Volatiles were removed under vacuum, and the solid was taken up in 50 mL of petroleum ether, filtered, concentrated, and cooled to −78 °C. Cold filtering and drying under vacuum afforded 2.73 g (65.5%) of yellow crystalline 7. Anal. Calcd for $C_{16}H_9F_{20}MoNO_3P_2$: C, 23.99; H, 1.13. Found: C, 24.05; H, 0.98. IR (KCl, cm^{-1}): 1996 vs, 1937 s, 1881 vs, 1300 s, 1205 vs, 1118 s, 1090 s, 958 s, 749 m. ^1H NMR (benzene-d_6, 22 °C): δ 1.89 (m, 4 H, PCH_2), 0.92 (q, 2 H, $^3J_{HH} = 7.7$ Hz, $NCCH_2$), 0.19 (t, 3 H, $^3J_{HH} = 7.7$ Hz, CH_3). ^{13}C NMR (benzene-d_6, 22 °C): δ 211.9 (m, 2 CO), 211.1 (s, br, 1 CO), 128.9 (s, br, NC), 119.0 (qm, $^1J_{CF} \approx 296$ Hz, CF_3), 20.4 (tt, $^1J_{CH} = 138$ Hz, $J_{CP} = 15$ Hz, PCH_2), 12.1 (t, $^1J_{CH} = 135$ Hz, $NCCH_2$), 9.5 (q, $^1J_{CH} = 133$ Hz, CH_3). ^{31}P NMR (benzene-d_6, 25 °C): δ 101.3 (m). ^{19}F NMR (benzene-d_6, 375.6 MHz, 22 °C): δ 78.2 (s, CF_3), 79.1 (s, CF_3), 107.2 (ABX, $\nu(A) - \nu(B) = 542$ Hz, $^2J_{FF} = 315$ Hz, $^2J_{FP} = 105, 58$ Hz, CF_2P), 108.8 (ABX, $\nu(A) \approx \nu(B)$, $^2J_{FP}(av) = 68$ Hz, CF_2P).

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Preparation and Spectroscopic Characterization of CF_3-Substituted Amides, Phosphides, and Arsenides, $M(CF_3)_2^-$ (M = N, P, As)

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The formation and isolation of $Na(CF_3)_2E$ (E = P, As) and of $Cs(CF_3)_2E$ (E = N, P, As) are reported. Whereas cesium bis(trifluoromethyl)amide is stable at room temperature and can be obtained from the reaction of cesium fluoride with $CF_3N{=}CF_2$ or $CF_3N{=}CFN(CF_3)_2$, the novel alkali-metal derivatives of $(CF_3)_2PH$ and $(CF_3)_2AsH$ are obtained via the interaction of the phosphane or arsane with an alkali metal in liquid ammonia. The alkali-metal bis(trifluoromethyl)phosphides and -arsenides undergo decomposition above 215 K. All compounds are characterized by multinuclear (^{13}C, ^{14}N, ^{19}F, ^{31}P) NMR techniques. The infrared and Raman spectra of $Cs(CF_3)_2N$ are presented and discussed. Several reactions, including the thermolysis of $Na(CF_3)_2P$ and $Cs(CF_3)_2P$ to give $CF_3P{=}CF_2$, demonstrate the synthetic potential of these salts.

Introduction

Metalated derivatives of the compounds HER_2 (E = N, P, As; R = alkyl, aryl substituent) have long been known and are of widespread importance in inorganic and organic synthetic pathways.[1] In spite of this and the increased interest in fluorine-containing compounds during the last decades, only very few salt-like bis(perfluoroorgano)element–metal compounds $ME(R_F)_2$ (M = electropositive metal; $R_F = CF_3$, C_6F_5, etc.) have been reported in the literature.[2-4] These types of compounds are considered to be very unstable because of the energetically favored formation of MF, especially in the case of small cations.[5] Hence, for the purpose of transfering $(CF_3)_2P$ groups, more difficult preparative routes to covalently bonded reagents such as $(CH_3)_3SiP(CF_3)_2$ and $(CH_3)_3SnP(CF_3)_2$ have been developed.[5-8]

However, the synthetic potential of cesium bis(trifluoromethyl)amide, $Cs(CF_3)_2N$, has already been described in the literature;[2,3] it thus appeared necessary and worthwhile to try to obtain the corresponding P and As derivatives. We have now succeeded in the preparation and spectroscopic characterization of pure $Cs(CF_3)_2N$ as well as the novel and highly reactive homologues $M(CF_3)_2E$ (M = Na, Cs; E = P, As), alkali-metal bis(trifluoromethyl)phosphides and -arsenides.

