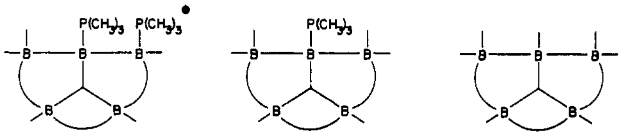
Figure 2. The extremely large value of J_{BP} (220 Hz) is noteworthy.

C. Pentaborane(9) and Trityl Tetrafluoroborate. Pentaborane(9) did not react with trityl tetrafluoroborate in dichloromethane at room temperature.

D. Conclusion. The reactions described above demonstrated that the attachment of electron-donating trimethylphosphine to pentaborane enhances the hydridic behavior of the borane hydrogen atoms: The ease of hydride abstraction by the trityl cation increases with the number of trimethylphosphines attached to pentaborane.

The new polyboron complex cation $B_5H_8{\cdot}2P(CH_3)_3^+$ is isostructural with its isoelectronic, neutral and anionic counterparts $B_5H_9{\cdot}P(CH_3)_3$[5,6] and $B_5H_{10}^-$:[7]



Thus, the isoelectronic–isostructural feature observed for the triboron and tetraboron trios is now extended to the pentaboron trio. It is noted that, among $B_5H_9{\cdot}2P(CH_3)_3^+$, $B_5H_9{\cdot}P(CH_3)_3$, and $B_5H_{10}^-$, the anion is most fluxional with respect to its borane hydrogen atom migration[6,7] and the cation is least fluxional. The same trend has been observed for the corresponding trios of tri- and tetraboron.[1,3] The other new cation, $B_5H_8{\cdot}P(CH_3)_3^+$, belongs to a new family of polyboron complex cations with the general formula $B_nH_{n+3}{\cdot}P(CH_3)_3^+$, and it is isostructural also with its isoelectronic, neutral counterpart B_5H_9.

Two different salts of the trityl cation were used in this study. The BF_4^- salt yielded reasonably stable salts of the pentaboron cations, but the PF_6^- salt did not. Whenever the PF_6^- salt was used, BF_4^- and $BF_3{\cdot}P(CH_3)_3$ were formed. The interaction of the PF_6^- ion with borane species is an interesting subject of a separate study, and the results will be reported at a later date upon completion of the study.

Experimental Section

General Information. Conventional vacuum-line techniques were used throughout for the handling of air-sensitive, volatile compounds. Nitrogen gas filled, plastic bags were used for the transfer of air-sensitive solids. Pentaborane(9) (Callery Chemical Co.) was fractionated and treated with trimethylphosphine (laboratory stock, prepared by a literature method[8]) to prepare the samples of $B_5H_9{\cdot}2P(CH_3)_3$.[9] The sample of $B_5H_9{\cdot}P(CH_3)_3$ was prepared from B_5H_{11} and $B_2H_4{\cdot}2P(CH_3)_3$ by the method described previously.[6] The BF_4^- and PF_6^- salts of the trityl cation (Aldrich Chemical Co. and Alfa Products) were recrystallized from dichloromethane. The NMR spectra were recorded on a Varian XL-100 or XL-300 spectrometer. Chemical shifts for ^{11}B and ^{31}P resonances were recorded with reference to the $BF_3{\cdot}O(C_2H_5)_2$ and 85% orthophosphoric acid signals, respectively. For ^1H resonances, the shift of dichloromethane was taken to be at 5.28 ppm. The reactions of the pentaborane compounds with the trityl salts were performed in 10-mm-o.d. Pyrex tubes. The tubes containing reaction mixtures were placed in the probe of the NMR instrument to monitor the reactions.

