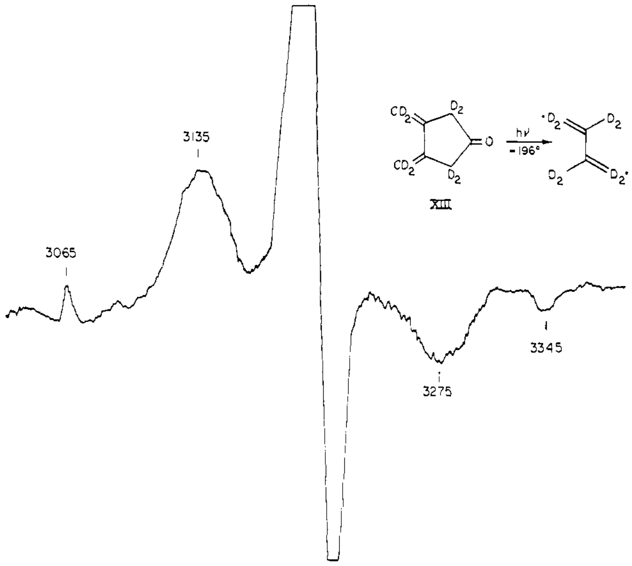

Figure 1. Epr spectrum of tetramethyleneethane-d_8.

serving the epr spectrum simultaneously. The instability of the molecule may also be responsible for the lack of resolution of the x,y lines whose presence is indicated by the broadness of the inner two lines. The central line is a distinct, more stable radical as indicated by the fact that the intensity of this line is undiminished on standing for a period of time at −196°.

The above results constitute the first direct observation of a 1,4 diradical by physical means.[15] Efforts to trap this species chemically are currently in progress.

Acknowledgment. This work was generously supported by the National Science Foundation (Grant No. GP 6667).

(15) Strong evidence for the intermediacy of 1,4 diradicals in cycloaddition reactions has been presented by P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964). See also subsequent papers in that series.

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Stereochemically Nonrigid Six-Coordinate Hydrides

Sir:

We report the first unambiguous example of stereochemically nonrigid behavior in six-coordinate complexes. Barriers to intramolecular rearrangement in such complexes are usually relatively high[1] as exemplified by $C_6H_5SF_5$ whose AB_4 ^{19}F nmr spectrum we find is unaltered at 215°.

Rapid intramolecular rearrangements have been established for $H_2Fe[P(OC_2H_5)_4]_4$[2] (**1**) and $H_2Fe[C_6H_5P(OEt)_2]_4$ (**2**) by analysis of the temperature-dependent ^{31}P and ^1H nmr spectra. The 220-MHz ^1H nmr spectra at −50° for the hydride regions of complexes **1** and **2** are shown in Figure 1, together with spectra simulated on a Calcomp plotter. Spectra for both compounds

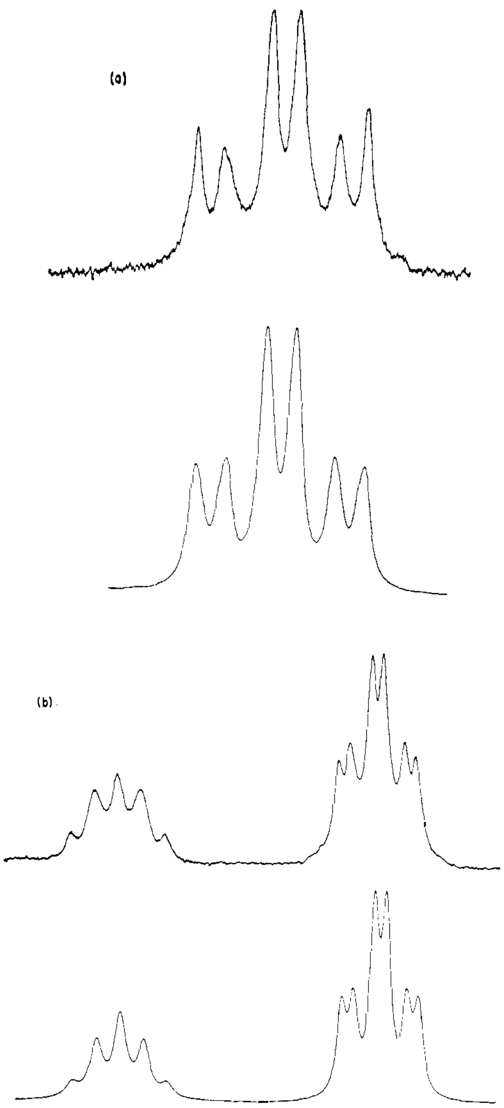

Figure 1. Observed and simulated 220-MHz ^1H nmr spectra of hydride region of complex **1** (a) and complex **2** (b) (−50°).

