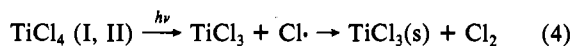**Figure 2.** Models for titanium(IV) chloride in argon matrices: A, perturbation; B, coordination; C and D, dimerization. • = Ti, O = Cl, and ○ = other ligand.

Simultaneous annealing and UV irradiation only caused all Ti–Cl bands attributed to I and II to disappear gradually in exchange for a broad feature around 300–350 cm^{-1}, probably due to the reactions

$$TiCl_4 \text{ (I, II)} \xrightarrow{h\nu} TiCl_3 + Cl\cdot \rightarrow TiCl_3(s) + Cl_2 \quad (4)$$

The formation of a lower valent titanium chloride is supported by the appearance of a brown-yellow color of the matrix. It can be concluded that species I is as stable as species II at 12–35 K and that neither interact with the strong Lewis acid trimethylaluminum.

Species II is the well-known tetrahedral $TiCl_4$ molecule with matrix bands at 524 ($\nu_1 + \nu_4$, F_2) and 503 cm^{-1} (ν_3, F_2).[5] The antisymmetric stretching, ν_3, has a low-frequency shoulder due to isotopic splitting. The same interpretation is offered for the shoulder on the 544-cm^{-1} band of I. The remaining bands of the new compound may be explained by any of the four I(A–D) models in Figure 2. They all give three IR-active $TiCl_t$ terminal stretching fundamentals as observed. Deformations and bridge stretches are expected well below 300 cm^{-1}.[6,7] Distribution of the $TiCl_t$ modes among the irreducible representations of the appropriate point groups are given in eq 5–8, where IR and R

$$\Gamma(T_d) = A_1 \text{ (R)} + F_2 \text{ (IR, R)} \quad (5)$$

$$\Gamma(C_{3v}) = 2 A_1 \text{ (IR, R)} + E \text{ (IR, R)} \quad (6)$$

$$\Gamma(D_{2h}) = 2 A_g \text{ (R)} + B_{2g} \text{ (R)} + B_{1u} \text{ (IR)} + 2 B_{3u} \text{ (IR)} \quad (7)$$

$$\Gamma(C_{2h}) = 2 A_g \text{ (R)} + B_g \text{ (R)} + A_u \text{ (IR)} + 2 B_u \text{ (IR)} \quad (8)$$

denote infrared and Raman activity, respectively. One of the frequencies, 390 cm^{-1}, is in the same position as ν_1 (A_1) of $TiCl_4$ (T_d).[5] This Raman mode is activated in the IR region by a perturbation model such as I(A) in Figure 2, e.g., caused by a weak interaction with a solvent atom. However, the considerable splitting of ν_3 (F_2), 503 → 544 + 456 cm^{-1}, can only have its origin in the formation of a normal chemical bond, as in I(B). Nevertheless, this model appears improbable because an impurity donor like N_2, O_2, or CO is required. Carbon monoxide is not found in the matrices, and N_2 or O_2 is hardly present in large enough amounts to give the observed effect. Besides, no ligand bands that may be attributed to such complex formation can be identified.[6]

The possibilities left are models I(C) and I(D), which both imply a bridged dimer with five-coordinated titanium atoms. Of these, I(D) definitely is assumed to be the more stable. Since it forms the bridges by employing one axial and one equatorial bond of each tbp $TiCl_5$ part of the dimer, the ideal Cl_b–Ti–Cl_b angle is 90° compared to 120° for I(C). Observed angles,[8,9] in other

complexes with similar Ti–Cl$_2$–Ti bridges are 80 ± 2°, and I(D) therefore requires a far less distortion of the ideal structure. In addition, similar structures have been found for the oxygen-bridged molecules $Ti_2Cl_4(OC_6H_5)_4$ and $Ti_2Cl_4(OC_2H_5)_4$.[10]