Experimental Section

Materials and Apparatus. Literature methods were used for the synthesis of $CF_3N{=}CFN(CF_3)_2$,[9] $(CF_3)_2PH$,[10] and $(CF_3)_2AsH$.[10] $CF_3N{=}CF_2$ was received from the Bayer Co., Leverkusen, FRG, as a gift. Cesium fluoride (99.99 %, Aldrich Co.) was fused in a platinum crucible and powdered in a drybox prior to use. Elemental sodium was doubly distilled before use; cesium was obtained in high purity from the Aldrich Co. (99.95+ %, Gold Label). Both alkali metals were loaded into and handled in sealed thin-walled glass vessels by techniques described in the literature.[11] Solvents were purified by standard methods.[12] 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 Mettler Model TA 1 instrument. Infrared spectra were recorded on a Perkin-Elmer Model 580 B spectrometer; Raman spectra were run on a Coderg T 800 spectrometer equipped with an Ar^+ laser (Spectra Physics) operating at $\lambda = 488.0$ nm.

The NMR spectra were recorded on a Bruker Model AM 300 spectrometer (^{13}C, 75.5 MHz; ^{14}N, 21.7 MHz; ^{19}F, 282.5 MHz; ^{31}P, 121.5 MHz) with positive shifts being downfield from the external standards TMS (^{13}C), CH_3NO_2 (^{14}N), $CFCl_3$ (^{19}F), and 85% orthophosphoric acid (^{31}P).

Preparation of $Cs(CF_3)_2N$. Cesium fluoride (10 mmol), suspended in 25 mL of acetonitrile, and 15 mmol of $CF_3N{=}CF_2$ or 7.5 mmol of $CF_3N{=}CFN(CF_3)_2$, respectively, were combined in a 50-mL vessel equipped with a Young stopcock. The reaction mixture was magnetically stirred for 6 h at room temperature and eventually filtered off from undissolved cesium fluoride. When 25 mL of methylene chloride was added, $Cs(CF_3)_2N$ precipitated. After filtration, washing with methylene chloride and removal of the remaining solvent by pumping, colorless finely crystalline $Cs(CF_3)_2N$ was obtained in a yield of 80%. Its purity was checked by ^{19}F NMR spectroscopy and was better than 99%.

Preparation of $Na(CF_3)_2P$ and $Cs(CF_3)_2P$. In a typical run, 2.65 mmol of Na or Cs, contained in a sealed thin-walled glass vessel, was placed into one section of a two-bulbed glass vessel connected to the vacuum line and equipped with a magnetic stirrer. The thin-walled glass vessel was broken in an inert N_2 atmosphere and 2.5 mL of liquid ammonia was condensed at 77 K onto the alkali metal. The mixture was stirred at 200 K and again cooled to 77 K. $(CF_3)_2PH$ (2.5 mmol) was then added in portions of approximate 0.25 mmol each; each addition was followed by stirring the mixture at 200 K for 10 min, cooling it to 77 K, and pumping off the evolved H_2. In order to obtain pure $Na(CF_3)_2P$ and $Cs(CF_3)_2P$, ammonia was removed by pumping at 190 K. The residue was treated with 5 mL of liquid dimethyl ether and stirred at 190 K.

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Eventually the solution was decanted and the solvent was removed by pumping at 190 K, leaving behind pale grey $Na(CF_3)_2P$ and $Cs(CF_3)_2P$. Their purity was checked by means of ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy and was better than 95%. Main impurities were CHF_3, $[(CF_3)_2P]_2NH$, $CHF_2(CF_3)PNH_2$, and $CH_2F(CF_3)PNH_2$, as established by their NMR spectra.[13]

The pale yellow solutions of the phosphides in liquid ammonia or dimethyl ether were stable for 2 weeks at 200 K or even up to 230 K for short periods.

