Similar permutations with simultaneous rotations of the α-naphthyl groups about their respective P–CN1 bonds (and in the case of V, rotation of $(CH_3)_2N$ group about the CN8–N bond) would provide a mechanism consistent with NMR data.[7] This exchange process follows the form of the distortion coordinate found for V and VI (Table IX).

In contrast, the X-ray study on the corresponding bis(biphenylylene) derivatives VII and VIII[16] containing substituents of lower steric requirements, methyl and phenyl, respectively, shows the distortion coordinate is not that followed for the naphthyl derivatives but is indicative of the C_{2v} pathway for the lower energy process.

It is possible then, as stated earlier,[13] that a changeover in ligand exchange mechanism takes place from the lower to the higher energy process as the steric requirements are increased for bis(biphenylylene) derivatives. This lends support to the detailed NMR line shape study of Whitesides et al.[12] which showed the lower energy process for the isopropylphenyl derivative I but the higher energy process for the more hindered triisopropylphenyl derivative II.

Acknowledgment. The support of this work by grants from the National Institutes of Health and the National Science Foundation is gratefully acknowledged. We thank Professor D. Hellwinkel for supplying samples of the bis(biphenylylenes) used in this investigation. We also express appreciation to the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. V, 52753-52-3; VI, 75082-07-4.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes for V and VI, thermal parameters (Table XII) and bond lengths and angles involving hydrogen atoms (Table XIII) for V, and thermal parameters (Table XIV) for VI (32 pages). Ordering information is given on any current masthead page.

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Molecular Structure of the Methyl and Phenyl Derivatives of Bis(2,2′-biphenylylene)phosphorane[1]

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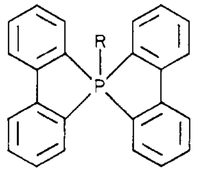
Single-crystal X-ray analysis of methylbis(2,2′-biphenylylene)phosphorane $(C_{12}H_8)_2PCH_3$ (III) and phenylbis(2,2′-biphenylylene)phosphorane $(C_{12}H_8)_2PC_6H_5$ (IV) reveals closely related structures which are nearly trigonal bipyramidal but displaced 16.9 and 15.0%, respectively, in a direction opposite to a coordinate connecting a rectangular pyramid that has the unique substituent apical. Data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer out to a maximum $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} = 55°$. III crystallizes in the monoclinic space group $C2/c$ with $a = 24.244$ (4) Å, $b = 7.138$ (3) Å, $c = 22.203$ (5) Å, $\beta = 104.08$ (2)°, and $Z = 8$ and has a pseudo-twofold axis along the phosphorus–methyl C bond. IV crystallizes as the benzene disolvate in space group $C2/c$ with $a = 16.169$ (4) Å, $b = 9.399$ (4) Å, $c = 20.961$ (8) Å, $\beta = 92.23$ (3)°, and $Z = 4$ and has a crystallographic two-fold axis along the phosphorus–phenyl C bond. Both structures were refined by full-matrix least-squares techniques: for III to final $R = 0.057$ and $R_w = 0.052$ for the 2712 reflections having $I \geq \sigma_I$; for IV to final $R = 0.051$ and $R_w = 0.053$ for the 2494 reflections having $I \geq \sigma_I$. Molecular mechanics calculations on these phosphoranes, III and IV, and the related [8-(dimethylamino)-1-naphthyl]bis(2,2′-biphenylylene)phosphorane (I) and (1-naphthyl)bis(2,2′-biphenylylene)phosphorane (II) gave reasonable agreement in reproducing structural parameters obtained in the X-ray studies. Strain energy comparisons support a changeover in intramolecular ligand-exchange mechanism as the size of the unique R group is increased.

Introduction

As shown in the preceding paper,[1b] both the 8-(dimethylamino)-1-naphthyl and the 1-naphthyl derivative of bis(2,2′-biphenylylene)phosphorane, I and II, respectively, have molecular structures displaced along a coordinate leading to a rectangular pyramid that contains the naphthyl group in a basal position. I was located about 65% along this coordinate, and II, about 25%. Usually the structures of spirocyclic phosphoranes are located along a coordinate leading to a rectangular pyramid that has the unique group in the apical position.[2-4] For PPh_5, the structure is very nearly trigonal bipyramidal.[5] Neither the presence of the unsaturated spirocyclic system nor the incorporation of five carbon atoms bonded to phosphorus then suggests the structural distortion coordinate found for I and II.



I, R = 8-$(CH_3)_2$N-1-Np
II, R = 1-Np
III, R = CH_3
IV, R = Ph
Np = naphthyl

We ascribed[1b] the structural preference to steric requirements of the naphthyl group. These requirements are magnified in the 8-$(CH_3)_2$N-Np derivative I. The extensive NMR studies of Hellwinkel and co-workers[6-10] on the fluxional be-

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(1) (a) Pentacoordinated Molecules. 37. (b) Part 36: Day, R. O.; Holmes, R. R. *Inorg. Chem.*, preceding paper in this issue.
(2) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.
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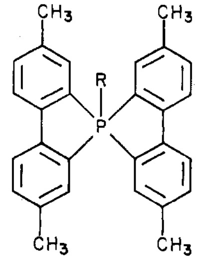
(6) Hellwinkel, D. *Chimia* **1968**, *22*, 488.

0020-1669/80/1319-3616$01.00/0

havior of bis(biphenylylenes) support the presence of steric effects. For example, with use of a ligand of relatively low steric requirements, 2-naphthyl, the coalesence temperature for the onset of facile intramolecular ligand exchange in V is −48 °C.[6] In comparison, the coalesence temperature for the 1-naphthyl derivative VI is +54 °C,[6] and for the 2,4,6-triisopropylphenyl derivative VII it is +202 °C.[11] The corresponding free energies of activation $\Delta G_c^\ddagger$ are <11.9 (V), 17.1 (VI), and 26.0 kcal/mol (VII).



