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ADDUCT FORMATION AND EXCHANGE REACTIONS OF DI(TERTIARY AMINOPHOSPHINES) WITH PF_5. PREPARATION OF $F_2P[B_{10}H_{10}C_2]PF_2$ AND THE NOVEL $[Me_2NP(B_{10}H_{10}C_2)PNMe_2](PF_6)_2$

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SUMMARY

Phosphorus pentafluoride reacts with the di(tertiary aminophosphines) of the type $RR'P[B_{10}H_{10}C_2]PR''R'''$ [$R=R'=C_6H_5$ or NMe_2, $R''=R'''=NMe_2$: $R=R''=NMe_2$, $R'=R'''=F$: $R=R'=C_6H_5$, $R''=NMe_2$, $R'''F$] to give adducts containing P(III)->P(V) bonds. Thermal decomposition of the adducts leads to products where an amino group is exchanged by fluorine. The adduct $Me_2N(F)P[B_{10}H_{10}C_2]P(F)NMe_2.2PF_5$ in CH_3CN solution exists in the ionic form $[Me_2NP(B_{10}H_{10}C_2)PNMe_2](PF_6)_2$ containing dicoordinate phosphorus. Thermal decomposition of this adduct gives the novel $F_2P[B_{10}H_{10}C_2]PF_2$.

INTRODUCTION

We have previously reported the preparation and characterization of a number of symmetrical and unsymmetrical di(tertiary)phosphines containing electronegative substituents.[1,2] Some of the fluorine containing di(tertiary) phosphines were prepared by reacting aminophosphines with PF_5 in a manner analogous to that reported by Sharp and co-workers.[3] While we speculated that these reactions proceeded via a covalent adduct formation, no evidence was presented to support this assumption. In fact a number of very interesting divalent cationic phosphorus compounds have been prepared[4,5] and it seemed

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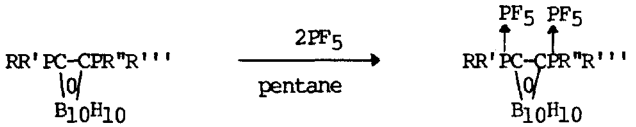
possible that the adducts reported by us might have ionic structures. We now report a detailed study on the solution chemistry of the adducts and we have now shown that cationic products are produced under certain conditions and that the hitherto unreported $F_2P[B_{10}H_{10}C_2]PF_2$ derivative can be synthesized by decomposition of these adducts.

RESULTS AND DISCUSSION

Phosphorus pentafluoride reacts with aminophosphine derivatives of orthocarborane to form white solid adducts (I-IV) according to the following reaction:



$$RR'PC\text{-}CPR''R''' \ (B_{10}H_{10}) \xrightarrow[\text{pentane}]{2PF_5} RR'\overset{PF_5}{\overset{\uparrow}{P}}C\text{-}C\overset{PF_5}{\overset{\uparrow}{P}}R''R''' \ (B_{10}H_{10})$$

I: $R=R'=R''=R'''=NMe_2$

III: $R=R''=NMe_2;R'=R'''=F$

II: $R=R'=C_6H_5;R''=R'''=NMe_2$

IV: $R=R'=C_6H_5;R''=F,R'''=NMe_2$

The solid adducts are moisture sensitive and are insoluble in hydrocarbon solvents. The stoichiometry ($2PF_5$: 1 phosphine) suggests a P(III)→P(V) bond in the adducts since a higher ratio would probably occur if N were the donor atom to the PF_5 moiety. Previous work by Sharp[3] and by Rudolph[6] has demonstrated that a P(III)→P(V) bond is preferred for amino phosphine adducts with PF_5. The P-N stretching frequencies in the adducts (I, 976cm^{-1}, 965cm^{-1}; II, 975 cm^{-1}, 961 cm^{-1}; III, 980 cm^{-1}; IV, 980 cm^{-1}) occur on the high energy side of the accepted region for these absorptions (940-980 cm^{-1}). This is a result of the nitrogen to phosphorus $p\pi \rightarrow d\pi$ interaction. The high electron withdrawing character of the carborane cage favors this interaction as does the presence of fluorine on the phosphorus. However, the P-N stretching frequencies for the adducts are not appreciably different from the P-N stretching vibrations of the free ligands[1,2] suggesting that the adducts contain $P \rightarrow PF_5$ bonds rather than $N \rightarrow PF_5$ bonds where the P-N stretch of the ligand would be expected to occur at much lower energy

(800 cm^{-1}). The strengthing of the P-NMe_2 bond by $p\pi \rightarrow d\pi$ interaction may account for the unsuccessful attempts by us to break the P-NMe_2 bonds by reaction with anhydrous HCl. Cleavage of the P-carborane cage bond was observed with every attempt. All adducts show strong absorptions in the 800-860 cm^{-1} region (assigned to the PF_5 moiety) as well as typical bands due to the B-H stretch (2620-2570 cm^{-1}) and the cage deformation vibration at 720 cm^{-1}.

