat substance decomposes at 320 °C (DTA/TG). Elemental analysis (calcd for C$_{15}$H$_{24}$F$_6$KO$_6$-PS$_2$): K 7.59 (7.13); S 11.73 (11.69); P 5.23 (5.65); F 20.27 (20.78); C 33.27 (32.84); H 5.03 (4.41). Infrared spectrum (cm^{-1}, KBr pellet): 2951 m, 2905 s, 2829 w, 2799 vw, 2748 vw, 2715 vw, 2692 vw, 1474 m, 1456 w, 1434 vw, 1353 s, 1327 vw, 1286 w, 1251 m, 1211 m, 1239 sh, 1176 vs, 1136 vs, 1107 vs, 1058 sh, 1038 s, 1001 w, 962 s, 839 m, 740 br, 565 vw, 553 w, 536 vw, 527 w, 504 w, 482 w, 443 m, 411 w. Raman (cm^{-1}): 2950 (14), 2913 (90), 2891 (100), 2846 (89), 2811 (46), 2788 (10), 2752 (6), 2730 (8), 2702 (7), 2683 (5), 1473 (53), 1455 (4), 1410 (9), 1274 (38), 1247 (25), 1137 (16), 1108 (8), 1080 (13), 1038 (9), 868 (36), 850 (36), 829 (21), 736 (18), 720 (4), 564 (6), 548 (19), 533 (sh), 504 (15), 483 (8), 443 (3), 412 (12), 364 (sh), 351 (10), 282 (21), 271 (sh), 238 (19) (3), 179 (18). NMR data (acetone-d_6, 243 K) of the [18-crown-6-K]$^+$ cation: $\delta(^1$H) 3.6 ppm; $\delta(^{13}$C) 70.4 ppm. NMR data of the [P(CF$_3$)$_2$CS$_2$]$^-$ anion: $\delta(^{31}$P) 8.2 ppm; ^2J(PF) 46.6 Hz; $\delta(^{19}$F) -54.6 ppm; $\delta(^{13}CF_3)$ 128.2 ppm; ^1J(CF) 323.1 Hz; ^1J(PC) 47.7 Hz; ^3J(CF) 4.9 Hz; $\delta(^{13}CS_2)$ 239.5 ppm; ^1J(CP) 41.5 Hz; ^3J(CF) 2.1 Hz.

Nucleophilic Displacement Reactions. Solutions of [18-crown-6-K][P(CF$_3$)$_2$CS$_2$] in CH$_2$Cl$_2$ containing also some CS$_2$ were treated at room temperature with an excess of ethyl tosylate, iodoethane, and Ph$_2$PCl, respectively. The products EtP(CF$_3$)$_2$[14] as well as Ph$_2$-PP(CF$_3$)$_2$ were identified by multinuclear NMR spectroscopy. NMR data of Ph$_2$PP(CF$_3$)$_2$ (CH$_2$Cl$_2$/CS$_2$; rt): $\delta(^{31}$PPh$_2$) -30.1 ppm; δ-(^{31}P(CF$_3$)$_2$) 4.7 ppm; $\delta(^{19}$F) -46.9 ppm; ^1J(PP) 180.0 Hz; ^2J(PF) 59.9 Hz; ^3J(PF) 9.0 Hz.

Preparation of Potassium Bis(trifluoromethyl)phosphan-odithioformate. A 1.275 g (7.502 mmol) portion of HP(CF$_3$)$_2$ was condensed onto a suspension of 0.308 g (4.730 mmol) of KCN in 20 mL of THF and 2 mL of CS$_2$. The suspension was stirred for 1 h at -78 °C while KCN dissolved giving a dark red solution. Removal of all volatile compounds in vacuo was performed during the warming up to room temperature. The remaining residue (1.307 g (4.598 mmol, 97%)), a very hygroscopic red solid, was extracted several times with pentane. The neat substance K[P(CF$_3$)$_2$CS$_2$] can be handled using Schlenk techniques at room temperature, but it immediately deliquesces on contact with wet air. The vibrational spectra are summarized in Table 1. Additionally, the Raman spectrum exhibits a less intense signal of unreacted cyanide at 2077 cm^{-1}. NMR data (acetone-d_6, 238 K) of the [P(CF$_3$)$_2$CS$_2$]$^-$ anion: $\delta(^{31}$P) 8.9 ppm; ^2J(PF) 47.2 Hz; $\delta(^{19}$F) -54.5 ppm; $\delta(^{13}CF_3)$ 128.2 ppm; ^1J(CF) 322.6 Hz; ^1J(PC) 45.9 Hz; ^3J(CF) 5.2 Hz; $\delta(^{13}CS_2)$ 239.9 ppm; ^1J(CP) 41.3 Hz; ^3J(CF) 1.9 Hz.

