to the Van Vleck equation with $g = 2.0 \pm 0.1$ and $-2J = 750 \pm 50$ cm^{-1}. The large scatter in the data obtained for this system and the narrow range of temperature over which measurements were made place large errors on the values of g and $-2J$, but the results clearly indicate a strongly antiferromagnetically coupled complex.

The fact that $Cu_2(PPD)(OH)Br_3 \cdot 1.5H_2O$ is diamagnetic at room temperature is unusual (repeated measurements with large samples gave the same result) and suggests very large antiferromagnetic exchange. Other examples of binuclear copper(II) complexes that are diamagnetic are rare and usually involve 1,3-azide or O-carbonate bridges.[38-44] In the carbonate-bridged systems a single oxygen atom bridges the two copper centers, and Cu–O–Cu angles of greater than 172° lead to room-temperature diamagnetism. A linear relationship between the exchange integral ($-2J$) and Cu–O–Cu bridge angle has been demonstrated for a series of related dihydroxo-bridged copper(II) systems[45] and also for a series of related monohydroxo-bridged copper(II) systems involving $d_{x^2-y^2}$ ground states with exchange increasing with bridge angle.[16,17] Such a relationship has, however, not been demonstrated with other oxygen bridge groups, and although the carbonate-bridged species are diamagnetic, it is not clear whether such large oxygen bridge angles are necessary to cause complete spin pairing at room temperature. An extrapolation of a linear plot of room-temperature magnetic moment against hydroxide bridge angle for a related series of monohydroxo-bridge copper(II) complexes with $d_{x^2-y^2}$ copper ion ground states[16,17] suggests that an angle of about 145° should lead to room-temperature diamagnetism. It is of interest to note that oxyhemocyanin is "diamagnetic" over the temperature range 5–260 K[46,47] ($-2J > 1100$–1250 cm^{-1}) and appears to have a single atom, endogenous bridge (probably an oxygen atom) according to EXAFS and other studies. Assuming reasonable values for the Cu–OR(bridge) (1.90 Å) and Cu–Cu (3.65 Å) separations in oxyhemocyanin a Cu–O–Cu angle of ~145° would result by simple trigonometry.[48]

Acknowledgment. We thank Dr. A. W. Addison, Drexel University, for the gift of an original sample of PPD and the Natural Sciences and Engineering Research Council of Canada for financial support, including the purchase of magnetometer equipment. Also we are indebted to Dr. M. J. Newlands and Dr. B. S. Ramaswamy for computing and graphics assistance.

Supplementary Material Available: Listings of anisotropic thermal parameters for V and VII (Tables III and VI), observed and calculated structure factor amplitudes for V and VII (Tables IV and VII), bond length and bond angle data pertaining to the ligand in V (Table X), bond length and bond angle data pertaining to the ligand and distant nitrate groups in VII (Table XIII), and least-squares-plane calculations for V and VII (Table XIV) (49 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Study of 2,4-Disubstituted 1,3-Diaryl-1,3,2,4-diazadiphosphetidines

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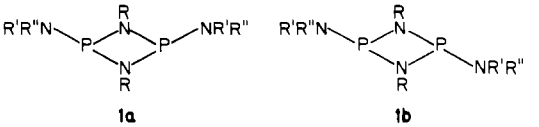
Received April 19, 1985

Reactions of *cis*-$[(C_6H_5N)PCl]_2$ (**5**) with $(C_6H_5)_2NH$, $(n\text{-}C_4H_9)_2NH$, or $i\text{-}C_3H_7NH_2$ yield the new *trans*-1,3,2,4-diazadiphosphetidines $[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**), $[(C_6H_5N)PN(n\text{-}C_4H_9)_2]_2$ (**10**), and $[(C_6H_5N)PNH(i\text{-}C_3H_7)]_2$ (**12**), respectively. **6**, **10**, and **12** have been characterized in solution by spectral data. **5** and **6** have been characterized by single-crystal X-ray crystallographic analysis. Lattice parameters and space group information are as follows. For **5**: $a = 16.034$ (5) Å, $b = 11.405$ (3) Å, $c = 7.826$ (2) Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, $Cmc2_1$, $Z = 4$. For **6**: $a = 7.795$ (3) Å, $b = 13.533$ (8) Å, $c = 17.046$ (7) Å, $\beta = 103.12$ (3)°, monoclinic, $P2_1/c$, $Z = 2$. Structures were solved and refined by direct methods to (**5**) $R = 0.061$ and $R_w = 0.077$ for 390 independent reflections and (**6**) $R = 0.097$ and $R_w = 0.108$ for 801 independent reflections. **5** is a cis isomer with a planar P_2N_2 ring (approximate C_{2v} molecular symmetry). **6** is a trans isomer (C_i molecular symmetry). **5**, **6**, **10**, and **12** are obtained in their thermodynamically favored isomeric forms. From **6**–$C_6H_5NH_2$ and $[(C_6H_5)_2N]_2PCl$–$C_6H_5NH_2$ [in the presence of $(C_2H_5)_3N$] reactions the thermodynamically stable *cis*-$[(C_6H_5N)_2P_2N(C_6H_5)_2(NHC_6H_5)]$ is obtained and characterized. *cis*-$[(C_6H_5N)_2P_2(Cl)N(C_6H_5)_2]$ is characterized tentatively as the major product of the reaction of a deficiency of $(C_6H_5)_2NH$ with **5**. Relative stabilities of cis and trans isomers in *N*(ring)-aryl-substituted diazadiphosphetidines and the factors that influence these are discussed.

Introduction

Structural properties of phosphorus(III) 1,3,2,4-diazadiphosphetidines,[2] especially 2,4-diamino-1,3-dialkyl-substituted species (**1**; R = alkyl), have received considerable recent attention.



1a **1b**

Cis–trans isomerism,[3-24] rotation around *exo*-P–N bonds,[20-22,25-27] and the factors that affect relative isomer stability have been

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(2) The 1,3,2,4-diazadiphosphetidine nomenclature system advocated by *Chem. Abstr.* and diazadiphosphetidine are used synonomously throughout this paper.
(3) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101 and references cited therein.

