various primary[1] and secondary[2,3] amines ("transamination"), amides,[2,3] imines,[4] amino alcohols,[5] and carbonyl compounds.[3] Iminobis(aminodiphenylphosphonium) chloride,[6] $[(C_6H_5)_2P(NH_2)\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)(C_6H_5)_2]^+Cl^-$ (I), and the corresponding free phosphinimine (II) offer a preformed five-membered chain for a ring-closure reaction as well as amino groups, and therefore we have investigated the reaction between $P[N(CH_3)_2]_3$ and II.

Experimental Section

Materials.—All solvents used were Spectrograde quality and practically water free. Compound I was made by ammonolysis of $(C_6H_5)_2PCl_3$ with dry ammonia[6] followed by dehydrochlorination to the corresponding phosphinimine (II) with a freshly prepared sodium methoxide solution.[7] Melting point and nmr spectra agreed with the published data. $P[N(CH_3)_2]_3$ was also prepared following a literature procedure.[8] All operations were carried out under nitrogen.

Analyses.—Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Melting points were obtained in sealed glass capillaries on a Mel-Temp melting point block and are uncorrected.

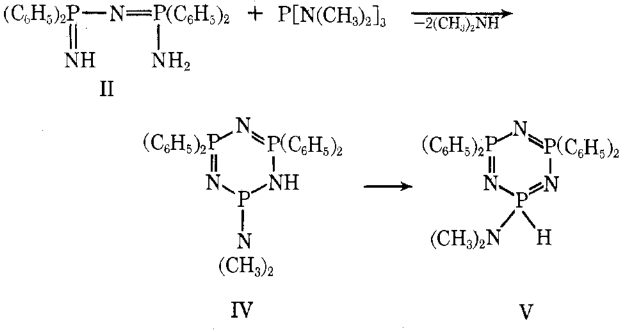
Spectra.—Infrared (ir) spectra were recorded in solution (CCl_4–CS_2) with a Beckman IR-10 spectrometer. The ^1H nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer in $CDCl_3$ solution, using TMS as an internal standard. The ^{31}P nmr spectra were run with a Varian XL-100-15 spectrometer, operating at a frequency of 40.55 MHz and locked onto the deuterium resonance of D_2O. The samples were contained in 5-mm o.d. tubes (solvent CH_2Cl_2) which were concentrically inserted, using Teflon spacers, into a thin-wall 12-mm o.d. tube containing the D_2O.

Reaction of II with $P[N(CH_3)_2]_3$.—In a typical reaction, 10.0 g of II and 3.92 g of $P[N(CH_3)_2]_3$ in 40 ml of bromobenzene were heated slowly to reflux. The reaction started at *ca.* 120° and the split-off dimethylamine was collected in a −78° trap. After 4 hr, 2.17 g of $(CH_3)_2NH$ (96% of theory) was collected; the yellow solution was concentrated to about 20 ml and chilled to 0°, and the unreacted II was filtered off. Evaporation to dryness yielded a heavy oil (III); addition of acetonitrile gave, upon standing, white crystals which were recrystallized from acetonitrile; yield 8.05 g (61% of theory based upon the quantity of II consumed); dec pt *ca.* 110°. *Anal.* Calcd for $C_{28}H_{30}N_5P_3$: C, 63.51; H, 5.71; N, 13.23; P, 17.55. Found: C, 63.07; H, 5.53; N, 13.29; P, 17.70. Nmr: proton spectrum: $\tau_{C_6H_5}$ 2.08, 2.30, 2.62 (complex multiplet); τ_{PH} 2.45 (d); τ_{CH_3} 7.48 (d); τ_{CH_3CN} 8.22; $^3J_{PNCH}$ = 13.5 Hz, $^1J_{PH}$ = 611 Hz; phosphorus spectrum: $\delta_{PC_6H_5}$ −14.1 ppm (s); $\delta_{PN(CH_3)_2}$ −7.5 (d, d); ratio $P_{C_6H_5}:P_{N(CH_3)_2} = 2:1$ (calcd 2:1).

The above compound represents an acetonitrile adduct of $(C_6H_5)_4P_3N_3H[N(CH_3)_2]$. This adduct may be destroyed by recrystallization from benzene to give the unsolvated compound; mp 179–181°. *Anal.* Calcd for $C_{26}H_{27}N_4P_3$: C, 63.93; H, 5.57; N, 11.47; P, 19.02. Found: C, 63.42, H, 5.04; N, 11.56; P, 19.28. Ir: 3080 (s, sh), 3060 (vs), 3020 (m), 2940–2920 (s), 2890 (m), 2840 (m), 2800 (m), 2370/2340 (s), 1480 (m), 1440 (s), 1200–1160 (vs), 1120 (vs), 1070 (s), 1030 (s), 970 (vs), 855 (s), 715 (s), 690 (vs), 605 cm⁻¹ (m). Nmr: as above but without the acetonitrile peak.

