(~7 mmol) in dry acetonitrile (20 mL) at −196 °C in a thick-walled tube was added (difluoroamino)difluoroacetonitrile (12 mmol) or trifluoroacetonitrile (12 mmol) under vacuum. The reaction mixture was warmed slowly to 25 °C and then heated at 65 °C with constant stirring until the mixture became a clear solution. While still hot, the solution was filtered under a dry atmosphere. After evaporation of CH_3CN, the respective tetrazolate salt remained in essentially quantitative yield. Further purification was realized by recrystallization from CH_3CN. Spectral data for $Na^+NF_2CF_2CNNNN^-$ (**2**): IR (KBr disk) 3620 w, 1618 m, br, 1492 s, 1420 w, 1230 vs, 1192 vs, 1170 vs, 1115 s, 1050 s, 960 s, 948 s, 920 s, 800 m, 765 w, 672 w, 633 m cm^{-1}; ^{19}F NMR, ϕ 19.81 (NF_2), −100.3 (CF_2). Anal. Calcd for $C_2F_4N_5Na$: Na, 11.91; N, 36.27. Found: Na, 11.17; N, 36.36.

Synthesis of 4 and 6. Sodium 5-((difluoroamino)difluoromethyl)tetrazolate (2 mmol) and manganese pentacarbonyl bromide (2 mmol) were dissolved in THF (5 mL) to form a clear solution that was heated at 40 °C for 36 h. Sodium bromide was removed by filtration and the solvent by evaporation to give the desired compound. Further purification resulted from paper chromatography under dry N_2; yield 56%. Spectral data for **6**: IR (KBr disk, Digilab FT), 3400 (H_2O), 2055 s, 1954 vs, 1949 vs, 1690 br, 1500 m, 1460 w, 1400 br, 1250 m, 1200 s, 1180 vs, 1110 m, 1070 m, 1035 m, 1025 m, 990 w, 950 m, 930 m, 920 s, 870 w, 850 w, 705 w, 620 w, 590 m cm^{-1}. Spectral data for **4** (CH_2Cl_2, Perkin-Elmer FT), 3055 w, 2989 w, 2056 vs, 1967 vs, 1658 br, 1638 br, 1495 m, 1461 w, 1439 w, 1423 w, 1385 w, 1266 vs, 1245 m, 1202 s, 1181 s, 1108 w, 1066 w, 1037 w, 972 vw, 950 w, 919 w, 898 w, 848 w, 794 vw, 741 vs, 706 s, 681 vw, 632 vw cm^{-1}; ^{19}F NMR (THF), ϕ 109.6 (CF_2), 16.4 (NF_2). Anal. Calcd for $C_5F_4MnN_5O_3$: C, 19.42; Mn, 17.77; N, 22.66. Found: C, 19.63; Mn, 17.70; N, 22.75.

Synthesis of 5, 7, and 8. Sodium 5-(trifluoromethyl)tetrazolate (2.2 mmol) and manganese pentacarbonyl bromide (2.2 mmol) were dissolved in THF (5 mL) to give a clear solution, which was heated at 40 °C for 48 h under vacuum. A crude filtration was accomplished while the solution was hot. Crystals were grown in a diglyme, petroleum ether, and $CHCl_3$ mixture (1:1:1). Compound **5** (**7**) was purified by using paper chromatography. The same experiment was repeated without removing the NaBr, and crystals were grown in the same mixture of solvents. The compound obtained was $[Mn_2(CO)_6(CF_3\overline{CNNNN})_3]^-Na^+\cdot 1.5diglyme\cdot CHCl_3\cdot H_2O$. Anal. Calcd for $[Mn_2(CO)_6(CF_3\overline{CNNNN})_3]Na\cdot 1.5(CH_3OC_2H_4)_2O\cdot CHCl_3\cdot H_2O$: C, 25.14; H, 2.19; N, 16.00. Found: C, 25.19; H, 2.57; N, 16.05. When the latter was recrystallized from diglyme, $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Na(digly)_2]^+$ (**8**) was found. The change in solvent of crystallization depended on the concentration of NaBr and the presence of trace amounts of H_2O. Spectral data for **8**: IR (Nujol), 2952 vs, 2926 vs, 2854 vs, 2042 m, 1959 s, 1949 m, 1461 s, 1377 s, 1369 m, 1306 vw, 1262 m, 1245 w, 1169 m, 1150 m, 1114 m, 1061 w, 1036 w, 975 w, 973 w, 954 vw, 736 s, 480 s cm^{-1}; IR (diglyme) two bands for ν_{CO} at 2030 m and 1915 s cm^{-1}; ^{19}F NMR (diglyme), ϕ −65.21 (CF_3).

