illustrated. The nonlinear least-squares method along with iteration for the free ligand concentration, e.g. pyridine, allows one to determine equilibrium constants with small values that would be overlooked by conventional methods. To stress the importance of this, plots of $10^{-\Delta E/0.06}$ vs. $[\mathrm{py}]_{\mathrm{added}}$ as determined by a linear least-squares regression analysis had slopes with correlation coefficients of 0.996 but intercepts of −15. After an iterative calculation for $[\mathrm{py}]_{\mathrm{free}}$, the intercept improved to 1.1 One might at first be tempted to discount the intercept as spurious and assign the equilibrium to a one-step process. Analysis of the data by the more rigorous nonlinear least-squares method, however, demonstrates in a convincing way the existence of a second step. This method, where applicable, may also be superior to absorption methods, which often are complicated by overlapping bands, low extinction coefficients, or a combination of the two.

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Synthesis and X-ray Structure of *cis*-1,3-Di-*tert*-butyl-2,4-bis(pentafluorophenoxy)-1,3,2,4-diazadiphosphetidine

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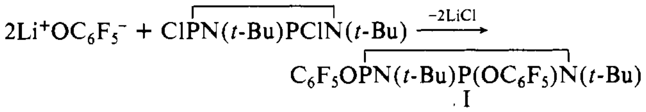
Substituted 1,3,2,4-diazadiphosphetidines have received much attention from both synthetic and structural chemists.[2] For this ring system it is possible to assign geometric isomers on the basis of ^{31}P NMR chemical shifts with roughly a 80–90 ppm difference in chemical shifts for the cis and trans isomers (Table I). However, in some cases there is considerable overlap of these shift values. In this instance, an X-ray crystal structure determination was used to confirm the cis conformation of the title compound.

When lithium pentafluorophenoxide was reacted with *cis*-1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazaphosphetidine in a mixture of diethyl ether and hexane at −78 °C, I was obtained:



$$2\mathrm{Li}^+\mathrm{OC_6F_5}^- + \mathrm{Cl}\overline{\mathrm{PN}(t\text{-Bu})\mathrm{PClN}}(t\text{-Bu}) \xrightarrow{-2\mathrm{LiCl}} \mathrm{C_6F_5O}\overline{\mathrm{PN}(t\text{-Bu})\mathrm{P(OC_6F_5)N}}(t\text{-Bu})$$

I

Upon recrystallization from pentane and diethyl ether, clear, colorless crystals were isolated (mp 78 °C; 70% yield). The major isomer that formed was cis in spite of the bulky pentafluorophenoxy groups substituted at phosphorus. This is in keeping with other examples.[3,4] However, the ^{31}P chemical shift of I is found considerably farther downfield than values for the cis isomers of other compounds with the exception of the chloro derivative. In fact, the chemical shift value falls in the upper range of chemical shifts for trans isomers (Table I).

Table I. ^{31}P NMR Chemical Shifts for Derivatives of 1,3,2,4-Diazadiphosphetidines (N Substituent = *tert*-Butyl)

	ppm[a]	
P substituent	trans (low field)	cis (high field)
$C_6F_5O^b$	252	162.6
$(CH_3)_2N^c$	184.7	95.0
$C_4H_8N^c$	165.1	76.7
$C_5H_{10}N^c$	182.3	91.5
$C_2H_5O^d$	209.7	131
Cl		207.7

[a] Relative to 85% H_3PO_4. [b] This work. [c] See ref 3. [d] See ref 4.

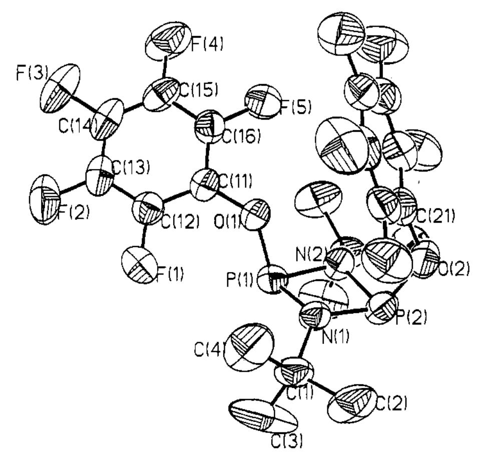


Figure 1. ORTEP view of *cis*-I showing the atom-numbering scheme. Important parameters [distances (Å); angles (deg)]: P(1)–N(2) = 1.694 (3), P(2)–N(2) = 1.701 (3), P(2)–N(1) = 1.701 (3), P(1)–N(1) = 1.695 (3), P(1)–O(1) = 1.697 (3), P(2)–O(2) = 1.675 (3), O(1)–C(11) = 1.359 (4); P(1)–O(1)–C(11) = 119.3 (2), N(1)–P(1)–N(2) = 82.5 (1), P(1)–N(1)–P(2) = 91.1 (1), N(1)–P(2)–N(2) = 82.1 (1), P(2)–O(2)–C(21) = 124.9 (2).

