Cis/Trans Isomerization and Conformational Properties of 2,4-Bis(primary amino)-1,3,2,4-Diazadiphosphetidines

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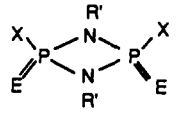
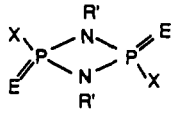
The new 1,3,2,4-diazadiphosphetidines *cis*- and *trans*-[(MeNH)PNMe]$_2$ (**8**, **9**), *cis*- and *trans*-[(EtNH)PNEt]$_2$ (**10**, **11**), *cis*- and *trans*-[(*i*-PrNH)PN-*i*-Pr]$_2$ (**13**, **14**), [(MeNH)P(S)NMe]$_2$ (**16**), *trans*-[(EtNH)P(S)NEt]$_2$ (**17**), [(*i*-PrNH)P(S)N-*i*-Pr]$_2$ (**19**), *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]$_2$ (**20**), and the cage compounds $P_4(NEt)_6$ (**12**) and $P_4S_4(NEt)_6$ (**18**) have been prepared and characterized. Structures of **17** and **20** have been determined by X-ray single-crystal analysis: **17**, orthorhombic, *Pbcn*, a = 12.558(2) Å, b = 8.889(1) Å, c = 14.432(2) Å, V = 1611.1(4) Å^3, Z = 4, R = 0.039, R_w = 0.052; **20**, monoclinic, $P2_1/n$, a = 10.728(2) Å, b = 15.503(3) Å, c = 14.652(2) Å, β = 103.7°, V = 2367(7) Å^3, Z = 4, R = 0.049, R_w = 0.078. Equilibration of *cis/trans* mixtures give equilibrium constants ($K_{cis/trans}$) for **8/9**, **10/11**, and **13/14** of 3, 8, and 15, respectively. Conformational structural properies of the P(III) and P(V) 1,3,2,4-diazadiphosphetidines **8–11**, **13**, **14**, **16**, **17**, **19**, and **20**, along with *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (**5**), *cis*-[(PhNH)PNPh]$_2$ (**4**), *cis*-(*t*-BuNH)P(N-*t*-Bu)$_2$PCl (**15**), and *trans*-[(PhNH)P(S)NPh]$_2$ (**7**), have been examined in variable-temperature ^{31}P and ^{1}H NMR studies. *Trans* isomers are temperature independent to −90 °C; however, the *cis* isomers **8**, **10**, **13**, **15**, and **20** undergo restricted *exo*-N(H)R group rotation. Rotational barriers are in the 9.5–12.9 kcal/mol range. Correlation of $^2J_{PNH}$ coupling constants of P–N(H)R groups with previously measured ^2J data and X-ray structural data, along with X-ray data obtained in this study for **17** and **20**, allow specific conclusions to be made as to the lowest energy conformation(s).

Introduction

Three- and four-coordinate 1,3,2,4-diazadiphosphetidines[2] (**1**, **2**; R′ = alkyl, aryl; X = alkoxy, halo, NRR″; E = lone pair, O, S, Se) offer potential for incorporation into phosphazane oligo-

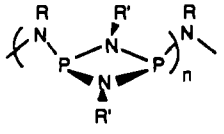


1 (cis)

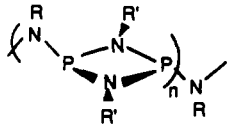


2 (trans)

mers/polymers (**3**)[3–6] because they can be made with a variety of substituents[5,7–22] and they are often the most stable members of a [XPN(R/R′)]$_n$ cyclooligomer series.[4–6,8,23–25] In connection



3A (cis)



3B (trans)

with their use in oligomers/polymers, it is of interest to understand in detail their reactivity and structural properties. Structural features of 2,4-diamino-substituted diazadiphosphetidines (**1**, **2**; X = NRR″) are important to the problem of diazadiphosphetidine incorporation into oligomeric/polymeric phosphazanes because (i) these features can be related to their properties as synthetic precursors and (ii) they offer insight into what to expect of extended molecules which contain them. It is recognized that diazadiphosphetidines can exist in *cis* and *trans* forms,[7–10,17,25–31] that the P_2N_2 *trans* rings are planar but depending upon

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substitutents the *cis* rings can be planar or bent,[5,6,9b,17,19,26,32,33] and that *exo*-NRR″ moieties (X = *exo* group) can show restricted rotation around the P–N bonds.[8,9,17,32–35] Although the conditions which favor *cis* or *trans* isomer formation[10,21,22,25,27,34–37] and which lead to restricted rotation[8,9,28,30,35,36] have been discussed, studies have centered on molecules which are *exo* substituted with bulky secondary amino, $-NR_2$ (R = alkyl or aryl), groups. Unfortunately, little structural chemistry is known about (primary amino)-substituted diazadiphosphetidines, **1** or **2** where X = N(H)R, systems of interest in oligomer/polymer synthesis because they contain functional N–H bonds and they are less sterically bulky. Further, P(III) diazadiphosphetidines which contain the small Me and Et in N(ring) positions, e.g. **1** or **2** (E = lone pair) where R′ = Me or Et, have not been prepared previously. Thus, in order to obtain new *exo*-N(H)R- and *N(ring)*-R′-substituted diazadiphosphetidines and to establish the conformational and isomerization properties of these systems, we conducted the study below.

Experimental Section

Apparatus and Materials. All operations were carried out in N_2-flushed glovebags and standard vacuum-line equipment.[38] Infrared and mass spectra were obtained using Beckman IR4250 and Varian MAT CH-5 spectrometers. Elemental analyses were performed by Huffman Analytical Laboratories, Golden, CO. X-ray crystallographic data were collected at room temperature using a Syntex P1 automated diffractometer (Mo Kα or Cu Kα radiation, graphite monochromator). ^{1}H NMR spectra were recorded at 89.6, 250.1, and 300 MHz using JEOL FX-90Q, Bruker WM-250 FT, and Varian 300VXR spectrometers, respectively. ^{31}P NMR spectra were obtained on JEOL FX-90Q (36.3 MHz), Bruker WM-250FT (101.2 MHz), and Varian 300 VXR (121.2 MHz) spectrometers. ^{1}H and ^{31}P NMR chemical shifts (+δ = downfield) were measured relative to internal Me_4Si and external 85% H_3PO_4, respectively. In cases where ^{31}P NMR relative spectral areas were important, the areas measured in decoupled [^{31}P{^{1}H}] spectra were compared to those in undecoupled [^{31}P] spectra and the instrumentation data collection conditions were varied over a wide range. In all cases, area agreement was within ±5%. Variable-temperature experiments were carried out in toluene/benzene-d_6 (10%) or toluene-d_8 unless otherwise stated. Temperature calibrations were accomplished using a Fluke thermocouple gauge and a standard methanol sample with a calibration error of ±0.5 °C. Simulated spectra were calculated on an Aspect 2000/A computer using the PANIC program, version 810515.1.

(ClPNPh)$_2$,[18] *cis*-[(PhNH)PNPh]$_2$ (**4**),[5] *cis*-(*t*-BuNH)P(N-*t*-Bu)$_2$PCl (**15**),[10] *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (**5**),[14] *trans*-[(*i*-PrNH)PNPh]$_2$ (**6**),[25] and *trans*-[(PhNH)P(S)NPh]$_2$ (**7**)[39] were prepared as described previously. PCl_3 (Aldrich) was distilled before use. *i*-$PrNH_2$ (Aldrich) and *t*-$BuNH_2$ (Aldrich) were distilled from CaH_2. Toluene and petroleum ether (Fisher Scientific) were distilled from Na/Pb alloy or Na/benzophenone. $EtNH_2$ and $MeNH_2$ (Matheson, anhyd) were passed through a BaO-packed column immediately prior to use. S_8, decane, benzene-d_6, and toluene-d_8 (Aldrich) were used as obtained.