When solutions of $Na(CF_3)_2P$ and $Cs(CF_3)_2P$ in liquid ammonia were warmed further, the formation of CH_3F was observed. Decomposition of the solid salts started at 215 K.

Preparation of $Na(CF_3)_2As$ and $Cs(CF_3)_2As$. These compounds could be obtained in high purity (≥98%, checked by means of ^{13}C and ^{19}F NMR spectroscopy) by a procedure analogous to that described for the phosphides, starting from $(CF_3)_2AsH$. CHF_3 was found as a main contaminant (due to hydrolysis or ammonolysis). Whereas the stability range of the alkali-metal bis(trifluoromethyl)arsenides is the same as that of the phosphides, their solutions are colorless.

Results and Discussion

Formation. In analogy to the formation of $Hg[(CF_3)_2N]_2$[6] from HgF_2 and $CF_3N{=}CF_2$, Gontar et al.[2,3] described the formation of $Cs(CF_3)_2N$ (eq 1). We found that this salt could also readily

$$CF_3N{=}CF_2 + CsF \xrightarrow{(CH_3CN)} Cs(CF_3)_2N \qquad (1)$$

be prepared at room temperature by starting from dimerized perfluoro(2-azapropene), $CF_3N{=}CFN(CF_3)_2$ (eq 2). This reaction (eq 2) is understandable only on the assumption that the dimer $CF_3N{=}CFN(CF_3)_2$ is depolymerized under the catalytic action of CsF (eq 3). The monomer so formed reacts according

$$CF_3N{=}CFN(CF_3)_2 + 2CsF \xrightarrow{(CH_3CN)} 2Cs(CF_3)_2N \qquad (2)$$

$$CF_3N{=}CFN(CF_3)_2 \overset{(CsF)}{\rightleftharpoons} 2CF_3N{=}CF_2 \qquad (3)$$

to eq 1 to give the amide. While the cesium fluoride catalyzed dimerization of $CF_3N{=}CF_2$ has already been described in the literature,[9] the reverse reaction has not. However, it was not possible to detect the monomer. ^{19}F NMR spectra of solutions containing cesium fluoride and an excess of $CF_3N{=}CF_2$ or $CF_3N{=}CFN(CF_3)_2$ in acetonitrile showed only signals due to $Cs(CF_3)_2N$ and $CF_3N{=}CFN(CF_3)_2$. Among numerous synthetic routes to phosphides and arsenides, the reaction of the phosphane or arsane with butyllithium in organic solvents and the reaction with alkali metals in liquid ammonia seemed to be especially promising for the synthesis of bis(trifluoromethyl)phosphides. Both techniques permit the reactions to occur in homogeneous phase, even at reduced temperature. However, the first method did not result in detectable formation of $(R_F)_2E^-$ salts.[5] The latter method requires some care in order to prevent side reactions of $(CF_3)_2PH$ or $(CF_3)_2AsH$ with ammonia. Experiments carried out by Burg[13] and Haszeldine et al.[14] showed that, e.g., $(CF_3)_2PH$ reacted with ammonia even at very low temperatures. We succeeded in reacting $(CF_3)_2PH$ and $(CF_3)_2AsH$ with alkali metals in liquid ammonia to give the pure salts. This was achieved by adding the phosphane or arsane in only small amounts to a solution containing an excess of the alkali metal (see Experimental Section). Due to the high acidity of $(CF_3)_2PH$ and $(CF_3)_2AsH$, the salt formation occurred in a very fast reaction[15,16] (eq 4).