Preparation of [18-Crown-6-K][P(CF$_3$)$_2$C(S)NPh)]. To a frozen solution of 0.453 g (0.959 mmol) of [18-crown-6-K]P(CF$_3$)$_2$ in 5 mL of acetone was added 0.3 mL (2.745 mmol) of PhNCS. The temperature was raised to -78 °C and the mixture stirred for 1 h. All volatile materials were removed during the warming up to 0 °C. Diethyl ether (10 mL) was distilled onto the yellow oil at -78 °C and stirred well, giving a red powder. The solvent was removed with a syringe. After washing three times with diethyl ether, the resulting yellow powder was dried in vacuo at 0 °C and for a short time at room temperature. A 0.456 g (0.751 mmol; 78%) portion of [18-crown-6-K][P(CF$_3$)$_2$C(S)NPh)] was obtained as a

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Table 1. Calculated (B3PW91/6-311G(d)) Vibrational Frequencies and Observed Infrared and Raman Spectra of the $[P(CF_3)_2CS_2]^-$ ion

approximated mode description[a]	[18-c-6-K][P(CF₃)₂CS₂]		K[P(CF₃)₂CS₂]		[P(CF₃)₂CS₂]⁻
	IR	Raman	IR	Raman[b]	calcd [IR][c] (Raman)[d]
ν(CF)	1176 vs		1178 vs		1194.7 [92] (8)
					1166.8 [9] (10)
			1147 vs		1153.6 [61] (14)
			1123 vs		1140.5 [100] (17)
			1102 vs		1117.9 [69] (17)
			1085 m		1089.2 [23] (38)
ν$_{as}$(CS₂)	1038 vs	1038(25)	1030 s, br	1042(12)	1058.0 [23] (37)
ν$_s$(CS₂)		850(100)	859 w	863(100)	828.3 [10] (100)
δ$_s$(CF₃)	740 br	720(12)	724 br		744.7 [1] (15)
		736(50)	739 w	737(17)	735.8 [0] (40)
δ$_{as}$(CF₃)	565 vw	564(18)	564 vw	564(6)	567.7 [2] (15)
	553 w		555 vw	552(13)	552.6 [3] (14)
	536 vw	533(sh)	537 vw	532(8)	536.3 [1] (6)
	527 w				528.5 [0] (1)
	504 w	504(42)	501 vw	502(17)	505.2 [2] (32)
δ(CS₂)	482 w	483(23)	488 vw	490(24)	489.8 [3] (38)
ν$_{as}$(PC₂)	443 m	443(8)	444 w	442(4)	441.7 [6] (14)
ν$_s$(PC₂)/δ(CS₂)	411 w	412(33)	418 vw	418(12)	414.3 [4] (45)
		351(28)		358(16)	356.8 [1] (37)
		271(sh)		284(5)	277.9 [0] (17)
				270(6)	264.6 [0] (16)
		238(54)		244(19)	242.1 [0] (15)
					227.1 [0] (41)
δ(CS₂)		179(50)		188(32)	179.7 [1] (36)
					129.2 [0] (3)
					124.8 [0] (10)
					106.3 [0] (9)
					69.0 [0] (5)
					47.7 [0] (11)
τ(CF₃)					35.4 [0] (46)

