shift (54 ppm) of the compound that is formed in smallest amount (2%) is very similar to that of one of the products of the reaction between B_2Br_4 and $CFBr_3$ that is discussed above.

There are a few ligand-exchange reactions of B_4Cl_4, such as those of the lithium alkyls, in which the tetraboron framework does stay intact,[19] but more commonly the reactions of B_4Cl_4 results in cage fragmentation, often generating mono- and diboranes that are related to those found in the $CFCl_3$ reaction. In the reaction of B_4Cl_4 with $HNMe_2$, for instance, $B(NMe_2)_3$ (50%), $B_2Cl_4{\cdot}2HNMe_2$ (25%), and $B_2Cl_2(NMe_2)_2$ (25%) are the major products observed.[20] Similarly, the reactions of B_4Cl_4 with the halogens Cl_2 and Br_2 result in the formation of B_2Cl_4 (18%) and B_2Br_4 (14%) along with the boron trihalides.[21]

The most satisfying single explanation for the similarity of the product distributions from these reactions is that all of these reagents initially attack one of the faces of the tetraboron tetrahedron, rather than one of the relatively inert B–Cl bonds; thus, the product similarities in these reactions primarily reflect the manner by which B_4Cl_4 fragments. Given the results from the halogenation reactions above, at 200 °C $CFCl_3$ might well be expected to react with B_4Cl_4, resulting in fluoroboranes, BF_2CCl_3, and B_9Cl_9, the last presumably resulting from the partial thermal decomposition of the diboron tetrahalide formed as one of the initial products of the cage fragmentation.

(Dihaloboryl)pentaboranes. As discussed in the Introduction, the bonding in $1\text{-}BCl_2B_5H_8$ and $1\text{-}BBr_2B_5H_8$ is a composite of almost all of the different types that are commonly found in boron hydride chemistry. Fluorination with $Hg(CF_3)_2$ proceeded smoothly to generate the previously unknown $BF_2B_5H_8$ in excellent yields, 96%, an indication that B–H bonds, the pentaborane cage, and B–B single bonds are all essentially unaffected by $Hg(CF_3)_2$ under these conditions.

Both the absence of C_2F_4 and $c\text{-}C_3F_6$ and the mass spectrometric results from the mercurials formed during the reaction are supportive of direct fluorination of the boron–chlorine bonds as the primary means by which the boron–fluorine bonds are formed. The properties of the product $BF_2B_5H_8$ will be commented upon separately,[10] but to the extent that this reaction of $BCl_2B_5H_8$ with $Hg(CF_3)_2$ can be taken as a test of the effectiveness of these new flourinating agents, it appears that on the scale employed here $Hg(CF_3)_2$ has performed quite well.

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(19) Davan, T.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 250. Emery, S. L.; Morrison, J. A. *Inorg. Chem.* **1985**, *24*, 1612.

(20) Emery, S. L. Ph.D. Thesis, University of Illinois at Chicago, 1985.

(21) Wartik, T.; McHale, J. M. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 113.

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Synthesis and Coordination Properties of Bis(bis(pentafluoroethyl)phosphino)ethane

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The efficient synthesis of $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) by direct alkylation of $Cl_2PCH_2CH_2PCl_2$ with C_2F_5Li at −95 °C is described. Thermal substitution reactions of dfepe and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) with $M(CO)_6$ (M = Cr, Mo, W) gave high yields of the corresponding tetracarbonyls $(\widehat{P\,P})M(CO)_4$ ($\widehat{P\,P}$ = dfppe, M = Cr, Mo, W; $\widehat{P\,P}$ = dfepe, M = Cr, Mo). The reaction of dfepe with *fac*-$Mo(EtCN)_3(CO)_3$ afforded *fac*-$Mo(dfepe)(EtCN)(CO)_3$. From a literature comparison of $(dfepe)Mo(CO)_4$ IR $\nu(CO)$ data with those of a range of analogous phosphine derivatives, it is concluded that dfepe rivals fluorophosphines in π-acceptor strength. Cone angle estimates for dfepe give a value of 123°, comparable to that of $Ph_2PCH_2CH_2PPh_2$ and significantly greater than typical cone angle values for fluorophosphines.