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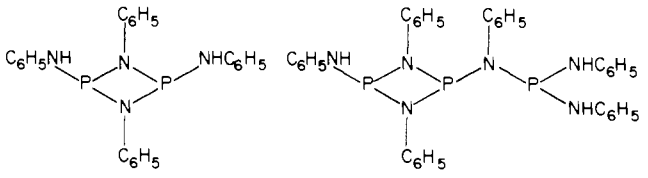
studied in detail.[3,5,23,24] For these *N*(ring)-alkyl- (endo-) substituted compounds, it is known that trans isomers (**1b**) are often kinetically favored during formation, cis isomers (**1a**) are generally thermodynamically preferred, and rates of isomer interconversion are largely dependent upon steric interactions among the *endo*-alkyl and *exo*-amino moieties.[5] Even with relatively large R and NR′R″ groups, (eg. R = *t*-C_4H_9; R′ = Me, R″ = $SiMe_3$), the cis isomers are thermodynamically favored.[5,21,23]

In contrast, for *N*(ring)-aryl-substituted diazadiphosphetidines, circumstances under which cis or trans isomers are favored either kinetically or thermodynamically are less clear.[13,23] In a series of 1,3-diaryl compounds, **1** (R′R″N = $(CH_3)_2N$, $(C_2H_5)_2N$, R = C_6H_5 and R′R″N = $(CH_3)_2N$, R = *p*-ClC_6H_4, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$), on the basis of ^{31}P NMR spectral correlations, it was determined that cis isomers are kinetically favored but the trans isomers are thermodynamically preferred.[23] We observed a different situation in 2,4-bis(phenylamino)-1,3-diphenyl-1,3,2,4-diazadiphosphetidines (**2–4**),[6,19] where only cis isomers are



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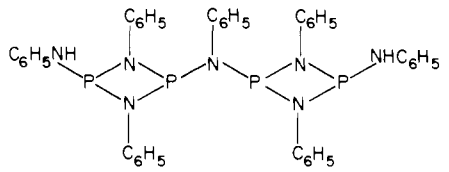

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observed, and they appear to be thermodynamically preferred. Therefore (i) to determine more clearly under what situations of substitution cis or trans isomers are thermodynamically stable, (ii) to confirm the validity of ^{31}P NMR spectral correlations in assigning isomer structures, and (iii) to determine the factors important in determining isomer stability in *N*(ring)-aryldiazadiphosphetidines, we have undertaken the preparation, structural characterization, and solution study of selected *N*-(ring)-aryl series members. The results of this work are described below.

Experimental Section

Apparatus and Materials. All inert-atmosphere manipulations were carried out in N_2-flushed glovebags and standard Schlenk-type glassware.[28] Infrared spectra (4000–400 cm^{-1}) were obtained by using Perkin-Elmer Model 337G and Beckman 4250 grating spectrometers. Mass spectra were obtained at 70 eV with a Varian MAT CH5 spectrometer. ^1H NMR spectra were obtained at 60.0 and 90.0 MHz with Varian A-60A and EM-390 spectrometers. Proton chemical shifts downfield from the standard [$(CH_3)_4Si$] are assigned positive, +δ, values. ^{31}P NMR spectra were obtained at 40.5 MHz on a JEOL PFT-100 Fourier transform spectrometer equipped with standard probe accessories. Chemical shifts downfield from the standard (H_3PO_4) are assigned positive, +δ, values. X-ray diffraction data were collected with a Syntex P$\bar{1}$ automated diffractometer (Mo Kα radiation, λ = 0.71069 Å) equipped with a graphite monochromator.

$C_6H_5N(PCl_2)_2$,[29] [(*t*-C_4H_9N)P(*t*-C_4H_9NH)]$_2$,[30] $(C_6H_5)_2NPCl_2$,[31] $[(C_6H_5)_2N]_2PCl$,[31] $[(C_6H_5N)P(NHC_6H_5)]_2$ (**2**),[16] and $[(C_6H_5N)PN(C_2H_5)_2]_2$[23] (**11**) were prepared as described elsewhere. $C_6H_5NH_2$ (Mallinckrodt, analytical), $(n\text{-}C_4H_9)_2NH$ (Fisher Scientific), $(C_2H_5)_2NH$ (Aldrich), and *i*-$C_3H_7NH_2$ (Aldrich) were distilled from CaH_2. $(C_6H_5)_2NH$ (Eastman, ACS reagent) was recrystallized before use. *cis*-$[(C_6H_5N)PCl]_2$ (**5**) was prepared generally from $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$ (**4**)–PCl_3 and literature[29] reactions. Toluene, benzene, and hexane (over Na–Pb alloy), $CHCl_3$ and CH_2Cl_2 (over P_4O_{10}), and PCl_3 (Fisher Scientific, reagent; over CaH_2) were distilled immediately prior to use.

Reactions materials from the reactions below were characterized by comparison of their physical and/or spectral properties with those reported in the literature or with samples prepared independently in our laboratories. Mass spectral data refer to the major peak of the envelope in question. Elemental analyses were performed by Huffman Laboratories Inc., Wheatridge, CO.

$[(C_6H_5N)PCl]_2$ (5). (A) $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$ (4)–PCl_3 Reaction. PCl_3 (100 mmol) in toluene was added dropwise under N_2 to a toluene solution of **4** (20 mmol) at 0 °C, and the mixture was warmed slowly to reflux. After 8–10 h, the reaction mixture was filtered to remove $C_6H_5NH_3Cl$, and the filtrate evaporated to dryness in vacuo. $C_6H_5N(PCl_2)_2$ was sublimed from the solid under vacuum at 50 °C. Recrystallization of the resulting solid from C_6H_6 yielded **5** (yield 69%; mp[29] 153–154 °C; ^{31}P NMR δ 199.5 (s)).

(B) $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$ (4)–HCl Reaction. Hydrogen chloride (6.2 mmol) was condensed into **4** (0.92 mmol) in CH_2Cl_2. The mixture was warmed slowly to room temperature, and the resulting suspension was filtered under nitrogen to remove $C_6H_5NH_3Cl$. ^{31}P NMR spectral analysis of the yellow filtrate confirmed the presence of **5**, $C_6H_5N(PCl_2)_2$, and PCl_3. Small quantities of other, as yet uncharacterized, intermediate materials were observed also. An additional 0.96 mmol of HCl was added, the resulting suspension filtered, and the filtrate evaporated to dryness to yield pure **5**.

(C) *trans*-$[(C_6H_5N)PN(C_6H_5)_2]_2$ (6)–HCl Reaction. Hydrogen chloride (4.20 mmol) was condensed into a CH_2Cl_2 solution of **6** (2.40 mmol). The mixture was warmed slowly to 25 °C and filtered. The ^{31}P NMR spectrum of the filtrate showed only singlet resonances at δ 200.0 (**5**) and δ 168.9 (unreacted **6**).