Reactions of PCl_3. (A) With $MeNH_2$ To Form *cis*-[(MeNH)PNMe]$_2$ (8) and *trans*-[(MeNH)PNMe]$_2$ (9). PCl_3 (27.5 g, 0.20 mol) was added dropwise to a solution of $MeNH_2$ (72.4 g, 1.61 mol) in petroleum ether (400 mL) at −78 °C. After the mixture warmed to 25 °C during 8 h, the ^{31}P{^{1}H} NMR spectrum showed mainly resonances at δ 117.6, 190.0, and 81.9 due to **8**, **9**, and $P_4(NMe)_6$,[40,41] respectively (3:1:6, m/m) and minor unassigned peaks (<15% spectral area) between δ 80 and δ 120. After filtration of $MeNH_3Cl$, evaporation of solvent, and cooling, an **8**:**9** (3:1, m/m) mixture crystallized. **8** and **9** could not be separated by fractional crytallization or chromatography; therefore, characterization data were obtained on the mixture. ^{31}P{^{1}H} NMR (toluene-d_8): δ 117.6 (s, **8**), 190.0 (s, **9**). ^{1}H NMR (C_6D_6): δ 2.50–2.90 (comp m, area 12; CH_3), 2.40 (br s, area 2; NH). MS (EI$^+$): M$^+$ *m/e* (rel int) 180 (100). Because the **8**/**9** mixture is thermally and oxidatively unstable, satisfactory elemental analytical data were not obtained.

Under the above reaction conditions, but at 10 times higher dilution in petroleum ether, the reaction produced **8** and **9** and only traces of $P_4(NMe)_6$, along with larger quantities of uncharacterized spurious peaks between δ 80 and δ 116. In the absence of solvent, $P_4(NMe)_6$ was the sole product.

Thermolysis of **8**/**9** at 100 °C resulted in evolution of $MeNH_2$ and the formation of $P_4(NMe)_6$. The **8**:**9** ratio (3:1) remained constant.

At a lower reactant ratio (5:1), the $MeNH_2/PCl_3$ reaction yielded a complex ^{31}P NMR spectrum exhibiting resonances between δ 80 and δ 220. Minor resonances due to $(ClPNMe)_3$ (δ 101.8, 127.1, 131.8)[23b,24] (<10% spectral area) were evident.

(B) With $EtNH_2$To Form *cis*-[(EtNH)PNEt]$_2$ (10), *trans*-[(EtNH)-PNEt]$_2$ (11), and $P_4(NEt)_6$ (12). PCl_3 (20.6 g, 0.15 mol) was added dropwise to $EtNH_2$ (53.1 g, 1.18 mol) in petroleum ether at −78 °C. After the mixture warmed slowly to 25 °C, the ^{31}P{^{1}H} NMR spectrum exhibited resonances at δ 105.0 and 177.7 due to **10** and **11**, respectively (**10**:**11** = 8:1 m/m), and smaller approximately equal-area peaks at δ 95.2 and 89.0. After thermolysis at 75 °C for 6 h, the **10**:**11** ratio remained at 8:1. Upon filtration of $EtNH_3Cl$ and removal of solvent in vacuo, a **10**/**11** solid crystallized; after redissolution it was found to be a **10**:**11** (8:1) mixture. Rapid isomer equilibration in solution prevented separation of **10** and **11**. **10**/**11**: ^{31}P{^{1}H} NMR (toluene-d_8) 107.0 (s, **10**), 178.3 (s, **11**); ^{1}H NMR (C_6D_6) δ 0.80–1.35 (comp m, area 12; CH_3), 3.0 (comp m, area 8; CH_2), 3.65 (br m, area 2; NH); MS (EI$^+$), M$^+$ *m/e* (rel. int.) 236 (10). Weak peaks due to **12** were also seen. Anal. Calcd for $C_8H_{22}N_4P_2$: C, 40.67; H, 9.39; N, 23.70. Found: C, 41.05; H, 10.10; N, 23.10.

In the absence of solvent, the $PCl_3/EtNH_2$ reaction yielded a **10**/**11**/**12** mixture (typically 8:1:20, m/m). Thermolysis at 90 °C for 10 h yielded only **12**; removal of solvent in vacuo left **12** as an oil. ^{31}P{^{1}H} NMR (toluene-d_8): δ 78.8. ^{1}H NMR (C_6D_6): δ 0.85–1.45 (br t, area 18; CH_3), 2.65–3.57 (comp m, area 12; CH_2). MS (EI$^+$): M$^+$ *m/e* (rel int) 382 (100). Anal. Calcd for $C_{12}H_{30}N_6P_4$: C, 37.69; H, 7.91; N, 21.97. Found: C, 36.85; H, 7.75; N, 21.40.

At a lower reactant ratio (5:1), the $EtNH_2/PCl_3$ reaction yielded mainly (>85%) a resonance at δ 228.5, tentatively attributed to $(ClPNEt)_2$, and resonances due to $(Cl_2P)_2NEt$ (δ 164.0)[31] and $(ClPNEt)_3$ (δ 104.0, 128.9, 135.3)[24] in a 1:7:4 mole ratio.

(C) With *i*-$PrNH_2$To Form *cis*-[(*i*-PrNH)PN-*i*-Pr]$_2$ (13) and *trans*-[(*i*-PrNH)PN-*i*-Pr]$_2$ (14). *i*-$PrNH_2$ (100.3 g, 1.7 mol) was added dropwise to PCl_3 (30.3 g, 0.22 mol) in petroleum ether at −78 °C. After the mixture warmed to 25 °C during 10 h, the ^{31}P{^{1}H} NMR spectrum showed resonances at δ 95.4, 169.3, and 84.0 due to **13**, **14**, and P_4(*i*-PrN)$_6$[42] (**13**:**14**:P_4(*i*-PrN)$_6$ = 2:2:1, m/m). An unidentified resonance at δ 90.2 was also present. Filtration of *i*-$PrNH_3Cl$ and removal of solvent in vacuo yielded crystalline **14**. ^{31}P{^{1}H} NMR (toluene-d_8): δ 167.2 (s). ^{1}H NMR (C_6D_6): δ 1.27 (d, area 12; CH_3), 1.40 (d, area 12; CH_3), 2.50 (br s, area 2; NH), 3.25–4.10 (comp m, area 4; CH). MS (EI$^+$): M$^+$ *m/e* 292. Anal. Calcd for $C_{12}H_{30}N_4P_2$: C, 49.30; H, 10.34; N, 19.17. Found: C, 48.80; H, 11.20; N, 18.80.

Thermolysis of **14** in toluene at 80 °C for 3–5 h produced **13**/**14** equilibrium mixtures ((14–17):1.0, m/m). Repeated crystallization yielded **13** contaminated with **14** (ca. 5%). **13**: ^{31}P{^{1}H} NMR (C_6H_6) δ 95.4 (s); ^{1}H NMR (C_6D_6) δ 1.25 (d, area 12; CH_3), 1.50 (d, area 12; CH_3), 2.80 (br s, area 2; NH), 3.55–4.10 (comp m, area 4; CH). MS (EI$^+$): M$^+$ *m/e* 292. Anal. Calcd for $C_{12}H_{30}N_4P_2$: C, 49.30; H, 10.34; N, 19.17. Found: C, 49.05; H, 10.05; N, 18.88. Upon further heating, the ^{31}P NMR resonance from **14** decreased, that for **13** increased, and that for P_4(*i*-PrN)$_6$[42] appeared.

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At a lower *i*-$PrNH_2$:PCl_3 reactant ratio (<5:1), the reaction yielded (ClPN-*i*-Pr)$_2$ (δ 221.7),[13] *i*-PrN$(PCl_2)_2$ (δ 169.2; assignment based on Me,[13] Et,[13] and *t*-Bu[11] analogs), and *i*-PrNHPCl_2 (δ 155.9; for *t*-BuNHPCl_2, δ = 164.0[13]) in a 35:1:1 mole ratio.

(D) With *t*-BuNH_2 To Form *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (5)[14] and *cis*-(*t*-BuNH)P(N-*t*-Bu)$_2$PCl (15). Typically, *t*-$BuNH_2$ reacts with PCl_3 (5:1, m/m) in toluene at 25 °C, yielding *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (**5**) as reported previously.[14] At lower reactant ratios, the products are 1:8:1 (ClPN-*t*-Bu)$_2$ (δ 206.7),[13] *t*-BuN$(PCl_2)_2$ (δ 169.8),[11] and *t*-BuNHPCl_2 (δ 163.9)[12,13] in a 6:1:6 mole ratio and 3:1 (ClPN-*t*-Bu)$_2$ (δ 206.7) and **15** (δ 195.2, 136.4)[10] in a 3:1 mole ratio.