Introduction

The development of new π-acceptor ligands and their associated coordination chemistry remain a conspicuous challenge to inorganic and organometallic chemists. In contrast to donor ligand classes such as PR_3, OR, and NR_2 (R = alkyl, aryl, amide, alkoxide, etc.), which have a wide range of accessible steric and electronic properties,[1] prototypical π-acceptor ligands (CO, NO, PF_3) lack suitable "handles" for modification. King[2] and Nixon[3] have noted in particular the absence of potentially chelating acceptor ligands and have examined the chemistry of heteroatom-bridged fluorophosphines, $RN(PF_2)_2$, with a variety of metal systems. Although these chelates efficiently displace carbon monoxide in many cases, the susceptibility of P–F and P–N bonds toward cleavage side reactions limits their general application as innocent spectator ligands. Other examples of substituted fluorophosphine ligands that have been reported include $F_2P(C_6H_{10})PF_2$, $F_2PCX_2CX_2PF_2$ (X = H, F),[4] and $(Y)_xPF_{3-x}$ (x = 1, 2; Y = Me, Pr, CF_3, Me_2N, $NC(CF_3)_2CO$).[5] It is noteworthy that the coordination chemistry of these ligands remains essentially undeveloped.

A potentially useful class of π-acceptor ligands that has received little attention is that of fluoroalkyl-substituted phosphines, $(R_f)_xPR_{3-x}$. Replacement of fluorine with inductively similar fluoroalkyl groups maintains the acceptor character of the phosphorus center while providing a means for steric control. Additionally, P–R_f bonds are considerably more inert than P–F bonds and should support applications where reactive, electron-deficient metal centers are generated.[6] Some time ago, Burg reported the synthesis of the fluoroalkyl-substituted phosphine chelates $(CF_3)_2PCX_2CX_2P(CF_3)_2$ (X = H, F).[7] Although these ligands were demonstrated to be strong π-acceptors, practical

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(1) (a) Tolman, C. A. *Chem. Rev.* **1977**, *109*, 313. (b) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977. (c) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1724.

(2) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243.

(3) Johnson, T. R.; Nixon, J. F. *J. Chem. Soc. A* **1969**, 2518.

(4) (a) Morse, K. W.; Morse, J. G. *Inorg. Chem.* **1975**, *14*, 565. (b) Gallup, D. L.; Morse, J. G. *J. Organomet. Chem.* **1978**, *159*, 477.

(5) (a) Mathieu, R.; Poilbanc, R. *Inorg. Chem.* **1972**, *11*, 1858. (b) Udovich, C. A.; Clark, R. J. *Inorg. Chem.* **1969**, *8*, 1066. (c) Burg, A. B.; Street, G. B. *Inorg. Chem.* **1966**, *5*, 1532. (d) Montemayor, R. G.; Sawyer, D. T.; Fleming, S. S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. (e) Douglas, W. M.; Ruff, J. K. *J. Chem. Soc. A* **1971**, 3558. (f) Bauer, D. P.; Ruff, J. K. *Inorg. Chem.* **1983**, *22*, 1686.

(6) Cleavage of P–CF_3 bonds in unligated phosphines has been observed under strongly basic conditions: (a) Burg, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 2226. (b) Cooper, P.; Fields, R.; Haszeldine, R. N. *J. Chem. Soc. C* **1971**, 3031.

(7) (a) Burg, A. B.; Street, G. B. *J. Am. Chem. Soc.* **1963**, *85*, 3522. (b) Grant, L. R. Ph.D. Dissertation, University of Southern California, 1961, pp 44–49.

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difficulties in their synthesis have severely limited potential applications.

We are interested in exploiting the unique advantages that (fluoroalkyl)phosphine acceptor ligands may afford. Substitution of sterically demanding chelating acceptor phosphines for conventional, small monodentate carbonyl ligands should provide access to electrophilic metal systems with unusual structural and electronic properties. As an initial step in our studies, we report here the efficient high-yield synthesis and characterization of a new (fluoroalkyl)phosphine chelate, $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$. Syntheses of a number of simple group VI mixed carbonyl derivatives with this ligand have been carried out in order to compare electronic properties with those of known phosphine analogues and to provide a benchmark for future studies.