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Supplementary Material Available: Listings of atomic positional and isotropic thermal parameters for non-hydrogen atoms, all bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and atomic positional and isotropic thermal parameters for hydrogen atoms (7 pages); a listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Cyanoborane Adducts of Dialkyl ((Dialkylamino)methyl)phosphonates

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Cyanoborane adducts of dialkyl ((dialkylamino)methyl)phosphonates were prepared from dialkyl ((dialkylamino)methyl)-phosphonates and macrocyclic cyanoborane oligomers,[6] by the reaction of the hydrochloride salts of dialkyl ((dialkylamino)-methyl)phosphonates with sodium cyanotrihydroborate and by a base displacement reaction. The products have been characterized by spectroscopy and elemental analysis. Comparison of the methods shows that the reaction with the cyanoborane oligomer is the method of choice due to the absence of decomposition products and ease of purification.

The synthesis and biological importance of an extensive series of amine–BH_2R (R = CN, COOH, COOR′, C(O)NHR′) adducts have recently been reported.[1-4] The isoelectronic and isostructural relationship of the amine–carboxyboranes with the dipolar form of the corresponding amino acid (e.g., $(CH_3)_3NBH_2CO_2H$ and betaine, $(CH_3)_3N^+CH_2COO^-$) was pointed out. The syntheses of cyanoborane adducts of dialkyl ((dialkylamino)methyl)-phosphonates were pursued with the goal of comparing their chemical and biological activity with that of amine–cyanoboranes. The inclusion of the phosphorus moiety will allow examination for the first time of the effect on biological activity of the (aminoalkyl)phosphonate moiety in cyanoborane compounds. In this paper we report the synthesis and characterization of cyanoborane adducts of $(RO)_2P(O)CH_2NR'_2$ (R = Me, Et, 2-Pr, Ph; R′ = Me, Et, H).

Experimental Section

Materials. All glass equipment was dried in an oven at 110 °C and assembled under a stream of dry nitrogen gas. All reactions were carried out under a N_2 atmosphere.

The ^1H NMR spectra were taken (TMS internal standard) on Varian XL-300 and JEOL FX-90Q spectrometers operating at 300 and 90 MHz, respectively. The ^{31}P NMR and ^{11}B NMR spectra were recorded on a JEOL FX-90Q instrument with the chemical shifts reported relative to 85% H_3PO_4 and $BF_3\cdot OEt_2$, respectively.

Infrared spectra were run as KBr disks or as neat liquids on a Perkin-Elmer 1750 FT spectrometer. Elemental analyses were preformed by M-H-W Laboratories, Phoenix, AZ 85018, and are reported in Table I. $NaBH_3CN$ (Sigma) and 1.0 M anhydrous HCl in diethyl ether (Aldrich) were used without further purification. Phosphonates were prepared by modification of the method reported by Fields.[5a] $(BH_2CN)_x$

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Table I. Physical Data for the Cyanoborane Adducts of Dialkyl ((Dialkylamino)methyl)phosphonates

compd	physical state	yield, %	^{11}B NMR, ppm[a]	^{31}P NMR, ppm	elemental anal., % calcd C	calcd H	calcd N	found C	found H	found N
$(CH_3O)_2P(O)CH_2N(Et)_2\cdot BH_2CN$ (**1**)	oil	49.72	−16.34 (101)	19.60	41.05	8.63	11.97	40.94	8.54	11.87
$(C_2H_5O)_2P(O)CH_2N(Et)_2\cdot BH_2CN$ (**2**)	oil	70.0	−16.05 (89)	16.67	45.82	9.25	10.69	46.03	9.24	10.58
$(2\text{-}C_3H_7O)_2P(O)CH_2N(Et)_2\cdot BH_2CN$ (**3**)	oil	73.0	−16.64 (107)	15.15	49.66	9.74	9.66	49.82	9.81	9.92
$(C_2H_5O)_2P(O)CH_2N(CH_3)_2\cdot BH_2CN$ (**4**)	oil	75.0	−11.76 (106)	16.89	41.05	8.63	11.97	40.96	8.54	12.32
$(PhO)_2P(O)CH_2NH_2\cdot BH_2CN$ (**5**)	solid (mp 146 °C)	74.6	−21.35 (92)	13.47	55.66	5.35	9.28	55.74	5.36	9.30

[a] *J* values (in Hz) given in parentheses.