Reactions of S_8. (A) With 8/9 To Form [(MeNH)P(S)NMe]$_2$ (16). Reaction of an **8/9** (3:1) mixture with excess S_8 in refluxed toluene for 6 h produced a yellow solid, which when recrystallized from toluene yielded **16**.[43] Attempts to obtain **16** completely free of S_8 failed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 58.2 (s). MS (EI): M^+ *m/e* (rel int) 244 (2).

(B) With 10/11 and 12 To Form *trans*-[(EtNH)P(S)NEt]$_2$ (17) and $P_4S_4(NEt)_6$ (18). Reaction of a **10/11** mixture or **12** with excess S_8 in toluene for 9 h at 95 °C, followed by recrystallization, yielded pure **17** (mp 174–176 °C; 60% yield) or **18**, respectively. **17**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 53.4 (s); ^1H NMR (C_6D_6) δ 0.79 (t, area 6, J = 7.5 Hz; CH_3), 1.09 (t, area 6, J = 7.5 Hz), 2.30–3.65 (m, area 10; CH_2, and NH); MS (EI^+): M^+ *m/e* (rel int) 300 (10). Anal. Calcd for $C_8H_{22}N_4P_2S_2$: C, 32.00; H, 7.39; N, 18.65. Found: C, 31.82; H, 7.62; N, 18.70. **18**: $^{31}P\{^1H\}$ NMR (C_6H_6) δ 64.8 (s); ^1H NMR (C_6D_6) δ 1.25 (t, area 18; CH_3), 3.50–4.25 (comp m, area 12; CH_2); MS (EI^+), M^+ *m/e* (rel int) 510 (1).

(C) With 13/14 To Form [(*i*-PrNH)P(S)N-*i*-Pr]$_2$ (19). Reaction of **13/14** with excess S_8 at 95 °C for 8 h in toluene, followed by recrystallization from toluene, yielded **19** (mp 144–145 °C; 45% yield). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 46.8 (s). ^1H NMR (C_6D_6): δ 0.77 (d, area 12, J = 6.8 Hz; CH_3), 1.31 (d, area 12, J = 6.8 Hz; CH_3), 2.60 (br s, area 2; NH), 3.44 (m, area 2; CH), 3.82 (m, area 2; CH). MS (EI): M^+ *m/e* (rel int) 356 (37). Anal. Calcd for $C_{12}H_{30}N_4P_2S_2$: C, 40.43; H, 8.48; N, 15.71. Found: C, 40.61; H, 8.62; N, 15.62.

(D) With 5 To Form *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]$_2$ (20). Reaction of **5** with excess S_8 for 12 h at toluene reflux, followed by recrystallization from toluene, yielded **20** (mp 165–167 °C; 90% yield). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 38.7. ^1H NMR (C_6D_6): δ 1.25 (s, area 18; CH_3), 1.70 (s, area 18; CH_3), 3.00 (br s, area 2; NH). MS (EI^+): M^+ *m/e* (rel int) 412 (21). Anal. Calcd for $C_{16}H_{38}N_4P_2S_2$: C, 46.58; H, 9.28; N, 13.57. Found: C, 46.68; H, 9.23; N, 13.60.

Variable-Temperature NMR Spectral Analysis. $^{31}P\{^1H\}$ NMR variable-temperature spectra were obtained for **4**, **6**, **7**, **13–17**, **19**, and **20** (in toluene-d_8) from 100 to –90 °C, for **8**, **9**, **10**, and **11**, as **8/9**, and **10/11** equilibrium mixtures in toluene-d_8, from +27 to –90 °C, and for **5** (in toluene-d_8 and mesitylene) from +150 to –90 °C. Spectra of **6**, **7**, **9**, **11**, **16**, **17**, and **19** showed only sharp singlets over the temperature range examined. Those of **4**, **5**, **8**, **10**, **13**, **14**, **15**, and **20** were temperature dependent. Spectral parameters measured at 25 and –90 °C for **4**, **8**, **10**, **13**, and **20** are given in Table 1. The singlet resonance of **14** broadened at low temperatures, but no interpretable spectral features were seen. The $^{31}P\{^1H\}$ spectum of **5** (toluene-d_8) consists of a narrow singlet at δ 89.4 ($\nu_{1/2}$ = 8–12 Hz) between –90 and +50 °C. Above 50 °C, line broadening occurs. $\nu_{1/2}$, Hz (°C): 48 (75), 66 (100), 102 (125), 108 (150). At –70 °C, the ^1H-coupled ^{31}P NMR spectrum consists of a single poorly resolved doublet, $^2J_{PNH} \cong 5$ Hz. The $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8) of **15** at 27 °C exhibits two equal-area coupled doublets at δ 195.2 and 136.4 (^2J = 42.9 Hz). Upon cooling, resonances broaden and collapse to broad singlets by –90 °C. Adequate spectral measurements below –90 °C were precluded by sample solution high viscosity. A reliable value for T_c was not obtained.

The ^1H NMR spectrum of **20** is temperature dependent: at 25 °C (toluene-d_8), δ 1.70 (s, area 18; CH_3), 1.25 (s, area 18; CH_3'), 3.00 (s, area 2; NH); at –90 °C, δ 1.66 (s, area 18; CH_3), 1.34 (s, area 9; CH_3'), 1.06 (s, area 9; CH_3'), 2.83 (br s, area 1; NH), 3.87 (br d, area 1, $^2J_{HNP}$ = 14.7 Hz; NH'); T_c = –50 °C.

The pseudo-first-order rate constants (k_c) for NMR site exchange were obtained using the rate constant approximation $k_c = \pi(\Delta\nu/\sqrt{2})$ at T_c, where $\Delta\nu$ is the difference in chemical shifts between the resonances (in hertz) in the absence of exchange.[44,45] The free energies of activation (ΔG^*) for the dynamic process were calculated from the relation $\Delta G^* = 2.303RT_c[10.32 + \log(T_c/k_c)]$ (Table 1). The ΔG^* values are taken to be accurate within 0.5 ± kJ/mol.

Table 1. Variable-Temperature ^{31}P NMR Data for *cis*-[(RNH)P(E)NR']$_2$ Diazadiphosphetidines[a]

compd	R	R'	E	δ (mult) 27 °C	δ (mult) –90 °C	T_c, °C	ΔG^*, kcal/mol
8	Me	Me	LP[b]	117.0 (s)	conf a:[c] 122.5 (br s), 106.7 (br s); conf b:[c] 105.3 (br s)	–50	9.5
10	Et	Et	LP	107.0 (s)	conf a:[d] 110.5 (br s), 95.3 (br s); conf b:[d] 93.5 (br s)	–51	9.5
13	*i*-Pr	*i*-Pr	LP	95.4 (s)	conf a:[e] 96.0 (s), 83.3 (d); $^2J_{PNH}$ = 39.8 Hz; conf b:[e] 80.4 (d); $^2J_{PNH}$ = 38.6 Hz	–30	10.4
4	Ph	Ph	LP	104.9 (s)	105.9 (d), 104.7(d of d); $^2J_{PP}$ = 9.1 Hz, $^2J_{PNH}$ = 38.4 Hz	0	12.9
20	*t*-Bu	*t*-Bu	S	38.6 (s)	38.1 (d), 36.2 (d of d); $^2J_{PP}$ = 37.1 Hz, $^2J_{PNH}$ = 14.2 Hz	–51	10.2

[a] Data from ^1H-coupled ^{31}P NMR spectrum unless specified otherwise. [b] LP = lone electron pair. [c] **8a:8b** = 2:1. [d] **10a:10b** = 2:1. [e] **13a:13b** = 1:1.