Results and Discussion

Preparation of ethylene-bridged diphosphines $R_2PCH_2CH_2PR_2$ are most readily carried out by direct alkylation of bis(dichlorophosphino)ethane with alkyllithium or Grignard reagents.[8] Applying this methodology to the synthesis of fluoroalkyl derivatives, however, is hampered by the well-documented thermal instability of perfluorocarbanions.[9] In the case of the simplest example, CF_3Li, facile elimination of LiF and generation of difluorocarbene occurs at temperatures below −100 °C, well before any alkylation chemistry can occur. Recently, Gassmann reported that (perfluoroethyl)lithium, C_2F_5Li, can be generated by metal–halogen exchange from C_2F_5I and MeLi at −78 °C.[10] In the presence of ketones, subsequent alkylation gave fluorocarbon-substituted alcohols in good yield. Significantly, qualitative experiments indicated the lifetime of C_2F_5Li to be approximately 5–10 min at this temperature.

Since P–Cl bonds in general alkylate quite rapidly, we felt that carrying out an alkylation with C_2F_5Li formed in situ at −95 °C would afford the desired fluorocarbon-substituted diphosphine. Initial experiments utilizing C_2F_5I/MeLi exchange in diethyl ether followed by dropwise addition of a solution of $Cl_2PCH_2CH_2PCl_2$ in ether did in fact give moderately pure $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ in poor to fair yield. Attempts, however, to scale up this reaction gave poor results due to the large exothermicity of Li–I exchange. To circumvent this problem, the kinetics of exchange between C_2F_5Cl and *n*-BuLi at −95 °C were monitored with the expectation that this reaction would be less exothermic. Addition of C_2F_5Cl to a solution of *n*-BuLi in ether at −95 °C followed by quenching with MeOH and GC analysis of the BuCl exchange product against a decane internal standard indicated that the exchange was complete within 35 min. Moreover, monitoring the temperature of this exchange showed only a very mild exotherm. When we switched to the C_2F_5Cl/*n*-BuLi/Et_2O system, essentially pure $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (abbreviated as "dfepe") was obtained as an odorless, colorless liquid (bp 105 °C, 80 Torr) in 68% yield (eq 1). Since C_2F_5Cl (Freon 115) is also considerably

$$4C_2F_5Cl \xrightarrow[-95\ ^\circ C,\ Et_2O]{n\text{-BuLi}} 4[C_2F_5Li] \xrightarrow[-95\ ^\circ C\ \rightarrow\ \text{room temp}]{Cl_2PCH_2CH_2PCl_2} \underset{\mathbf{1},\ 68\%}{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2} \quad (1)$$

cheaper than C_2F_5I, this modification of the procedure provides an efficient route to dfepe on a convenient large scale for study. The ^1H NMR spectrum of dfepe displays a simple apparent triplet at δ 2.40 (J_{PH} = 4 Hz) with no discernible long-range coupling to fluorine. Evidence for complete alkylation of the phosphorus centers is given by ^{13}C NMR data, which exhibit a single triplet at δ 14.9 ($^1J_{CH}$ = 137 Hz) for the ethylene backbone.

The substitution chemistry of dfepe as well as the known (perfluoroalkyl)diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (abbreviated as "dfppe") with group VI hexacarbonyls was investigated

Table I. Comparison of Infrared and Cone Angle Data for *cis*-$L_2Mo(CO)_4$

L_2	$\nu_{CO}(A_1{}^1)$, cm^{-1}	ref	cone angle, deg[a]
2 PF_3	2087	16	104
$F_2PCH_2CH_2PF_2$	2074	4b	98
$EtN(PF_2)_2$	2066	3	94
$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$	2064	this work	123[b]
$Cl_2PCH_2CH_2PCl_2$	2061	11	111
$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$	2041	11	151
$(CH_3O)_2PCH_2CH_2P(OCH_3)_2$	2033	17	100
$Ph_2PCH_2CH_2PPh_2$	2020	18	125
$Cy_2PCH_2CH_2PCy_2$	2016	19	142
$Et_2PCH_2CH_2PEt_2$	2012	18	115

[a] Values taken from ref 1a. [b] Estimated from structural data.[20,21]

in order to compare ligation properties with a wide range of known mixed alkylphosphine/carbonyl systems. With a single exception, direct thermal substitution of dfepe or dfppe with the hexacarbonyls in the appropriate solvent gave the tetracarbonyls $(\overset{\frown}{P\,P})M(CO)_4$ as pure crystalline solids in excellent yield (eq 2).