[a] Mode description is based on the displacement vectors of the calculated vibrational modes. [b] Very weak. ν(CF) modes could not be located with certainty. [c] Calculated Raman intensities in Å⁴/amu. [d] IR intensities in km/mol.

yellow powder which slowly decomposed at room temperature. Elemental analysis (calcd for $C_{21}H_{29}F_6KNO_6PS$): N 2.46 (2.31); C 41.22 (41.51); H 4.93 (4.81). NMR data (acetone-d_6, 243 K) of the [18-crown-6-K]⁺ cation: δ(¹H) 3.6 ppm; δ(¹³C) 70.4 ppm. NMR data of the [P(CF₃)₂C(S)Ph]⁻ anion: δ(³¹P) −16.6 ppm; ²J(PF) 45.7 Hz; δ(¹⁹F) −52.5 ppm.

Preparation of 18-Crown-6-potassium Bis(pentafluorophenyl)phosphanodithioformate. A solution of 1.980 g (6.011 mmol) of [18-crown-6-K]CN dissolved in 5 mL of CH_2Cl_2 was added dropwise to a mixture of 2.490 g (6.890 mmol) of HP(C₆F₅)₂ in 5 mL of CH_2Cl_2 and 2 mL of CS_2 at −78 °C. After stirring for 1 h at −78 °C, 70 mL of diethyl ether was distilled onto the well-stirred dark red solution from which [18-crown-6-K][P(C₆F₅)₂CS₂] precipitated. After precipitation appeared to be complete, the solvent was removed by use of a syringe, and the solid residue was washed several times with Et₂O. After drying the solid in vacuo, the temperature was raised to 0 °C over a period of 1 h. A 3.150 g (4.231 mmol, 70%) portion of [18-crown-6-K][P(C₆F₅)₂CS₂] was obtained as an orange-red powder at this temperature. The salt decomposes to a brown solid, upon warming to 20 °C.

Crystal Structure Determination. Crystals of [18-crown-6-K]-[P(C₆F₅)₂CS₂]·CH₂Cl₂ slowly grew while diethyl ether was distilled onto a CH_2Cl_2 solution of [18-crown-6-K][P(C₆F₅)₂CS₂] at −45 °C. An appropriate red single crystal was selected and sealed in a glass capillary tube (d = 0.3 mm). Single-crystal X-ray data were collected on an image plate diffractometer (STOE IPDS) using graphite-monochromatized Mo Kα radiation (λ = 71.069 pm).[15] The structure was solved by direct methods (SHELXS-86) and Fourier synthesis.[16] The refinement[17] was done by full matrix least-squares procedures using anisotropic thermal parameters. The H

Table 2. Crystal Data and Details of Data Collection and Structure Refinement

compound	[18-crown-6-K][P(C₆F₅)₂CS₂]·CH₂Cl₂
fw	829.56
cryst syst	monoclinic
space group	P 2₁/n (no. 14)
lattice parameters	a = 1151.8(1) pm
	b = 1498.1(2) pm
	c = 2018.2(2) pm
	β = 102.58(1) °
cell vol	3.3987(7) nm³
formula units/unit cell	Z = 4
T	170 K
ρ$_{calcd}$	1.621 g cm⁻³
μ$_{calcd}$ (Mo Kα)	0.577
F(000)	1680
2θ range	3.42−48.14
reflns	26677
obsd ($I_0 > 2σ(I)$)	3071
no. params	537
S$_{obsd/all}$	1.132/0.928
R1; wR2[a] ($I_0 > 2σ(I)$)	0.0666; 0.1525
R1; wR2 (all data)	0.1068; 0.1688
Δρ min/max	−0.710/0.946

[a] Weighting $w^{-1} = σ^2(|F_o|^2) + (0.0999·P)^2$ with $P = (|F_o|^2 + 2|F_c|^2)/3$. Extinction $F_c^* = kF_c[1 + 0.001 \times |F_c|^2λ^3/\sin(2θ)]^{-1/4}$. $R = \sum||F_o| - |F_c||/\sum|F_o|$; $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$. $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$.

atom positions were taken from the difference Fourier card at the end of the refinement. Further details are given in Table 2. A selection of bond lengths and angles is given in Table 3.