Table 2. Crystallographic Data for *trans*-[(EtNH)P(S)NEt]$_2$ (**17**) and *cis*-[(*t*-BuN)P(S)N*t*-Bu]$_2$ (**20**)

	17	**20**
formula	$C_8H_{22}N_4P_2S_2$	$C_{16}H_{38}N_4P_2S_2$
fw	300.37	412.58
space group	*Pbcn*	$P2_1/n$
a, Å[a]	12.558(2)	10.728(2)
b, Å	8.889(1)	15.503(3)
c, Å	14.432(2)	14.652(2)
α, deg	90.0	90.0
β, deg	90.0	103.7(1)
γ, deg	90.0	90.0
V, Å^3	1611.1(4)	2367.5(7)
d_{calc}, g cm^{-3}	1.24	1.15
Z	4	4
μ, cm^{-1}	4.98	33.5
λ, Å	Mo Kα: 0.71069	Cu Kα: 1.5418
T, K	174–176	165–167
R^b	0.039	0.049
R_w	0.052	0.078

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Based on observed data.

X-ray Structure Analyses. (A) *trans*-[(EtNH)P(S)NEt]$_2$ (17). An X-ray-quality crystal, obtained from toluene, was mounted on a glass fiber and coated with epoxy resin. Crystal data and details of the data collection and structure refinement are summarized in Table 2. Cell parameters were determined on the diffractometer and refined by a least-squares fit to 40 centered reflections in the range 28.5° ≤ 2θ ≤ 37.3°. The structure was solved by direct methods. The molecule was refined anisotropically, except for the hydrogen atoms, which were included in idealized positions. Amine hydrogens refined into positions corresponding to sp^2 hybridization and therefore were included in idealized positions. Final positional parameters for **17** are given in Table 3. Thermal parameters are included in the supplementary material.

(B) *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (20). An X-ray-quality crystal obtained from decane was mounted on a glass fiber. Crystal data and details of the data collection and structure refinement are summarized in Table 2. Cell parameters were determined on the diffractometer and refined by a least-squares fit to 24 centered reflections in the range 72.4° ≤ 2θ ≤ 102.6°. The structure was solved by direct methods. The molecule was refined anisotropically, except for the hydrogen atoms. Hydrogen atoms were included in idealized positions and, with the exception of the amine hydrogens, were refined riding on the atom to which they were attached

(43) Becke-Goehring, V. M.; Leichner, J.; Scharf, B. *Z. Anorg. Allg. Chem.* **1966**, *343*, 154.
(44) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.
(45) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

Table 3. Atomic Coordinates[a] (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for *trans*-[(EtNH)P(S)NEt]₂ (**17**)

	x/a	y/b	z/c	U_{eq}[b]
S(1)	1037(1)	2003(2)	1315(1)	71(1)
P(1)	3(1)	672(1)	764(1)	51(1)
N(1)	−413(3)	970(3)	−321(2)	51(1)
N(2)	−1011(3)	460(5)	1450(3)	71(1)*
C(1)	−1206(4)	2056(6)	−671(4)	86(2)*
C(2A)#	−781(31)	3259(40)	−1238(29)	151(12)*
C(2B)#	−638(29)	3476(22)	−947(26)	135(11)*
C(3A)#	−1847(12)	−672(15)	1345(9)	95(5)*
C(3B)#	−1961(33)	−476(69)	962(28)	181(23)*
C(4A)#	−2949(14)	−185(24)	1456(15)	103(7)*
C(4B)#	−2742(19)	−371(31)	1852(13)	140(9)*

[a] Atoms have occupancies of 1.0 except as marked with # above: C(2A), 0.50; C(2B), 0.50; C(3A), 0.75; C(3B), 0.25; C(4A), 0.50; C(4B), 0.50. [b] Asterisks indicate the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]₂ (**20**)

	x/a	y/b	z/c	U_{eq}[a]
S(1)	5740(1)	3468(1)	689(1)	64(1)
S(2)	2762(1)	1827(1)	2147(1)	61(1)
P(1)	3901(1)	3336(1)	271(1)	45(1)
P(2)	2397(1)	2505(1)	1021(1)	42(1)
N(1)	3238(3)	2353(2)	190(2)	42(1)
N(2)	2980(3)	3516(2)	1037(2)	40(1)
N(3)	3426(3)	3870(2)	−708(2)	52(1)
N(4)	874(3)	2519(2)	497(3)	54(1)
C(1)	3708(4)	1518(2)	−137(3)	58(2)
C(2)	3122(4)	4204(2)	1776(3)	55(1)
C(3)	2176(4)	4015(3)	−1384(3)	61(1)
C(4)	−328(4)	2166(3)	677(3)	65(2)
C(11)	4211(5)	1705(3)	−1017(3)	86(2)
C(12)	2599(4)	904(3)	−387(3)	76(2)
C(13)	4804(5)	1166(3)	629(3)	84(2)
C(21)	1904(5)	4244(3)	2108(3)	83(2)
C(22)	3406(5)	5059(2)	1352(3)	80(2)
C(23)	4265(4)	3979(3)	2605(3)	71(2)
C(31)	1564(4)	3186(3)	−1808(3)	70(2)
C(32)	2466(5)	4566(3)	−2186(3)	101(2)
C(33)	1276(5)	4523(4)	−910(4)	100(2)
C(41)	−1396(4)	2499(4)	−121(4)	89(2)
C(42)	−567(5)	2498(4)	1596(4)	103(3)
C(43)	−303(5)	1191(3)	664(4)	100(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

with one overall isotropic displacement parameter for the entire set of hydrogens. The amine hydrogens were refined with no positional constraints and individual isotropic displacement parameters. Final positional parameters for **20** are given in Table 4. Thermal parameters are included in the supplementary material.

Results and Discussion

Synthetic Studies. The 2,4-bis(primary alkylamino)-substituted diazadiphosphetidines [(RNH)PNR]₂ (R = Me, **8/9**; Et, **10/11**; *i*-Pr, **13/14**; *t*-Bu, **5**[14]) examined in this study were prepared from RNH_2/PCl_3 in toluene or petroleum ether solvent. Reactants were combined at −78 °C and then allowed to warm to 25 °C over an 8–10-h period. Products form according to

$$10RNH_2 + 2PCl_3 \rightarrow 6RNH_3Cl + \underset{\mathbf{8/9,\ 10/11,\ 13/14,\ 5}}{[(RNH)PNR]_2} \quad (1)$$

The RNH_2/PCl_3 (R = Me, Et, *i*-Pr) reactions produce both *cis*- and *trans*-2,4-diamino isomers. These products were obtained optimally using petroleum ether or toluene solvent and ca. 8:1 RNH_2:PCl_3 reactant ratios. Excess amine beyond the stoichiometric 5:1 ratio is necessary as a HCl scavenger; lower ratios result in considerable amounts of chloro(amino)phosphines. The previously reported (*t*-BuNH)P(*t*-BuN)₂PCl (**15**) was obtained from the 3:1 *t*-$BuNH_2$:PCl_3 reaction. Solvent is also essential. Neat reactions yield almost exclusively the tricyclic six-membered-ring-based cage products $P_4(NMe)_6$,[40] $P_4(NEt)_6$ (**12**), and P_4(*i*-PrN)₆.[42] No evidence was obtained for P_4(*t*-BuN)₆.

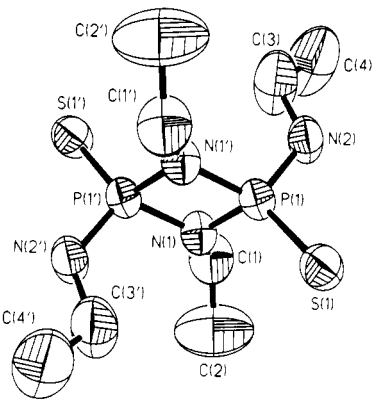


Figure 1. Structure of *trans*-[(EtNH)P(S)NEt]₂ (**17**) showing the numbering scheme. Thermal ellipsoids include 50% of the atom probability. Hydrogen are atoms omitted for clarity.