***trans*-$[(C_6H_5N)PN(C_6H_5)_2]_2$ (6). (A) $[(C_6H_5N)PCl]_2$ (5)–$(C_6H_5)_2NH$ Reaction.** Diphenylamine (10.1 mmol) in 25 mL of CH_2Cl_2 was added at 25 °C under N_2 to a CH_2Cl_2 solution of **5** (5.0 mmol) and $(C_2H_5)_3N$ (10.0 mmol). After 5 h, the solution was filtered and evaporated to dryness. Recrystallization from CH_2Cl_2 yields **6** as a CH_2Cl_2 solvate (mp 274.5–275.5 °C). Removal of CH_2Cl_2 in vacuo yields pure **6** (yield 90%). Anal. Calcd for $C_{36}H_{30}P_2N_4$: C, 74.48; H, 5.17; P, 10.69; N, 9.66. Found: C, 74.52; H, 5.13; P, 10.60; N, 9.59. ^1H NMR (10% in CD_2Cl_2): δ 6.70–7.40 (complex, C_6H_5). ^{31}P NMR (20% in $CDCl_3$): δ 169.0 (s). IR (Nujol mull): 1595 (vs), 1487 (vs), 1290 (vs), 1268 (s), 1184 (m), 1075 (m), 1028 (m), 958 (m), 905 (s), 883 (s), 750 (s), 735 (s), 692 (s),

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610 (w), 535 (m), 450 (w) cm^{-1}. MS (parent and five most intense envelopes): m/e (relative intensity) 580 (9), 412 (100), 290 (19), 198 (27), 169 (12), 122 (62).

6 is very soluble in $CHCl_3$, moderately soluble in CH_2Cl_2, and slightly soluble in C_6H_6 and $C_6H_5CH_3$.

To a solution of **5** (4.0 mmol) and $(C_2H_5)_3N$ (8.2 mmol) in $CHCl_3$ was added $(C_6H_5)_2NH$ (6.0 mmol) under conditions where the ^{31}P NMR spectra could be monitored periodically. After 25 min, the spectrum of the solution exhibited an equal area doublet ($^2J_{PNP}$ = 36.6 Hz) resonances at δ 124.9 and 163.0 ppm (relative area 8, intermediate **7**), and singlets at δ 168.9 (relative area 2, **6**), 180.2, and 210.4 (d of s, relative area 2, intermediate **8**), 200.7 (s, relative area 4, **5**). After 50 min, **5** disappeared and the δ 168.9 resonance had grown. Attempts to separate reaction components by chromatography or fractional crystallization were unsuccessful.

(B) $C_6H_2N(PCl_2)_2$–$(C_6H_5)_2NH$ Reaction. Diphenylamine (20.0 mmol) in 25 mL of CH_2Cl_2 was added slowly under N_2 to a CH_2Cl_2 solution of $C_6H_5N(PCl_2)_2$ (5.0 mmol) and $(C_2H_5)_3N$ (20.0 mmol). After 7 h, the reaction mixture was filtered and the filtrate evaporated to dryness. Recrystallization from CH_2Cl_2 yielded **6** (mp 274.5–275.5 °C; 60% yield).

(C) $(C_6H_5)_2NPCl_2$–$C_6H_5NH_2$ Reaction. Aniline (11 mmol) was added slowly at 25 °C to a stirred $(C_2H_5)_2O$ solution of $(C_6H_5)_2NPCl_2$ (9.5 mmol). The ^{31}P NMR spectrum of the filtered solution in $CDCl_3$ showed major resonances at δ 117.7 ($[(C_6H_5)_2N](C_6H_5NH)PCl$), 124.9, and 162.9 (d of d, intermediate **7**), 180.1 and 210.2 (d of s, intermediate **8**), and 200.4 (s, **5**) and a resonance for unreacted $(C_6H_5)_2NPCl_2$. Minor resonances appeared at δ 100.4 and 105.0 (**9**) also. Upon further addition of $C_6H_5NH_2$, resonances due to **9** increased, and a resonance at δ 168.8 (s, **6**) appeared. After addition of 13.2 mmol of $C_6H_5NH_2$ and 2 h of refluxing, the sample showed mainly **9** and **6** and only small resonances due to **5**, **7**, and **8**. In some reactions, minor resonances from **3** and **4** were seen also. Attempts to isolate **7** or **8** were unsuccessful.

***cis*-$[(C_6H_5N)_2P_2N(C_6H_5)_2(NHC_6H_5)]$ (9). (A) $C_6H_5NH_2$–6 Reaction.** A $CHCl_3$ solution of $C_6H_5NH_2$ (12 mmol) was added to a solution of **6** (3 mmol) at ambient temperature. After 6 h, the ^{31}P NMR spectrum showed a minor resonance at δ 105.2 (**2**), equal area doublet resonances at δ 100.9 and 104.9 (**9**), and a major resonance at δ 168.8 (unreacted **6**). Further reaction at 25 °C yielded additional **2**; the relative amount of **9** was unchanged. Removal of solvent in vacuo and repeated recrystallization from CH_2Cl_2 yielded **9** (mp 164–166 °C; 55% yield). Anal. Calcd for $C_{30}H_{26}P_2N_4$: C, 71.42; H, 5.19; N, 11.11. Found: C, 72.00; H, 5.23; N, 10.96. ^1H NMR: δ 6.8–7.3 (complex, C_6H_5, area 25), 3.64 (d, $^2J_{PNH}$ = 6.0 Hz, NH, area 1). ^{31}P NMR: δ 104.9 (broad, area 1, d in $^{31}P\{^1H\}$), 100.9 (d, $^2J_{PNP}$ = 12.2 Hz, area 1). IR (KBr): 2880–2970 (vs), 1600 (s), 1500 (s), 1465 (s), 1385 (m), 1290 (s), 1225 (w), 910 (m), 890 (w), 870 (w), 850 (w), 790 (w), 750 (m), 690 (m), 660 (w), 500 (w) cm^{-1}. MS: main envelope at m/e 504 (parent).

The $C_6H_5NH_2$–**6** reaction rate appeared accelerated by traces of $(C_2H_5)_3NHCl$, which is difficult to remove from **6**. Reactions of the most highly purified **6** proceeded only slowly at 25 °C.