Table II. ^{1}H NMR Chemical Shifts,[a] Multiplicities,[b] and Coupling Constants[c] for Compounds **1–5**

compd	HCCOP	HCOP	HCP	HN	HCN	HCCN
1		3.83 (d) [11.1]	3.24 (d) [10.8]		3.25 (q) [7.0, HCCH]	1.30 (t) [7.0, HCCH]
2	1.37 (t) [6.9, HCCH]	4.18 (m)	3.26 (d) [12.9]		3.29 (q) [7.2, HCCH]	1.34 (t) [7.2, HCCH]
3	1.36 (d) [6.3, HCCH]	4.75 (m)	3.20 (d) [12.9]		3.30 (q) [7.2, HCCH] 3.31 (q) [7.2, HCCH]	1.35 (t) [6.9, HCCH]
4	1.37 (t) [7.1, HCCH]	4.27 (m) [7.1] [8.9, HCOP]	3.28 (d) [12.3]		2.96 (s)	
5		7.32 (m)	3.62 (m) [12.3]	6.34 (bs)		

[a] Values are reported in ppm. [b] Given in parentheses: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; b = broad. [c] Coupling constants (in brackets) are reported in Hz, ±0.3 Hz.

Table III. IR Data for Compounds **1–5**

compd	ν, cm^{-1} P=O	B—H	N—B	C≡N	N—H
1	1260	2430, 2372	674	2199	
2	1242	2437, 2365	678	2191	
3	1249	2430, 2372	678	2199	
4	1257	2432, 2336	708	2199	
5	1241	2425, 2310	689	2203	3428

was prepared by adapting the method reported by Spielvogel et al.[6] but was not isolated or purified in order to avoid an explosion hazard.[7] The HCl salts of the phosphonates were prepared by bubbling anhydrous HCl gas (Matheson) into an anhydrous ether solution of the phosphonate. The salt was isolated and dried in vacuo before further use. Diethyl ether and tetrahydrofuran (THF) were dried by refluxing over and distilling from sodium metal. Hydrogen gas evolution was monitored by using an oil bubbler.

General Method of Preparation of Cyanoborane Adducts 1–3 of $(RO)_2P(O)CH_2NR'_2$ Using $(BH_2CN)_x$. In a modification of the method of Spielvogel et al.,[6] $NaBH_3CN$ (8.8 g, 0.14 mol) was added with stirring under a stream of dry N_2 to 200 mL of ice-cooled anhydrous diethyl ether. A 1.0 M solution of HCl in anhydrous ether (140 mL) was added dropwise with stirring until the evolution of H_2 ceased (ca. 1 h). The above mixture was refluxed for 1 h, cooled, and filtered and a majority of the solvent removed under reduced pressure. The resulting viscous oil was washed with anhydrous ether (3 × 100 mL) and the ether removed under reduced pressure. At no time was the oligomer handled dry.[7]

Fresh anhydrous ether (200 mL) was added to $(BH_2CN)_x$ followed by the addition of 0.11 mol of the (aminomethyl)phosphonate, and the mixture was stirred at room temperature for 72 h. The residue, after solvent was removed, was dissolved in a small amount of water followed by extraction of the product with ether (4 × 100 mL). The combined ether extracts were dried over anhydrous K_2CO_3. The oily liquid obtained after removal of K_2CO_3 and solvent was washed with hexane to remove traces of phosphonate formed during the water purification. The product was dried under vacuum and the purity of the products assayed by elemental analysis and spectroscopy (Tables I–III).

Preparation of Cyanoborane Adduct $(C_2H_5O)_2P(O)CH_2N(CH_3)_2\cdot BH_2CN$ (4) Using $NaBH_3CN$. By a procedure similar to that described by Spielvogel et al.,[2] $(C_2H_5O)_2P(O)CH_2N(CH_3)_2\cdot HCl$ (33.00 g, 0.14 mol) and $NaBH_3CN$ (9.10 g, 0.13 mol) were combined in anhydrous THF and the mixture was stirred at room temperature until the H_2 gas evolution slowed (ca. 30 min). The resulting suspension was refluxed for 84 h. The reaction mixture was cooled and filtered and the solid washed with anhydrous THF (2 × 20 mL). The THF washings were combined with the filtrate, and the THF was removed at reduced pressure, leaving a viscous oil. The oil was dissolved in 200 mL of anhydrous diethyl ether, resulting in a cloudy solution, which was filtered. Anhydrous HCl gas was bubbled into the solution, removing the unreacted phosphonate as the insoluble HCl salt. The cloudy solution was cooled and stored at −20 °C, yielding a small amount of the salt as a viscous oil. The ether layer was decanted off, and the oil was washed with anhydrous ether (2 × 50 mL). The washings were combined, and the ether was removed at reduced pressure to yield the product. Analytical and spectroscopic data are summarized in Tables I–III.