$$M(CO)_6 + \overset{\frown}{P\,P} \xrightarrow[-2CO]{\Delta} (\overset{\frown}{P\,P})M(CO)_4 \quad (2)$$

$$\begin{aligned} \mathbf{2}&:\ \overset{\frown}{P\,P} = \text{dfppe},\ M = Cr\\ \mathbf{3}&:\ \overset{\frown}{P\,P} = \text{dfppe},\ M = Mo\\ \mathbf{4}&:\ \overset{\frown}{P\,P} = \text{dfppe},\ M = W\\ \mathbf{5}&:\ \overset{\frown}{P\,P} = \text{dfepe},\ M = Cr\\ \mathbf{6}&:\ \overset{\frown}{P\,P} = \text{dfepe},\ M = Mo \end{aligned}$$

For molybdenum, refluxing toluene or octane was sufficient for displacement of CO ligands. For the less labile chromium and tungsten hexacarbonyls, refluxing in diglyme for 24 h or in octane for several days was necessary to drive the reaction to completion. In no case did exhaustive thermolysis or photolysis in the presence of excess diphosphine yield detectable quantities of disubstituted products $(\overset{\frown}{P\,P})_2M(CO)_2$. Thermolysis of dfepe and $W(CO)_6$ in diglyme did not yield any of the expected (dfepe)$W(CO)_4$ product. Dfepe complexes **5** and **6** are highly soluble in aromatic solvents and moderately soluble in hydrocarbon solvents and have been fully characterized by NMR and IR spectroscopy and analytical data. ^{31}P, ^{13}C, and ^{19}F NMR data are all consistent with their formulation as monomeric octahedral complexes. Complexes **2** and **3** have been previously prepared by reaction of dfppe with (nbd)$M(CO)_4$ (M = Cr, Mo).[11]

The reactions of dfepe with other labile Mo(0) carbonyl precursor systems have also been examined. Although treatment of (cycloheptatriene)$M(CO)_3$ (M = Mo, W) with bulky donor phosphines (P^tBu_3, P^iPr_3) under mild conditions has been reported to give the novel five-coordinate complexes *trans*-$M(PR_3)_2(CO)_3$,[12] no displacement of cycloheptatriene from $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ with dfepe or dfppe was observed even after prolonged thermolysis in refluxing octane. In addition, no discernible reaction between dfepe and the bis(piperidine) complex $(C_5N_{11}N)_2Mo(CO)_4$ took place in refluxing toluene, though reactions with donor phosphines such as PPh_3 are known to be facile at 40 °C.[13] Substitution of propionitrile ligands in *fac*-$Mo(EtCN)_3(CO)_3$ by dfepe after refluxing 3 days in hexane did, however, afford the tricarbonyl complex *fac*-Mo(dfepe)(EtCN)$(CO)_3$ (**7**) in good yield (eq 3).

$$fac\text{-}Mo(EtCN)_3(CO)_3 + \text{dfepe} \xrightarrow{\Delta} \underset{\mathbf{7}}{fac\text{-}Mo(\text{dfepe})(EtCN)(CO)_3} + 2EtCN \quad (3)$$

The assigned facial geometry of **7** is consistent with the ^{31}P NMR spectrum, which exhibits a single resonance at 101.3 (m) ppm instead of the two resonances expected for a meridional isomer. Carbonyl infared bands appear at 1996, 1937, and 1881 cm^{-1}, predictably higher than values reported for analogous donor phosphine complexes *fac*-Mo(dppe)(MeCN)$(CO)_3$ (ν(CO) =

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(8) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.

(9) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; pp 344–349.

(10) Gassman, P. G.; O'Reilly, N. J. *Tetrahedron* **1985**, *26*, 5243.

(11) Cook, R. L.; Morse, J. G. *Inorg. Chem.* **1984**, *23*, 2332.

(12) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61.

(13) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1975**, *17*, 2680.

1933, 1840, 1819 cm^{-1})[14] and *fac*-Mo(dppm)(MeCN)$(CO)_3$ (ν(CO) = 1930, 1837, 1823 cm^{-1}).[15]

A comparison of ν(CO) IR data and cone angle estimates for **2** with those of a wide range of known *cis*-$L_2Mo(CO)_4$ phosphine systems is given in Table I. As anticipated, the electronic influence of fluoroalkyl-substituted dfepe is similar to that of fluorophosphines. Cone angle estimates from structural data[20] and molecular models give a value of 123°,[21] indicating that dfepe is similar in size to $Ph_2PCH_2CH_2PPh_2$ and is significantly larger than other ligands possessing a high degree of π-acceptor ability. The observed failure of dfepe to react with (η^6-C_7H_8)$Mo(CO)_3$ or $(C_5H_{11}N)_2Mo(CO)_4$ contrasts with the facile substitution chemistry observed for donor phosphines of equal or greater steric influence and lends support to the contention that dfepe is a relatively weak σ donor.