Reaction of $B_5H_9{\cdot}2P(CH_3)_3$ with Trityl Cation. A 0.49-mmol sample of $B_5H_9{\cdot}2P(CH_3)_3$ was dissolved in about 2 mL of CH_2Cl_2 in the reaction tube, and a 0.61-mmol sample of $C(C_6H_5)_3^+BF_4^-$ was added in the tube above the frozen solution. As the reaction mixture was agitated by shaking the tube in a −80 °C bath, the dark yellow color of the trityl cation changed rapidly to a faint yellow. At this stage the original $B_5H_9{\cdot}2P(CH_3)_3$ had been completely converted into the $B_5H_8{\cdot}2P(CH_3)_3^+$ cation. As the tube was allowed to warm to room temperature, a clear, straw yellow solution resulted. At this point the solution did not contain any boron compound other than the BF_4^- salt of the pentaboron cation. The volatile components were evaporated under vacuum, and the resulting pale yellow residue was washed with toluene and then leached with CH_2Cl_2. By evaporation of the solvent from the leachate, a white solid of the $B_5H_8{\cdot}2P(CH_3)_3^+BF_4^-$ salt was obtained. The solid was contaminated slightly with small amounts of decomposition products, which were produced during the isolation process. The reaction with $C(C_6H_5)_3^+PF_6^-$ (1:1 molar ratio, 0.46 mmol of each reactant) proceeded similarly. However, the formation of BF_4^- was observed at higher temperatures (about −20 °C) and was fast above 0 °C.

Reaction of $B_5H_9{\cdot}P(CH_3)_3$ with Trityl Cation. A 0.59-mmol sample of $B_5H_9{\cdot}P(CH_3)_3$ and 0.64 mmol of $(C_6H_5)_3^+BF_4^-$ were mixed in about 2 mL of CH_2Cl_2 in a reaction tube. At −80 °C most of the trityl salt remained undissolved, and the solution was dark yellow. When the mixture was allowed to warm to −30 °C and agitated by shaking, the trityl salt quickly disappeared and the solution became pale yellow and turbid. At this point $B_5H_9{\cdot}P(CH_3)_3$ had been converted into the $B_5H_8{\cdot}P(CH_3)_3^+$ cation. As the tube was allowed to warm to room temperature, the solution became clear. To isolate the $B_5H_8{\cdot}P(CH_3)_3^+BF_4^-$ salt, this solution was treated in the same manner as the $B_5H_8{\cdot}2P(CH_3)_3^+$ cation solution. (See above.) During this isolation process, however, a small portion of the salt decomposed; thus, the product was contaminated. It was noted that as the salt was freed from triphenylmethane, its solubility in CH_2Cl_2 decreased markedly.

Mixtures of B_5H_9 and Trityl Salt. Approximately 0.84-mmol samples of $C(C_6H_5)_3^+BF_4^-$ were mixed with B_5H_9 in 1:2 and 2:1 molar ratios in 2-mL portions of CH_2Cl_2. When allowed to warm to room temperature, the reaction mixtures were dark brownish yellow. The ^{11}B NMR spectra of these solutions contained only the signals of B_5H_9 and BF_4^- and were found to be unchanged when examined 2 days later.

Acknowledgment. We acknowledge support of this work by the U.S. Army Research Office through Grant DAAG 29-85-K-0034.

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Contribution from the Department of Chemistry,
The University of North Carolina at Charlotte,
Charlotte, North Carolina 28223

Reactivity of $[Cu(TIM)]^{2+}$ with Pyridine: Formation Constants Determined by Cyclic Voltammetry

David E. Whitmoyer and D. Paul Rillema*

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Recently we reported the unusual reactivity of $[Cu(TIM)]^{2+}$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) with chloride ion in methylene chloride[1] (Figure 1). The formation constant in methylene chloride of the 1:1 adduct was $2 \times 10^7\ M^{-1}$, a value which indicates that the reaction had proceeded far to the right. The method used to determine this very large constant was a modified version of a cyclic voltammetric simulation program, reported by Philp and co-workers.[2]

In this study we examine the reactivity of $[Cu(TIM)]^{2+}$ with pyridine in methylene chloride. The formation constants for this case were considerably smaller than with chloride ion and were determined by conventional electrochemical and spectral techniques. We also demonstrate the usefulness of the cyclic voltammetric simulation technique for formation constant determi-

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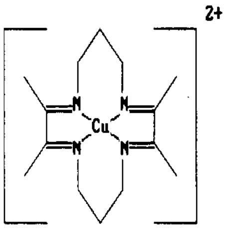

Figure 1. $[Cu(TIM)]^{2+}$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene).

nations of values considerably smaller than ~10^7 M^{-1}.

Experimental Section

Materials. $[Cu(TIM)](ClO_4)_2$ was available from a previous study.[3] Spectranalyzed methylene chloride was dried over 4-Å molecular sieves for 48 h before use. ACS grade pyridine was distilled under N_2 from KOH just prior to use. Tetrabutylammonium hexafluorophosphate (TBAH) was electrograde purchased from Southwestern Analytical, Inc.