The new P(III) diazadiphosphetidines **8/9**, **10/11**, and **13/14** and the cage phosphazane **12** were characterized by spectral data; **8/9** and **10/11** were characterized as mixtures since they were too unstable with respect to equilibration for their *cis*/*trans* isomer mixtures to be separated. The ^{31}P NMR chemical shift regions expected for *cis* and *trans* isomers of amine-substituted diazadiphosphetidines are well established;[4-6,8,10,26,27,29] the *cis* isomers **8**, **10**, and **13** and the *trans* isomers **9**, **11**, and **14** display resonances in the high field (δ 81.9–107.0) and low-field (δ 168.0–190.0) regions expected. **12** exhibits a ^{31}P NMR resonance at δ 78.8, close to those for $P_4(NMe)_6$ (δ 78.4)[40] and P_4(*i*-PrN)₆ (δ 84).[42] All new compounds show mass spectral parent ions (M^+), indicating conclusively that compounds **8/9**, **10/11**, and **13/14** are cyclodiphosphazanes and not higher oligomers.

Reactions of **8/9**, **10/11**, **13/14** and *cis*-[(*t*-BuNH)PN-*t*-Bu]₂ (**5**) with S_8 yield the P(V) diazadiphosphetidine disulfides. Reaction of **12** with S_8 yields $P_4S_4(NEt)_6$ (**18**) quantitatively. From each diazadiphosphetidine/S_8 reaction we isolated only one isomer: [(MeNH)P(S)NMe]₂ (**16**), *trans*-[(EtNH)P(S)NEt]₂ (**17**), [(*i*-PrNH)P(S)N-*i*-Pr]₂ (**19**), and *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]₂ (**20**). If the second isomers were present, they were in quantities too small to identify or characterize. **20** displays a ^{31}P NMR resonance at δ 38.7. In comparison, **16**, **17**, and **19** exhibit somewhat lower shifts from δ 46.8 to δ 59.2. Although we might expect that **20**, like its precursor **5**, was the *cis* isomer, isomer identification of **16**, **17**, and **19** from ^{31}P NMR is ambiguous because the range in their δ values is relatively large when compared to the relatively small chemical shift differences between known *cis* and *trans* diazadiphosphetidine disulfides. For example, for [(Me₂N)P(S)N-*t*-Bu]₂ the δ_{cis} and δ_{trans} values are 44.8 and 53.8, respectively.[37] Since δ_{cis} and δ_{trans} values are not very different, we sought X-ray confirmation of the structures. Unfortunately, we were unable to obtain X-ray quality crystals of **16** and **19**. We were able to establish that **17** is the *trans* isomer (see below), and given that the δ values for **16**, **17**, and **19** are all upfield and closely similar, we conclude they are all *trans* isomers.

The X-ray structures of **17** and **20**, *trans* and *cis* diazadiphosphetidines, respectively, are shown in Figures 1 and 2. The structures and structural parameters (Tables 5 and 6) for both are entirely consistent with previously reported diazadiphosphetidine disulfides.[7,19,37,39] Both crystallize with four molecules per unit cell. The P_2N_2 ring of **17** is planar, but that of **20** is significantly bent like that seen in the related *cis*-(ClPN-*t*-Bu)₂.[33] The dihedral angle between P(2)/N(1)/N(2) and P(1)/N(1)/

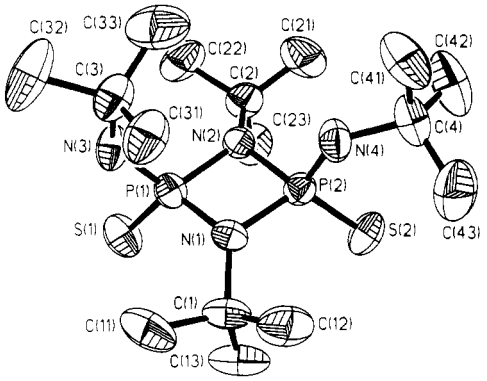


Figure 2. Structure of *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]$_2$ (**20**) showing the numbering scheme. Thermal ellipsoids include 50% of the atom probability. Hydrogen atoms are omitted for clarity.

Table 5. Selected Structural Parameters for *trans*-[(EtNH)P(S)NEt]$_2$ (**17**)

(a) Distances, Å

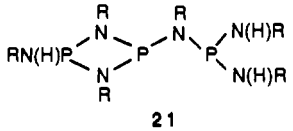
P(1)–S(1)	1.928(2)	P(1)–N(2)	1.616(4)
P(1)–N(1)	1.673(3)	N(1)–P(1′)	1.674(3)
P(1)–N(1′)	1.674(3)	N(1)–C(1)	1.476(6)
N(2)–C(3)	1.474(7)	P(1)···P(1′)	2.508(2)

(b) Angles, deg

S(1)–P(1)–N(1)	119.9(1)	S(1)–P(1)–N(2)	110.7(1)
N(1)–P(1)–N(2)	109.9(2)	S(1)–P(1)–N(1′)	119.0(1)
N(1)–P(1)–N(1′)	83.0(2)	N(2)–P(1)–N(1′)	111.7(2)
P(1)–N(1)–C(1)	129.6(3)	P(1)–N(1)–P(1′)	97.0(2)
C(1)–N(1)–P(1′)	130.2(3)	P(1)–N(2)–C(3)	124.6(3)

N(2) planes in **20** is 5.5°. The P–N distances and angles in **17** and **20** are typical; the mean ring P–N distances of 1.67 and 1.69 Å for **17** and **20**, respectively, are somewhat longer than the *exo* P–N distances of 1.62 and 1.63 Å. The –N(H)Et groups in **17** are rotated such that the N–H bond in each is approximately *cis* to the P=S bond. In contrast, in **20**, one –N(H)-*t*-Bu group is rotated so that its N–H bond is *cis* to the P=S bond and the other –N(H)-*t*-Bu is positioned with the N–H bond approximately *trans* to the P=S bond.

The products of RNH_2/PCl_3 reactions carried out under mild temperature conditions, –78 to +25 °C, in toluene at reactant ratios <8:1, were also examined in order to establish if under some conditions diazadiphosphetidine-based triphosphazanes (**21**) or tetraphosphazanes (**22**) analogous to [(PhNH)PNPh]$_3$[4,6] and



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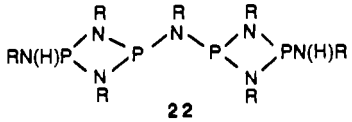

22

$(PhNH)_2P_4(NPh)_5$[5] might form and/or be intermediates in the formation of the tricyclic $P_4(NR)_6$ cages. The RNH_2/PCl_3 reactions carried out under these conditions were more complex and generally produced a variety of chloro(amino)phosphines. The *t*-$BuNH_2/PCl_3$ reaction at a low ratio (1.8:1) yields the chlorophosphine products (ClPN-*t*-Bu)$_2$,[13] *t*-BuN$(PCl_2)_2$,[11] and *t*-BuNHPCl_2;[12,13] at a 3:1 ratio, the partially aminated diazadiphosphetidine (*t*-BuNH)P(N-*t*-Bu)$_2$PCl (**15**) appears;[10] and at 8:1, *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (**5**) is virtually the only product. Consistent with data reported earlier for *t*-$BuNH_2/PCl_3$ reactions, we found no evidence for *trans*-[(*t*-BuNH)PN-*t*-Bu]$_2$,[12-14] six-membered-ring products,[23,24] a tetraphosphorus cage P_4(N-*t*-Bu)$_6$,[41] or diazadiphosphetidine-based type **21** and **22** products.[5,6] Apparently, the large *t*-Bu group precludes formation of all but the single-ring, four-membered-ring phosphazanes. In contrast, we observed six-membered-ring products from the *i*-$PrNH_2$, $EtNH_2$, and $MeNH_2/PCl_3$ reactions. *i*-$PrNH_2/PCl_3$ ((3–5):1) reactions yield mainly (ClPN-*i*-Pr)$_2$,[13] *i*-PrN$(PCl_2)_2$, and *i*-PrNHPCl_2; at higher reactant ratios, *cis*- and *trans*-[(*i*-PrNH)PN-*i*-Pr]$_2$ (**13**, **14**) and the known cage P_4(*i*-PrN)$_6$[42] appear. The $EtNH_2/PCl_3$ and $MeNH_2/PCl_3$ reactions ((3–5):1, m/m), in addition to products identified tentatively as $RN(PCl_2)_2$ and $(ClPNR)_2$,[11] yield the known chlorocyclotriphosphazane (ClPNR)$_3$.[23,24] We observed no resonances which could be unambiguously assigned to bicyclo-$Cl_2P_4(NR)_5$.[24] At slightly higher ratios ((5–6.5):1), reactions produce significant amounts of the diazadiphosphetidines **8**/**9** and **10**/**11** and cage compounds $P_4(NMe)_6$ and $P_4(NEt)_6$ (**12**). Again, we saw no characteristic ^{31}P NMR ABX or AA′XX′ patterns[5,6] expected for type **21** or **22** phosphazanes. Synthesis and characterization details for **12**, although the compound has been mentioned earlier,[24] have never appeared. In the $MeNH_2/PCl_3$ reactions and, to a lesser degree, in the $EtNH_2/PCl_3$ systems, additional minor unidentifiable resonances were seen in the ^{31}P NMR spectrum. Due to the thermal, oxidative, and hydrolytic instability of these reaction products, repeated attempts at their isolation and characterization failed.