(B) $[(C_6H_5)_2N]_2PCl$–$C_6H_5NH_2$ Reaction. To $[(C_6H_5)_2N]_2PCl$ (3.0 mmol) in $(C_2H_5)_2O$ at 0 °C was added a $(C_2H_5)_2O$ solution of $C_6H_5NH_2$ dropwise. The ^{31}P NMR spectrum of the reaction mixture initially showed a resonance at δ 117.7 ($(C_6H_5)_2N(C_6H_5NH)PCl$). Upon further addition of $C_6H_5NH_2$ (up to 5.0 mmol) and 2 h of refluxing, the mixture exhibited minor resonances from $[(C_6H_5N)P(NHC_6H_5)]_3$ (**3**), $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$ (**4**), and **9**. Repeated recrystallization from $(C_2H_5)_2O$ and C_6H_6 yielded pure **9**.

***trans*-$[(C_6H_5N)PN(n\text{-}C_4H_9)_2]_2$ (10).** Di-*n*-butylamine (10.0 mmol) in CH_2Cl_2 (10 ml) was added slowly under N_2 to a stirred solution of **5** (5.1 mmol) and $(C_2H_5)_3N$ (10.0 mmol) in CH_2Cl_2 at 0 °C. After 1 h, the solution was warmed to 25 °C and 50 mL $(C_2H_5)_2O$ was added. Filtration of the $(n\text{-}C_4H_9)_2NH_2Cl$, evaporation of the solution to dryness in vacuo, and recrystallization from CH_2Cl_2 yielded pure **10** (mp 259–261.5 °C; 85% yield). Anal. Calcd for $C_{28}H_{46}N_4P_2$: C, 67.20; H, 9.20; N, 11.20; P, 12.40. Found: C, 66.98; H, 9.10; N, 11.20; P, 12.72. ^1H NMR (15% in $CDCl_3$): δ 6.75–7.30 (area 10, C_6H_5), 0.70–1.0 (area 12, CH_3), 1.20–1.50 (area 16, β- and γ-CH_2) and 2.90–3.25 ppm (area 8, α-CH_2). ^{31}P NMR (20% in $CDCl_3$): δ 164.4 (s). IR (Nujol mull): 1600 (s), 1496 (s), 1280 (s), 1235 (w), 1176 (m), 1075 (w), 1030 (m), 999 (m), 890 (m), 750 (s), 690 (m), 655 (m), 618 (w), 510 (w) cm^{-1}. MS (parent and eight most intense envelopes): m/e (relative intensity) 502 (1), 372 (11), 261 (13), 250 (24), 158 (42), 122 (51), 92 (81), 85 (100), 57 (39).

10 is soluble in CH_2Cl_2 and $CHCl_3$ and moderately soluble in C_6H_6 and $(C_2H_5)_2O$.

***trans*-$[(C_6H_5N)PN(C_2H_5)_2]_2$ (11).** Under conditions analogous to those used in the **5**–$(t\text{-}C_4H_9)_2NH$ reaction, **5**, $(C_2H_5)_3N$, and $(C_2H_5)_2NH$ were allowed to react. Removal of $(C_2H_5)_3NHCl$ by filtration, evaporation of the reaction solution to dryness in vacuo, and recrystallization of the resulting solid from CH_2Cl_2 yield pure **11** (80% yield; mp 104–106 °C; ^{31}P NMR δ 162.6 (lit.[23] mp 104–105 °C; ^{31}P NMR δ 162.2)).

Table I. Crystal and Data Collection Parameters for **5** and **6**

	5[b]	**6**
formula	$[(C_6H_5N)PCl]_2$	$[(C_6H_5N)PN(C_6H_5)_2]_2 \cdot CH_2Cl_2$
M_r	315.08	665.545
mp, °C	153–154	274.5–275.5
space group	$Cmc2_1$	$P2_1/c$
a, Å[a]	16.034 (5)	7.795 (3)
b, Å	11.405 (3)	13.533 (8)
c, Å	7.826 (2)	17.046 (7)
β, deg		103.12 (3)
V, Å^3	1431 (1)	1751 (1)
d_c, g cm^{-3}	1.462	1.26
d_o, g cm^{-3}	1.42	1.30
Z	4	2
$F(000)$	640	692
μ(Mo Kα), cm^{-1}	6.57	3.05
cryst size, mm	0.10 × 0.11 × 0.18; 0.25 × 0.27 × 0.38	0.2 × 0.4 × 0.5
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα
temp, K	290–295	290–295
hkl values scanned	$+h,+k,+l$	$+h,-k,\pm l$
scan type	ω–2θ; θ–2θ	θ–2θ
scan speed, deg min^{-1}	4.0–24.0	4.0–24.0
$2\theta_{max}$, deg	3.0–40.0; 3.0–50.0	3.0–45.0
no. of reflcns collcd	483; 706	2144
abs cor	none	none
no. of reflcns observed	390	801
no. of variables refined	46	88
R	0.061	0.097
R_w	0.077	0.108

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Double entries refer to data for set I and set II, respectively.

***trans*-$[(C_6H_5N)PNH(i\text{-}C_3H_7)]_2$ (12).** $C_3H_7NH_2$ (8.1 mmol) and $(C_2H_5)_3N$ (8.1 mmol) were added dropwise at 24 °C to a stirred toluene solution of **5** (4.06 mmol). After 12 h, $(C_2H_5)_3NHCl$ was removed by filtration and the reaction solution was reduced to one-third volume. ^{31}P NMR spectral analysis showed resonances at δ 150.5 and 97.7 in an 11:1 ratio. Upon further removal of solvent, pure **12** crystallized from solution (yield 75%; mp 127–130 °C). Anal. Calcd for $C_{18}H_{26}N_4P_2$: C, 60.00; H, 7.22; N, 15.56; P, 17.22. Found: C, 60.03; H, 7.23; N, 15.39; P, 17.01. ^1H NMR (20% in C_6H_6): δ 7.20–6.83 (complex, area 10, C_6H_5), 3.63 (multiplet, area 2, CH), 2.50 (d of d, area 2, $^3J_{HNCH}$ = 7.5 Hz, $^2J_{PNH}$ = 32.5 Hz, NH), 0.75 (d, area 12, $^3J_{HCCH}$ = 5.0 Hz, CH_3). $^{31}P\{^1H\}$NMR (20% in $CH_3C_6H_5$): 150.5 (s). IR (KBr pellet): 3350 (w), 2970 (w), 1599 (s), 1497 (s), 1402 (w), 1386 (w), 1369 (w), 1287 (s), 1238 (w), 1185 (w), 1169 (w), 1140 (w), 1080 (w), 1032 (w), 1011 (w), 997 (w), 954 (w), 911 (m), 895 (m), 879 (m), 745 (m), 687 (w), 659 (w), 502 (w), 375 (w) cm^{-1}. MS (parent and four most intense envelopes): m/e (relative intensity) 360 (19), 180 (52), 122 (90), 87 (56).