Preparation of the Cyanoborane Adduct $(C_2H_5O)_2P(O)CH_2N(CH_3)_2\cdot BH_2CN$ (4) by Base Replacement Reaction. Samples of $(C_2H_5O)_2P(O)CH_2N(CH_3)_2$ (10.00 g, 0.045 mol) and $C_6H_5NH_2\cdot BH_2CN$ (4.00 g, 0.030 mol) were placed in a flask, and the reaction mixture was stirred for 84 h at room temperature. The oily mixture was dissolved in 200 mL of anhydrous ether, and HCl gas was bubbled into the solution, removing the unreacted phosphonate and aniline as their HCl salts. The cloudy solution was cooled at −20 °C for 2 h, yielding the salts in a viscous oil. The ether layer was decanted off, and the oil was washed with anhydrous ether (2 × 20 mL). The ether washings were combined, and the ether was removed at reduced pressure, to yield the product. The analytical data (IR, NMR) are consistent with those obtained from the analysis of the product formed in the preceding reaction.

Preparation of $(C_6H_5O)_2P(O)CH_2NH_2\cdot BH_2CN$ (5). The $(BH_2CN)_x$ oligomer was prepared as previously described. After $(C_6H_5O)_2P(O)CH_2NH_2$ (28.93 g, 0.11 mol) was added, the reaction mixture was stirred at room temperature for 2 h. A solid was collected and rinsed three times with anhydrous ether, followed by washing with hot (60 °C) water twice. The solid was dried under vacuum. The product can be recrystallized from THF/hexane. Analytical data are summarized in Tables I–III.

Results and Discussion

Three routes for the synthesis of cyanoborane adducts of $(RO)_2P(O)CH_2NR'_2$ may be envisaged. First, the reaction of the HCl salt of the phosphonate with $NaBH_3CN$, based on Spielvogel's work,[2] should give a cyanoborane (eq 1). The

$$(RO)_2P(O)CH_2NR'_2\cdot HCl + NaBH_3CN \rightarrow (RO)_2P(O)CH_2NR'_2\cdot BH_2CN + H_2 + NaCl \quad (1)$$

cyanoborane adduct of $(C_2H_5O)_2P(O)CH_2N(CH_3)_2$ was synthesized by this method in good yield. However, this method is not uniformly applicable to the synthesis of all cyanoborane adducts of $(RO)_2P(O)CH(R'')NR'_2$. When this method was tried with $R'' = CH_3$, C_2H_5, considerable ester cleavage as well as P—C bond cleavage was observed, leading to low yields of the adduct.[8] These observations may be rationalized by the presence of intramolecular hydrogen bonding between the P=O group and the

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proton on the nitrogen, thereby facilitating bond cleavage.[5b]

A second route to cyanoboranes of this type uses a base displacement reaction between $(RO)_2P(O)CH_2NR'_2$ and a cyanoborane adduct. An example would be the utilization of an amine–cyanoborane[7a] or $(CH_3)_2S{\cdot}BH_2CN$[9] as a weak base–cyanoborane adduct reacting with the (aminoalkyl)phosphonate. This process successfully produced the desired cyanoborane (eq 2) in good yield, but production of the donor adduct was time-consuming, and the subsequent product purification was a cumbersome process.

$$PhNH_2{\cdot}BH_2CN + (C_2H_5O)_2P(O)CH_2N(CH_3)_2 \rightarrow (C_2H_5O)_2P(O)CH_2N(CH_3)_2{\cdot}BH_2CN + PhNH_2 \quad (2)$$

In view of the actual and potential usefulness of macrocyclic cyanoborane oligomers, prepared as described above, a more straightforward and convenient procedure for synthesizing $(RO)_2P(O)CH_2NR'_2{\cdot}BH_2CN$ is possible. This procedure affords a simple, less time-consuming method for producing this type of compound in high yield. The cyclic oligomer $(BH_2CN)_x$ reacts with $(RO)_2P(O)CH_2NR'_2$ at room temperature with stirring for 72 h, yielding a product mixture that contains very few contaminants. Heating the reaction mixture leads to decomposition of the starting materials with one decomposition product involving P–C bond cleavage. This results in a lower yield as well as formation of a mixture of products that are difficult to identify. A room-temperature reaction is therefore advantageous and necessary to obtain pure product in higher yield. This temperature dependence of the reaction is in direct contrast to that seen for the amine–cyanoboranes, which are normally refluxed for 3 days.[2] Compounds **1–4** are colorless, oily liquids (Table I); compound **5** is a white crystalline solid.