Primary alkylamine/PCl_3 reactions have been reported previously,[8,12-14,18,24] but with significantly different results for the $MeNH_2/PCl_3$ and $EtNH_2/PCl_3$ reactions. Diazadiphosphetidine products had been demonstrated only from RNH_2/PCl_3 (R = *i*-Pr, *t*-Bu) reactions. The metal carbonyl stabilized $(CO)_5$Mo[(MeNH)PNMe]$_2$Mo$(CO)_5$ is known, but it was obtained by Et_3N-promoted dehydrohalogenation of $(CO)_5$MoP-$(NHMe)_2Cl$.[46] We attribute our obtaining [(RNH)PNR]$_2$ (R = Me, Et), **8**/**9**, and **10**/**11** to the use of high amine:PCl_3 ratios and conditions of moderately high dilution. In previous studies, low amine:PCl_3 ratios were used, ratios which are more likely to allow formation of incompletely aminated chlorophosphino products. From the RNH_2/PCl_3 (R = Me, Et) reactions larger-ring products were also identified, e.g. cyclotrimers $(ClPNR)_3$ and bicyclic rings based on fused cyclotrimers; from neat $MeNH_2/PCl_3$ reactions $P_4(NMe)_6$ is formed almost quantitatively. Under our conditions of high reaction dilution, intermolecular conden-

Table 6. Selected Structural Parameters for *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]$_2$ (**20**)

(a) Distances, Å

P(1)–S(1)	1.933(1)	P(2)–S(2)	1.917(1)
P(1)–N(1)	1.675(3)	P(2)–N(1)	1.695(3)
P(1)–N(2)	1.685(3)	P(2)–N(2)	1.685(3)
P(1)–N(3)	1.630(3)	P(2)–N(4)	1.632(3)
N(1)–C(1)	1.507(5)	N(2)–C(2)	1.506(3)
N(3)–C(3)	1.483(5)	N(4)–C(4)	1.481(6)
N(3)–H(1)	0.88(4)	N(4)–H(2)	0.74(4)

(b) Angles, deg

S(1)–P(1)–N(1)	120.2(1)	S(1)–P(1)–N(2)	119.2(1)
N(1)–P(1)–N(2)	83.8(1)	S(1)–P(1)–N(3)	107.9(1)
N(1)–P(1)–N(3)	111.2(1)	N(2)–P(1)–N(3)	113.0(2)
S(2)–P(2)–N(1)	120.5(1)	S(2)–P(2)–N(2)	119.9(1)
N(1)–P(2)–N(2)	83.1(1)	S(2)–P(2)–N(4)	112.9(1)
N(1)–P(2)–N(4)	107.9(2)	N(2)–P(2)–N(4)	108.7(2)
P(1)–N(1)–P(2)	96.4(1)	P(1)–N(1)–C(1)	129.4(3)
P(2)–N(1)–C(1)	128.6(2)	P(1)–N(2)–P(2)	96.4(1)
P(1)–N(2)–C(2)	128.5(2)	P(2)–N(2)–C(2)	130.1(2)
P(1)–N(3)–C(3)	135.2(3)	P(2)–N(4)–C(4)	136.7(3)

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Table 7. Equilibrium Isomer Composition of *N(ring)*-Alkyl 1,3,2,4-Diazadiphosphetidines

compd	*N(ring)*-R′ substitutents		*exo*-NRR″ group	$K_{cis/trans}$
$[(MeNH)PNMe]_2$ (**8/9**)	Me	Me	MeNH	3 ● 0.5
$[(EtNH)PNEt]_2$ (**10/11**)	Et	Et	EtNH	8 ± 1
$[(i\text{-PrNH})PN\text{-}i\text{-Pr}]_2$ (**13/14**)	*i*-Pr	*i*-Pr	*i*-PrNH	15 ± 1
$(Me_2N)_2P_2(NMe)(N\text{-}t\text{-Bu})$ (**23**)[a]	Me	*t*-Bu	Me_2N	1.5
$(Me_2N)_2P_2(NEt)(N\text{-}t\text{-Bu})$ (**24**)[a]	Et	*t*-Bu	Me_2N	2
$[(Me_2N)PN\text{-}t\text{-Bu}]_2$ (**25**)[a]	*t*-Bu	*t*-Bu	Me_2N	10
$[(Et_2N)PN\text{-}t\text{-Bu}]_2$ (**26**)[a]	*t*-Bu	*t*-Bu	Et_2N	∞[b]
$[(t\text{-BuNH})PN\text{-}t\text{-Bu}]_2$ (**5**)	*t*-Bu	*t*-Bu	*t*-BuNH	∞[b]

[a] Data from ref 10. [b] Within limits of experimental detection, no *trans* isomer was present.

sations necessary to give $P_4(NMe)_6$ are disfavored relative to the four-membered rings. It is noteworthy that **8/9**, **10/11**, and **13/14** upon thermolysis all yield the $P_4(NR)_6$ cage compounds. However, it is unclear whether these diazadiphosphetidines are intermediates that precede formation of six-membered-ring products or if the new diazadiphosphetidines are highly labile and readily rearrange to six-membered-ring products prior to cage condensation.

Isomer and Conformational Studies. Compounds **8/9**, **10/11**, and **13/14** undergo facile *cis/trans* isomer equilibration (eq 2), and from thermally equilibrated mixtures in toluene we deter-

$$trans\text{-}[(RNH)PNR]_2 \rightleftharpoons cis\text{-}[(RNH)PNR]_2 \qquad (2)$$

mined *cis/trans* equilibrium constants $K_{cis/trans}$ ($K_{cis/trans} = [cis]/[trans]$). In the alkylamine/$PCl_3$ reactions studied, two isomers are always seen; however, as is the case with the *N(ring)*-*t*-Bu diazadiphosphetidines[9,10,25] the *trans* isomer appears to be the kinetic product. Conversion to the more stable *cis* isomer occurs upon standing or mild thermolysis. Even though some decomposition accompanies thermolysis of **8/9** and **10/11** mixtures, we obtained reasonable values of $K_{cis/trans}$. In the Me (**8/9**), Et (**10/11**), and *i*-Pr (**13/14**) systems, $K_{cis/trans}$ values are 3 ± 0.5, 8 ± 1, and 15 ± 1, respectively. In no case did we observe a dependence of K on T; our data were likely inadequate to show the expected small differences. $[(t\text{-BuNH})P(S)N\text{-}t\text{-Bu}]_2$ (**20**) never shows a *trans* product;[10] possibly the *trans* → *cis* conversion occurs fast and is complete by the time product isolation begins.