Attempts to isolate and characterize the δ 97.7 isomer, presumed to be cis, were unsuccessful.

Data Collection and Structural Analysis for *cis*-$[(C_6H_5N)PCl]_2$ (5) and *trans*-$[(C_6H_5N)PN(C_6H_5)_2]_2$ (6). Colorless crystals of **5** and of **6** were mounted and coated with epoxy resin. Cell parameters were determined on the diffractometer and were refined by least-squares fit of the parameters to 15 centered reflections. Crystal and data collection parameters are given in Table I. Because of the high air sensitivity of **5**, several data sets were collected on different crystals. The two best of these were corrected for decline, scaled to the same absolute scale, and averaged (R_{av} = 0.056). Details of the data collection procedures have been discussed previously.[32] The structures were solved by using direct methods[33] and

(32) Chang, C.-C.; Haltiwanger, R. C.; Thompson, M. L.; Chen H.-J.; Norman, A. D. *Inorg. Chem.* **1979**, *18*, 1899.
(33) Manin, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. "MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", University of York, England, and Louvain, Belguim, 1978.

Table II. Final Atomic Positional Parameters for **5** and **6**[a]

atom	*x*	*y*	*z*
	A. Nongroup Atoms of **5**		
P(1)	0	0.2118 (4)	3/4
P(2)	0	0.0656 (4)	0.4967 (8)
Cl(1)	0	0.3811 (3)	0.653 (1)
Cl(2)	0	0.1648 (5)	0.2708 (9)
N(1)	0.0681 (5)	0.1385 (7)	0.623 (1)
	B. Nongroup Atoms of **6**		
P(1)	0.6367 (5)	0.4512 (3)	0.0426 (2)
N(1)	0.412 (1)	0.4413 (7)	0.0097 (5)
N(2)	0.663 (1)	0.4852 (6)	0.1412 (5)
Cl(1)	−0.628 (4)	0.578 (2)	0.533 (3)
Cl(2)	−0.554 (3)	0.507 (2)	0.397 (1)
Cl(3)	−0.345 (3)	0.426 (2)	0.529 (1)
Cl(4)	−0.442 (4)	0.443 (2)	0.429 (2)
Cl(5)	−0.373 (3)	0.438 (2)	0.599 (1)
Cl(1)	−0.558 (7)	0.481 (5)	0.493 (4)

[a] Rigid group parameters are given in the supplementary material.

refined by using full-matrix least-squares procedures.[34] Statistical weights[32] and scattering curves for neutral atoms were used.[35] Tables of observed and calculated structure factor amplitudes are available.[36] For **6**, we were unable to determine a completely satisfactory model for the dichloromethane molecule of solvation. At the point we terminated our efforts, the top two peaks in a difference Fourier resulted from the CH_2Cl_2. Of the top 25 difference peaks, 7 resulted from the CH_2Cl_2, 13 from phenyl hydrogens, and 5 were noise in the vicinity of the rigid groups. Final positional parameters for **5** and **6** are given in Table II.

Results and Discussion

cis-$[(C_6H_5N)PCl]_2$ (**5**) was obtained from the previously reported reactions of excess PCl_3 with aniline (eq 1),[29] from the thermolysis of $C_6H_5N(PCl_2)_2$ (eq 2),[29] and from new reactions

$$2PCl_3 + 6C_6H_5NH_2 \rightarrow 4C_6H_5NH_3Cl + \mathbf{5} \quad (1)$$

$$2C_6H_5N(PCl_2)_2 \rightarrow 2PCl_3 + \mathbf{5} \quad (2)$$

of $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$ (**4**) with PCl_3 (eq 3) or HCl (eq 4) and *trans*-$[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**) with HCl (eq 5).

$$[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5 + 6PCl_3 \xrightarrow[-2(C_2H_5)_3NHCl]{2(C_2H_5)_3N} 3C_6H_5N(PCl_2)_2 + 2(\mathbf{5}) \quad (3)$$

$$[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5 + 7HCl \rightarrow 3C_6H_5NH_3Cl + 2(\mathbf{5}) \quad (4)$$

$$[(C_6H_5N)PN(C_6H_5)_2]_2 + 4HCl \rightarrow 2(C_6H_5)_2NH_2Cl + \mathbf{5} \quad (5)$$

From each reaction, **5** is obtained in only the cis isomeric form (see characterization below). ^{31}P NMR spectral analyses of reaction mixtures in every case showed no reasonance(s) attributable to the trans isomer. No tendency for cis–trans isomerism was observed. Even after **5** was heated in toluene for 24 h at 100 °C, only the cis isomer is present. Thus we conclude that for **5**, like its N(ring)–alkyl analogue $[(t\text{-}C_4H_9N)PCl]_2$, the cis isomer is the thermodynamically stable form.

Compound **5** reacts with $(C_6H_5)_2NH$, $(n\text{-}C_4H_9)_2NH$, $i\text{-}C_3H_7NH_2$, or $(C_2H_5)_2NH$, in the presence of $(C_2H_5)_3N$ (eq 6)

$$[(C_6H_5N)PCl]_2 + 2RR'NH \xrightarrow[-2(C_2H_5)_3NHCl]{2(C_2H_5)_3N} [(C_6H_5N)PNRR']_2 \quad (6)$$

R, R′ = C_6H_5, C_6H_5 (**6**); $n\text{-}C_4H_9$, $n\text{-}C_4H_9$ (**10**); H, $i\text{-}C_3H_7$ (**12**); C_2H_5, C_2H_5 (**11**)

to form the new 2,4-diamino-1,3-diphenyl-1,3,2,4-diazadiphosphetidines $[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**), $[(C_6H_5N)PN(n\text{-}C_4H_9)_2]_2$ (**10**), and $[(C_6H_5N)P(i\text{-}C_3H_7NH)]_2$ (**12**) and the previously reported $[(C_6H_5N)PN(C_2H_5)_2]_2$ (**11**).[23] Examination of **5**–$(C_6H_5)_2NH$, **5**–n-$(C_4H_9)_2NH$, or **5**–$(C_2H_5)_2NH$ reaction mixtures shows only single low-field ^{31}P NMR resonances, in the δ 162.2–169.0 range. From the **5**–$i\text{-}C_3H_7NH_2$ reaction two products form, giving resonances at δ 150.5 and 97.7 in a 10–11:1 ratio. From a single-crystal X-ray study of **6** (below) and the close correlation of ^{31}P NMR chemical shifts of **6**, **10**, **11**, and **12**, we conclude that the sole (or dominant in the case of **12**) isomer to be the trans isomer. If initial information of a cis product occurs, isomerization occurs too rapidly to allow detection in our ex-