Results and Discussion

As in the case of the reaction of $RP(OC_6H_5)_2$ with II,[9] the isolated product is not the phospha(III)diphospha(V)triazine derivative IV but its tautomer V, a PH phosphazene. Evidence for the ring closure is given by the infrared spectrum which shows at 1200–1160 and at 1120 cm^{-1} the characteristic P═N bands. Evidence for V is provided by the insensitivity of the compound to oxygen, by the ir frequencies at 2370 and 2340 cm^{-1} (ν_{PH} vibrations), and by the high coupling constant J_{PH} = 611 Hz. The observed ^{31}P chemical shifts are also in accord with this structure.



II

IV

V

It should be noted that in one experiment out of nine carried out, the ^{31}P nmr spectrum of a CH_2Cl_2 solution of III was found to exhibit only two peaks of δ_P −63.0 ppm and δ_P −40.9 ppm (ratio: calcd, 1:2; found, 1:2.1), the former being split into a multiplet (theoretical septet) with $^3J_{PNCH}$ = 14.0 Hz. This experiment could, however, not be repeated, but it seems we have here observed form IV as the sole product which then transformed into V upon crystallization.

It is further interesting to note that V gives an adduct with acetonitrile as do the related phosphazatriene derivatives $(C_6H_5)_4P_3N_3Cl_2$[10] and $[(C_6H_5)_2PN]_3$[11] (the latter with *sym*-$C_2H_2Cl_4$); no such adduct was reported for the previously mentioned[9] PH phosphazenes.

Acknowledgment.—We wish to thank the National Science Foundation (Grant No. GP-9525) for partial financial support and Dr. A. D. F. Toy of the Stauffer Chemical Co. for a generous gift of diphenylphosphinous chloride.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112,
AND UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48105

The Synthesis of Tetrafluorodiphosphine–Bis(borane(3))

BY R. T. PAINE[1a] AND R. W. PARRY*[1b]

Received June 30, 1971

In an earlier communication[2] from this laboratory

[1] (a) University of Michigan. (b) University of Utah.

[2] K. W. Morse and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 172 (1967).

the synthesis of $F_4P_2 \cdot BH_3$ from F_4P_2 and B_2H_6 was reported, but all efforts to produce $F_4P_2 \cdot 2BH_3$ by this reaction were unsuccessful. Since F_4P_2 contains two potential coordination sites, the absence of coordination at the second site was a curious phenomenon which suggested some possible double bonding or other peculiarity in the P–P linkage.

Recently we have shown that $F_4P_2 \cdot 2BH_3$ can be synthesized using $OCBH_3$ as the borane source. The process proceeds by a stepwise base-displacement sequence

$$F_4P_2(g) + OCBH_3(g) \xrightarrow{-78°} F_4P_2 \cdot BH_3(g) + CO(g)$$

$$F_4P_2 \cdot BH_3(g) + OCBH_3(g) \xrightarrow[2.\ \ -196°]{1.\ \ -45°} F_4P_2 \cdot 2BH_3(g) + CO(g)$$

The $F_4P_2 \cdot 2BH_3$ complex was found to be very unstable toward dissociation and decomposition at 0°. The complex reacted, on contact with trimethylamine, to give $(CH_3)_3N \cdot BH_3$, P_2F_4, and PF_3. This reaction served as an analytical reaction for determining the number of borane(3) units coordinated to the ligand.

The ^{11}B nmr spectrum was recorded at 32.1 MHz and at −40° in $CFCl_3$ solvent. The spectrum consisted of a 1:3:3:1 quartet with δ 130.7 ppm relative to $(CH_3)_3B$ and J_{BH} = 115 Hz. No further splitting of the ^{11}B signal was observed. The ^{19}F nmr spectrum was recorded at 94.1 and 56.4 MHz at −40°. The spectrum in each case was found to be second order, as shown in Figure 1, with δ 10.0 ppm relative to F_3CCOOH. The second-order feature was not unexpected since an earlier study of P_2F_4[3] showed that the ligand exhibited an $X_2AA'X'_2$ type ^{19}F nmr spectrum. On expansion, the inner members of the $F_4P_2 \cdot 2BH_3$ spectrum showed a 1:3:3:1 quartet structure, $J_{FPBH} \cong 25$ Hz. The small, outer members showed no resolvable fine structure.