From eq 8, it is seen that the IR-active Ti_2Cl_8 terminal stretching modes belong to $A_u + 2 B_u$. The corresponding assignments are 544 (axial Ti–Cl$_t$ stretch (B_u)), 456 (antisymmetric equatorial $TiCl_t$ stretch (A_u)), and 390 cm^{-1} (symmetric equatorial Ti–Cl$_t$ stretch (B_u)), where axial and equatorial refer to the tbp $TiCl_5$ units. The highest frequency deserves special attention. On the basis of a splitting of the 503-cm^{-1} band (ν_3, F_2) of $TiCl_4$, 544 cm^{-1} does not seem unreasonable. It should be noted, however, that this is the highest frequency assigned to a Ti(IV)–Cl normal mode.[1,6–8] Therefore, it is gratifying that a strong axial Ti–Cl terminal bond is compatible with the trans influence found in octahedral Ti(IV) complexes;[8] cf. the short $TiCl_t$ distance (2.258 (2) Å) trans to bridging atoms with the other terminal bond lengths (2.296 (3) Å) in $Ti_2Cl_{10}^{2-}$.[9]

To summarize, the Ti_2Cl_8 molecule is proposed to be stable at cryogenic temperatures, although the dependency on the deposition parameters suggests that the kinetics for production of dimers is important. A very limited stability range is indicated by the failure to initiate dimerization at liquid-N_2 temperature.[11] We may continue the efforts to characterize the new complex by employing an all-vacuum, matrix-isolation FTIR system.[12]

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Mechanism of Formation of Bicyclic Phosphazenes. Isolation of a Versatile Tetrakis(amino) Intermediate, $N_4P_4Cl_4(NMe_2)_2(NHEt)_2$

Sir:

Novel bicyclic phosphazenes of types $N_4P_4(NHR)_6(NR)$ (I) and $N_4P_4(NMe_2)_5(NR)(NHR')$ (II) have been isolated in the
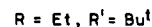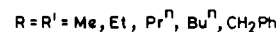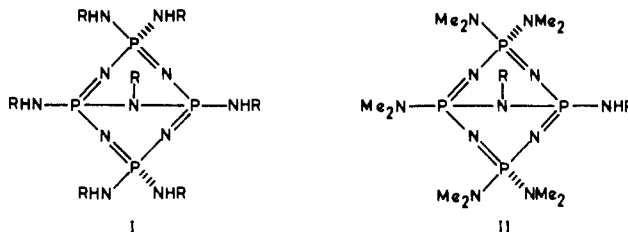
aminolysis reactions of octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) and its bis(primary amino) derivatives, $N_4P_4(NHR)_2Cl_6$ or $N_4P_4(NHR)(NHR')Cl_6$.[1–4] The effects of solvent, substitutent,

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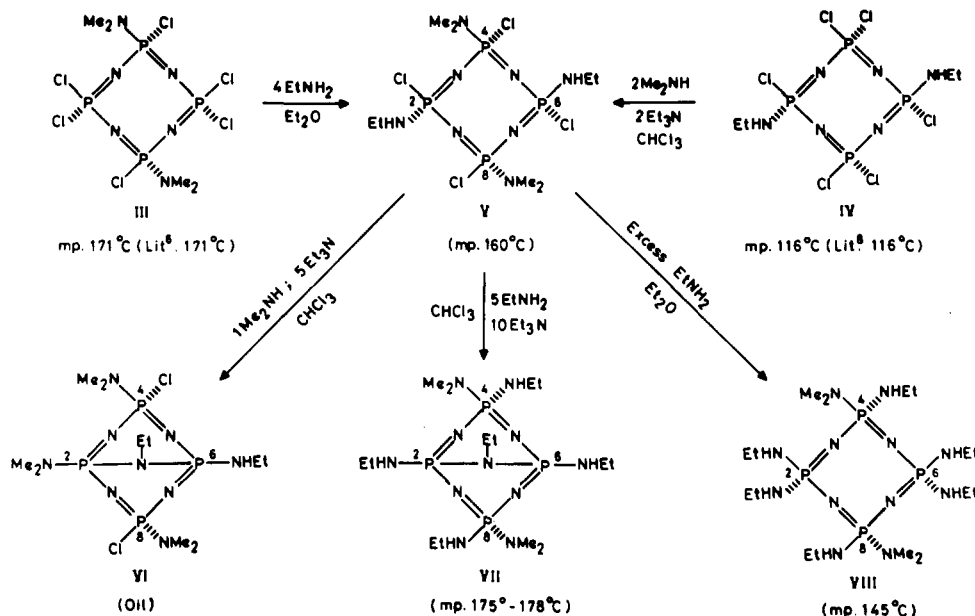
Figure 1. Synthesis and reactions of the tetrakis(amino) derivative $N_4P_4(NMe_2)_2(NHEt)_2Cl_4$.