$$2(CF_3)_2EH + 2M \xrightarrow{(NH_3)} 2(CF_3)_2EM + H_2 \qquad (4)$$

$$M = Na, Cs;\ E = P, As$$

Properties and Reactions. According to differential thermal analysis, $Cs(CF_3)_2N$ decomposes above 365 K according to the reverse of eq 2 in a slightly endothermic reaction. Like $Hg[(CF_3)_2N]_2$,[17] it turned out to behave as a mild fluorinating agent; e.g., hexachloroantimonates ($(C_6H_5)_4As^+SbCl_6^-$, $K^+SbCl_6^-$) were converted in acetonitrile solution into the corresponding hexafluoroantimonates with liberation of $CF_3N{=}CFN(CF_3)_2$. In a complicated and yet not quite understood reaction, $Cs(CF_3)_2N$ and $(CF_3S)_2PH$[18] gave $CsPF_6$. A precipitate of $CsSbF_6$ was obtained from the interaction of the amide and $(C_6H_5)_4As^+SbF_6^-$ or $(C_2H_5)_4N^+SbF_6^-$ in acetonitrile. ^{19}F NMR spectra of the solutions proved the existence of $(C_6H_5)_4As^+(CF_3)_2N^-$ and $(C_2H_5)_4N^+(CF_3)_2N^-$ ($\delta_F = -37.0$ ppm), respectively. However, the pure salts could not be isolated. The reactions of $Cs(CF_3)_2N$ with organic compounds containing halogen have been reported by Gontar et al.[2,3]

Table I. Observed Infrared and Raman Frequencies (cm^{-1}) of Solid $Cs(CF_3)_2N$ and Comparison with Those of Isoelectronic $(CF_3)_2O$[a]

$Cs(CF_3)_2N$		$(CF_3)_2O$		
IR[b,c] solid	Raman solid	IR[21] gas	Raman[21] liq	assgnts[21] and approx descripns
n.m.	180 (9)	n.m.	178 w	ν_7 (a_1) δ(CXC)
n.o.	341 (25)	n.o.	n.o.	ν_{10} (a_2) $\rho(CF_3)$
366 (50)	368 (21)	358.4	355 w, sh	ν_{16} (b_1) $\rho(CF_3)$
383 (45)	384 (37)	n.o.	368 s	ν_5 (a_1) $\rho(CF_3)$
512 sh	521 (12)	526.7 m	527 w	ν_4 (a_1) $\delta_{as}(CF_3)$
550 (65)	552 (18)	573.2 m	574 w	ν_{15} (b_1) $\delta_{as}(CF_3)$
n.o.	600 (4)	n.o.	n.o.	ν_9 (a_2) $\delta_{as}(CF_3)$
647 (45)	648 (12)	655 m	650 vw	ν_{20} (b_2) $\rho(CF_3)$
663 (70)	n.o.	696.3 s	690 vw	ν_{13} (b_1) $\delta_s(CF_3)$
716 sh	713 (45)	747 m	747 m	ν_2 (a_1) $\delta_s(CF_3)$
816 (60)	818 (100)	854 vvw	852 vs	ν_6 (a_1) ν(CX)
876 (55)	876 (13)	971.0 s	970 vvw	ν_{17} (b_1) ν(CX)
1183 (75)	n.o.	1173.4 vvs	1170 vvw	ν_{12} (b_1) $\nu_s(CF_3)$
1222 (100)	n.o.	1255.6 vvs	1250 vvw	ν_{14} (b_1) $\nu_{as}(CF_3)$
n.o.	n.o.	n.o.	1279 w	ν_1 (a_1) $\nu_s(CF_3)$
1263 (65)	n.o.	1328.9 vvs	1329 w	ν_3 (a_1) $\nu_{as}(CF_3)$

[a] Abbreviations used: n.m., not measured; n.o., not observed; sh, shoulder; v, very; s, strong; m, medium; w, weak. [b] The following combination tones were observed: 434 w ($\nu_6 - \nu_5$), 466 w ($\nu_{20} - \nu_7$), 599 w ($\nu_3 - \nu_{13}$), 616 w ($\nu_3 - \nu_{20}$), 667 w ($\nu_{12} - \nu_4$). [c] Nujol mull, CsBr windows.