Previous studies of small series of *N(ring)*-alkyl- and *N(ring)*-aryl-substituted P(III) diazadiphosphetidines[9,10,25] have allowed limited conclusions about the relative thermodynamic stability of *cis* (**1**) and *trans* (**2**) isomers. For the *N(ring)*-aryl compounds, *cis* isomers are favored except when the *endo*-group substitutents are very large, e.g. $-NR_2 = -NMe_2$, $-NEt_2$, and $-NPh_2$. By comparison, the situation with the *N(ring)*-alkyldiazadiphosphetidines seems more complex. Data from our studies and those reported by others earlier are summarized in Table 7. In general, *cis* isomers are favored; however, as the steric bulk of the *N(ring)*-R′ and *exo*-NRR″ group is increased, dominance of the *cis* over the *trans* isomer increases. As the steric bulk of both the *N(ring)*-R″ and *exo*-N(H)R′ groups increases, as with **8/9** < **10/11** < **13/14**, $K_{cis/trans}$ increases in favor of the *cis* isomer. However, increasing the size of either *N(ring)*-alkyl or *exo*-NRR′ groups also affects the ratio. Replacement of one *endo*-NMe group of **23** with an NEt (**24**) unit causes $K_{cis/trans}$ to increase from 1.5 to 2, while substitution of an N-*t*-Bu (**25**) with an NEt unit (**24**) decreases $K_{cis/trans}$ from 10 to 2. **5** and **26**, which contain *N(ring)*-*t*-Bu groups and the large NEt_2 or N(H)-*t*-Bu *exo* groups, show only the *cis* isomers. How the effects of group size on isomer ratio can be explained remains unclear, although it should be noted that in both *cis*-$(ClPN\text{-}t\text{-Bu})_2$[37] and *cis*-$[(t\text{-BuNH})P(S)N\text{-}t\text{-Bu}]_2$ (**20**) the P_2N_2 ring is bent significantly so as to increase the distance between the *exo*-NRR″ groups. Perhaps this bending is enough that the pairwise interactions that occur between *N(ring)*-R and *exo*-NRR″ groups are better minimized in the *cis* than in the *trans* isomer.[8] Futher studies of this problem, with more complete diazadiphosphetidine series and X-ray structural data, are needed.

The new compounds **8–11**, **13**, **14**, **16**, **17**, and **20** and the known *cis*-$[(PhNH)PNPh]_2$ (**4**), *cis*-$[(t\text{-BuNH})PN\text{-}t\text{-Bu}]_2$ (**5**), *trans*-$[(i\text{-PrNH})PNPh]_2$ (**6**), *trans*-$[(PhNH)P(S)NPh]_2$ (**7**), and *cis*-*t*-$BuNHP(N\text{-}t\text{-Bu})_2PCl$ (**15**) are an interesting series of P(III) and P(V) diazadiphosphetidines in which to compare temperature effects on *exo*-group conformational properties; hence, ^{31}P and selected ^1H NMR spectra were examined as a function of temperature. Compounds **4–7**, **13–17**, **19**, and **20** were studied from +100 to −90 °C, **8–11** were examined between +25 and −90 °C, and **5** was studied from +150 to −95 °C. The *trans* compounds, except for **14**, appeared temperature independent. In contrast, the *cis* isomers showed spectral temperature dependence which could be correlated with specific isomer conformations.

The temperature-dependent ^{31}P NMR spectral behavior of *cis* diazadiphosphetidines **4**, **8**, **10**, **13**, and **20** (Table 1) and **15** is of two types. Compounds **8**, **10**, and **13** all show spectral singlets at 27 °C which broaden upon cooling, go through coalesence, and "freeze" out to spectra of two (**a** and **b**) conformations. In each case, the **a** and **b** conformations are present in a 1:1 ratio. Typical spectra, in the low-temperature regime, for **13** are shown in Figure 3. At low temperature (Figure 3A) the $^{31}P\{^1H\}$ spectrum is a pair of equal-area singlet resonances at δ 96.0 and 83.3 (conformation **13a**) and a lone singlet at δ 80.4 (conformation **13b**). Conformation **13a** must be unsymmetrical with inequivalent phosphorus atoms; **13b** is symmetrical. With ^1H coupling (Figure 3B), the δ 96.0 member of **13a** is essentially unaffected. However, the δ 83.3 peak of **13a** and the **13b** peak at δ 80.4 are split into doublets, $^2J_{PNH} = 39.8$ and 38.6 Hz, respectively, indicating that P atoms attributable to these resonances are coupled to an exo-oriented −N(H)R proton.

Different spectral behavior is shown by **4**, **20**, and perhaps **15**, because at low temperature they show only one conformation. The singlets seen at 25 °C broaden as the samples are cooled, coalesce, and sharpen to an AX pair of doublets at −90 °C. The $^{31}P\{^1H\}$ NMR spectrum of **20**, which is typical of **4** and **20**, is shown in Figure 4A. The existence of two resonances indicates the presence of a single, unsymmetrical conformation. The $^2J_{PNP}$ couplings of 9.1 and 37.1 Hz in **4** and **20**, respectively, are consistent with the coupling expected between nonequivalent phosphorus atoms in P(III)–P(III) and P(V)–P(V) diazadiphosphetidines.[5,6,9,22,50] The high-field doublets of both **4** and **20** upon ^1H coupling each split into a doublet of doublets (Figure 4B); however, the low-field resonances are unaffected. The new coupling is assigned to $^2J_{PNH}$, attributed to coupling between one phosphorus center and the proton of the attached −N(H)R group. The spectral situtation for **15** at −90 °C is less well defined because even at −90 °C the spectrum had not fully coalesced. However, the barrier to rotation must be less than the 16.9 kcal/mol barrier reported for the analogous but sterically more encumbered *cis*-$Me_2NP(N\text{-}t\text{-Bu})_2PCl$.[35]

(50) Burdon, J.; Hotchkiss, J. C.; Jennings, W. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1052.

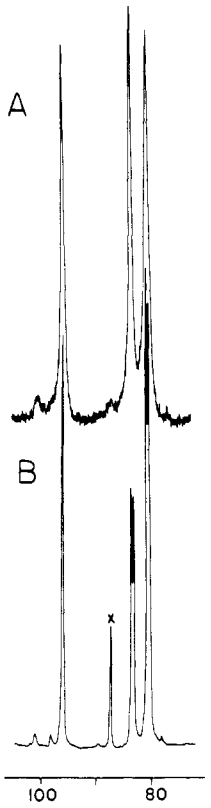


Figure 3. ^{31}P NMR spectra of *cis*-[(*i*-PrNH)PN-*i*-Pr]$_2$ (**13**) at −90 °C: ^1H decoupled (A); ^1H coupled (B).

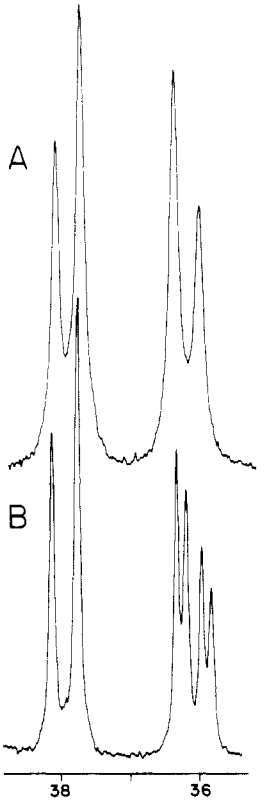
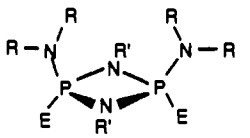


Figure 4. ^{31}P NMR spectra of *cis*-[(*t*-BuNH)P(S)N-*t*-Bu]$_2$ (**20**) at −90 °C: ^1H decoupled (A); ^1H coupled (B).

Coalescence temperatures (T_c) were determined for **4**, **8**, **10**, **13**, and **20**. From these, the activation barriers to rotation around the P–N(H)R bonds (ΔG^*) were determined (Table 1).[44,45] In general, the barriers were in the range of those reported earlier for P–N bonds in acyclic phosphazanes and other *cis*- bis(dialkylamino)-substituted diazadiphosphetidines.[8,29,35-37] The rotational barriers in **8**, **10**, and **13** were essentially equal (9.5–10.4 kcal/mol). Within experimental error, steric effects on barriers in this series were not detectable. The barrier of 12.9 kcal/mol for **4** is significantly higher than those for the other *cis* isomers, perhaps due to electronic effects that are characteristic of aryl group substitution in the *N(ring)*-R′ and *exo*-N(H)R sites. The 10.2 kcal/mol barrier to rotation of –N(H)-*t*-Bu groups in **20** is not as large as might be expected; the barrier in the analogous *cis*-[(Me$_2$N)P(S)N-*t*-Bu]$_2$ is 11.8 kcal/mol.[35] Perhaps greater ring puckering occurs in **20**, an effect which allows the *exo*-*t*-BuNH groups to experience lowered intergroup interaction.