and the attacking nucleophile on the relative yields of bicyclic phosphazenes and fully aminolyzed cyclotetraphosphazenes have been invesitgated, but the stage of chlorine replacement at which the formation of the trans annular P–N–P bridge occurs remains a matter of conjecture.[1,3] In the present study, we conclusively establish that the formation of bicyclic phosphazene occurs only after the tetrakis stage of chlorine replacement. This result has an important bearing on the mechanism of the reaction and opens up a general synthetic route for bicyclic phosphazenes containing different substituents.

The key result of the present investigation is the synthesis of the bis(dimethylamino) bis(ethylamino) tetrachloro derivative, $N_4P_4(NMe_2)_2(NHEt)_2Cl_4$ (V), by two different routes starting from 2,6-*trans*-$N_4P_4(NMe_2)_2Cl_6$ (III)[6,7] or 2,6-*trans*-N_4P_4-$(NHEt)_2Cl_6$ (IV)[8] as shown in Figure 1. The structure of compound V follows unambigously from its NMR spectral data.[9] When V is treated with 1 mol equiv of dimethylamine in the presence of triethylamine in chloroform[10] and the ^{31}P NMR spectrum[11] of the reaction mixture examined, two groups of signals in the regions δ 15–21 and 0–4 are observed, which are attributable to a bicyclic phosphazene and an (amino)cyclotetraphosphazene, respectively.[1] Thin-layer chromatography and IR spectroscopy can also be used to distinguish the two types of products.[1,12] By the extraction of the reaction mixture with petroleum ether (bp 60–80 °C), it has been possible to isolate an oil that is essentially the bicyclic derivative, $N_4P_4(NMe_2)_3(NHEt)(NEt)Cl_2$ (VI), containing traces of an (amino)chlorocyclotetraphosphazene as shown by ^{31}P NMR,[13] IR, and TLC evidence and elemental

analyses. Further treatment of this oil with 4 mol equiv of diemthylamine in diethyl ether results in the isolation of the well-known bicyclic compound $N_4P_4(NMe_2)_5(NHEt)(NEt)^{2,15}$ in 80% yield.[16] In the same way, when V is treated with 1 mol equiv of ethylamine, morpholine, or isopropylamine in the presence of triethylamine in chloroform, a bicyclic phosphazene-,$N_4P_4Cl_2(NMe_2)_2(NHEt)(NEt)(R)$ (R = NHEt, NC_4H_8O, NH-*i*-Pr), is formed in good yield (60–80%) in addition to an (amino)cyclotetraphosphazene derivative (40–20%) as determined from the ^{31}P NMR spectra of the reaction mixtures.[1,3]

The utility of the tetrakis(amino) derivative V as a versatile intermediate for the synthesis of bicyclic phosphazenes is further illustrated by the isolation of a new crystalline bicyclic compound, $N_4P_4(NMe_2)_2(NHEt)_4(NEt)$ (VII) (65% yield), from the reaction of V with 5 mol equiv of ethylamine in the presence of a twofold excess of triethylamine in chloroform. The fully aminolyzed cyclotetraphosphazene derivative, $N_4P_4(NMe_2)_2(NHEt)_6$ (VIII), is also formed in this reaction (^{31}P NMR evidence).[17] Compound VIII can be isolated in 70% yield by the treatment of compound V with an excess of ethylamine in diethyl ether (Figure 1).