Contrary to the behavior of $Hg[(CF_3)_2P]_2$, which yielded elemental Hg and $(CF_3)_4P_2$ on heating[8], but in accordance with the behavior of $Cs(CF_3)_2N$, the thermolysis of $Na(CF_3)_2P$ and $Cs(CF_3)_2P$ gave $CF_3P{=}CF_2$ and sodium or cesium fluoride. $CF_3P{=}CF_2$ was identified from its infrared spectrum.[19] The reactions of the phosphides with CH_3I in liquid dimethyl ether lead to the formation of $CH_3P(CF_3)_2$, which was characterized by its ^{19}F NMR spectrum.[20]

Vibrational Spectra of $Cs(CF_3)_2N$. Whereas with respect to its physical properties $Hg[(CF_3)_2N]_2$ (mp 17.5 °C; bp 127 °C[6,7]) is a covalent compound, $Cs(CF_3)_2N$ did not melt without decomposition, indicating it to possess more of a salt character. The interpretation of its infrared and Raman spectra we therefore carried out by analogy with the vibrational spectra of isoelectronic $(CF_3)_2O$ (Table I). Assuming C_{2v} symmetry for $(CF_3)_2O$ and local C_3 symmetry for the CF_3 groups, Bürger and Pawelke[21] found that there are 21 fundamental vibrations, distributed as 7 a_1, 4 a_2, 6 b_1, and 4 b_2. With the exception of the a_2 vibrations, which are only Raman active, all vibration modes should be infrared and Raman active. Calculations on a valence-shell electron-pair repulsion basis published in the literature[22] support the assumption of the same symmetry for $(CF_3)_2N^-$.

Figures 1 and 2 reproduce the infrared and Raman spectra of $Cs(CF_3)_2N$; Table I summarizes the data and compares them with the frequencies of $(CF_3)_2O$. CF_3 stretching modes are of low intensity in the Raman spectrum and were not observed for the amide, whereas they gave rise to intense absorptions in the infrared

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Table II. NMR Parameters of Alkali-Metal Bis(trifluoromethyl)amides, -phosphides, and -arsenides[a]

compd	solvent; temp, K	$\delta(^{13}C)$	$\delta(^{19}F)$	$\delta(E)$	$^1J_{FC}$	$^3J_{FC}$	$^4J_{FF}$	$^1\Delta^b$
$Cs(CF_3)_2N^c$	DMF; 293	n.o.	−34.8 s	n.o.	237.2	n.o.	9.3	−0.120
	$(CH_3)_2O$, 293	n.o.	−36.8 s	n.o.	n.o.	n.o.	n.o.	n.o.
	CH_3CN; 293	+125.3 qq	−37.8 s	−286 s, br[d]	243.0	10.4	n.o.	n.o.
$Na(CF_3)_2P^{e,f}$	NH_3; 211	+144.4 qdq	−28.7 d	−3.1 sept	315.1	10.8	n.o.	n.o.
	$(CH_3)_2O$; 211	n.m.	−29.3 d	+0.6 sept	n.m.	n.m.	n.o.	n.o.
$Na(CF_3)_2As^f$	NH_3; 211	+140.3 qq	−27.0 s	n.m.	340.8	7.7	7.2	−0.157

[a] δ in ppm, J in Hz. Abbreviations used: n.m., not measured; n.o., not observed; s, singlet; d, doublet; qq, quartet of quartets; sept, septet; br, broad. [b] $^1\Delta^{19}F$ ($^{12/13}C$),[24] measured in ppm; the data satisfy Frankiss' relationship.[25] [c] Saturated solutions are employed. [d] $\delta(^{14}N)$; half-height width = 300 Hz. [e] $^2J_{PF}$ = 47.3 Hz, $^1J_{PC}$ = 88.0 Hz. [f] The Cs salts gave identical data.