V, R = 2-Np
VI, R = 1-Np
VII, R = 2,4,6-(*i*-Pr)$_3$Ph
VIII, R = 2-*i*-PrPh

To investigate the structural aspects of this series more thoroughly and probe effects which may cause a preference for one particular distortion coordinate over another, we undertook a study of bis(biphenylylenes) having relatively low steric requirements, the methyl III and phenyl IV derivatives. Reported here are the results of an X-ray analysis of their solid-state structures and the use of molecular mechanics as an aid in defining specific interactions giving rise to these structures.

Experimental Section

Sample Preparation. Samples of methylbis(2,2′-biphenylylene)phosphorane (III) and phenylbis(2,2′-biphenylylene)phosphorane (IV) were kindly provided by Professor D. Hellwinkel, Organisch-Chemisches Institut der Universität, Heidelberg, Germany. The X-ray analyses of both compounds were complicated by difficulties in obtaining suitable crystals. For III, the crystals were either cut from aggregates and diffracted poorly or were single, but smaller than desirable. Attempts to grow larger single crystals from acetone, benzene, or ether proved unsuccessful. For IV, the apparent space group and unit cell volume depended on the solvent used for recrystallization, suggesting that the solvent was being incorporated into the crystal lattice. The best crystals, obtained from benzene, had the form of truncated distorted rhomboidal bipyramids. These proved to be twinned along the basal plane and deteriorated overnight when removed from the mother liquor. However, a suitable crystal resulted from careful cleavage of a twin which showed no sign of deterioration when sealed in a capillary.

Space Group Determination and Data Collection for III. A well-formed crystal having dimensions of 0.13 × 0.15 × 0.40 mm was glued to the interior of a thin-walled glass capillary which was sealed as a precaution against moisture sensitivity. Preliminary investigations using an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle 3.1°, $\lambda(K\alpha_1)$ 0.709 26 Å, $\lambda(K\alpha_2)$ 0.713 54 Å) indicated monoclinic (2/*m*) symmetry. From the observed extinctions *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, the space group was determined as either *C*2/*c* or *Cc*. The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $11.00° \le \theta_{\mathrm{Mo}\,K\bar{\alpha}} \le 15.16°$ and measured at an ambient laboratory temperature of 23 ± 2 °C are $a = 24.244$ (4) Å, $b = 7.138$ (3) Å, $c = 22.203$ (5) Å, and $\beta = 104.08$ (2)°. A unit cell content of eight molecules gives a calculated density of 1.249 g/cm^3 or a volume of 17.9 Å^3 per nonhydrogen atom, both of which are in the range to be expected for such compounds. The space group *C*2/*c* (C_{2h}^6, No. 15)[12] was thus chosen. This choice was confirmed by all later stages of solution and refinement.

Data were collected by using the θ–2θ scan mode with a θ scan range of $(0.75 + 0.35 \tan \theta)°$ centered about the calculated Mo $K\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.65 to 4.02° θ/min, the rate to be used for each reflection having been determined by a prescan. The intensity, *I*, for each reflection is then given by $I = (FF/S)(P - 2(B_1 + B_2))$ where *P* is the counts accumulated during the peak scan, B_1 and B_2 are the left and right background counts, *S* is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = ((FF)^2/S^2)(P + 4(B_1 + B_2)) + 0.002I^2$.

A total of 4279 independent reflections (+*h*, +*k*, ±*l*) having $2° \le 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \le 55°$ were measured. Six standard reflections monitored after every 12 000 s of X-ray exposure time gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\mathrm{Mo}\,K\bar{\alpha}} = 0.157$ mm^{-1}), and the intensities were reduced to relative amplitudes, F_o, by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

Solution and Refinement of Structure for III. Initial coordinates for the 26 independent nonhydrogen atoms were obtained by direct methods (MULTAN). Isotropic unit-weighted full-matrix least-squares refinement[13] of the structural parameters for these atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.106 and a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.103 for the 1691 reflections having $I \ge \sigma_I$ and $(\sin \theta)/\lambda \le 0.52$ Å^{-1}. Anisotropic refinement led to $R = 0.079$ and $R_w = 0.082$.

Initial coordinates for the 3 methyl hydrogen atoms were then obtained from a difference Fourier synthesis, while initial coordinates for the remaining aromatic hydrogen atoms were inferred from the required geometry of the molecule. Subsequent refinement employing variable weights ($w^{1/2} = 2F_oLp/\sigma_I$) and including the 19 independent hydrogen atoms as isotropic contributions gave $R = 0.039$ and $R_w = 0.043$. Inclusion of the high-angle data in the refinement led to the final values of $R = 0.057$, $R_w = 0.052$, and S[14] = 1.23 for the 2712 reflections having $I \ge \sigma_I$ and $2° \le 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \le 55°$. During the final cycle of refinement the largest shift in any parameter was 0.08 times its estimated standard deviation (esd). A final difference Fourier synthesis showed a maximum density of 0.25 e/Å^3.

Space Group Determination and Data Collection for IV. Experimental conditions were the same as described for III, unless otherwise noted. A single crystal was obtained by cleaving a twin grown from benzene as previously described, along the basal plane. The crystal, having approximate dimensions of 0.25 mm × 0.40 mm × 0.60 mm, was wedged into a thin-walled glass capillary, which was sealed with a flame to prevent deterioration by loss of benzene. Initial diffractometric investigations indicated monoclinic (2/*m*) symmetry. From the observed extinctions *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, the space group was determined as either *C*2/*c* or *Cc*. the lattice constants, as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.07° \le \theta_{\mathrm{Mo}\,K\bar{\alpha}} \le 17.51°$, are $a = 16.169$ (4) Å, $b = 9.399$ (4) Å, $c = 20.961$ (8) Å, and $\beta = 92.23$ (3)°. A unit cell content of four molecules of IV and eight molecules of benzene gives a calculated density of 1.187 g/cm^3 or a volume of 18.5 Å^3 per nonhydrogen atom. These values would be consonant either with space group *Cc* with one moleucle of IV and two molecules of C_6H_6 per asymmetric unit or with space group *C*2/*c* with the phosphorane moiety lying on a twofold axis and the benzene molecule in a general position.

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(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 101.

