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Transformations between Monomeric, Dimeric, and Trimeric Phosphazanes: Oligomerizing NP Analogues of Olefins

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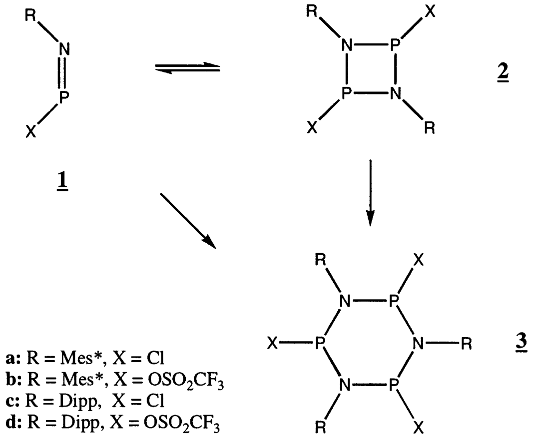
Although a variety of inorganic polymers are now well established,[1] polymerization of inorganic analogues of olefins has not been developed due to the limited availability of appropriate monomers. Ethene monomer is kinetically stable with respect to the thermodynamically favored cyclobutane dimer, oligomer, or polymer. In contrast, isolation of compounds containing π-bonds involving the heavier p-block elements requires the presence of bulky substituents,[2−6] which modify[5] both the kinetic and thermodynamic factors that are responsible for the relative stability of the π-bonded monomer. For example, Mes*NPCl (Mes* = 2,4,6-tri-*tert*-butylphenyl) is observed as an iminophosphine monomer (**1a**)[7] in the solid state, while the slightly smaller substituent at nitrogen (Dipp = 2,6-diisopropylphenyl) in DippNPCl allows for the more familiar phosphetidine dimeric arrangement (**2c**).[9] Appropriate selection of substituents provides for an energetic balance to enable facile transformations between monomer, dimer, and oligomers. We now present evidence for an iminophosphine/phosphetidine, monomer/dimer equilibrium (**1b**[8]/**2b**) and report a Lewis acid-induced oligomerization reaction to give **3c·GaCl₃** from **2c**.



Isolation procedures previously described for **1b** involve low temperature (−30 °C) and Schlenk conditions.[8] We have now discovered that slow evaporation of hexane solutions over a period of days under vacuum at room temperature gives a mixture of crystals with distinctly different morphologies, that can be manually separated. Monomer **1b**[8] and dimer **2b**[10] have been spectroscopically and crystallographically characterized. While isotropic chemical shifts (**1b** δ_{iso} 49 ppm; **2b** δ_{iso} 250 ppm) observed in the solid-state ^{31}P CPMAS NMR spectra are distinct, both crystals dissolve to give ^{31}P NMR δ 50 ppm, implying quantitative dissociation of the dimer in solution. On heating, crystals of **2b** first become orange and then melt at the same temperature as those of **1b**. The cooled melt exhibits all of the IR characteristics for **1b**, indicating dissociation of **2b** in the melt.

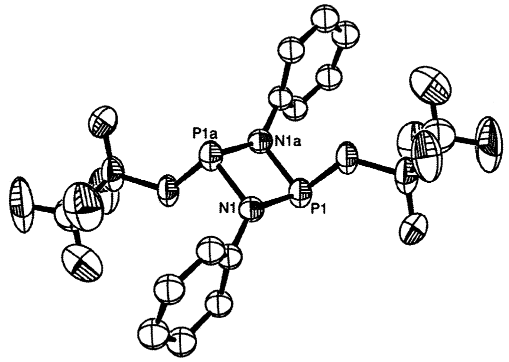


Figure 1. Molecular structure of **2b** in the solid state. Hydrogen atoms and *tert*-butyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−N1 = 1.705(7); N1−P1a = 1.721(7); P1a−N1a = 1.705(7); N1a−P1 = 1.721(7); P1−N1−P1a = 97.3(3); N1−P1−N1a = 82.7(3); P1a−N1a−P1 = 97.3(3); N1a−P1a−N1 = 82.7(3).

The solid-state structure of **2b** (Figure 1) is analogous to that of DippNPOSO$_2$CF$_3$ **2d**,[11] which has a nearly square PNPN core containing crystallographically indistinguishable N−P bonds [1.695(6), 1.707(6) Å] that are typical of 2,4-diphosph-1,3-azanes[12,13] and dramatically longer than the formal N−P multiple bond in the monomer **1b** [1.477(5) Å].[8] Consistently, the intense N−P stretches[14] at 1464 cm^{-1} in the IR and 1475 cm^{-1} in the Raman spectra of **1b** are absent in the spectra of **2b**.