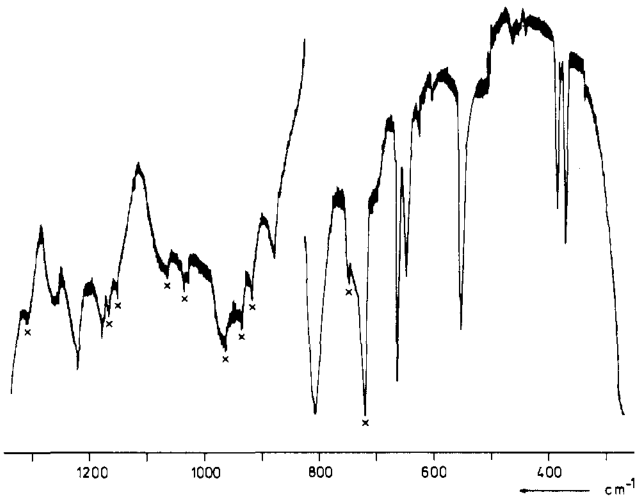

Figure 1. Infrared spectrum of $Cs(CF_3)_2N$ (Nujol mull, CsBr windows). The ordinate is in arbitrary units of absorption. Bands marked with an asteriks arise from Nujol.

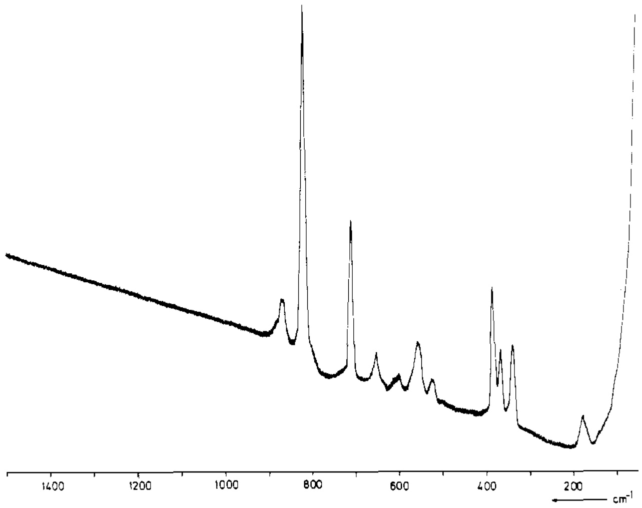

Figure 2. Raman spectrum of solid $Cs(CF_3)_2N$. The ordinate is in arbitrary units of scattering intensity.

spectrum at 1183, 1222, and 1263 cm^{-1}. Five of the six expected CF_3 deformations were observed. With the exception of $\delta_s(CF_3)$ at 713 cm^{-1} the measured frequencies correspond to typical literature values. As was shown by a normal coordinate analysis of $(CF_3)_2O$,[21] $\delta_s(CF_3)$ in particular may be influenced by coupling effects. The intense Raman band at 818 cm^{-1} and a weak feature at 876 cm^{-1} are interpreted as C–N stretches; compared to the C–O stretches in $(CF_3)_2O$, they are shifted to lower frequencies. This may be caused by the negative charge of the amide anion.[23] The four $\rho(CF_3)$ modes as well as δ(CNC) can be associated with proper frequencies corresponding to the analogous frequencies of $(CF_3)_2O$. The remaining two torsional modes, $\tau(CF_3)$, were not observed; they are expected to occur at frequencies below 100 cm^{-1}.

NMR Spectra of the Alkali-Metal Bis(trifluoromethyl)amides, -phosphides, and -arsenides. Table II summarizes the NMR parameters obtained from a multinuclear (^{13}C, ^{14}N, ^{19}F, ^{31}P) NMR investigation. The observed signal splittings and line widths agree with the presence of $(CF_3)_2EM$ compounds.

The chemical shifts δ and coupling constants ^nJ are, however, influenced by different and often counteracting parameters. The ^{13}C nuclei in the series amide, phosphide, and arsenide should experience an increasing shielding with decreasing electronegativity and increasing polarizability of the central atom;[26] the opposite trend is, however, supported by decreasing C–E double-bonding effects.[27] The observed ^{13}C chemical shifts show that neither of these factors dominates in this series; compared to $(CF_3)_2EH$[28,29] a considerable shift to low field occurs. It is known for some other classes of compounds that $^1J_{FC}$ is proportional to the size of the central atom;[26,30,31] the chemical relationship of the salts is clearly evidenced by the plot of $^1J_{FC}$ versus $\delta(^{19}F)$ (Figure 3). Figure 4 points out the chemical relationship between the anions and the isoelectronic bis(trifluoromethyl)chalcogenides. Provided that the paramagnetic term remains nearly constant, electronegative ligands