Since the original submission of this article, the synthesis of $[(CF_3)_2PCH_2CH_2P(CF_3)_2]Mo(CO)_4$ has been published.[26] The ν(CO) IR data for this molecule are essentially identical with those reported for compound **3**.

Experimental Section

General Considerations. All manipulations were conducted under an atmosphere of nitrogen by using Schlenk, high-vacuum-line, and/or glovebox techniques. Unless otherwise noted, reactions were carried out under a reduced ambient pressure of approximately 590 Torr (approximately 7200-ft. elevation). Dry, oxygen-free solvents were vacuum-distilled prior to use. Elemental analyses were performed by Desert Analytics. Mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation facility (Grant No. CHE 8211164). Infrared spectra were recorded on a Mattson Cygnus 100 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL JNM-FX270 or GSX-400 instrument (GSX spectra courtesy of JEOL USA, Inc.). ^{19}F spectra were referenced to CF_3CO_2Et as an internal standard (75.32 ppm vs $CFCl_3$, with upfield chemical shifts taken to be positive). ^{31}P spectra were referenced to an 85% H_3PO_4 external standard. $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (Aldrich) and C_2F_5Cl (SCM Specialty Chemicals) were used as received. Bis(dichlorophosphino)ethane was prepared by a literature procedure.[22] $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ was prepared by a modification of literature procedures.[23]

$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (1). A 175-mL aliquot of 1.6 M *n*-BuLi (280 mmol) was transferred into a 500-mL two-neck flask fitted with a vacuum adapter and a low-temperature thermometer. Hexane was removed, *n*-BuLi was taken up in 250 mL of diethyl ether, and the solution was cooled to −95 °C by using a toluene/N_2 slush bath. A 32-mL aliquot of C_2F_5Cl (bp −34 °C, density 1.88 g/mL, 389 mmol) was measured out into a calibrated volume at −78 °C and vacuum-transferred into a 50-mL flask equipped with a stirbar and maintained at −78 °C. C_2F_5Cl was slowly added to the *n*-BuLi solution by vacuum transfer so as to maintain the reaction temperature below −90 °C. After 10 min the addition was complete and the solution was stirred for an additional 1 h, during which time the reaction mixture became slightly cloudy. A solution of $Cl_2PCH_2CH_2PCl_2$ (13.00 g, 56 mmol) in 50 mL of diethyl ether was added by cannula under nitrogen counterflow in 1-mL aliquots over a period of 20 min to maintain the temperature below −90 °C. Upon addition the solution turned brown, and after the addition was complete, the mixture was maintained at −95 °C an additional 10 min and then allowed to warm slowly (approximately 2 h to ambient temperature). At approximately 0 °C a white precipitate began to form. After 1 h at ambient temperature, ether and *n*-BuCl were distilled off at atmospheric pressure, the pressure was reduced to 80 Torr, and 21.48 g (68%) of product was collected at 100–108 °C. The ^1H NMR spectrum of the water-white liquid showed essentially pure **1**. A small portion was redistilled (bp 104–108 °C) for analysis. Anal. Calcd for $C_{10}H_4F_{20}P_2$: C, 21.22; H, 0.71; F, 67.13. Found: C, 21.44; H, 0.56; F, 60.86. (Note: F analyses were consistently low; C analyses were variable.) High-resolution EI mass spectrum: *m/e* 565.9460 (565.9468 calcd, M), 546.9500 (546.9484 calcd, $[M - F]^+$), 446.9538 (446.9548 calcd, $[M - C_2F_5]^+$); relative intensities 0.47:2.89:100, respectively. IR (neat, KCl, cm^{-1}): 1423 w, 1310 s, 1215 s, 1130 s, 956 s, 748 m, 611 w. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C): δ 2.40 (t, J_{PH} = 4 Hz). ^{13}C NMR (benzene-d_6, 67.8 MHz, 22 °C): δ 106.1 (qtd, $^1J_{CF}$ = 286 Hz, $^2J_{CF}$ = 32 Hz, $^2J_{CP}$ = 22 Hz, $CF_2\mathit{C}F_3$), 106.0 (tdq, $^1J_{CF}$ = 290 Hz, $^2J_{CF} \approx {}^2J_{CP} \approx$ 42 Hz, $\mathit{C}F_2CF_3$), 14.9 (t, $^1J_{CH}$ = 137 Hz, CH_2). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C): δ 7.4 (m). ^{19}F NMR (benzene-d_6, 253.7 MHz, 22 °C): δ 82.3 (s, CF_3), 112.1 (tm, $^2J_{FP}$ = 43 Hz, CF_2).