(13) The function minimized is $\sum w(|F_o| - |F_c|)^2$. Atomic form factors for nonhydrogen atoms were taken from: Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104. Scattering factors for hydrogen atoms were taken from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(14) Goodness of fit $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$. N_o = number of observations = 2712; N_v = number of variables = 311.

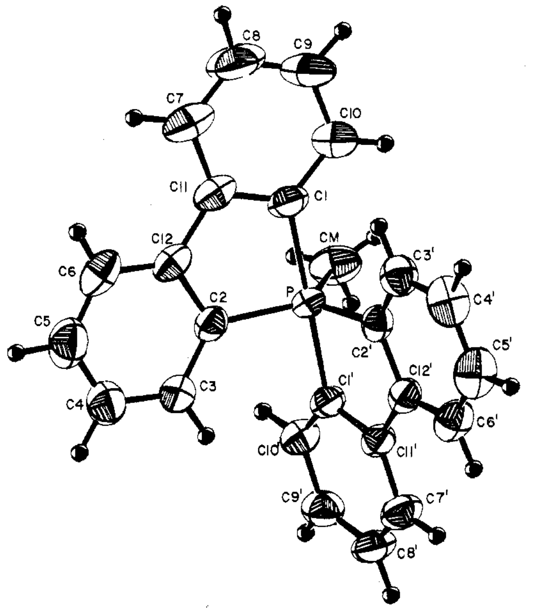

Figure 1. ORTEP plot of the $(C_{12}H_8)_2PMe$ molecule (III) with thermal ellipsoids for nonhydrogen atoms at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary radius.

Data were collected as for III, except that the θ scan range was $(0.65 + 0.35 \tan \theta)°$ and the scan rates varied from 0.59 to 4.02° θ/min. A total of 3644 independent reflections were measured. The six standard reflections gave no indication of deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\text{Mo K}\bar{\alpha}} = 0.120$ mm^{-1}).

Solution and Refinement of Structure for IV. A solution by direct methods (MULTAN) was attempted in both $C2/c$ and Cc. Equivalent results were obtained in each of the two space groups and led to the choice of $C2/c$[12] with the phosphorus atom and atoms 1 and 4 of the attached phenyl group lying on the twofold axis. Conditions for refinement were the same as described for III. Isotropic unit-weighted refinement of the structural parameters for the 23 independent nonhydrogen atoms and a scale factor gave $R = 0.111$ and $R_w = 0.107$ for the 1354 reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$ Å^{-1}. Anisotropic refinement then gave $R = 0.083$ and $R_w = 0.081$ for the 1543 reflections having $I \geq \sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$ Å^{-1}.

Initial coordinates for the 17 independent hydrogen atoms were inferred from the required geometry of the molecule. Inclusion of the hydrogen atoms as isotropic contributions gave $R = 0.039$ and $R_w = 0.037$ for 1543 reflections. The final cycles of refinement included the high-angle data and employed variable weights and led to the final values of $R = 0.051$, $R_w = 0.053$, and $S = 1.36$[15] ($N_o = 2494$, $N_v = 262$) for the 2494 reflections having $I \geq \sigma_I$ and $2° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 55°$. During the last cycle of refinement the largest shift in any parameter was 0.01 times its esd. A final difference Fourier synthesis showed a maximum density of 0.18 e/Å^3.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) by using the direct methods program, MULTAN, by Main, Germain, and Woolfson; Zalkin's Fourier program, FORDAP; Prewitt's full-matrix least-squares program, SFLS; Johnson's thermal ellipsoid plot program, ORTEP; and several locally written programs.

Results and Discussion

The atom labeling scheme for methylbis(2,2′-biphenylylene)phosphorane (III) is shown in Figure 1 and that for phenylbis(2,2′-biphenylylene)phosphorane (IV) in Figure 2. For both compounds the hydrogen atoms are labeled according to the carbon atoms to which they are bonded. III has an approximate twofold axis lying along the P–CM bond. The extent to which the twofold symmetry is obeyed can be seen in the pictorial bond length and angle summary of Figure 3, where the primed atoms are related to the unprimed ones by the pseudo-twofold axis. IV has an exact crystallographic twofold axis lying along the P–CP1 bond. For IV, in the following discussion and in the tables and figures, the primed atoms are related to the unprimed ones by the crystallographic twofold axis. For IV, bond lengths and angles are summarized pictorially in Figure 4. Bond lengths and angles for nonhydrogen atoms of III are listed in Tables I and II, respectively. Corresponding bond parameter data for IV are found in Tables III and IV. Atomic coordinates are given for III in Tables V and VI and for IV in Table VII and VIII. Thermal parameters and bond angles involving hydrogen atoms are provided as supplementary material (refer to the end of this article).

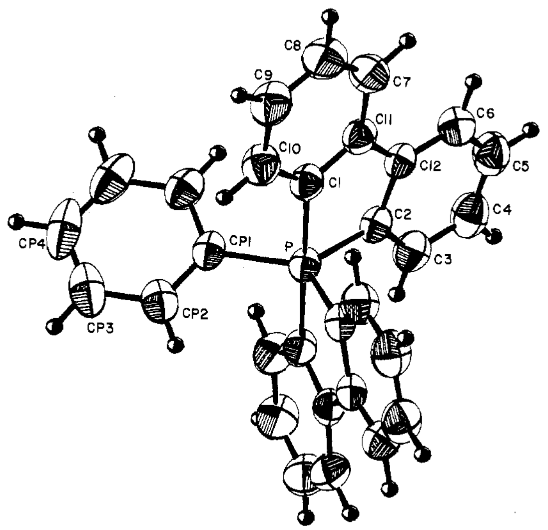

Figure 2. ORTEP plot of the $(C_{12}H_8)_2PPh$ molecule (IV) with thermal ellipsoids for nonhydrogen atoms at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. The benzene molecule, CB1–CB6 and HB1–HB6, is not shown.