(15) IPDS-Bedienungsanleitung, Stoe Darmstadt, 1997.

(16) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

(17) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for
[18-Crown-6-K][P(C_6F_5)$_2CS_2$]·CH_2Cl_2

|			
P1−C11	183.1(6)	C15−C16	135.6(8)
P1−C21	185.0(6)	C16−F17	135.7(6)
P1−C1	186.8(6)	C21−C26	139.4(8)
C1−S11	166.4(6)	C21−C22	140.1(8)
C1−S12	167.5(6)	C22−F22	132.5(6)
F23−K1	283.1(4)	C22−C23	138.7(8)
C11−C16	139.3(8)	C23−F23	133.0(6)
C11−C12	140.2(8)	C23−C24	136.8(8)
C12−F12	133.4(6)	C24−F24	136.1(6)
C12−C13	137.0(8)	C24−C25	137.0(8)
C13−F13	134.2(6)	C25−F25	134.5(6)
C13−C14	137.7(8)	C25−C26	138.2(8)
C14−F14	133.4(7)	C26−F26	134.5(6)
C14−C15	138.2(8)	C4−Cl41	172.7(10)
C15−F15	135.3(7)	C4−Cl42	173.9(9)
C11−P1−C21	103.7(3)	S11−C1−P1	120.4(3)
C11−P1−C1	102.7(3)	S12−C1−P1	109.6(3)
C21−P1−C1	104.8(3)	C16−C11−P1	126.0(5)
S11−C1−S12	129.3(4)	C12−C11−P1	118.9(4)

Results and Discussion

The bis(trifluoromethyl)phosphanide ion, P(CF₃)₂⁻, (ref 5) decomposes slowly above −30 °C in CH_2Cl_2 and THF solution. Stabilization of the P(CF₃)₂⁻ ion by formation of bis(trifluoromethyl)phosphanido complexes such as [Hg{P-(CF₃)₂}₂(PR₃)₂] ((PR₃)₂ = (PMe₃)₂, dppe)[3] or [Ag{P(CF₃)₂}₂]⁻ is accompanied by a decrease in reactivity. An increase of thermal stability of the P(CF₃)₂⁻ moiety in solution is observed if excess CS_2 is added, giving dark red solutions. The P(CF₃)₂⁻ moiety is stabilized because of the formation of a bis(trifluoromethyl)phosphanodithioformate anion, which is easily monitored by NMR spectroscopy. Depending on the reversible behavior of the [P(CF₃)₂CS₂]⁻ ion, it may also be described as a CS_2 adduct of the P(CF₃)₂⁻ ion.

$$[cat]P(CF_3)_2 + CS_2 \rightleftharpoons [cat][P(CF_3)_2CS_2] \qquad (3)$$

$$[cat]^+ = [NEt_4]^+, [18\text{-crown-6-K}]^+$$
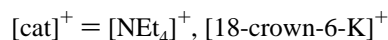
After treatment of an [18-crown-6-K]P(CF₃)₂ solution in THF, CH_2Cl_2, or acetone with 1 equiv of CS_2, the mixture exhibits NMR signals of the P(CF₃)₂⁻ ion ($\delta(^{31}P)$ −1.9 ppm; $\delta(^{19}F)$ −31.4 ppm; $^2J(PF)$ 47.2 Hz)[5] and the [P(CF₃)₂CS₂]⁻ ion (($\delta(^{31}P)$ 8.2 ppm; $\delta(^{19}F)$ −54.6 ppm; $^2J(PF)$ 46.6 Hz; see Experimental Section) in an 1:3 ratio. Only by use of excess CS_2 is complete conversion into the CS_2 adduct observed. The CS_2 adduct is isolated upon removal of the solvent and excess CS_2 in vacuo. When the isolated product is dissolved, its NMR spectrum exhibits the expected signals for the P(CF₃)₂⁻ ion and the CS_2 adduct. Solutions containing the [P(CF₃)₂CS₂]⁻ ion slowly decompose at room temperature, even in the presence of excess CS_2. The isolated red powder decomposes above 320 °C, while [18-crown-6-K]P-(CF₃)₂ decomposes at 145 °C.[5]
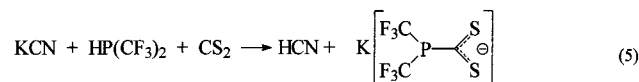
Solutions of a [P(CF₃)₂CS₂]⁻ salt still act as a source of P(CF₃)₂⁻, even in the presence of excess CS_2, because of the equilibrium, shown in eq 3. The originally formed CS_2 adduct does not lead to side products and allows us to run the nucleophilic displacement reactions at higher temperatures in comparison with reactions in CH_2Cl_2 or THF without