$[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]Mo(CO)_4$ (3). A mixture of $Mo(CO)_6$ (2.0 g, 7.6 mmol), $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (5.74 g, 7.6 mmol), and 25 mL of toluene was refluxed under 760 Torr of nitrogen pressure for 12 h. (Note: refluxing at ambient pressure resulted in incomplete reaction due to the lower boiling point.) By this time, $Mo(CO)_6$ had ceased to sublime out of solution and a small quantity of black solid (Mo) had begun to deposit on the flask walls. The solution was filtered, and toluene was removed under vacuum. The residue was slurried in petroleum ether, filtered, and dried in vacuo to give 6.87 g (94%) of white crystalline **3**. Anal. Calcd for $C_{30}H_4F_{20}MoO_4P_2$: C, 37.29; H, 0.42. Found: C, 37.30; H, 0.34. IR (KCl, cm^{-1}): 2041 s, 1965 s, 1935 vs, 1912 vs, 1645 m, 1522 s, 1386 m, 1378 sh, 1293 m, 1095 s, 977 s.

$[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]Cr(CO)_4$ (2). The procedure used to prepare the molybdenum analogue was followed except that diglyme was used as the solvent and the reaction mixture was refluxed for 24 h. Workup afforded yellow **2** in 82% yield. Anal. Calcd for $C_{30}H_4CrF_{20}O_4P_2$: C, 39.07; H, 0.44. Found: C, 38.87; H, 0.38. IR (KCl, cm^{-1}): 2032 s, 1962 s, 1932 vs, 1909 vs, 1644 m, 1522 s, 1291 m, 1095 s, 977 s.

$[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]W(CO)_4$ (4). A procedure analogous to that used for **3** afforded pale yellow **4** in 94% yield. Anal. Calcd for $C_{30}H_4F_{20}O_4P_2W$: C, 34.18; H, 0.38. Found: C, 33.94; H, 0.34. IR (KCl, cm^{-1}): 2038 s, 1959 s, 1929 vs, 1908 vs, 1645 m, 1522 s, 1292 m, 1096 s, 977 s.

$[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]Cr(CO)_4$ (5). A mixture of $Cr(CO)_6$ (0.176 g, 0.800 mmol) and $(C_2F_5)_2PCH_2CH_2(C_2F_5)_2$ (0.500 g, 0.883 mmol) in 10 mL of octane was refluxed for 48 h. Octane was removed under vacuum, the solid residue was taken up in 20 mL of petroleum ether, and a small amount of black material was removed by filtration. Concentration and cooling of the filtrate to −78 °C afforded 0.435 g (74.6%) of white crystalline **5**. Anal. Calcd for $C_{14}H_4CrF_{20}O_4P_2$: C, 23.03; H, 0.55. Found: C, 23.10; H, 0.50. IR (KCl, cm^{-1}): 2046 s, 1974 vs, 1946 vs, 1306 m, 1211 vs. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C): δ 1.73 (m). $^{13}C\{^1H\}$ NMR (benzene-d_6, 67.8 MHz, 30 °C): δ 220.7 (d, $^2J_{CP}$ = 12 Hz, CO_{eq}), 215.1 (t, $^2J_{CP}$ = 9 Hz, CO_{ax}), 119.2 (qm, $^1J_{CF}$ = 287 Hz, CF_3), 20.7 (t, J_{CP} = 18 Hz, CH_2). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C): δ 136.1 (pm, $^2J_{PF}$ = 77 Hz). ^{19}F NMR (benzene-d_6, 375.6 MHz, 22 °C): δ 78.4 (s, CF_3), 108.2 (ABX, $\nu(A) \approx \nu(B)$, $^2J_{FP}$(av) = 78 Hz; CF_2P).