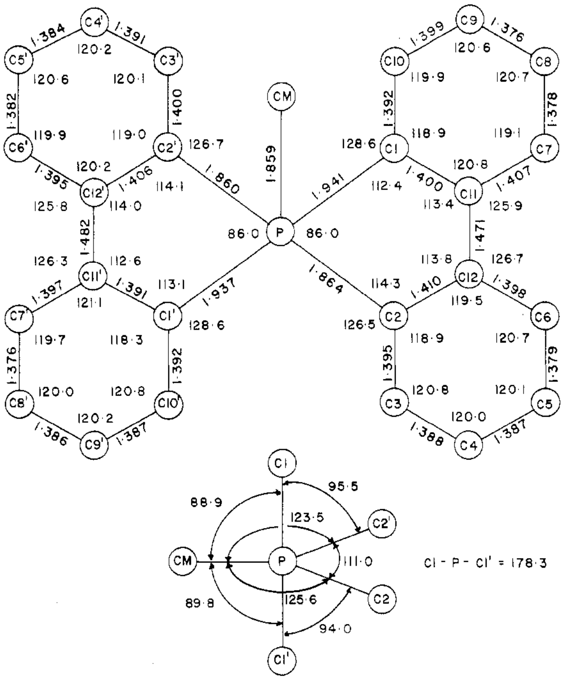

Figure 3. Selected bond lengths (Å) and angles (deg) for $(C_{12}H_8)_2PMe$ (III).

The basic structural form for both III and IV is a trigonal bipyramid. A comparison of the bond lengths and angles for the two structures (Tables I–IV) shows a remarkable similarity. Along with the high degree of trigonal bipyramidal

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[15] As defined in ref 14.

Table I. Bond Lengths (Å) in Crystalline $(C_{12}H_8)_2PCH_3$ (III)[a]

type[b]	bond length	type[b]	bond length
P–CM	1.859 (2)	C10–C1	1.392 (2)
P–C1	1.941 (1)	C10′–C1′	1.392 (2)
P–C1′	1.937 (1)	C1–C11	1.400 (2)
P–C2	1.864 (1)	C1′–C11′	1.391 (1)
P–C2′	1.860 (1)	C2–C12	1.410 (1)
C11–C12	1.471 (2)	C2′–C12′	1.406 (1)
C11′–C12′	1.482 (1)	C3–H3	0.97 (1)
C2–C3	1.395 (2)	C4–H4	0.99 (1)
C2′–C3′	1.400 (2)	C5–H5	1.00 (1)
C3–C4	1.388 (2)	C6–H6	0.93 (1)
C3′–C4′	1.391 (2)	C7–H7	1.02 (1)
C4–C5	1.387 (2)	C8–H8	0.93 (1)
C4′–C5′	1.384 (2)	C9–H9	0.94 (1)
C5–C6	1.379 (2)	C10–H10	0.96 (1)
C5′–C6′	1.382 (2)	C3′–H3′	0.97 (1)
C6–C12	1.398 (2)	C4′–H4′	0.98 (1)
C6′–C12′	1.395 (2)	C5′–H5′	0.93 (1)
C11–C7	1.407 (2)	C6′–H6′	0.94 (1)
C11′–C7′	1.397 (2)	C7′–H7′	0.91 (1)
C7–C8	1.378 (3)	C8′–H8′	0.97 (1)
C7′–C8′	1.376 (2)	C9′–H9′	0.98 (1)
C8–C9	1.376 (3)	C10′–H10′	0.98 (1)
C8′–C9′	1.386 (2)	CM–HM1	0.88 (2)
C9–C10	1.399 (2)	CM–HM2	0.93 (2)
C9′–C10′	1.387 (2)	CM–HM3	0.84 (2)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

Table II. Bond Angles (Deg) for Nonhydrogen Atoms in Crystalline $(C_{12}H_8)_2PCH_3$ (III)[a]

type	bond angle	type	bond angle
C1–P–C1′	178.3 (1)	C7′–C11′–C12′	126.3 (1)
C2–P–C2′	111.0 (1)	C12–C2–C3	118.9 (1)
C2–P–CM	125.6 (1)	C12′–C2′–C3′	119.0 (1)
C2′–P–CM	123.5 (1)	C2–C3–C4	120.8 (1)
C1–P–C2	86.0 (1)	C2′–C3′–C4′	120.1 (1)
C1′–P–C2′	86.0 (1)	C3–C4–C5	120.0 (1)
C1–P–C2′	95.5 (1)	C3′–C4′–C5′	120.2 (1)
C1′–P–C2	94.0 (1)	C4–C5–C6	120.1 (1)
C1–P–CM	88.9 (1)	C4′–C5′–C6′	120.6 (1)
C1′–P–CM	89.8 (1)	C5–C6–C12	120.7 (1)
P–C1–C11	112.4 (1)	C5′–C6′–C12′	119.9 (1)
P–C1′–C11′	113.1 (1)	C6–C12–C2	119.5 (1)
P–C2–C12	114.3 (1)	C6′–C12′–C2′	120.2 (1)
P–C2′–C12′	114.1 (1)	C10–C1–C11	118.9 (1)
C1–C11–C12	113.4 (1)	C10′–C1′–C11′	118.3 (1)
C1′–C11′–C12′	112.6 (1)	C1–C11–C7	120.8 (1)
C2–C12–C11	113.8 (1)	C1′–C11′–C7′	121.1 (1)
C2′–C12′–C11′	114.0 (1)	C11–C7–C8	119.1 (7)
P–C1–C10	128.6 (1)	C11′–C7′–C8′	119.7 (1)
P–C1′–C10′	128.6 (1)	C7–C8–C9	120.7 (2)
P–C2–C3	126.5 (1)	C7′–C8′–C9′	120.0 (1)
P–C2′–C3′	126.7 (1)	C8–C9–C10	120.6 (2)
C6–C12–C11	126.7 (1)	C8′–C9′–C10′	120.2 (1)
C6′–C12′–C11′	125.8 (1)	C9–C10–C1	119.9 (1)
C7–C11–C12	125.9 (1)	C9′–C10′–C1′	120.8 (1)

[a] See footnotes to Table I.