Electrochemical and Spectral Measurements. Cyclic voltammetry measurements were made with a PAR 173 potentiostat/galvanostat, 179 digital coulometer and 175 universal programmer. The measurements were made with a Pt-disk working electrode, a Pt-wire counter electrode, and an SSCE (saturated sodium calomel electrode) reference electrode. The measurements were made in a conventional H-cell with the reference compartment separated from the main compartment by a fine glass frit and the auxiliary compartment separated from the main compartment by a medium glass frit. $[Cu(TIM)]^{2+}$ solutions were ~1×10^{-3} M in 0.10 M TBAH and were degassed with N_2 immediately prior to use. Cyclic voltammetric changes were recorded as degassed pyridine was added dropwise with a gastight syringe. Coulometry was effected with the PAR 173 potentiostat and the PAR 179 digital coulometer. The electrolysis was performed in a Vacuum Atmospheres Dri-Lab. $[Cu(TIM)]^+$ was generated electrochemically ($n = 0.95$) in the H-cell at a Pt-gauze electrode. A Pt wire functioned as the auxiliary electrode; another Pt wire functioned as a pseudoreference. Prior to and after electrolysis, cyclic voltammograms were run in order to probe the electrochemical reversibility of the two copper species. $E_{1/2}$ values were determined from the peaks of the oxidation and reduction waves according to the relationship $E_{1/2} = (E_{pa} + E_{pc})/2$. The peak to peak separation was 80 mV. Theoretically,[4] it should be 60 mV/n, where n is the number of electrons transferred for the redox couple. ΔE_p values are often larger than this in nonaqueous solvents and are rationalized on the basis of uncompensated solution resistance.[5]

The absorption spectra were determined with a Perkin-Elmer Lambda Array 3840 instrument, and absorption spectra changes were monitored with a Cary 14 spectrophotometer. Spectra of $[Cu(TIM)]^{2+}$ were obtained in 1-cm quartz cells. Spectra of $[Cu(TIM)]^+$ were obtained in 1-mm cylindrical quartz cells that were filled in the Dri-Lab and tightly sealed with serum caps. $[Cu(TIM)]^+$ shows a unique absorption at 757 nm ($\epsilon = 999$ M^{-1} cm^{-1}).

Computational Procedures. The computer system used was an IBM-PC/XT with 512K RAM and a 10-meg fixed disk. A Hercules Graphics card and a Panasonic 1091 dot-matrix printer were used for the curve-fitting and simulation-plotting routines. The computer graphics software was provided by R. W. Ramette.[6] The program EASYPLOT was modified to work in conjunction with the Hercules card and was used for both the curve-fitting routine and the cyclic voltammetric simulation.

The curve-fitting routine for cyclic voltammetric titration data was a rigorous, nonlinear least-squares method adapted from E. Meyer.[7] Initially, formation constants were estimated from the concentration of pyridine added. These formation constants were used to calculate the "free" pyridine concentrations. New formation constants were then determined from the "free" pyridine concentrations, and so forth, until the pyridine concentration in solution converged.

Cyclic voltammetric simulations were obtained after modifications of a program provided by R. Philp.[2] The modifications were primarily made to take advantage of disk file storage and the Microsoft basic compiler for the IBM-PC/XT in order to increase the speed of data analysis.

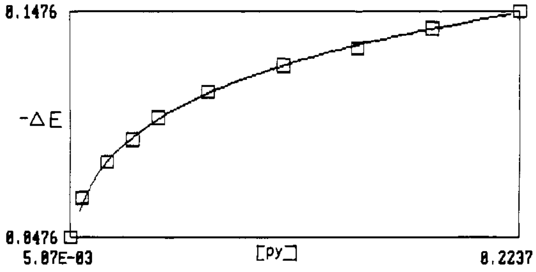

Figure 2. Computer fit of data obtained for $E_{1/2}$(py) as pyridine was added to the solution. The equation for the fit is $-\Delta E = 0.0591 \log (1 + \beta_1[py] + \beta_2[py]^2)$.

Table I. Equilibrium Constants for Formation of Five-Coordinate (K_1) and Six-Coordinates (K_2) $[Cu(TIM)]^{2+}$ Pyridine Adducts[a]

	K_1, M^{-1}	K_2, M^{-1}		K_1, M^{-1}	K_2, M^{-1}
run 1	1100	2.73	$\bar{X}$	995	2.35
run 2	933	2.02	SD	91.4 (9%)	0.36 (15%)
run 3	952	2.31			

[a] Conditions: $T = 20 \pm 1$ °C, methylene chloride.