addition of CS_2. On the other hand, this increase of thermal stability in solution, after adding CS_2, is accompanied by a lower nucleophilicity of the P(CF₃)₂⁻ moiety, preventing reactions with alkyl tosylates. This type of reaction is
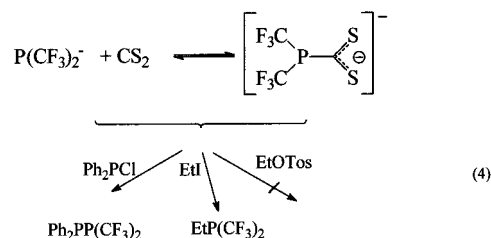
comparable with the reaction of [PPh₂CO₂]⁻ with iodoalkanes giving RPPh₂ (R = Me, Et) accompanied by a liberation of CO_2.[18]

To investigate the bonding situation in the CS_2 adduct by vibrational spectroscopy, in combination with quantum chemical calculations, it was necessary to synthesize the CS_2 adduct with a simple cation. Otherwise, some of the vibrational modes are hidden by intensive cation bands. Because of the instability of alkali metal P(CF₃)₂⁻ salts, these compounds are not available as starting materials. On the other hand, the synthesis of K[P(CF₃)₂CS₂] was successful if the intermediately formed KP(CF₃)₂ was stabilized by the presence of an excess of CS_2. The very hygroscopic orange-


red solid gives nearly the same NMR spectra as the [18-crown-6-K] salt. The ^{13}C NMR signal of the $^{13}CS_2$ unit is located at 239.9 ppm (d, sept: $^1J(CP)$ 41.3; $^3J(CF)$ 1.9 Hz), 47 ppm low field from excess CS_2.

The observed vibrational frequencies of the [P(CF₃)₂CS₂] moiety in its potassium and 18-crown-6 potassium salts are listed in Table 1. The experimental frequencies are in excellent agreement with the data calculated at the B3P91/6-311G(d) level of theory. The reliability of vibrational and structural data for trifluoromethyl derivatives of oxygen, sulfur, and phosphorus, calculated with the hybrid density functional method (HDFT) B3PW91, was demonstrated earlier.[5] The program, Gaussian 98, was used for the structure and frequency calculations.[19]

The geometry of the [P(CF₃)₂CS₂]⁻ ion optimized at the B3PW91/6-311G(d) level is shown in Figure 1. As expected,