The crystal structure analysis[5] was based on 3514 total reflections refined to $R = 0.0522$. Even though the pentafluorophenyl rings are indeed cis, one ring is exo relative to the P_2N_2 ring, as would be expected, while the other is found at an angle of 60° with respect to the first C_6F_5 ring and also is endo to the extent that a line passing through the center and perpendicular

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(1) Department of Chemistry, Washington State University, Pullman, WA 99164.

(2) Keat, R. *Top. Curr. Chem.* **1982**, *102*, 89 and references therein.

(3) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1980**, 321.

(4) Keat, R.; Rycroft, D. S.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1224.

(5) A colorless crystal of dimensions 0.18 mm × 0.37 mm × 0.44 mm was coated in epoxy glue and mounted on the end of a glass fiber. Data were collected on a Nicolet R3m/E automated four-circle diffractometer using Mo Kα ($\bar{\lambda} = 0.71069$ Å) radiation with a graphite monochromator.[6] The following data were obtained from a least-squares refinement of the angular settings of 25 well-centered reflections in the range $20° < 2\theta < 31°$ at room temperature for $C_{20}H_{18}N_2O_2F_{10}P_2N_2$: monoclinic space group $P2_1/n$, with $a = 9.941$ (3) Å, $b = 17.842$ (4) Å, $c = 13.645$ (4) Å, $\beta = 90.87$ (2)°, $V = 2420$ (1) Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.57$ g cm^{-3}. Data were collected to $2\theta(\max) = 45°$ in the $h, k \geq 0$, all l octants via 2° ω scans, and three check reflections, (261), $(31\bar{4})$, and (323), were monitored every 50 reflections. Eleven reflections were rejected from the data set because of asymmetric peak shapes, and an Lp correction and a crystal decay correction, based on a curve fitted to the intensities of standards, were applied. An empirical absorption correction was also applied to the data ($\mu = 2.9$ cm^{-1}, $T(\max) = 0.80$, $T(\min) = 0.78$, $R_{\mathrm{merge}} = 0.123$ before and 0.0116 after the correction). A total of 3514 reflections were collected, yielding 3149 unique reflections of which 2260 with $|F| > 3\sigma$ were retained. The Nicolet SHELXTL program package was used for structure solution and refinement with direct methods as the solution technique. Positions of all but three non-hydrogen atoms were identified from the electron density map produced after direct-methods solution and refinement. The rest of the atom positions, including hydrogen, were identified from subsequent electron density difference maps. The structure was refined by using a cascading blocked least-squares method. Refinement of all non-hydrogen atom positions with isotropic thermal parameters and unit weights gave $R = 0.132$. Refinement of 326 parameters yielded $R = 0.0528$, $R_w = 0.0407$, and GOF = 1.576. The C–H bond distance was constrained to 0.96 Å. $\Delta/\sigma(\mathrm{mean}) = 0.013$. $\Delta/\sigma(\max) = 0.042$. Largest peak on final difference map: 0.239 e/Å^3, 1.02 Å from HZc.

(6) Campana, C. F.; Shepard, D. F.; Litchman, W. M. *Inorg. Chem.* **1981**, *20*, 4039.

0020-1669/87/1326-2015$01.50/0

to the P_2N_2 plane intersects the para carbon atom of this second phenyl ring (Figure 1).