$[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]Mo(CO)_4$ (6). The procedure was analogous to that used for **5** except that the reaction mixture was refluxed in octane for 8 h. Workup gave yellow-orange crystalline **6** in 74.5% yield. Anal. Calcd for $C_{14}H_4F_{20}MoO_4P_2$: C, 21.72; H, 0.52. Found: C, 21.70; H, 0.44. IR (KCl, cm^{-1}): 2064 s, 2012 sh, 1993 s, 1982 s, 1955 vs, 1302 m, 1208 vs, 1125 s, 1097 m, 1084 m, 963 m. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C): δ 1.65 (m). ^{13}C NMR (benzene-d_6, 67.8 MHz, 22 °C): δ 208.3 (dd, $^2J_{CP}$(trans) = 33 Hz, $^2J_{CP}$(cis) = 9 Hz, CO_{eq}), 204.4 (s, br; CO_{ax}), 119.2 (qm, $^1J_{CF}$ = 285 Hz, CF_3), 20.4 (tt, $^1J_{CH}$ = 139 Hz, J_{CP} = 14 Hz, CH_2). ^{31}P NMR (benzene-d_6, 109 MHz, 22 °C): δ 107.2 (m, $^2J_{PF}$ = 81 Hz). ^{19}F NMR (benzene-d_6, 375.6 MHz, 22 °C): δ 78.3 (s, CF_3), 109.0 (ABX, $\nu(A) - \nu(B)$ = 337 Hz, $^2J_{FF}$ = 315 Hz, $^2J_{FP}$ = 74, 37 Hz, CF_2P).

$[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]Mo(CO)_3(CH_3CH_2CN)$ (7). A solution of $Mo(CO)_3(EtCN)_3$[24] (1.82 g, 5.27 mmol) and $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (3.33 g, 5.88 mmol) in 50 mL of hexane was refluxed for 72 h.

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(14) Kubas, G. J.; Jarvinen, G. D.; Ryan, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 1883.

(15) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727.

(16) Dobson, G. R.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 1.

(17) King, R. B.; Rhee, W. M. *Inorg. Chem.* **1978**, *17*, 2961.

(18) Chatt, J.; Watson, H. R. *J. Chem. Soc.* **1961**, 4980.

(19) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1975**, *94*, 55.

(20) Ernst, M. F.; Roddick, D. M. Manuscript in preparation.

(21) The effective cone angle θ was estimated by Tolman's method, with use of $\theta_i/2$ = 85° for the ligand backbone: Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

(22) Henderson, R. A.; Hussain, W.; Leigh, G. J.; Normanton, F. B. *Inorg. Synth.* **1985**, *23*, 141.

(23) (a) The procedure described in ref 23b was followed, with the modification that metal–halogen exchange between C_6F_5Br and *n*-BuLi was carried out at −78 °C for a minimum of 30 min. More efficient generation of C_6F_5Li results in yields after crystallization from THF/MeOH of greater than 80%. (b) Chatt, J.; Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1131.

(24) Prepared by using the procedure described in ref 25. IR (ν(CO), Nujol, cm^{-1}): 1909 s, 1779 vs.

(25) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

(26) Phillips, I. G.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* **1988**, *27*, 4038.

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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(1) For reviews see: Allen, D. W. *Organophosphorus Chem.* **1987**, *18*, 3. Refer to preceeding volumes also.
(2) Gontar, A. G.; Bykovskaya, E. G.; Knunyants, I. L. *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1975**, **20**, 232; *Chem. Abstr.* **1975**, *83*, 9063.
(3) Gontar, A. G.; Bykovskaya, E. G.; Knunyants, I. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1975**, *20*, 232; *Chem. Abstr.* **1976**, *84*, 121781.
(4) Fild, M. Dissertation 1966 Göttingen, FRG.
(5) Ansari, S.; Grobe, J.; Schmid, P. *J. Fluorine Chem.* **1972/73**, *2*, 281.
(6) Young, J. A.; Tsoukalas, S. N.; Dresdner, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3604.
(7) Emeléus, H. J.; Hurst, G. L. *J. Chem. Soc.* **1964**, 396.
(8) Grobe, J.; Demuth, R. *Angew. Chem.* **1972**, *84*, 1153.
(9) Minkwitz, R.; Kerbachi, R.; Nass, R.; Bernstein, D.; Preut, H. *J. Fluorine Chem.* **1987**, *37*, 259.
(10) Cavell, R. G.; Dobbie, R. C. *J. Chem. Soc.* A **1967**, 1308.
(11) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; F. Enke: Stuttgart, FRG, 1978; Vol. II, p 942.
(12) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, England, 1980.

0020-1669/89/1328-1627$01.50/0