The suspensions in hydrocarbon solvents or chloroform solutions of the adduct (I) are decomposed upon heating to give $Me_2N(F)P[B_{10}H_{10}C_2]P(F)NMe_2$(VI) as previously reported. The exchange of substitutents probably takes place while the P-P bond is retained.[3] No oxidation-reduction occurs as no PF_3 or derivative of PF_3 is observed in the volatile by-products and no evidence of pentavalent phosphorus is seen in the ^{31}P nmr spectra. The only volatile by-product is Me_2NPF_4.

Adduct (III) is formed by reaction of excess PF_5 with (VI) in pentane solutions. Solutions of adduct (III) in CH_3CN at 25°C show a broad singlet at +358 ppm (85% H_3PO_4 external reference) diagnostic of a divalent phosphorus cation[4,5] and a septet at -145.3 ppm ($^1J_{P-F}$ = 707 Hz) typical of PF_6^-. The identity of the PF_6^- ion is further confirmed by the ^{19}F nmr spectrum which shows a doublet at +71 ppm (CCl_3F, internal reference) and $^1J_{P-F}$ = 706 Hz. Conductivity measurements of a 10^{-3} M solution at 25°C gave a molar conductivity of 232.5 ohm^{-1} cm^2 mol^{-1} typical of a 2:1 electrolyte.[6] Thus, the solution species is assigned the ionic structure $[Me_2NP(B_{10}H_{10}C_2)PNMe_2]^{+2}$ with two PF_6^- counterions.

Thermal decomposition of adduct (III) in a pentane slurry gave the hitherto unreported $F_2P[B_{10}H_{10}C_2]PF_2$(VII) in ca. 45% yield. The ^{31}P and ^{19}F nmr were analyzed as a $X_2AA'X'_2$ spin system. The chemical shifts and coupling constants are in the expected ranges for this type of fluorophosphine.

Adduct (II) is decomposed upon heating a pentane suspension or acetonitrile solution to give $(C_6H_5)_2P[B_{10}H_{10}C_2]P(F)NMe_2$ (VIII) in 60% yield. However a small amount of the compound $(C_6H_5)_2P[B_{10}H_{10}C_2]PF_2$(IX) was also observed as well as some $(C_6H_5)_2P[B_{10}H_{10}C_2]H$. The latter results from some $(Me_2N)_2P$-carborane bond cleavage. Decomposition of adduct (IV) gave much higher yields of (IX) but also more $(C_6H_5)_2P[B_{10}H_{10}C_2]H$ was observed. No cationic divalent phophorus could be observed in CH_3CN solutions in spite of the observation of some PF_6^-. Since the $(C_6H_5)_2P\rightarrow PF_5$ bond is easily broken, excess $PF_5\cdot$ solvent could be in solution and could react further with the Me_2NP center.

It should be pointed out that adduct (I) had a higher decomposition point (135-140°C) than adduct (II) (95°C) reflecting the greater basicity of the $P(NMe_2)_2$ group compared to the $P(C_6H_5)_2$ group. Of interest is the fact that the $(C_6H_5)_2P[B_{10}H_{10}C_2]H\cdot PF_5$ adduct dissociates below 50°C. Similarly the lower decomposition points of the $FPNMe_2$-containing adducts (60°C) reflect the lower basicity of this group compared to the $P(NMe_2)_2$ group.

EXPERIMENTAL

The aminophosphines were prepared as previously described.[1,2] Phosphorus trifluoride and phosphorus pentafluoride were obtained from Ozark-Mahoning Company and purified by fractional condensation. Acetonitrile was distilled from P_4O_{10} prior to use. Other solvents were dried over molecular sieves (4A) prior to use. Glassware was dried in an oven at 110°C overnight prior to use. All volatile reactants and products were handled using high vacuum techniques. Non-volatile solids were handled in an argon atmosphere in a dry box.