The P_2N_2 ring is very slightly puckered, with the nitrogen atoms lying 0.05 Å above the least-squares plane calculated from the position of the phosphorus–nitrogen atoms with the phosphorus atoms lying 0.05 Å below the plane. This is particularly interesting because the cis isomer would be expected to have a more puckered P_2N_2 plane in order to relieve the steric interactions of the phenyl rings.[7] Since this has not occurred, the steric repulsions are alleviated by structural modifications that are observed only rarely in similar systems. Thus, the P(2)–O(2)–C(21) and P(1)–O(1)–C(11) angles are 124.9 (2) and 119.3 (2)°, respectively. These are relatively large compared with the expected approximately tetrahedral angle. The magnitudes of the P–N bond lengths are the same within experimental error (1.698 (3) Å). These bond lengths are comparable to the P–N bond length of the parent *cis*-1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazaphosphetidine,[8] where the P–N bond is 1.689 (5) Å.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Natioal Science Foundation (Grant CHE 84-04974), and to the U.S. Air Force Office of Scientific Research (Grant 82-0247) for support of this research. The support of NSF Grant CHE-8408407 and of the Boeing Co. for the establishment of the X-ray diffraction facility at Washington State University is gratefully acknowledged.

Supplementary Material Available: Listings of atomic positional and thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(7) Keat, R.; Keith, A. N.; MacPhee, A.; Muir, K. W.; Thompson, D. G. *J. Chem. Soc., Chem. Commun.* **1978**, 372.

(8) Muir, K. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1971**, 1405.

Additions and Corrections

1986, Volume 25

Shin-ichi Nishikiori and Toschitake Iwamoto*: Crystal Structures of (α,ω-Diaminoalkane)cadmium(II) Tetracyanonickelate(II)–Aromatic Molecule Inclusion Compounds. 3. (1,4-Diaminobutane)cadmium(II) Tetracyanonickelate(II)–Pyrrole (1/1), (1,4-Diaminobutane)cadmium(II) Tetracyanonickelate(II)–Aniline (2/3), and (1,4-Diaminobutane)cadmium(II) Tetracyanonickelate(II)–*N*,*N*-Dimethylaniline (1/1).

Page 791. The values in Table IV are incorrect. A revised version of this table is printed below.

Supplementary Material Available: A revised table of anisotropic thermal parameters for **3** (1 page). Ordering information is given on any current masthead page.

Table IV. Final Atomic Parameters for **3**

	G	x/a	y/b	z/c	$B_{eq}/\text{Å}^2$
Cd	0.5	−0.02612 (5)	0.25	−0.02234 (7)	2.01 (1)
Ni	0.5	0.0	0.0	0.5	2.02 (2)
C(1)	1.0	0.0168 (5)	0.0885 (3)	0.3333 (6)	2.5 (2)
C(2)	1.0	−0.0479 (5)	0.0852 (3)	0.6484 (6)	2.5 (1)
C(3)	0.5	0.2521 (9)	0.25	−0.162 (1)	5.2 (4)
C(4)	0.5	0.411 (1)	0.25	−0.127 (1)	5.1 (4)
C(5)	0.5	0.455 (1)	0.25	−0.283 (2)	8.2 (7)
C(6)	0.5	0.6119 (8)	0.25	−0.254 (1)	4.7 (4)
C(7)	0.5	0.5	0.0	0.0	5.0
C(8)	0.5	0.354 (1)	−0.0197 (9)	−0.052 (2)	5.0
C(9)	1.0	0.2983 (7)	0.0188 (4)	0.106 (1)	5.0
C(10)	0.5	0.391 (1)	0.054 (1)	0.260 (2)	5.0
C(11)	1.0	0.5463 (7)	0.0747 (5)	0.313 (1)	5.0
C(12)	0.5	0.609 (1)	0.034 (1)	0.164 (2)	5.0
N(1)	1.0	0.0243 (5)	0.1423 (3)	0.2312 (6)	3.7 (2)
N(2)	1.0	−0.0730 (5)	0.1373 (3)	0.7401 (6)	3.4 (2)
N(3)	0.5	0.2174 (6)	0.25	0.010 (1)	4.1 (3)
N(4)	0.5	0.7326 (7)	0.25	−0.064 (1)	4.9 (3)
N(5)	0.5	0.562 (1)	−0.0426 (8)	−0.160 (2)	5.0
H(1)	1.0	0.2704	0.1924	0.0958	5.0
H(2)	1.0	0.2086	0.1924	−0.2481	5.0
H(3)	1.0	0.4653	0.1924	−0.0248	5.0
H(4)	1.0	0.4120	0.1924	−0.3847	5.0
H(5)	1.0	0.6270	0.1924	−0.3291	5.0
H(6)	1.0	0.7161	0.1924	0.0105	5.0

—Toschitake Iwamoto