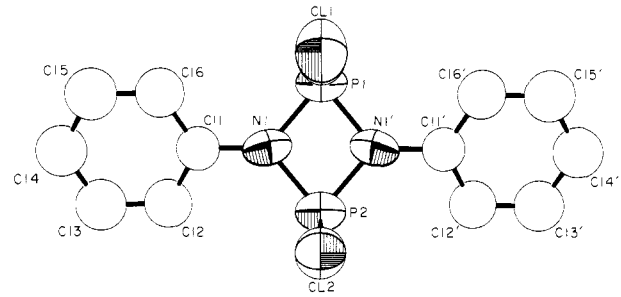

Figure 1. Structure of *cis*-$[(C_6H_5N)PCl]_2$ (**5**). ORTEP thermal ellipsoids represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

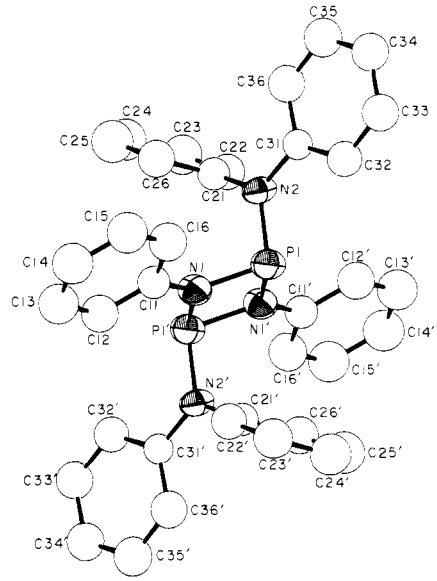

Figure 2. Structure of *trans*-$[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**). ORTEP thermal ellipsoids represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

Table III. Selected Structural Parameters for *cis*-$[(C_6H_5N)PCl]_2$ (**5**) and *trans*-$[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**)

5		**6**	
	(a) Bond Distances (Å)		
P(1)–N(1)	1.698 (10)	P(1)–N(1)	1.722 (9)
P(2)–N(1)	1.691 (10)	P(1)–N(1)′	1.703 (9)
P(1)–Cl(1)	2.075 (6)	P(1)–N(2)	1.709 (9)
P(2)–Cl(2)	2.099 (9)	N(1)–C(11)	1.404 (13)
N(1)–C(11)	1.423 (9)	N(1)–C(21)	1.438 (13)
		N(1)–C(31)	1.429 (10)
	(b) Bond Angles (deg)		
P(1)–N(1)–P(2)	99.7 (4)	P(1)–N(1)–P(1)′	101.1 (5)
N(1)–P(1)–N(1)′	80.1 (3)	N(1)–P(1)–N(1)′	78.9 (5)
N(1)–P(2)–N(1)′	80.5 (4)	N(1)–P(1)–N(2)	103.1 (5)
Cl(1)–P(1)–N(1)	104.1 (4)	N(1)–P(1)–N(2)′	104.3 (4)
Cl(2)–P(2)–N(1)	103.1 (4)	P(1)–N(1)–C(11)	129.1 (7)
P(1)–N(1)–C(11)	130.9 (8)	P(1)′–N(1)–C(11)	129.7 (7)
P(2)–N(1)–C(11)	129.3 (8)	P(1)–N(2)–C(21)	120.2 (6)
		P(1)–N(2)–C(31)	121.0 (7)
		C(21)–N(1)–C(31)	118.8 (7)

(34) Ibers, J. A. Northwestern Crystallographic Computing Library, Northwestern University, Evanston, IL, 1975.
(35) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(36) See paragraph at end of paper regarding supplementary material.

periments. Also, these data further substantiate the general correlation[5] that in both the N(ring)–alkyl- and N(ring)–aryldiazadiphosphetidines the "low" and "high" field ^{31}P NMR resonances correlate with trans and cis isomers, respectively.

Single-crystal X-ray structural analyses show **5** and **6** to have the cis and trans structures shown in Figures 1 and 2, respectively. Selected bond distance and bond angle data are listed in Table III. Compounds **5** and **6** have crystallographically imposed C_s and C_i molecular symmetry, respectively. **5** contains a plane of symmetry perpendicular to the P_2N_2 ring, which includes atoms P(1), C(11), P(2), and C(12). **6** contains an inversion center of symmetry. In both **5** and **6**, the N atoms of the P_2N_2 rings are trigonal planar, the angles around N atoms summing to ca. 360 °C. The C_6H_5 rings attached to the P_2N_2 ring approach coplanarity with the latter; dihedral angles between the C_6H_5 and P_2N_2 rings are 18.7° and 8.5° in **5** and **6**, respectively. A tendency towards aryl group–P_2N_2 ring coplanarity has been observed in other 1,3-diaryldiazadiphosphetidines,[6,19] and it is possible that deviations from coplanarity result from packing forces in the solid. The *exo*-$(C_6H_5)_2N$ moieties in **6** assume an orientation around the *exo*-P–N bonds such that the P(1), N(2), C(31), and C(21) plane is nearly perpendicular (dihedral angle = 91.0°) to the P_2N_2 plane, again a conformational situation seen previously in other phosphorus(III) diazadiphosphetidines.[3,6,10,22,19]

The bond distances and angles in **5** and **6** are closely similar to those of other previously reported phosphorus(III) diazadiphosphetidines, particularly *cis*-$[(t\text{-}C_4H_9N)PCl]_2$ (**17**)[7] and the 2,4-bis(phenylamino)substituted 1,3-diphenyldiazadiphosphetidines **2**–**4**.[6,19] Irrespective of the substituents on either the ring N or P atoms, ring angles and distances vary only slightly. The P_2N_2 ring parameters of **5** agree closely with those of **17**, except that the ring in **5** within experimental error is planar and in **17** is slightly bent.[7] Ring puckering in **17** occurs so as to allow an increase in the Cl---Cl intramolecular nonbonded distance. The Cl---Cl distance in **5** is 3.88 (1) Å (4.10 Å in **18**), slightly longer than the van der Waals distance of 3.6–3.8 Å.[37] The intermolecular distance of 3.392 (8) Å between P(2)–Cl(2) at coordinate positions $-x, -y, {}^1/_2 + z$ is short and may suggest the occurrence of weak Cl bridge bonding between molecules, as can occur in phosphorus(V) halides.[38] This interaction might cause lengthening of the intramolecular P(2)–Cl(2) distance; however, we are unable to determine if the P(1)–Cl(1) and P(2)–Cl(2) distances of 2.099 (9) and 2.075 (6) Å are statistically different.