Results and Discussion

Addition of pyridine to $[Cu(TIM)]^{2+}$ solutions in methylene chloride containing 0.10 M TBAH results in smooth cyclic voltammetric changes. A single wave shifts toward more negative values as the quantity of added pyridine increases. The effect is indicative of pyridine coordination to $[Cu(TIM)]^{2+}$. This can be written in a general way as

$$[Cu(TIM)]^{2+} + q\text{py} \xrightarrow{\beta_q} [Cu(TIM)(py)_q]^{2+} \qquad (1)$$

It leads to eq 2 relating the $E_{1/2}$ shift to the concentration of species

$$E_{1/2}(\text{py}) = E_{1/2}([CuTIM]^{2+}) - 0.06 \log \beta_q - 0.06q \log [\text{py}] \qquad (2)$$

in solution. The derivation of eq 2 assumes $[Cu(TIM)]^+$ is four-coordinate and does not bind pyridine or, if it does, does so very weakly.[8] A plot of $E_{1/2}$(py) vs. log $[\text{py}]_{\text{added}}$ results in a slope of 1.12, indicating that one or more pyridine molecules coordinate to $[Cu(TIM)]^{2+}$. Equations 3 and 4 are then taken to describe the system.

$$[Cu(TIM)]^{2+} + \text{py} \overset{K_1}{\rightleftharpoons} [Cu(TIM)(py)]^{2+} \qquad (3)$$

$$[Cu(TIM)(py)]^{2+} + \text{py} \overset{K_2}{\rightleftharpoons} [Cu(TIM)(py)_2]^{2+} \qquad (4)$$

The equilibrium constants can be determined from the formation constants (β values), and the β values can be determined from eq 5, a variation of eq 2, where $\Delta E = E_{1/2}(\text{py}) - E_{1/2}([Cu(TIM)]^{2+})$.[9,10]

$$10^{-\Delta E/0.06} = 1 + \beta_1[\text{py}] + \beta_2[\text{py}]^2 \qquad (5)$$

An initial linear least-squares fit of the data with the relationship $10^{-\Delta E/0.06}$ vs. $[\text{py}]_{\text{added}}$ gave an intercept of −15, which is in considerable disagreement with the theoretical value of 1. The data analysis was significantly improved by using the relationship in eq 5. A least-squares polynomial fit gave initial β estimates and an acceptable intercept of 1.1. In order to treat the data with a better curve-fitting technique, a rigorous nonlinear least-squares method along with an iterative procedure (Newton–Raphson) was used for final β-value determinations.[11,12] Equations 6 and 7,

$$C_{[Cu(TIM)]^{2+}} = [[Cu(TIM)]^{2+}](1 + \beta_1[\text{py}] + \beta_2[\text{py}]^2) \qquad (6)$$

$$C_{\text{py}} = [\text{py}] + \beta_1[[Cu(TIM)]^{2+}][\text{py}] + 2\beta_2[[(CuTIM)]^{2+}][\text{py}]^2 \qquad (7)$$

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Table II. Comparison between Experimental and Calculated $E_{1/2}$ Value Shifts as a Function of Added Pyridine[a]

$[py]_{added}$, M	ΔE(exptl), V[b]	ΔE(calcd), V[b]	$[py]_{added}$, M	ΔE(exptl), V[b]	ΔE(calcd), V[b]
1×10^{-7}	0	0	0.0740	0.119	0.116
0.0124	0.067	0.066	0.111	0.129	0.128
0.0495	0.105	0.104	0.220	0.153	0.151

[a] Simulation based on $K_1 = 995$ M^{-1} and $K_2 = 2.35$ M^{-1} for reactions 3 and 4 in methylene chloride. $[[Cu(TIM)]^{2+}]_{in} = 1.0 \times 10^{-3}$ M. [b] $\Delta E = E_{1/2}([Cu(TIM)(py)_x]^{2+}) - E_{1/2}([Cu(TIM)]^{2+})$, ΔE ±0.003 V.