The X-ray structures of several *cis*- and *trans*-2,4-(R$_2$N)$_2$-substituted diazadiphosphetidines[5-7,9,17,19,28,39] have been determined. From these, generalizations can be made about the preferred orientations of the –NR$_2$ groups with respect to the P$_2$N$_2$ plane of the molecule. In nearly every case, the groups orient so that the one R group is over the P$_2$N$_2$ plane and one is out from the plane. The R groups are in approximate *cis* and *trans* conformations relative to the P–E unit (E = lone pair, S, O) of the phosphorus to which the NR$_2$ group is bonded (**29**). This observation indicates that such a conformation is lowest in



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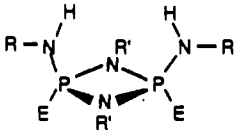
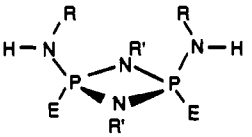
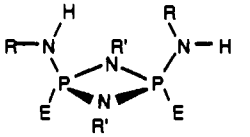


30A



30B



30C

energy for the NRR groups and may therefore also be the conformation to be expected in solution at low temperature. Keat and co-workers have argued[8] that conformations which have the NRR (NCC) plane parallel to the P···P molecular axis are preferred because they keep the NR$_2$ group N and P lone-pair electrons orthogonal and thereby minimize intergroup repulsions.

Our data allow us to make conclusions about (i) the –N(H)R group conformational orientations in **4**, **8**, **10**, **13**, and **20** and (ii) how to assign ^{31}P NMR resonances to specific P–N(H)R groups. Because the spectrum of **15** did not reach full coalesence, no conclusions were made about the –N(H)-*t*-Bu orientation at low temperatures. Assuming that the lowest energy conformations of *cis*-(N(H)R)$_2$-substituted diazadiphosphetidines in solution parallel those seen in the solid, three conformations for a *cis* isomer can be considered: **30A** and **30B**, symmetrical conformations with the –N(H)R group N–H bonds oriented over or away from the P$_2$N$_2$ ring, respectively, and an unsymmetrical conformation **30C**. **4** (E = LP) and **20** (E = S), which freeze to unsymmetrical conformations, are assumed to be of conformation type **30C**. Assuming that $^2J_{PNH}$ coupling constants in –N(H)R-substituted compounds behave like $^2J_{PNC}$ and $^3J_{PNCH}$ couplings in tervalent phosphazanes[8,32,52,53] and *exo*-substituted diazadiphosphetidines[8,29,36] or $^2J_{PNP}$ couplings in diphosp-

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(53) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1977**, 1674.

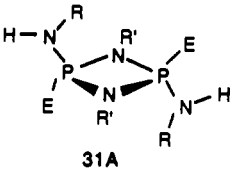
hazanes[8,9,31,54] and depend on the angular relationships between the P–N–H, P–N–C, or P–N–P group P–lone pair (or P=E bond) and the N–H, N–C, or N–P bond vector, respectively, $^2J_{PNH}$ for an N–H oriented *cis* to the P–E bond will be larger than for one oriented *trans*. Thus, the high-field resonances, δ 104.7 for **4** and δ 36.2 for **20**, since they show large $^2J_{PNH}$ couplings (38.4 and 14.2 Hz), are assigned to the P–N(H)R groups in which the N–H points "out". The low-field resonances, δ 105.9 for **4** and δ 38.1 for **20**, are assigned to P–N(H)R environments which have the N–H oriented "in".

Compounds **8**, **10**, and **13** (E = LP) freeze to mixtures of two conformations, one symmetrical and one unsymmetrical. Resolution of spectra for **8** and **10** is inadequate to show small $^2J_{PNH}$ couplings if they are present. However, for **13a**, the higher field resonance shows a strong $^2J_{PNH}$ coupling (39.8 Hz). As with **4** and **20**, the higher field doublet is assigned to –N(H)R groups with the N–H "out", **30c**. Since the $^2J_{PNH}$ coupling (35 Hz) seen for **13b** is essentially the same as for the upper member in **13a**, we conclude that this symmetrical isomer is one with both N–H groups oriented out, i.e. **30B**. It is unclear why a conformation which has the two *i*-Pr groups pointing toward one another over the ring, as is required in **30B**, should be favored over one with the R groups out (**30A**). However, it may be that the P_2N_2 ring is sufficiently bent that the R groups are not in each other's way and/or that there is some electronic advantage to having *cis* P–lone pair arrangements or P–E (E = O, S) bonds. This problem warrants futher experimental and theoretical study.

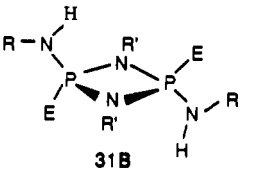
The solution conformational properties of *cis*-[(*t*-BuNH)PN-*t*-Bu]$_2$ (**5**) are different from those of the other *cis* compounds. **5** exhibits a singlet ^{31}P NMR peak over the temperature range studied; no spectral change occurs at low temperatures. At higher temperatures, the spectral line width increases and the half-height width ($\nu_{1/2}$) increases from 12 Hz at 50 °C to 108 Hz at 150 °C. Only at higher temperatures does rotation around the P–N(H)-*t*-Bu bond become fast on the NMR time scale. The line broadening above 50 °C indicates the introduction of a conformation(s) which has larger $^2J_{PNH}$ values, e.g. **30B** or **30C**, into the conformational population.

(54) (a) Hill, T. G.; Haltiwanger, R. C.; Prout, T. R.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 3461. (b) Prout, T. R.; Imiolczyk, T. W.; Barthelemy, F.; Young, S. M.; Haltiwanger, R. C.; Norman, A. D. Submitted for publication.

In contrast to what is observed for the *cis* isomers, the ^{31}P NMR spectra of *trans* diazadiphosphetidines appear to be temperature independent. *A priori* it is unclear whether the compounds are frozen in one symmetrical conformation or, alternatively, the –N(H)R groups are completely averaged (freely rotating) over the entire temperature range. Between +100 and –90 °C, **6**, **7**, **9**, **11**, **16**, **17**, and **19** show only singlet ^{31}P{^{1}H} spectra; no spectral collapse behavior is observed. With ^{1}H coupling, the spectra are little changed. No resolvable $^2J_{PNH}$ coupling appears as would be expected if at low temperatures the compounds froze to a symmetrical conformation with the N–H bonds pointing outward (**31A**) as occurs for *trans*-[(PhNH)P-



31A



31B

(S)NPh]$_2$ (**7**)[19] and *trans*-[(EtNH)P(S)NEt]$_2$ (**17**) in the solid. A symmetrical conformation in which the N–H bonds point "in" (**31B**) is possible; however, it is unclear why for the *trans* isomers, unlike the for the *cis* isomers, the lowest energy conformation in solution would be different from what occurs in the solid. Thus our data suggest that the –N(H)R groups for these compounds are freely rotating at –90 °C and that the barriers to rotation around the *exo* P–N bonds in *trans* isomers are significantly lower than those for the analogous *cis* isomers. This observation contrasts that reported for several (dialkylamino)-substituted diazadiphosphetidines[30,35] where rotation barriers (ΔG^*, in kcal/mol) are higher for the *trans* than for the *cis* isomers, e.g. [(Me_2N)P(O)N-*t*-Bu]$_2$ (*trans*, 15.9; *cis*, 11.6) and [(Me_2N)P(S)N-*t*-Bu]$_2$ (*trans*, 13.8; *cis*, 11.8).[35] The difference in behavior observed between –N(H)R and –NR_2 exo-substituted diazadiphosphetidines warrants further study.

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Supplementary Material Available: Tables of crystal data and refinement details, anisotropic thermal parameters, hydrogen atom positions, nonessential bond distances and angles, and least squares planes for **17** and **20** (17 pages). Ordering information is given on any current masthead page.