In contrast to **2b**, **2c** (^{31}P CP-MAS δ_{iso} 211 ppm) is resilient in solution (CH$_2$Cl$_2$, ^{31}P δ 211 ppm) and in the melt but **2c** reacts rapidly with GaCl$_3$ to give an intense orange solution from which **3c·GaCl₃** has been isolated[15] and crystallographically characterized (Figure 2). NMR spectra of solutions containing **3c·GaCl₃** do not show distinctive peaks, even at low temperature, implicating a dynamic system. The solid-state structure of **3c·GaCl₃** is best described as a heterocyclic trimer of **1c** associated with gallium chloride. The incipient heterolytic dissociation of one chloride is evident in the P−Cl distances [*cis* configured chlorine centers, 2.0806(9), 2.0879(9) Å, cf. PCl$_3$, 2.038(6) Å,[16] *trans* configured P(3)−Cl(3) 2.704(1) Å]. In this context, the molecule is a hybrid of phosphazane (P1 and P2) and "phosphenium" (P3) fragments, which is evidenced by the slightly shorter N−P3 bonds (Figure 2). Reaction of **3c·GaCl₃** with triphenylphosphine or 4-(dimethylamino)pyridine effects release of **3c**, which is characterized in solution

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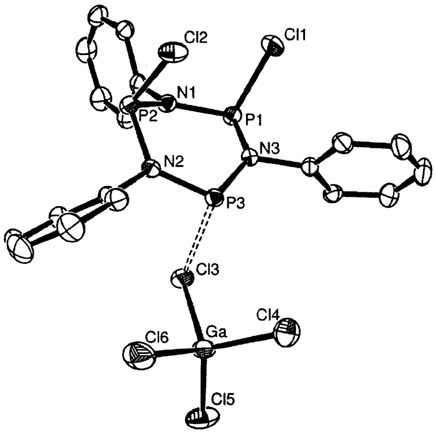

Figure 2. Molecular structure of **3c·GaCl₃** in the solid state. Hydrogen atoms and isopropyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−N1 = 1.697(2); P1−N3 = 1.753(2); P2−N1 = 1.703(2); P2−N2 = 1.736(2); P3−N2 = 1.656(2); P3−N3 1.650(2); P1−Cl1 = 2.0806(9); P2−Cl2 = 2.0879(9); P3−Cl3 = 2.704(1); Ga−Cl3 = 2.2492(7); Ga−Cl4 = 2.1556(8); Ga−Cl5 = 2.1493(8); Ga−Cl6 = 2.1497(9); N1−P1−N3 = 99.40(9); P1−N1−P2 = 131.8(1); N1−P2−N2 = 100.8(1); P2−N2−P31 = 129.5(1); N2−P3−N3 = 105.1(1); P1−N3−P3 = 134.5(1).

by ^{31}P NMR spectroscopy (110, 116 ppm; relative intensity 1:2) as a *cis*−*trans* heterocycle.

Formation of **3c·GaCl$_3$** contrasts the spectroscopic identification of the phosphazanium aluminate formed in the reaction of **2** (R = ^{t}Bu or NMe$_2$) with AlCl$_3$,[17] and represents a formal insertion of iminophosphine **1c** into phosphazane **2c**. In the context of the delicate energetic balance between sterically loaded derivatives of NP monomer and dimer (**1**/**2**), GaCl$_3$-assisted dissociation of the dimer **2c** is facilitated by the intermediate steric bulk of the Dipp substituent. Although rare examples of trimeric[18−21] and tetrameric[22,23] phosphazanes have been reported, the chemistry of [RNPX]$_n$ compounds is dominated by the observation of four-membered "phosphetidine" rings. The ring expansion demonstrated here represents a new synthetic approach to the higher oligomers and is a potentially versatile polymerization process.