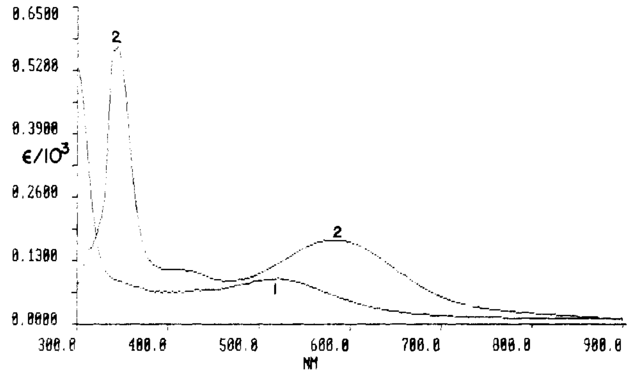

Figure 3. Comparison of the visible spectrum of $[Cu(TIM)]^{2+}$ in methylene chloride (1) to that in pyridine (2). The spectrum in pyridine is taken to be that of $[Cu(TIM)(py)_2]^{2+}$.

which equate the total metal ion concentration and the total ligand concentration to species in solution, were used in the iterative process until the concentration of free pyridine in solution converged (hence, also β values coverge). A computer fit of the data is illustrated in Figure 2, and the data obtained for three runs are given in Table I. The average K_1 value is 995 (±90) M^{-1}, and the average K_2 value is 2.35 (±0.35) M^{-1}. The 10% error can be related to the accuracy of the $E_{1/2}$ determinations.

Spectral measurements were made in order to verify the reaction stoichiometry and the magnitude of the equilibrium constants. Spectra of $[Cu(TIM)]^{2+}$ in methylene chloride and in pyridine are shown in Figure 3. There are two observable spectral changes, one in the visible region where the band located at 517 nm in methylene chloride shifts to 585 nm in pyridine and the second in the near-UV region where a new band located at 340 nm appears as pyridine is added. This band is associated with pyridine adduct formation since the absorbance of free pyridine occurs at 250 nm. Attempts were made to take advantage of these absorption changes in order to determine formation constants of Job's continuous variation method[13] and by spectral titration procedures.[14] Both methods were thwarted by the low extinction coefficients and solubility of $[Cu(TIM)]^{2+}$ in methylene chloride (5×10^{-3} M). However, as shown in Figure 4, two sets of behavior are observed in the visible region, one for dilute pyridine solutions and the other for more concentrated pyridine solutions. The spectral changes were in agreement with formation of both five- and six-coordinate pyridine adducts. The absorption changes were gradual, and no distinct separation between absorption changes associated with formation of the five-coordinate and six-coordinate species could be made. Thus, neither Job's method nor the titration process resulted in data useful for equilibrium constant determinations.

The equilibrium constants were verified by computer-simulated cyclic voltammograms based on the processes occurring in eq 3 and 4. The results are tabulated in Table II. The agreement between observed and calculated $E_{1/2}$ values is noteworthy. It should be pointed out that the simulation program assumes $[Cu(TIM)]^+$ is four-coordinate.

The results found here are similar to those for the homologue Cu^{II}(cyclops), for which Gagne and co-workers[9] report a K_1 value of 1×10^2 M^{-1} in acetone, but different from the results of Addison and co-workers,[10] who report formation of both five-coordinate Cu^{2+} and Cu$^+$ adducts in acetonitrile, with further evidence of six-coordinae pyridine adduct formation. The formation of five-coordinate adducts of Cu$^+$ appears to be a function of the type of axial base chosen[9] and the dielectric constant of the solvent.[10]