Table III. Bond Lengths (Å) in Crystalline $(C_{12}H_8)_2PPh$ (IV)[a]

type[b]	bond length	type[b]	bond length
P–C1	1.934 (1)	CB3–CB4	1.362 (4)
P–C2	1.862 (1)	CB4–CB5	1.356 (5)
P–CP1	1.859 (2)	CB5–CB6	1.355 (4)
CP1–CP2	1.386 (2)	CB6–CB1	1.341 (4)
CP2–CP3	1.391 (2)	C3–H3	0.96 (1)
CP3–CP4	1.368 (2)	C4–H4	0.96 (2)
C1–C11	1.385 (2)	C5–H5	0.94 (1)
C2–C12	1.408 (2)	C6–H6	0.98 (2)
C11–C12	1.483 (2)	C7–H7	0.99 (1)
C2–C3	1.406 (2)	C8–H8	0.91 (2)
C3–C4	1.387 (2)	C9–H9	0.95 (2)
C4–C5	1.373 (3)	C10–H10	0.97 (1)
C5–C6	1.391 (2)	CP2–HP2	0.96 (1)
C6–C12	1.389 (2)	CP3–HP3	0.96 (2)
C7–C11	1.403 (2)	CP4–HP4	0.92 (3)
C7–C8	1.387 (2)	CB1–HB1	0.92 (3)
C8–C9	1.372 (3)	CB2–HB2	0.89 (2)
C9–C10	1.390 (2)	CB3–HB3	0.94 (2)
C10–C1	1.400 (2)	CB4–HB4	0.94 (3)
CB1–CB2	1.375 (4)	CB5–HB5	0.97 (3)
CB2–CB3	1.357 (5)	CB6–HB6	0.97 (2)

[a] See footnote *a* to Table I. [b] Atoms are labeled to agree with Figure 2.

Table IV. Bond Angles (Deg) for Nonhydrogen Atoms in Crystalline $(C_{12}H_8)_2PPh$ (IV)[a]

type[b]	bond angle	type[b]	bond angle
C1–P–CP1	89.6 (1)	C5–C6–C12	120.3 (1)
C1–P–C2	86.1 (1)	C6–C12–C2	120.1 (1)
C1–P–C2′	94.3 (1)	C10–C1–C11	118.7 (1)
C2–P–C2′	111.5 (1)	C1–C11–C7	121.3 (1)
C2–P–CP1	124.3 (1)	C11–C7–C8	118.8 (1)
C1–P–C1′	179.3 (1)	C7–C8–C9	120.6 (2)
P–C1–C11	113.3 (1)	C8–C9–C10	120.6 (2)
P–C2–C12	113.8 (1)	C9–C10–C1	120.0 (1)
P–C1–C10	128.1 (1)	P–CP1–CP2	120.8 (1)
P–C2–C3	127.3 (1)	CP2′–CP1–CP2	118.5 (1)
C1–C11–C12	112.6 (1)	CP1–CP2–CP3	120.4 (1)
C2–C12–C11	114.2 (1)	CP2–CP3–CP4	120.4 (2)
C7–C11–C12	126.1 (1)	CP3–CP4–CP3′	119.8 (2)
C6–C12–C11	125.7 (1)	CB1–CB2–CB3	119.9 (3)
C12–C2–C3	118.7 (1)	CB2–CB3–CB4	119.3 (3)
C2–C3–C4	120.0 (1)	CB3–CB4–CB5	120.2 (4)
C3–C4–C5	121.0 (1)	CB4–CB5–CB6	120.6 (3)
C4–C5–C6	119.8 (1)	CB5–CB6–CB1	119.7 (3)
		CB6–CB1–CB2	120.3 (3)

[a] See footnote *a* to Table I. [b] Atoms are labeled to agree with Figure 2. Primed atoms are related by the crystallographic twofold axis to unprimed ones.

character, the P–C axial ring bonds average 0.077 Å longer than the P–C equatorial ring bonds in III and are 0.072 Å longer in IV.

By use of the dihedral angles procedure as applied to cyclic phosphoranes,[2,3] an accurate description of the structural distortion from idealized symmetries is obtained (Table IX). In terms of differences in dihedral angle sums between the trigonal bipyramid and rectangular pyramid, III and IV are displaced in a direction away from each of the idealized structures, −16.9% for III and −15.0% for IV relative to the trigonal bipyramid. This type of distortion, which is normally not present in cyclic phosphoranes[2-4] (but is seen in sulfuranes and CH_3PF_4 where relative electron-pair repulsion effects take on increasing importance[2]) is due to the slight tilt of the axial ligands away from the unique ligand accompanying the compression of the C2–P–C2′ equatorial angle in each case. The near equality of the terms *B* and *C* for III and equality of these terms for IV show that the distortion follows a C_{2v} constraint. Thus, the distortion is along the usual Berry coordinate for spirocyclic phosphoranes[2] but in a slightly negative direction.

From the least-squares mean planes listed in Tables X and XI, it is also apparent that the structures are displaced along a C_{2v} coordinate from the ideal trigonal-bipyramidal geometry. For the methyl derivative III the equatorial plane, I, and the axial plane, II, of Table X form a dihedral angle of 84.7°. For the phenyl derivative IV, these same planes in Table XI form a dihedral angle of 85.0°. The atoms in these planes for IV are required by symmetry to be coplanar; in III, only small atom deviations from the respective planes are evident. There is also very small atom deviation from the ring-containing planes for each derivative.

We found that the structures of biphenylylenes containing the 8-$(CH_3)_2$N-1-Np group (I) and the unsubstituted 1-naphthyl group (II) follow a distortion coordinate leading to