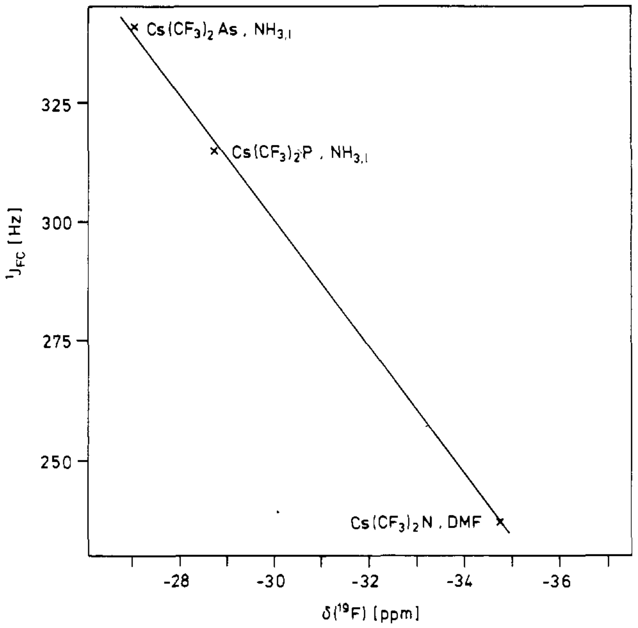

Figure 3. Plot of $^1J_{FC}$ vs δ_F of the alkali-metal bis(trifluoromethyl)amides, -phosphides, and -arsenides.

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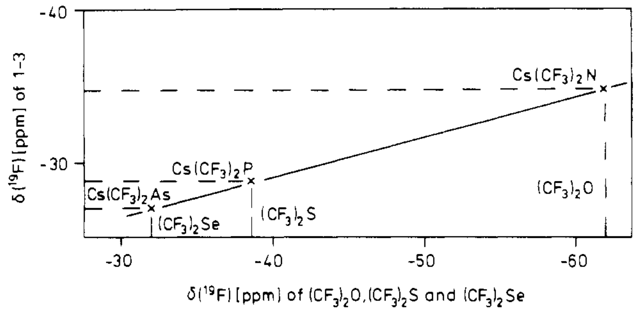

Figure 4. Plot of δ_F of the alkali-metal bis(trifluoromethyl)amides, -phosphides, and -arsenides vs δ_F of bis(trifluoromethyl)chalcogenides. Values were taken from ref 26 and 32.

cause deshielding of ^{14}N nuclei.[33] Compared to published ^{14}N chemical shifts of $(CH_3)_2NLi$[34] and $[(CH_3)_3Si]_2NNa$,[35] this effect is observed for $Cs(CF_3)_2N$ (Table II).

Whereas alkali-metal amides are assumed to dissociate in ionizing solvents, alkali-metal phosphides apparently seldom do[36,37] (excluding complexation with crown ethers[38]). As an example, $\delta(^{31}P)$ shifts of diphenylphosphides depend on the cation.[39] Contrary to this, the ^{31}P chemical shifts of the bis(trifluoromethyl)phosphides are identical within the accuracy of measurement. The very small value of $^2J_{PF}$ (47.3 Hz) may serve as a further piece of evidence for ionic dissociation of the phosphides. In comparison with phosphines of the type $(CF_3)_2PY$ (Y = H, F, Cl, Br, I), which give rise to considerably greater values of $^2J_{PF}$, substantial changes in bonding must be assumed. Burg[28] has published values for $^1J_{PC}$ of the phosphanes $(CF_3)_2PY$. $^1J_{PC}$ increases with increasing polarizability of the Y ligand and reaches a maximum value of 42.8 Hz for Y = iodine. With respect to the value of 88.0 Hz exhibited by $Na(CF_3)_2P$ and $Cs(CF_3)_2P$, we conclude that the alkali-metal bis(trifluoromethyl)phosphides dissociate in solution.