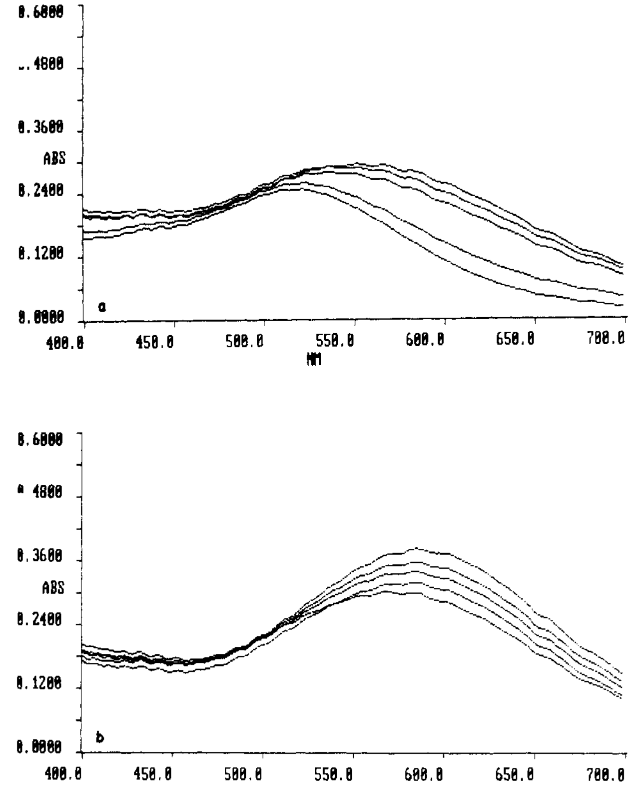

Figure 4. Comparison of spectral changes at low pyridine concentration ((a) $0 \leqslant [py] < 0.09$ M) to those at higher pyridine concentration ((b) $0.09 \text{ M} < [py] < 0.28$ M) for $[Cu(TIM)]^{2+}$ in methylene chloride. Spectra obtained at intermediate pyridine concentrations overlap appreciably.

To test for formation of pyridine adducts of $[Cu(TIM)]^+$, $[Cu(TIM)]^{2+}$ was reduced electrochemically ($n = 0.95$). Spectra of $[Cu(TIM)]^+$ in methylene chloride and of $[Cu(TIM)]^+$ in methylene chloride containing a small amount of pyridine (~0.04 M) obtained ~5 min after mixing were nearly identical. The characteristic absorption manifolds of $[Cu(TIM)]^+$ remained unchanged in the presence of pyridine. However, a very slow reaction did occur. The reaction appeared to be complex overall, but initially it followed first-order kinetics. A pseudo-first-order rate constant of 8.23×10^{-5} s^{-1} ([py] = 0.049 M) was obtained over the range of 3 half-lives. Extrapolation of the plot of the pseudo-first-order rate to time zero gave an initial absorbance of 0.52 compared to 0.55 for a sample of $[Cu(TIM)]^+$ in methylene chloride with no pyridine added. Thus, we conclude that pyridine does react with $[Cu(TIM)]^+$ and perhaps displaces or partially displaces the macrocycle from the coordination sphere but there is no significant coordination of pyridine with $[Cu(TIM)]^+$ on the cyclic voltammetric time scale.

In conclusion, the methods of formation constant determinations using various electrochemical and computer techniques have been

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Inorg. Chem. **1987**, *26*, 2015–2016

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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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

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

W. Ahmad Kamil, Marcus R. Bond,[1] and Jean'ne M. Shreeve*

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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:

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

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.

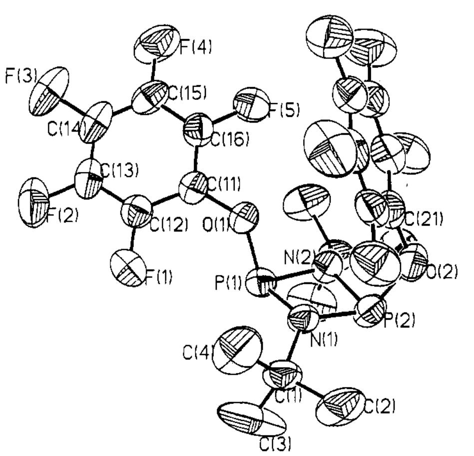

Figure 1. ORTEP view of *cis*-I showing the atom-numbering scheme. Important parameters [distances (Å); angles (deg)]: P(1)–N(2) = 1.694 (3), P(2)–N(2) = 1.701 (3), P(2)–N(1) = 1.701 (3), P(1)–N(1) = 1.695 (3), P(1)–O(1) = 1.697 (3), P(2)–O(2) = 1.675 (3), O(1)–C(11) = 1.359 (4); P(1)–O(1)–C(11) = 119.3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

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(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 $2\theta(\mathrm{max}) = 45°$ 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}, $T(\mathrm{max}) = 0.80$, $T(\mathrm{min}) = 0.78$, $R_{\mathrm{merge}} = 0.123$ 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. $\Delta/\sigma(\mathrm{mean}) = 0.013$. $\Delta/\sigma(\mathrm{max}) = 0.042$. Largest peak on final difference map: 0.239 e/Å^3, 1.02 Å from HZc.

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