It is not surprising that the cis isomer of **5** forms readily in condensation reactions (eq 1 and 2) since freely rotating acyclic intermediates are undoubtedly involved prior to final P_2N_2 ring closure. Also, in cleavage reactions (eq 3 and 4) if both *exo*-P–N bonds of the cis reactants are cleaved (by either HCl or PCl_3) by the same mechanism, a cis product is expected. However, formation of *cis*-**5** in the **6**–HCl reaction (eq 5) is more complex. If **5** forms without P_2N_2 ring opening and if both *exo*-P–N bonds are cleaved by the same mechanism, a trans isomer should form. If this occurs and ring opening does not occur, an unusually low barrier to inversion at phosphorus must be present, an unlikely situation since these are generally in the 25–33 kcal/mol range.[38,39] It seems more likely that the P_2N_2 ring system dissociates partially or completely to species that upon recombination yield the more stable cis isomer.

From several reactions, unsymmetrically substituted diazadiphosphetidines were obtained and their isomeric forms determined. Reaction of **6** with $C_6H_5NH_2$ results in the stepwise formation of **2** via formation of intermediate **9**:

$$\underset{\mathbf{6}}{[(C_6H_5N)PN(C_6H_5)_2]_2} + C_6H_5NH_2 \rightarrow (C_6H_5)_2NH + \underset{\mathbf{9}}{[(C_6H_5N)_2P_2N(C_6H_5)_2(NHC_6H_5)]} \quad (7)$$

Table IV. Equilibrium Isomer Composition of Selected 1,3,2,4-Diazadiphosphetidines

compd	N(ring) substituents	exo substituents	preferred isomer[a]
2[b]	C_6H_5	NHC_6H_5, NHC_6H_5	cis
3[c]	C_6H_5	$N(C_6H_5)P(NHC_6H_5)_2$, NHC_6H_5	cis
4[d]	C_6H_5	$N(C_6H_5)P_2(NC_6H_5)_2NHC_6H_5$, NHC_6H_5	cis
5	C_6H_5	Cl, Cl	cis
6	C_6H_5	$N(C_6H_5)_2$, $N(C_6H_5)_2$	trans
9	C_6H_5	$N(C_6H_5)_2$, NHC_6H_5	cis
10	C_6H_5	$N(n\text{-}C_4H_9)_2$, $N(n\text{-}C_4H_9)_2$	trans
11[e]	C_6H_5	$N(C_2H_5)_2$, $N(C_2H_5)_2$	trans
12	C_6H_5	$NH(i\text{-}C_3H_7)$, $NH(i\text{-}C_3H_7)$	trans:cis = 11:1
13[e]	C_6H_5	$N(CH_3)_2$, $N(CH_3)_2$	trans:cis = 10:1
14[e]	$p\text{-}ClC_6H_4$	$N(CH_3)_2$, $N(CH_3)_2$	trans
15[e]	$p\text{-}CH_3C_6H_4$	$N(CH_3)_2$, $N(CH_3)_2$	trans
16[e]	$p\text{-}CH_3OC_6H_4$	$N(CH_3)_2$, $N(CH_3)_2$	trans
17[f]	$t\text{-}C_4H_9$	Cl, Cl	cis
18[e]	$t\text{-}C_4H_9$	$N(CH_3)_2$, $N(CH_3)_2$	cis
19[e]	$t\text{-}C_4H_9$	$N(C_2H_5)_2$, $N(C_2H_5)_2$	cis

[a] Only one isomer observed, unless indicated otherwise. [b] Reference 40. [c] Reference 19. [d] Reference 6. [e] Reference 23. [f] Reference 7.

9, which exhibits a pair of ^{31}P NMR spectral doublet resonances at δ 100.9 and 104.0, is the only species seen in the reaction prior to formation of **2**. Reaction of $[(C_6H_5)_2N]_2PCl$ with $C_6H_5NH_2$ in the presence of $(C_2H_5)_3N$ proceeds smoothly to **9** along with **3** and **4** as the only diazadiphosphetidine products. The close correlation between the ^{31}P NMR chemical shifts of **9** and those of other *cis*-(phenylamino)-*N*(ring)-aryldiazadiphosphetidines, e.g. **2**–**4**,[6,19] suggests that **9** is a cis isomer. Since no evidence for a trans form of **9** is obtained in either the exo group cleavage reaction (**6**–$C_6H_5NH_2$) or the ring formation reaction ($[(C_6H_5)_2N]_2PCl$–$(C_6H_5NH_2)$), we conclude the cis isomer of **9** is thermodynamically favored.

Evidence for mixed chloro/amino unsymmetrically substituted diazadiphosphetidines and information about their cis vs trans isomer preference were obtained, although the species could not be isolated or characterized free of their respective reaction mixtures. Reaction of **5** with a deficiency of $(C_6H_5)_2NH$ in the presence of $(C_6H_5)_3N$, produced initially a major pair of equal area doublets at δ 124.9 and 163.0 (intermediate **7**) and a less intense pair of singlets at δ 180.2 and 200.7 (intermediate **8**). Upon further reaction with $(C_6H_5)_2NH$ these disappeared, and the product $[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**) formed. Identical ^{31}P NMR resonances appear in reactions of $(C_6H_5)_2NPCl_2$ with $C_6H_5NH_2$. Compounds **7** and **8**, from their ^{31}P NMR spectral and solution behavior are tentatively characterized as *cis*- and *trans*-$[(C_6H_5N)_2P_2(Cl)N(C_6H_5)_2]$. The δ 124.9 and 163.0 peaks are assigned to $(N)_3P$- and $(N)_2(Cl)P$-bonded phosphorus atoms, respectively, of a cis isomer. The $^2J_{PP}$ value of 36.6 Hz for **7** is close to that seen in other unsymmetrically substituted *cis*-P_2N_2 diazadiphosphetidines.[19,26] The absence of coupling between phosphorus atoms in **8** is perhaps not surprising, since in trans isomers coupling constants are known frequently to be smaller than in the cis analogues.[5,26]

The structural information about phosphorus(III) *N*(ring)-aryldiazadiphosphetidines now available and summarized in Table IV allows several generalizations and comparisons to be made:

(i) The *N*(ring)-aryldiazadiphosphetidines prefer trans isomers when both *exo*-amino groups are relatively bulky (e.g. **6**, **10**–**16**). With smaller substituents the cis form becomes more stable (e.g. **12** and **14**) and is found exclusively in systems containing at least one primary amino (RNH) group (**2**–**4**, **9**). In contrast, with *N*(ring)-alkyl-substituted diazadiphosphetidines the cis isomers generally predominate or are favored completely.[3–24] This has been shown for 2,4-dihalo, 2,4-dialkoxy, and 2,4-bis(dialkylamino) [RR'N = $(CH_3)_2N$, $(C_6H_5)_2N$ $C_5H_{10}N$, etc.] derivatives by others[3–24] and for monoalkylamino derivatives [RNH = CH_3NH, C_2H_5NH, $i\text{-}C_3H_7NH$, and $t\text{-}C_4H_9NH$] by us.[40,41]

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(ii) Both $[(C_6H_5N)PCl]_2$ (**5**) and $[(t\text{-}C_4H_9N)PCl]_2$ (**17**)[7] are thermodynamically stable as cis isomers.[2] In neither case has evidence for a trans isomer been obtained. Apparently, the *cis* Cl-PN_2P-Cl ring unit is sufficiently stable that replacement of *N*(ring)-C_6H_5 with *t*-C_4H_9 groups is not electronically or sterically significant enough to cause a change in isomer preference.

(iii) The P_2N_2 rings of the *cis*-*N*(ring)-aryldiazadiphosphetidines X-ray crystallographically characterized so far (**3**[6], **4**[19] and **5**) are planar or nearly planar. In contrast, the P_2N_2 rings of *cis*-*N*-(ring)-alkyldiazadiphosphetidines are puckered,[5] bent so as to increase the exo-substituent intramolecular distances. This stabilization of a P_2N_2 ring could arise through aryl group π interaction with p orbitals of the ring nitrogen atoms. Because the *N*(ring)-aryl-substituted P_2N_2 rings pucker only slightly to allow minimization of endo-exo- or exo-exo-group interactions,[5] their ground-state energies may be increased relative to those of the trans isomers and relative to those of cis-*N*(ring)-alkyl-substituted compoounds. This effect, in systems with large exo groups (e.g. **6**, **10-16**), could ultimately cause cis isomers to become less stable than the trans forms.

(iv) Trans isomers are favored for $[(C_6H_5N)PN(C_2H_5)_2]_2$ (**11**) and the series **13-16**. In contrast, the *N*(ring)-alkyl analogues $[(t\text{-}C_4H_9N)PN(CH_3)_2]_2$ (**18**) and $[(t\text{-}C_4H_9N)PN(C_2H_5)_2]_2$ (**19**) prefer the cis form. Since the *t*-C_4H_9 groups are bulkier than the C_6H_5 units, this result appears *contra* steric. However, this paradox might arise because the P_2N_2 ring in **11** and **13-16** does not pucker and yield a stable cis form. In **18** and **19**, ring puckering allows relief of exo-group-endo-group repulsion and causes the assumption of the stable cis isomeric form.

The results obtained so far suggest that *N*(ring)-aryldiazadiphosphetidine isomer preference is more sensitive to exo-group substitution than are the *N*(ring)-alkyl-substituted analogues. This might be related to the tendency toward P_2N_2 ring planarity in *N*(ring)-aryl systems vs. nonplanarity in the *N*-(ring)-alkyl compounds. This possibility is being investigated further currently.

Acknowledgment. Support of this work by grants from the National Science Foundation (CHE-7909497 and CHE-8312856) and a fellowship for H.-J.C. from the Chinese Ministry of Defense are gratefully acknowledged.

Supplementary Material Available: Listings of observed and calculated structure factors, thermal and positional parameters, derived and rigid group positional and thermal parameters, and equations of planes and atom derivations from planes (11 pages). Ordering information is given on any current masthead page.

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Coordination Compounds of a Pentadentate Pyrazole Derivative of Diaminopropane. Crystal Structure of Aqua(*N*,*N*,*N*′-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane)cobalt(II) Diperchlorate Hydrate, $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$

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Received May 1, 1985

Coordination compounds of the type $M(ap3d)(anion)_2(H_2O)_x$ are described in which M is one of the divalent metals Co, Ni, Cu, and Zn, the anion is ClO_4^- and BF_4^-, ap3d stands for $C_{21}H_{34}N_8$ or *N*,*N*,*N*′-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane, and $x = 1-3$. The compounds have been characterized by several analytical techniques and spectroscopic methods. In all compounds the ligand is pentadentate. The six-coordination is completed by one water molecule. The coordination geometry is distorted-octahedral as deduced from ligand field spectra for Co(II), Ni(II), and Cu(II) and powder isomorphism within this group. The noncoordinating water molecules are hydrogen bonded to the anions. The compound $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$ crystallizes in the space group $P2_1/n$ (monoclinic) with $a = 16.927$ (4) Å, $b = 18.853$ (4) Å, $c = 9.926$ (7) Å, $\beta = 102.02$ (3)°, and $Z = 4$. The structure has been solved by heavy-atom techniques and refined by least-squares methods to a residual *R* value of 0.050 ($R_w = 0.057$). The coordination geometry around the Co(II) ion can be described as a distorted octahedron formed by the five nitrogen atoms of the ligand ap3d and a water molecule. The bonding distances are about 2.1 Å. A second water molecule is hydrogen bonded to the coordinated water molecule and to the perchlorate ions.

Introduction

As part of a research program on the synthesis and structure of coordination compounds modeling the active site in metalloproteins we reported a novel method for the synthesis of N-substituted pyrazole chelates and a number of their coordination compounds.[1-5] One of the factors governing the properties of a metalloprotein is the steric constraint exerted by the protein on the active site containing the metal ion. Seven-coordinate compounds of the pyrazole derivative of 1,2-diaminoethane have been reported[5] with unusually long metal-nitrogen distances, their geometry being described as bicapped-octahedral. To verify whether only sterical factors are involved in producing this unusual coordination geometry, a study of the coordination behavior of a pyrazole derivative of 1,3-diaminopropane has been undertaken. Several coordination compounds of *N*,*N*,*N*′-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane (ap3d) have been synthesized, and the crystal structure of $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$ has been solved.

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Experimental Section

The compound *N*,*N*,*N*′-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane (ap3d) was synthesized by the condensation of 1,3-diaminopropane and *N*-(hydroxymethyl)-3,5-dimethylpyrazole in acetonitrile as described by Driessen.[1]

All other chemicals were commercially available, were of sufficient purity, and were used without further treatment.

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