Table V. Atomic Coordinates in Crystalline $(C_{12}H_8)_2PMe$ (III)[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
P	6651.5 (1)	7267.4 (4)	3667.6 (1)
CM	7045 (1)	5008 (2)	3784 (1)
C1	5962 (1)	5913 (2)	3687 (1)
C2	6492 (1)	8752 (2)	4295 (1)
C1P	7352 (1)	8570 (1)	3667 (1)
C2P	6365 (1)	8345 (1)	2892 (1)
C3	6785 (1)	10356 (2)	4553 (1)
C4	6593 (1)	11429 (2)	4982 (1)
C5	6100 (1)	10925 (2)	5154 (1)
C6	5803 (1)	9347 (2)	4903 (1)
C7	5214 (1)	5731 (2)	4248 (1)
C8	4994 (1)	4180 (3)	3902 (1)
C9	5241 (1)	3505 (3)	3450 (1)
C10	5728 (1)	4352 (2)	3342 (1)
C11	5703 (1)	6598 (2)	4141 (1)
C12	5988 (1)	8257 (2)	4467 (1)
C3′	5814 (1)	8140 (2)	2515 (1)
C4′	5651 (1)	9126 (2)	1959 (1)
C5′	6030 (1)	10326 (2)	1779 (1)
C6′	6574 (1)	10559 (2)	2147 (1)
C7′	7787 (1)	10635 (2)	3045 (1)
C8′	8297 (1)	10531 (2)	3483 (1)
C9′	8340 (1)	9461 (2)	4014 (1)
C10′	7872 (1)	8487 (2)	4104 (1)
C11′	7316 (1)	9654 (1)	3138 (1)
C12′	6745 (1)	9571 (1)	2704 (1)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

Table VI. Refined Parameters for Hydrogen Atoms in Crystalline $(C_{12}H_8)_2PMe$ (III)[a]

	coordinates			
atom type[b]	10^3x	10^3y	10^3z	B_{iso}, Å^2 [c]
HM1	693 (1)	422 (3)	347 (1)	13.5 (8)
HM2	742 (1)	519 (3)	378 (1)	10.2 (7)
HM3	709 (1)	476 (3)	416 (1)	12.1 (8)
H3	711 (1)	1073 (2)	441 (1)	4.1 (3)
H4	681 (1)	1253 (2)	519 (1)	6.0 (3)
H5	599 (1)	1172 (2)	548 (1)	7.0 (4)
H6	546 (1)	898 (2)	499 (1)	4.7 (3)
H7	504 (1)	624 (2)	459 (1)	8.0 (4)
H8	466 (1)	360 (2)	393 (1)	7.5 (4)
H9	508 (1)	251 (2)	319 (1)	6.5 (4)
H10	589 (1)	385 (2)	303 (1)	6.4 (4)
H3′	556 (1)	730 (2)	266 (1)	4.0 (3)
H4′	526 (1)	899 (2)	170 (1)	5.1 (3)
H5′	591 (1)	1089 (2)	139 (1)	5.8 (3)
H6′	683 (1)	1135 (2)	201 (1)	4.4 (3)
H7′	776 (1)	1128 (2)	268 (1)	4.8 (3)
H8′	863 (1)	1115 (2)	342 (1)	4.9 (3)
H9′	871 (1)	935 (1)	431 (1)	3.7 (2)
H10′	790 (1)	776 (1)	449 (1)	3.3 (2)

[a] See footnote *a* to Table V. [b] Hydrogen atoms are identified according to the carbon atoms to which they are bonded. See Figure 1. [c] B_{iso} is the isotropic thermal parameter.

a rectangular pyramid for which one of the bis(biphenylylene) rings lies in an apical–basal orientation.[1b] In contrast, the present structures give no evidence for adherence to this coordinate. The structural evidence for the naphthyl derivatives I and II, giving rise to the latter coordinate, suggested[1b] the operation of a steric effect between the naphthyl groups and the bis(biphenylylene) rings. The structure of I was located 64% and that of II 25% along this coordinate toward the rectangular pyramid. The relatively small methyl and phenyl groups most likely are insufficient in size to cause any distortion in this direction. The equatorial angle C2–P–C2′ remains very constant near 111° in structures II–IV. Not until introduction of the 8-$(CH_3)_2N$-1-Np ligand does this angle

Table VII. Atomic Coordinates in Crystalline $(C_{12}H_8)_2PPh{\cdot}2C_6H_6$ (IV)[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
P	5000	7236.2 (5)	2500
CP1	5000	9214 (2)	2500
CP4	5000	12179 (3)	2500
CP2	4739 (1)	9968 (2)	3024 (1)
CP3	4756 (1)	11448 (2)	3025 (1)
C1	6166 (1)	7249 (1)	2325 (1)
C2	4865 (1)	6121 (1)	1769 (1)
C3	4126 (1)	5528 (2)	1515 (1)
C4	4143 (1)	4618 (2)	995 (1)
C5	4876 (1)	4279 (2)	722 (1)
C6	5614 (1)	4854 (2)	967 (1)
C7	7175 (1)	6287 (2)	1612 (1)
C8	7798 (1)	6997 (2)	1955 (1)
C9	7615 (1)	7848 (2)	2462 (1)
C10	6804 (1)	7992 (2)	2649 (1)
C11	6357 (1)	6422 (1)	1804 (1)
C12	5615 (1)	5768 (1)	1487 (1)
CB1	1468 (2)	6700 (3)	9 (1)
CB2	1781 (2)	6151 (3)	577 (1)
CB3	1761 (1)	4726 (3)	681 (1)
CB4	1431 (2)	3857 (3)	218 (2)
CB5	1119 (2)	4414 (4)	−338 (2)
CB6	1130 (2)	5838 (3)	−439 (1)

[a] See footnote *a* to Table V. [b] Atoms are labeled to agree with Figure 2.

Table VIII. Refined Parameters for Hydrogen Atoms in Crystalline $(C_{12}H_8)_2PPh{\cdot}2C_6H_6$ (IV)[a]

	coordinates			
atom type[b]	10^3x	10^3y	10^3z	B_{iso}, Å^2 [c]
HP4	500	1316 (3)	250	7.6 (7)
HP2	456 (1)	946 (2)	339 (1)	5.2 (4)
HP3	456 (1)	1194 (2)	339 (1)	7.2 (5)
H3	361 (1)	576 (2)	171 (1)	4.4 (3)
H4	362 (1)	423 (2)	85 (1)	6.5 (4)
H5	487 (1)	366 (2)	37 (1)	5.0 (3)
H6	614 (1)	461 (2)	77 (1)	5.5 (4)
H7	729 (1)	570 (2)	124 (1)	5.2 (3)
H8	832 (1)	695 (2)	181 (1)	6.3 (4)
H9	803 (1)	836 (2)	270 (1)	6.6 (4)
H10	668 (1)	856 (2)	302 (1)	5.0 (3)
HB1	153 (1)	766 (3)	−8 (1)	10.1 (7)
HB2	205 (1)	671 (2)	86 (1)	9.8 (7)
HB3	199 (1)	436 (2)	106 (1)	8.9 (6)
HB4	139 (2)	288 (3)	31 (1)	14.2 (9)
HB5	91 (2)	382 (3)	−68 (1)	13.3 (9)
HB6	93 (1)	619 (2)	−85 (1)	10.2 (6)

[a] See footnote *a* to Table V. [b] Hydrogen atoms are identified according to the carbon atom to which they are bonded. See Figure 2. [c] B_{iso} is the isotropic thermal parameter.