Conclusion

In this paper we have shown that the alkali-metal bis(trifluoromethyl)amides, -phophides, and -arsenides are available in a pure form by a one-step reaction. Initial experiments demonstrate their high nucleophilic reactivity. These salts exhibit consistent spectroscopic data not only within the homologues but also in comparison with the isoelectronic bis(trifluoromethyl)-chalcogenides.

Addendum

The reaction of $(CF_3S)_2PH$ with Na or Cs metal in liquid ammonia, carried out as described in the preparation of alkali-metal bis(trifluoromethyl)phosphides, did not result in the formation of $(CF_3S)_2PNa$ but gave high yields of a yellow precipitate that contained all the phosphorus used. It is thought to be highly polymeric.

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Registry No. $Cs(CF_3)_2N$, 66566-92-5; CsF, 13400-13-0; $CF_3N{=}CF_2$, 371-71-1; $CF_3N{=}CFN(CF_3)_2$, 686-39-5; $Na(CF_3)_2P$, 119326-83-9; $Cs(CF_3)_2P$, 119326-79-3; Na, 7440-23-5; Cs, 7440-46-2; $(CF_3)_2PH$, 460-96-8; $Na(CF_3)_2As$, 119326-84-0; $Cs(CF_3)_2As$, 119326-85-1; $(CF_3)_2AsH$, 371-74-4; $(C_6H_5)_4As^+SbCl_6^-$, 119326-80-6; $K^+SbCl_6^-$, 29933-38-8; $(CF_3S)_2PH$, 1648-71-1; $CsPF_6$, 16893-41-7; $CsSbF_6$, 16949-12-5; $(C_6H_5)_4As^+SbF_6^-$, 30185-61-6; $(C_2H_5)_4N^+SbF_6^-$, 4455-34-9; $(C_6H_5)_4As^+(CF_3)_2N^-$, 119326-81-7; $(C_2H_5)_4N^+(CF_3)_2N^-$, 119326-82-8; $CF_3P{=}CF_2$, 72344-34-4; CH_3I, 74-88-4; $CH_3P(CF_3)_2$, 1605-54-5.

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Spectroscopic and Chemical Studies of Nickel(II) Hydrides

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The trans influence of X ligands on the spectroscopic properties of the Ni–H bond is reported for the series of square-planar nickel hydrides *trans*-$HNi(X)(PCy_3)_2$ (X = Me, Ph, CN, SCN, I, Br, Cl, SPh, S(*p*-tol), SH, OAc, O_2CH, O_2CPh, O_2CCF_3, OPh) prepared by oxidative addition of HX to $[Ni(PCy_3)_2]_2N_2$ or derivatives of subsequent products. The infrared-derived parameter ν(Ni–H) shows a similar ligand dependence as the proton chemical shift of the hydride ligand, with more covalently bound ligands such as methyl or phenyl producing lower ν(Ni–H) and smaller upfield chemical shifts as compared to those ligands that bind to Ni(II) with more electrostatic character such as anionic O-donor ligands. Comparisons with other ligand influenced, spectroscopic scales are made. Carbon dioxide and iodomethane were used as chemical probes of reactivity at the Ni–X or Ni–H bond. The derivatives with stronger Ni–H bonds (S and O donors) show no reactivity at the hydride while the C-bond derivatives exhibit CO_2 insertion at the hydride. The Ni–H functionality is active toward iodomethane in the C-donor derivatives. A mechanism of hydrogen atom abstraction by methyl radicals is consistent with literature precedents as well as the Ni–H bond strengths determined by spectroscopies.

Introduction

A broad series of square-planar nickel(II) hydrides, *trans*-$HNi(X)P(C_6H_{11})_3)_2$, is accessible from the dinitrogen complex[1] (eq 1) or derivatives of subsequent products (eq 2 and 3) as reported[2,3] for X = CH_3, C_6H_5, OAc, CN, SCN, I, Br, Cl, OC_6H_5, S(*p*-$C_6H_4CH_3$), and SC_6H_5 and extended in our laboratories to include SH, O_2CH, $O_2CC_6H_5$, and O_2CCF_3. This series provides

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