Infrared spectra of the solids were recorded in nujol mulls or fluorolube mulls on a Perkin-Elmer 580 Infrared Spectrophotometer. Proton nmr and ^{19}F nmr were obtained on a Varian EM 390 spectrometer operating at 90 MHz and 84.6 MHz respectively. Phosphorus-31 nmr spectra were obtained on a Varian CFT 20 spectrometer at 32.1 MHz. Conductivities were measured in acetonitrile at 25°C using a platinum dipping electrode and a conductivity bridge.

Preparation of the Adducts

The adducts were prepared by condensing excess PF_5 (fourfold) into a high pressure tube containing a solution of the aminophosphine (3-6 mmol) in the appropriate solvent and allowing the reaction mixture of warm to room temperature with constant shaking. After standing at room temperature for 0.5h the excess PF_5 was removed in vacuo and the remaining slurry was filtered and the solid dried. The stiochiometry of the reaction was determined by pressure measurements of the PF_5. The exchange products were synthesized by heating the adducts as suspensions in hydrocarbons in a high pressure tube.

$(Me_2N)_2P[B_{10}H_{10}C_2]P(NMe_2)_2.2PF_5$ (I)

Decomposition point, 135-140°C. Infrared spectrum of the analytically significant bands (cm^{-1}): 2620-2560, vs, br; 975, s; 969, s;855, vs;825, vs;805,vs;720, ms. Analysis, calc'd. (found):C, 19.0 (18.8); H, 5.4 (5.6);P, 19.6)19.5); F, 30.1 (29.9).

$(C_6H_5)_2P[B_{10}H_{10}C_2]P(NMe_2)_2 \cdot 2PF_5$(II)

Decomposition point, 95°C. Infrared spectrum of the analytically significant bands (cm^{-1}): 2640-2530 vs, br; 1431,vs (phenyl ring deformation); 1091,vs (P-C aryl stretch);975, s; 961, s; 860,vs;845,vs;800, vs;722, ms. Anaylsis, calc'd (found): C, 30.9 (30.0); H, 4.6 (4.8); P, 17.8 (17.6); F, 27.2 (26.9).

$(Me_2N)(F)P[B_{10}H_{10}C_2]P(F)(NMe_2) \cdot 2PF_5$(III)

Decomposition point, 55-60°C. Decomposes at room temperature in solution. Infrared spectrum of analytically significant bands (cm^{-1})· 2640-2570, vs, br;980, vs; 840 vs, br 820 vs, br; 740, vs;727, m. Analysis, calc'd (found); C, 12.4 (12.2.); H, 3.8 (3.9); P, 21.3 (21.0); F, 39.2 (39.0).

$(C_6H_5)_2P[B_{10}H_{10}C_2]P(F)(NMe_2) \cdot 2PF_5$(IV)

Decomposition point, 60°C. Decomposes at room temperature in solution. Infrared spectrum of the analytically significant bands (cm^{-1}); 2620-2560, vs, br 1435, vs (phenyl ring deformation); 1092,vs (P-C aryl stretch);980, vs, br; 870, vs, br;820, vs;747,vs;719,m. Analysis, calc'd (found); C, 28.5 (28.3);H, 3.9 (4.1); P, 18.4 (18.1); F, 31.1 (30.8).

$F_2P[B_{10}H_{10}C_2]PF_2$(V)

Moisture sensitive solid. NMR data $CDCl_3$ solution: δ_P=+171 (downfield from external 85% H_3PO_4); δ_F =+79ppm (upfield from internal CCl_3F); $^1J_{P-F}$=1274 Hz; $^4J_{P-F}$=55 Hz; $^3J_{P-P}$=70 Hz(Both ^{19}F and ^{31}P spectra belong to the X_2 AA'X'$_2$ spin system).

$(Me_2NP[B_{10}H_{10}C_2]PNMe_2)(PF_6)_2$

White solid, NMR data, $CDCl_3$ Solution: δ_P =+358 ppm (downfield from external 85% H_3PO_4); $\delta_{PF_6^-}$ =-145.3 ppm (upfield from external 85% H_3PO_4), $^1J_{P-F}$=707 Hz; δ_F=+71ppm (upfield from internal CCl_3F); δ_H=2.65 ppm (downfield from internal $Si(CH_3)_4$). Molar conductivity, 10^{-3}M solution in CH_3CN at 25°C, 232.5 $ohm^{-1}cm^2\ mol^{-1}$.

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