Table IX. Structural Distortion for $(C_{12}H_8)_2PCH_3$ (III) and $(C_{12}H_8)_2PPh$ (IV)[a,b]

	III	IV
A (deg) = $\Sigma_i \lvert \delta i(C) - \delta i(RP) \rvert$	253.7	250.3
B (deg) = $\Sigma_i \lvert \delta i(C) - \delta i(TP) \rvert$	37.4	32.6
C (deg) = $217.7° - A$	−36.0	−32.6
D = %(TP → RP)[c]	−16.9	−15.0

[a] Based on the dihedral angle method applied in ref 3. The coordination polyhedron is defined by unit vectors along the bonds from the P atom to the five atoms bonded to it. [b] A is the sum of the dihedral angles calculated for the compound relative to those for an idealized rectangular pyramid (RP) containing the carbon atom of the methyl or phenyl group at the apical position. B is a similar sum relative to an ideal trigonal bipyramid (TP) having a carbon atom of the methyl or phenyl group at an equatorial site. The value of 217.7° is the difference in the dihedral summation between the idealized geometries. [c] $D = (-B + C)/2(217.7)$.

Table X. Deviations from Some Least-Squares Mean Planes (Å) for $(C_{12}H_8)_2PMe$ (III)[a, b]

I		II		III		IV		V		VI	
P	−0.001	P	−0.011	C2	0.007	C1	0.001	C2′	−0.002	C1′	0.000
C2	0.000	C1	0.006	C3	−0.003	C7	−0.003	C3′	0.004	C7′	0.000
C2′	0.000	C1′	0.006	C4	0.000	C8	0.007	C4′	−0.002	C8′	−0.001
CM	0.000	CM	−0.000	C5	−0.001	C9	−0.006	C5′	−0.002	C9′	0.001
				C6	0.005	C10	0.002	C6′	0.003	C10′	0.000
				C12	−0.008	C11	0.000	C12′	−0.001	C11′	0.000

[a] Atoms are labeled to agree with Figure 1. [b] Dihedral angles (deg) between planes indicated: I and II, 84.7; III and IV, 5.5; V and VI, 4.3.

Table XI. Deviations from Some Least-Squares Mean Planes (Å) for $(C_{12}H_8)_2PPh$ (IV)[a, b]

I[c]		II[c]		III		IV		V		VI	
P	0.0	P	0.0	C1	0.014	C2	−0.001	CP1	0.000	CB1	−0.009
C2	0.0	C1	0.0	C7	−0.008	C3	0.001	CP4	0.000	CB2	0.002
C2′	0.0	C1′	0.0	C8	0.012	C4	0.000	CP2	−0.013	CB3	0.005
CP1	0.0	CP1	0.0	C9	−0.002	C5	0.000	CP3	0.013	CB4	−0.004
				C10	−0.011	C6	−0.001	CP2′	0.013	CB5	−0.003
				C11	−0.005	C12	0.001	CP3′	−0.013	CB6	0.009

[a] Atoms are labeled to agree with Figure 2. Primed atoms are two-fold related. [b] Dihedral angles (deg) between planes indicated: I and II, 85.0; I and V, 28.3; III and IV, 1.2. [c] Required by symmetry to be coplanar.

Table XII. Computed and X-ray Values of Bond Angles (Deg) at Phosphorus in R-bis(biphenylylenes)

	R = 8-$(CH_3)_2$N-1-Np (I)		R = 1-Np (II)		R = CH_3 (III)		R = Ph (IV)	
type[a]	calcd	X-ray	calcd	X-ray	calcd	X-ray	calcd	X-ray
C1-P-C1′	178.4	175.5	177.0	177.4	178.4	178.3	176.6	179.3
C1-P-C2	87.8	87.4	88.2	86.2	87.7	86.0	88.1	86.1
C1-P-C2′	93.0	92.5	92.9	94.2	93.2	95.5	94.0	94.3
C1-P-CX	87.9	85.8	87.7	87.7	88.7	88.9	88.7	89.6
C2-P-C1′	93.0	97.1	94.2	95.9	93.0	94.0	93.4	94.3[b]
C1′-P-C2′	88.2	85.9	88.0	86.6	87.8	86.0	88.2	86.1[b]
CX-P-C1′	90.5	93.6	89.6	90.0	89.7	89.8	87.9	89.6[b]
C2-P-C2′	104.3	101.8	109.3	110.9	113.1	111.0	112.3	111.5
C2-P-CX	117.3	106.1	118.5	116.4	125.6	125.6	125.7	124.3
CX-P-C2′	138.3	151.9	132.2	132.6	121.3	123.5	122.0	124.3[b]

[a] Labeled according to Figures 1 and 3 of ref 1b for derivatives I and II, respectively, and Figures 1 and 2 here for derivatives III and IV, respectively. X is N1 for I and II, M for III, and P1 for IV. [b] These values are required by the two-fold axis to equal the related value listed above.

decrease. In I, it has a value of 101.8°.[1b]

To further probe the role of steric effects on geometry in this series, we carried out a molecular mechanics calculation based on our earlier studies using this method.[16] We have found the method useful in examining possible intermolecular effects[17] and outlining probable reaction pathways for both enzymatic[18] and nonenzymatic[19] systems.

For each of the bis(biphenylylenes) I–IV, energy minimimization was carried out for three pentacoordinated geometries, a trigonal-bipyramidal form which has the unique substituent R positioned equatorially (A) and two rectangular-pyramidal forms which have the substituent either in the basal position (B) or at an apical (C) position. In addition, the calculation was extended to a trigonal bipyramid for I and II which contained the α-naphthyl group in an axial site (D).