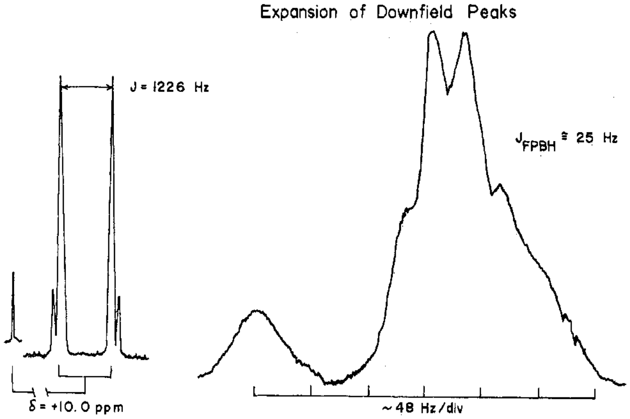

Figure 1.—The ^{19}F nmr spectrum of $F_4P_2 \cdot 2BH_3$ and expansion of the downfield peaks.

In the original paper by Parry[2] it was suggested that the borane group of $F_4P_2 \cdot BH_3$ oscillates between phosphorus sites since no splitting of the ^{11}B nmr signal by phosphorus was detected. This suggestion now appears to be incorrect since the ^{11}B spectrum of $F_4P_2 \cdot 2BH_3$ shows no splitting by phosphorus under the conditions used and oscillation is now clearly impossible. Furthermore Hodges and Rudolph[4] have recently detected the elusive splitting of the ^{11}B signal by phosphorus in $F_4P_2 \cdot BH_3$.

Experimental Section

In a typical preparation, 3.6 mmol of tetrafluorodiphosphine[5] and 4.0 mmol of borane carbonyl[6] were condensed together in a 300-ml bulb attached to a standard high-vacuum line. The bulb was then closed off by a stopcock and held at −78° for 2–3 days. During this reaction period the bulb and contents were periodically frozen at −196° and the liberated carbon monoxide pumped away. This served to drive the reaction to completion. When the carbon monoxide evolution ceased, the reaction was considered complete. The volatile products were passed through −78, −100, and −196° traps. The monoborane(3) complex was retained at −100°. A 2.0-mmol sample of pure $F_4P_2 \cdot BH_3$ was then combined with 3.0 mmol of borane carbonyl in a 300-ml flask and closed off from the vacuum line. The flask was then warmed to −45° for 1 min and then cooled to −196°, and the evolved carbon monoxide was pumped away. The warming–cooling cycle was repeated until no further carbon monoxide was evolved. The volatile products were passed through −78, −100, and −196° traps. The desired product, $F_4P_2 \cdot 2BH_3$, was retained at −78° in 60% yield based on the amount of $F_4P_2 \cdot BH_3$ used.

The mass spectrum of $F_4P_2 \cdot 2BH_3$ showed a parent peak, $F_4P_2 \cdot 2BH_3^+$ 166 (0.5), and the principal fragments: $F_4P_2 \cdot BH_3^+$, 152 (1.3); $F_4P_2^+$, 138 (11.5); $F_3P \cdot BH_3^+$, 102 (11.4); F_3P^+, 88 (9.4); F_2P^+, 69 (100); and FP^+, 50 (25.6), with the indicated mass numbers and (relative intensities). The overall pattern was consistent with the assigned formula. Infrared absorptions were observed: 2440 (ν_{BH}) (m); 2410 (ν_{BH}) (m, br); 1095 (δ_{BH_3}) (w, br); 1035 (δ_{BH_3}) (m, br); 930 (?) (sh); 915 (ν_{PF}) (vvs); 885 (ν_{PF}) (s); 860 (impurity); 845 (impurity); 660 (?) (m); and 585 (ν_{PB}) (w). (The symbols used above are defined as follows: ν, stretch; δ, deformation.)

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation and the National Aeronautics and Space Administration who supported a traineeship at the University of Michigan for R. T. P., 1966–1969.

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CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL AND
CHEMICAL RESEARCH, WAKO-SHI, SAITAMA, JAPAN

Studies on Interactions of Isocyanides with Transition Metal Complexes. VIII.[1] Reactions of Alkyl Isocyanide with Dicarbonyl-π-cyclopentadienylalkyliron

BY YASUHIRO YAMAMOTO* AND HIROSHI YAMAZAKI

Received June 8, 1971

Recently we have reported that the treatment of *tert*-butyl and cyclohexyl isocyanides with tricarbonyl-π-cyclopentadienylmethylmolybdenum undergoes readily a carbonyl insertion, affording the corresponding acyl complexes,[2] and that the reactions of cyclohexyl isocyanide with benzyl derivatives take place by an isocyanide insertion to give the iminoacyl complexes.[3] Of particular interest is the fact that only

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