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Supporting Information Available: Crystallographic data for structures **2b**, **2d** and **3c·GaCl$_3$** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) **1b**/**2b**: Mes*NPCl (2.4 mmol) and AgOSO$_2$CF$_3$ (2.5 mmol) in hexane for 4 days (30 mL), solution was filtered, and slow removal of the solvent gave a mixture of two types of crystals, total yield 82%; Anal. Calcd (Found) C, 51.93 (51.20); H, 6.65 (7.09); N, 3.19 (3.09); two types of crystal (monomer **1b** and dimer **2b**:**1b**, orange; mp 124-126 °C; FT-IR: 1599(9), 1464(1), 1398(15), 1366(3), 1296(sh), 1266(14), 1235(7), 1196-(6), 1184(5), 1150(4), 1134(11), 914(2), 886(10), 629(8), 585(12), 532-(13); FT-Raman: 2971(2), 2911(3), 1598(4), 1475(1), 1368(12), 1292(13), 1266(14), 1203(8), 1134(5), 1070(6), 926(15), 823(7), 781(11), 764(10), 571(16), 103(9); **2b**, yellow; d.p. 113 °C (resulting orange solid mp 124-126 °C and IR data consistent with that of **1b**); FT-IR: 1598(14), 1462-(2), 1408(3), 1363(6), 1241(7), 1208(1), 1142(5), 1101(8), 1027(15), 916(13), 884(9), 827(4), 755(11), 638(12), 602(10); FT-Raman: 3016-(17), 2973(1), 2914(2), 1598(4), 1468(13), 1447(12), 1230(8), 1206(9), 1152(10), 1029(11), 925(16), 824(3), 767(15), 568(7), 139(5), 117(6), 83-(14); ^{31}P CP-MAS NMR of crystal mixture: 49, 250; Solution NMR of crystal mixture redissolved in CD$_2$Cl$_2$: ^{31}P 50;. Crystal data for **2b** C$_{38}$H$_{58}$F$_6$N$_2$-O$_6$P$_2$S$_2$, MW = 878.92 g mol^{-1}, monoclinic $P2_1/n$, $a = 11.368(2)$ Å, $b = 16.429$ Å, $c = 12.013(2)$ Å, $\beta = 90.59(3)°$, $V = 2243.5(7)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo Kα) = 2.346 mm^{-1}, 3857 measured reflections, 3323 unique, 254 refined parameters, $R[I > 2\sigma(I)] = 0.0579$, wR = 0.1596.
(11) **2d**: [DippNPCl]$_2$ (0.75 mmol) and AgOTf (1.57 mmol) in hexane (30 mL), solution was filtered, and slow removal of the solvent gave a mixture of two types of crystals, total yield 68%; mp 127−130 °C, mp 182−184 °C; Anal. Calcd (Found): C, 43.94 (44.10), H, 4.82 (4.87), N, 3.94 (4.39)%; FT-IR: 1444 (*9*), 1406(*3*), 1386 (*12*), 1367 (*13*), 1317 (*17*), 1239 (*5*), 1213 (*1*), 1186 (*7*), 1139 (*6*), 1104 (*18*), 925 (*14*), 871 (*10*), 836 (*2*), 801 (*4*), 766 (*11*), 665 (*16*), 634 (*19*), 603 (*8*), 427 (*20*), 382 (*15*); NMR (CD$_2$Cl$_2$) ^{31}P 175 (75%, assigned as monomer), 274 (25% assigned as dimer **2d**); Crystal data for **2d** C$_{26}$H$_{34}$F$_6$N$_2$O$_6$P$_2$S$_2$, MW = 710.62 g mol^{-1}, monoclinic $P2_1/c$, $a = 10.772(2)$ Å, $b = 29.335(3)$ Å, $c = 11.170(2)$ Å, $\beta = 160.53(1)°$, $V = 3384.0(9)$ Å^3, $T = 296(1)$ K, $Z = 4$, μ(Mo Kα) = 2.982 mm^{-1}, 5948 measured reflections, 5625 unique, 397 refined parameters, $R[I > 2\sigma(I)] = 0.048$, wR = 0.05.
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(15) **3c·GaCl$_3$**: GaCl$_3$ (1.72 mmol) and **2b** (2.59 mmol) in CH$_2$Cl$_2$ (30 mL) overnight, solvent removed in vacuo (static) recrystallized from minimal CH$_2$Cl$_2$ at 4 °C, yield 27%; Anal. Calcd (Found) C, 45.07 (44.77); H, 5.42 (5.36); N, 4.20 (4.41); mp 136-139 °C; FT-IR: 3061(29), 1436(6), 1384 (8), 1364(9), 1349 (24), 1316(25), 1264(28), 1180(26), 1152 (10), 1095(7), 1056(23), 1041(14), 1006 (13), 977 (1), 970(3), 962 (2), 932-(19), 888(30), 856(18), 849(17), 803(4), 801(5), 712(21), 488(11), 472-(16), 466(20), 427(15), 401(12), 363(27), 343(22); FT-Raman: 3069 (13), 2964(3), 2909(1), 2868(2), 2765(14), 1588(9), 1463(12), 1442(17), 1280-(15), 1240(8), 1164(16), 1103(11), 1044(18), 436(10), 361(7), 287(6), 202-(5), 138(4); Crystal data for C$_{36}$H$_{51}$N$_3$P$_3$Cl$_6$Ga, MW = 901.30 g mol^{-1}, triclinic, P-1; $a = 10.4687(8)$ Å, $b = 13.9849(10)$ Å, $c = 16.4674(12)$ Å, $\alpha = 87.2367(12)°$, $\beta = 81.3528(12)°$, $\gamma = 78.8655(12)°$, $V = 2338.2(3)$ Å^3, $T = 293(1)$ K, $Z = 2$, μ(Mo Kα) = 1.178 mm^{-1}, 11817 measured reflections, 9403 unique, 469 refined parameters, $R[I > 2\sigma(I)] = 0.0375$, wR = 0.0981.
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