Strainless parameters (bond lengths and force constants) appropriate for each geometry were used. As constraints in the calculations, the atoms comprising the respective ring systems were maintained coplanar for all geometries; for R

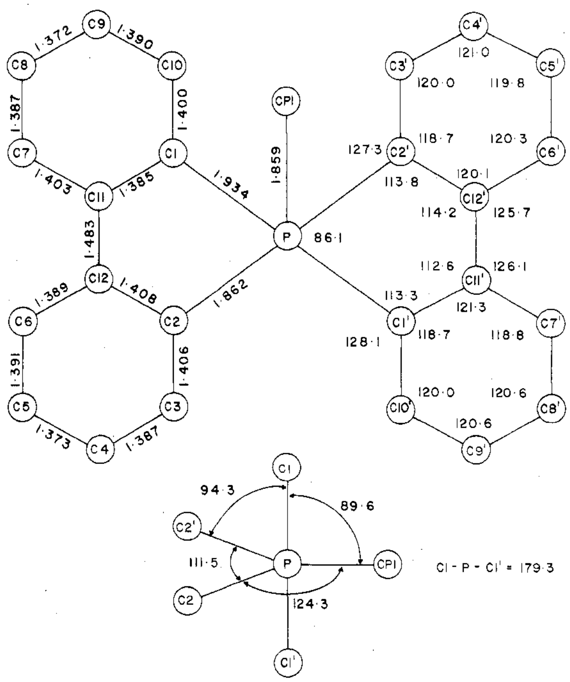

Figure 4. Selected bond lengths (Å) and angles (deg) for $(C_{12}H_8)_2PPh$ (IV). The primed atoms are related to the unprimed ones by the crystallographic twofold axis.

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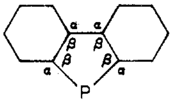
apical in the rectangular pyramid, it was necessary to maintain the biphenylylene ring carbon atoms attached to phosphorus coplanar; otherwise the geometry would transform to the trigonal bipyramid with R equatorial. For an energy minimization for I and II in a trigonal-bipyramidal geometry with R axial, coplanarity of the biphenylylene group, situated at an axial–equatorial location, and the phosphorus–carbon bond of the attached R group was required to avoid severe distortions from this geometry. The coordinates for the biphenylylene ring were representative of those obtained in the X-ray studies; e.g., some angle parameters are shown here.



$\alpha = 126.5°$, $\beta = 113.5°$

A strainless bond length of 1.47 Å was assumed for the central C–C bond.

With use of the trigonal bipyramid A as the ground-state structure, reasonable agreement with the X-ray parameters was obtained. Bond angles at phosphorus are compared in Table XII.

For the 8-$(CH_3)_2$N-1-Np derivative I, the calculated value of the equatorial angle CN1–P–C2′ is only 138.3° compared to the X-ray value[1b] of 151.9°. This results from opening of the angles at CN1, CN9, and CN8 to a greater degree than found experimentally in order to accommodate the presence of the $(CH_3)_2N$ group. If one reduces the equatorial bending force constant at phosphorus, better agreement between observed and calculated exocyclic angles of the α-naphthyl group and that of the equatorial angle at phosphorus is obtained. For both I and II, minimum-energy structures result when the plane of the naphthyl group is approximately at right angles to the basal plane of B or, in the case of A, when it lies near the equatorial plane, as found in the X-ray analyses.

The calculations show that the rectangular pyramid with R apical (type C) is the most strained and that the strain energy increases progressively, relative to conformation of types A or B, as the size of the R group increases along the series. When viewed relative to the type of structural displacement coordinates found from the X-ray data for I and II as opposed to that for III and IV, the results suggest, in agreement with the conclusion from the X-ray structural studies, that intramolecular ligand exchange through transition states of the type C may become disfavored in preference to pseudorotations proceeding via trigonal bipyramids with R apical (type D). This apparently is the case on going from the 2-isopropylphenyl derivative (VIII) to the 2,4,6-triisopropylphenyl derivative (VII) where ligand exchange was interpreted in terms of a transition state of the type C for VIII and in terms of a transition state or intermediate of the type D for the more sterically hindered phosphorane VII.

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Registry No. III, 3151-21-1; IV, 3572-91-6.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes for III and IV, thermal parameters (Table XIII) and bond angles involving hydrogen atoms (Table XIV) for III, and similar data (Tables XV, XVI) for IV (24 pages). Ordering information is given on any current masthead page.

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Proof of a Linear Fe–N–O Linkage, Perpendicular to the S_4 Plane in $Fe(NO)(S_2CN\{CH(CH_3)_2\}_2)_2$. A New (Aerobic) Synthesis of the Complex and Its Crystal Structure

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The title complex [Fe(NO)(*i*-Prdtc)$_2$] was prepared by the action of ferric nitrate on Fe(*i*-Prdtc)$_3$, and its crystal structure was determined. The meticulously air-free conditions normally used for such syntheses were not required. The crystal structure is by far the most accurate of any "d^7" M–N–O complex and is the first [Fe(NO)(dtc)$_2$] complex for which the ligand geometry can be established unambiguously. The controversial Fe–N–O geometry was found to be linear (179°) and perpendicular to the S_4 plane in a rectangular-base pyramid of ligand atoms. The Fe–N and N–O distances are 1.676 (3) and 1.161 (3) Å, respectively. Earlier spectroscopic structural assignments are reevaluated. Crystal data for [Fe(NO)(*i*-Prdtc)$_2$]: space group $P2_1/n$; $Z = 4$; $a = 9.242$ (6) Å, $b = 16.932$ (1) Å, $c = 14.223$ (4) Å; $\beta = 107.40$ (4)°; $V = 2124$ Å^3; $R = 4.6\%$ for 2069 reflections.

Introduction

As part of a program on the synthesis, properties, and structure of iron and cobalt dithiocarbamates (dtc),[2-5] we have been interested in their nitroso derivatives, [M(No)(dtc)$_2$], on which there is already a considerable body of literature.[6-16]

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