The above results show that the formation of bicyclic phosphazene in the aminolysis reactions of chloro(amino)cyclotetraphosphazenes occurs only after the replacement of a chlorine at all four PCl_2 centers to yield a nongeminal tetrakis(amino) derivative.[18] The treatment of the tetrachloro derivative V with an excess of triethylamine (without the addition of dimethylamine) in boiling chloroform results in the quantitative recovery of the

(4) Trans annular bridged cyclotetraphosphazene derivatives have been obtained recently by an organometallic route.[5]

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(9) Satisfactory C, H, and N analyses were obtained for compound V. Infrared spectrum (cm^{-1}, Nujol mull): 1280 and 1320 (split band, vs, ν_{PN}), 570 (s, ν_{PCl}). ^{31}P NMR (proton decoupled), A_2B_2 type: δ_A 0.9 [P(NHEt)Cl], δ_B 5.6 [P(NMe$_2$)Cl, J_{PNP} = 43.8 Hz]. The nongeminal structure is further confirmed by the magnitude of $^3J_{PH}$ for N(CH$_3$)$_2$ (16.2 Hz) and N(CH_2CH$_3$) (14.3 Hz) protons.[6,8]

(10) Two molar equivalents of triethylamine hydrochloride is isolated in this reaction.

(11) The ^{31}P{^{1}H} NMR spectra were recorded at 32.2 MHz in CHCl$_3$ on a Varian FT 80A spectrometer. The chemical shifts are with reference to 85% H$_3$PO$_4$ (external); upfield shifts are negative.

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(16) The isolation of 2 mol equiv of dimethylamine hydrochloride in this step confirms the presence of two P–Cl bonds in the bicyclic derivative (VI).

(17) Compounds VII and VIII give satisfactory elemental analyses and are further characterized by ^{31}P NMR and IR spectroscopy. VII: infrared spectrum (cm^{-1}, Nujol mull) 1180 and 1220 (split band, s, ν_{PN}); ^{31}P NMR (proton decoupled) δ 18.6 (A_2B_2 spectrum approaching the A_4 limit). VIII: infrared spectrum (cm^{-1}, Nujol mull) 1290 (s, ν_{PN}); ^{31}P NMR (A_2B_2 spectrum) δ_A 3.6 [P(NHEt)$_2$], δ_B 6.2 [P(NHEt)(NMe$_2$), J_{PNP} = 37.5 Hz]. VII and VIII (relative yields 3:2) can also be obtained when III is treated directly with the required stoichiometric quantity of ethylamine in the presence of a twofold excess of triethylamine in chloroform.

(18) The formation of the bicyclic derivative, N$_4$P$_4$(NHEt)$_6$(NEt), from the reaction of N$_4$P$_4$Cl$_8$ with ethylamine[2] also presumably involves the intermediacy of a nongeminal tetrakis derivative, N$_4$P$_4$Cl$_4$(NHEt)$_4$.[8]

starting material, and the formation of a bicyclic phosphazene cannot be detected. This result suggests that the formation of the intramolecular P–N–P bridge and the replacement of the chlorine at the junction P atom(s) [P(2), P(6)] by the attacking nucleophile are synchronous. Further work to extend the scope of the synthetic strategy outlined above for the preparation of bicyclic phosphazenes containing a variety of substituents is in progress.

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Articles

Synthesis and Stereochemistry of Reactive Mono(amido phosphine) Derivatives of Zirconium(IV) and Hafnium(IV). X-ray Crystal Structures of *fac*-HfCl₃[N(SiMe₂CH₂PMe₂)₂] and *mer*-ZrCl₃[N(SiMe₂CH₂P(CHMe₂)₂)₂]

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The tetrahalides of Zr and Hf react with 1 equiv of the potentially tridentate hybrid ligand, $LiN(SiMe_2CH_2PR_2)_2$ (R = Me, *i*-Pr, *t*-Bu), to generate the corresponding mono(ligand) complexes $MCl_3[N(SiMe_2CH_2PR_2)_2]$ (M = Zr, Hf). The stereochemistries of $HfCl_3[N(SiMe_2CH_2PMe_2)_2]$ and $ZrCl_3[N(SiMe_2CH_2P(CHMe_2)_2)_2]$ are described. In the case of the hafnium derivative, two different solid-state structures are observed: (a) monoclinic, space group $P2_1/n$, $a = 9.6894$ (10) Å, $b = 16.5806$ (6) Å, $c = 13.6613$ (13) Å, $\alpha = \gamma = 90°$, $\beta = 92.214$ (4)°, $Z = 4$, $R = 0.024$, $R_w = 0.030$; (b) orthorhombic, space group $Pbcn$, $a = 13.3517$ (8) Å, $b = 20.595$ (2) Å, $c = 15.9398$ (7) Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$, $R = 0.043$, $R_w = 0.046$. In both the monoclinic and orthorhombic modifications, the ligand in $HfCl_3[N(SiMe_2CH_2PMe_2)_2]$ is bound in a tridentate facial mode that deviates from a pure octahedral geometry. The zirconium complex, $ZrCl_3[N(SiMe_2CH_2P(CHMe_2)_2)_2]$, crystallizes in an orthorhombic crystal system, space group $P2_12_12_1$, $a = 9.0512$ (5) Å, $b = 17.0325$ (11) Å, $c = 17.2332$ (6) Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $R = 0.029$, $R_w = 0.034$; this solid-state structure shows a distorted octahedral geometry, wherein the tridentate ligand is bound in a meridional fashion. In solution the ligand adopts a meridional binding mode for all the $MCl_3[N(SiMe_2CH_2PR_2)_2]$ derivatives. The origins of the solid-state and solution structures are discussed.