As noted for amine–cyanoboranes,[2] the C≡N absorption in the IR spectra of $(RO)_2P(O)CH_2NR'_2{\cdot}BH_2CN$ indicates that the cyano and not the isocyano isomer is formed. Characteristic B—H absorptions in the region 2437–2309 cm^{-1} were observed for each compound. A strong NH_2 absorption further distinguished compound **5**. A moderately strong band in the region of 708–674 cm^{-1} is observed for each of these compounds, supporting the presence of a B—N donor/acceptor bond.[10] All the compounds exhibit absorptions in the region 1260–1241 cm^{-1}, which have been assigned to the P=O stretch and are within the range of values observed for the corresponding phosphonates.[5b,11]

The ^1H NMR spectra exhibit features that are consistent with those expected from the structural assignments for the cyanoborane adducts. All of the signals exhibit a downfield shift from the chemical shift values observed in the corresponding phosphonates. As might be expected, the magnitudes of the shifts are largest for those moieties closest to the N–B bond. In compounds **1–4**, the $P–CH_2$ group exhibits a large doublet, indicating the presence of the P–C bond. Compound **5** shows a broad multiplet, which collapses to the characteristic doublet when the N–H resonance is irradiated.

The ^{11}B and ^{31}P NMR data are summarized in Table I for ease of comparison. The ^{11}B NMR spectra for all the compounds show 1:2:1 triplets characteristic of BH_2 moieties. The range of chemical shifts as well as the range of coupling constants is consistent with that of other amine–cyanoboranes and tetracoordinate boron adducts.[12] The ^{31}P NMR data also confirm the formation of the cyanoborane adducts, with the signals showing an upfield shift comparable in magnitude to that observed when the parent phosphonates are compared to their HCl salts.[5b,13]

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Addition Reactions of a Silylated Iminomethylenephosphorane

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Reactions of the iminomethylenephosphorane $(Me_3Si)_2NP(=NSiMe_3)=CHSiMe_3$ (**2**), a stable three-coordinate P^V species, with some electrophilic and nucleophilic reagents have been studied. Treatment of **2** with various chlorophosphines gave the novel $P^V–C–P^{III}$ systems $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH(SiMe_3)P(X)R$ (**3**, R = X = Ph; **4**, R = X = NMe_2; **5**, R = Ph, X = Cl) via addition across the P=C double bond. The P–Cl derivative **5** readily eliminated Me_3SiCl to afford the cyclic product **6**, an unusual $P^VNP^{III}C$ four-membered-ring system. Compound **2** also underwent rapid addition reactions with both secondary amines and CF_3CH_2OH to yield the four-coordinate aminophosphoranimines $(Me_3Si)_2NP(=NSiMe_3)(CH_2SiMe_3)NR_2$ (**7**, R = Me; **8**, R = Et) and the *P*-(trifluoroethoxy)phosphoranimine $(Me_3Si)_2NP(=NSiMe_3)(CH_2SiMe_3)OCH_2CF_3$ (**9**), respectively. Heating of **9** resulted in elimination of $Me_3SiOCH_2CF_3$ and formation of the P_2N_2 dimer $[Me_3SiNP(=NSiMe_3)CH_2SiMe_3]_2$ (**10**). Addition of methyllithium to **2**, followed by quenching of the intermediate carbanion with either Me_3SiCl or Me_2SiCl_2, gave the highly silylated *P*-methylphosphoranimines $(Me_3Si)_2NP(Me)(=NSiMe_3)CH(SiMe_3)SiMe_2X$ (**11**, X = Me; **12**, X = Cl). When heated, the chlorosilyl derivative **12** readily underwent loss of Me_3SiCl and cyclization to give the novel PNCSi four-membered-ring product **13**. On the basis of these representative reactions, the reactivity of the P=C bond in the iminomethylenephosphorane **2** is contrasted with that in the analogous two-coordinate P^{III} system, the methylenephosphine $(Me_3Si)_2NP=CHSiMe_3$ (**1**).

Introduction

Since the first reports in the 1970s of the synthesis of stable methylenephosphines (A)[1] and iminophosphines (B),[2] the preparative chemistry,[3] reactivity,[4] and coordination chemistry[5] of these two-coordinate P^{III} species have been developed to a considerable

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