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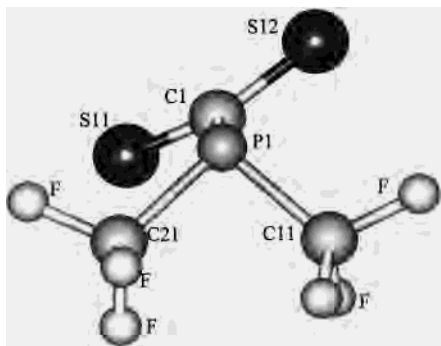
Figure 1. Geometry of the $[P(CF_3)_2CS_2]^-$ ion optimized at the B3PW91/6-311G(d) level.
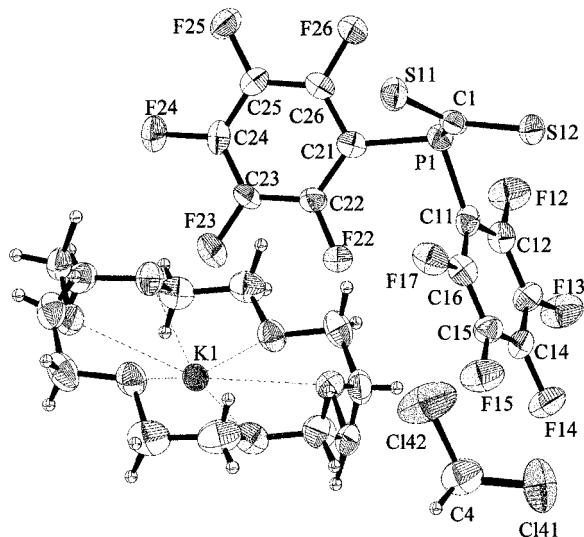
Figure 2. Molecular structure of $[18\text{-}crown\text{-}6\text{-}K][P(C_6F_5)_2CS_2] \cdot CH_2Cl_2$ and the atom numbering scheme. Probability amplitude displacement ellipsoids (50%) are shown.
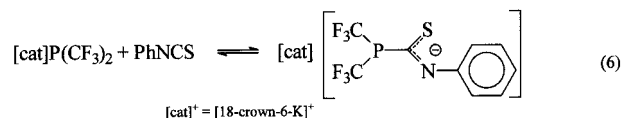
Table 4. Experimental Geometric Parameters of the $[P(C_6F_5)_2CS_2]$ Anion Versus the Calculated Data of the $[P(C_6F_5)_2CS_2]^-$ and $[P(CF_3)_2CS_2]^-$ Ion at the B3PPW91/6-311G(d) Level of Theory

	$[P(C_6F_5)_2CS_2]^-$		$[P(CF_3)_2CS_2]^-$
	X-ray	B3PW91	B3PW91
$d(C1-S12)$ (pm)	167.5(6)	168.1	168.7
$d(C1-S11)$ (pm)	166.4(6)	167.1	166.6
$d(P1-C1)$ (pm)	186.8(6)	186.2	186.8
$d(P1-C21)$ (pm)	185.0(6)	186.8	191.7
$d(P1-C11)$ (pm)	183.1(6)	186.0	190.6
$d(C-F)_\varnothing$ (pm)	134.3	133.7	134.9
$\angle(S1-C1-S2)$	129.3(4)°	130.7°	130.4°
$\angle(C21-P1-C11)$	103.7(3)°	103.1°	94.8°
$\Sigma\angle(C-P1-C)$	311.1°	312.3°	302.7°

the P−CF$_3$ bonds are elongated by 5 pm whereas the C−F bonds are shortened by approximately 2 pm in comparison with the calculated geometry of the P(CF$_3$)$_2^-$ ion.[5] Comparing the ν(CF) modes of the P(CF$_3$)$_2^-$ ion and the CS$_2$ adduct, the latter ones are shifted by about 50 cm^{-1} to higher frequency, indicating a strengthening of the C−F bonds in the CS$_2$ adduct. The displacement vectors of the calculated vibrational modes at 441.7 and 414.3 cm^{-1}, which were assigned to P−(CF$_3$)$_2$ stretching modes (Table 1), exhibit for both modes a considerable contribution of a CS$_2$ deformation and thus are not comparable with those of the P(CF$_3$)$_2^-$ anion. The reduced electron density of the phos-

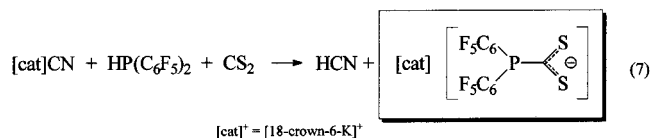phorus atom in the $[P(CF_3)_2CS_2]^-$ ion reduces the negative hyperconjugation.[20] Therefore, the P−C and C−F bond lengths are comparable to those of neutral trifluoromethylphosphanes such as (CF$_3$)$_2$PP(CF$_3$)$_2$.[21] In [18-crown-6-K][P(CF$_3$)$_2$CS$_2$] as well as in K[P(CF$_3$)$_2$CS$_2$], ν_{as}(CS$_2$) and ν_s-(CS$_2$) lie close to the positions previously reported for K[PPh$_2$CS$_2$].[22]