Introduction

The stereochemistry of the group 4 transition-metal coordination compounds that do not contain cyclopentadienyl type ligands is relatively unexplored.[2] This is no doubt due to a number of factors including the absence of a particular stereochemical preference for early-transition-metal complexes,[3] their propensity for high coordination numbers, and their high lability[4] especially with neutral ligands. One potential inroad to overcoming some of these problems is through the incorporation of a multidentate ligand both to control stereochemistry and to reduce the lability of certain donors. We have recently reported[5,6] the synthesis of a chelating ligand containing both "hard" and "soft" donors and its incorporation onto Zr(IV) and Hf(IV). We report here the synthesis of reactive mono(ligand) derivatives of the general formula $MCl_3[N(SiMe_2CH_2PR_2)_2]$ (M = Zr, Hf; R = Me, *i*-Pr, *t*-Bu) and their stereochemistries both in the solid state and in solution.

Experimental Section

General Information. All manipulations were performed under prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system or in standard Schlenk-type glassware. $ZrCl_4$ (Aldrich) and $HfCl_4$ (Alfa) were sublimed prior to use.

The secondary phosphines, $HPMe_2$,[7] $HP(i-Pr)_2$,[8] and $HP(t-Bu)_2$[9] were prepared according to literature procedures. Solvents were dried, distilled, and degassed by standard procedures. Melting points were determined on a Mel-Temp apparatus in sealed capillaries under nitrogen and are uncorrected. Carbon, hydrogen, nitrogen, and halogen analyses were performed by P. Borda of this department. ^1H NMR spectra were performed on one of the following instruments, depending on the complexity of the particular spectrum: Varian EM-360L, Bruker WP-80, Varian XL-100, Bruker WH-400. $^{31}P\{^1H\}$ NMR spectra were run at 32.442 MHz on the WP-80 or at 40.5 MHz on the XL-100; all ^{31}P chemical shifts are referenced to external $P(OMe)_3$ set at +141.0 ppm relative to 85% H_3PO_4. Solution $^{13}C\{^1H\}$ NMR spectra were run at 20.11 MHz on the WP-80. Infrared spectra were run on a Nicolet 5D-X instrument. Deuterated benzene (C_6D_6) and deuterated toluene (C_7D_8) were obtained from Aldrich, dried over activated 4-Å molecular sieves, and vacuum transferred prior to use. Deuterated methylene chloride (CD_2Cl_2) was dried by refluxing over CaH_2 for a few days and vacuum transferred before use.

LiN(SiMe₂CH₂PMe₂)₂. Dimethylphosphine (10 g, 0.161 mol) was vacuum transferred to a cooled (−80 °C) flask containing a solution of *n*-butyllithium (120 mL, 1.6 M in hexanes, 0.192 mol) in hexanes (100 mL). The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The resulting white precipitate was filtered off under nitrogen, washed with plenty of hexanes to remove the excess *n*-BuLi, and dried under vacuum. All of the lithium dimethylphosphide was dissolved in tetrahydrofuran (THF) (100 mL) and the resultant mixture cooled to −4 °C, whereupon neat 1,3-bis(chloromethyl)tetramethyldisilazane, $HN(SiMe_2CH_2Cl)_2$[10] (11.7 g, 0.053 mol), was added dropwise with

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