The P(CF$_3$)$_2^-$ ion forms also a reversible adduct with phenyl isothiocyanate, which can also be used as a nucleophilic P(CF$_3$)$_2^-$ source. In contrast to the stabilization of the

$$[cat]P(CF_3)_2 + PhNCS \;\rightleftharpoons\; [cat]\left[\begin{array}{c} F_3C \\ F_3C \end{array} P \underset{N}{\overset{S}{\diagdown}} \ominus \bigcirc \right] \quad (6)$$

$$[cat]^+ = [18\text{-}crown\text{-}6\text{-}K]^+$$

P(CF$_3$)$_2^-$ ion by the formation of CS$_2$ adducts, the isolated compound is less stable than [18-crown-6-K]P(CF$_3$)$_2$. The decomposition process already starts at room temperature. The phenylisothiocyanate does not destabilize the P(CF$_3$)$_2^-$ moiety. It just forms a weak adduct that decomposes at a lower temperature than the P(CF$_3$)$_2^-$ salt. All attempts to synthesize a CO$_2$ adduct of the P(CF$_3$)$_2^-$ ion were unsuccessful.

To synthesize bis(pentafluorophenyl)phosphanide salts, bis(pentafluorophenyl)phosphane, HP(C$_6$F$_5$)$_2$, was treated with cyanide salts at low temperature. The thermally unstable P(C$_6$F$_5$)$_2^-$ ion decomposes even at −78 °C in CH$_2$Cl$_2$ or acetone solution giving polymeric material.[12] Reaction in the presence of excess CS$_2$ allows the isolation of the thermally sensitive CS$_2$ adduct in 70% yield. The salt decomposes to a brown solid, upon warming to 20 °C. The [18-crown-6-

$$[cat]CN + HP(C_6F_5)_2 + CS_2 \;\longrightarrow\; HCN + [cat]\left[\begin{array}{c} F_5C_6 \\ F_5C_6 \end{array} P \underset{S}{\overset{S}{\diagdown}} \ominus \right] \quad (7)$$

$$[cat]^+ = [18\text{-}crown\text{-}6\text{-}K]^+$$

K] salt crystallizes with one solvent molecule CH$_2$Cl$_2$ in the monoclinic space group $P2_1/n$. A perspective drawing of the compound [18-crown-6-K][P(C$_6$F$_5$)$_2$CS$_2$]·CH$_2$Cl$_2$ is given in Figure 2. The bond lengths in the PCS$_2$ unit, found for the [P(C$_6$F$_5$)$_2$CS$_2$]$^-$ anion, are nearly identical with those of the [PPh$_2$CS$_2$]$^-$ ion[23] and agree with the data calculated for the free gaseous [P(CF$_3$)$_2$CS$_2$]$^-$ anion. To prove the reliability of the optimized geometric parameters of the [P(CF$_3$)$_2$CS$_2$]$^-$ ion at the B3PW91/6-311G(d) level of theory, we also optimized the geometry of the [P(C$_6$F$_5$)$_2$CS$_2$]$^-$ anion at the same level. As outlined in Table 4, experimental X-ray data are in excellent agreement with the calculated values. The pure orange-red solid as well as solutions with an excess of CS$_2$ decompose slowly upon warming to ambient tempera-

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ture. All attempts to use the $[P(C_6F_5)_2CS_2]^-$ compound as a source of $P(C_6F_5)_2^-$ have been unsuccessful so far.

Supporting Information Available: Crystallographic file in CIF format for the compound [18-crown-6-K][P(C₆F₅)₂CS₂]·CH₂Cl₂. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0112950

(24) Program available at http://www.uni-koeln.de/themen/Chemie/software/g98ff/.