show pronounced line-shape effects as the temperature is increased, and at +50° both give rise to simple quintet resonances. Similarly, the 40.5-MHz ^{31}P nmr spectra of compound **2** at low temperatures with and without proton noise decoupling are shown in Figure 2. The ^{31}P nmr spectra for both complexes at +50° show a simple triplet structure with the same splitting as the high-temperature proton quintets. Nuclear resonance data are given in Table I.

Averaging of nuclear environments and retention of H–P spin–spin coupling at the high temperatures operationally defines these molecules as stereochemically nonrigid. Consistently, the temperature-dependent hydride spectra are invariant to concentration changes and to addition of free phosphite. Also the high-temperature apparent coupling constants are equal to the average of the assigned low-temperature coupling constants.

At high temperatures the molecules are nonrigid and the four phosphorus atoms appear magnetically equivalent. As the temperature is lowered, specific *cis* and *trans* forms become apparent. For compound **2**, the two isomers have similar energies at −50°. One isomer is clearly the *trans* dihydride (Figure 3) with a sym-

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[1] E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968), and references therein.

[2] W. Kruse and R. H. Atalla [*Chem. Commun.*, 921 (1968)] incorrectly assign a distorted *trans* ground-state structure (see Figure 3).

Table I

A. ^1H Hydride Nmr Data

Compound (temp, °C)	δ, ppm[a]	J_{PH},[b] Hz
cis-$H_2Fe[C_6H_5P(OEt)_2]_4$ (−50°)	12.93	$J_{13} = J_{14} = J_{23} = J_{24} = 66.5$ $J_{15} = J_{26}$ (small) }[d] $J_{16} = J_{25} = 24$ }
trans-$H_2Fe[C_6H_5P(OEt)_2]_4$ (−50°)	10.55	$J_{PH} = 48$
Av $H_2Fe[C_6H_5P(OEt)_2]_4$ (+50°)	12.80	$J_{PH} = 40.5$
cis-$H_2Fe[P(OEt)_3]_4$ (−50°)	13.91	$J_{13} = J_{14} = J_{23} = J_{24} = 61.5$ $J_{15} = J_{26}$ (small) } $J_{16} = J_{25} = 25$ }
Av $H_2Fe[P(OEt)_3]_4$ (+50°)	13.92	$J_{PH} = 38.5$

B. ^{31}P Nmr Data

Compound (temp, °C)	δ_{34}, ppm[c]	δ_{56}, ppm[c]	J_{PP}, Hz
cis-$H_2Fe[C_6H_5P(OEt)_2]_4$ (−40°)	−198.6	−188.0	$J_{35} = J_{36} = J_{46} = J_{45} = 45.0$ J_{56} (small)

[a] Hydride chemical shifts in ppm upfield from TMS. [b] Numbering as in Figure 3. J_{HH} is small. [c] ^{31}P chemical shifts in ppm downfield from 85% H_3PO_4. [d] Couplings with braces cannot be separately assigned from the spectra.

metrical quintet resonance. The *trans* structure should distort in the manner indicated in the figure to relieve steric crowding in the plane. A "fixed" distorted structure could give a more complex splitting pattern. However, the barrier to inversion of the phosphorus ligands through the plane may be very small (*vide infra*), or there may be strong phosphorus–phosphorus coupling. The *cis* isomeric form of **2** has a hydride resonance pattern (<−20°) approximating a triplet of doublets. The main triplet splitting must arise from the magnetically equivalent phosphorus atoms 3 and 4 (Figure 3). The coupling constant is 66.5 Hz, comparable to the *cis* coupling of 48 Hz in the *trans* isomer. The doublet splitting of about 25 Hz arises either from 1,5 or 2,5 coupling with the other coupling being small. The overall assignment of *cis* geometry is supported by the ^{31}P spectra (Figure 2). The proton noise decoupled ^{31}P spectrum of **2** shows the symmetrical A_2B_2 pattern expected for *cis* geometry.[3] The ^{31}P spectrum of **2** without proton noise decoupling confirms the assignments of hydrogen to phosphorus couplings obtained from the hydride spectrum.

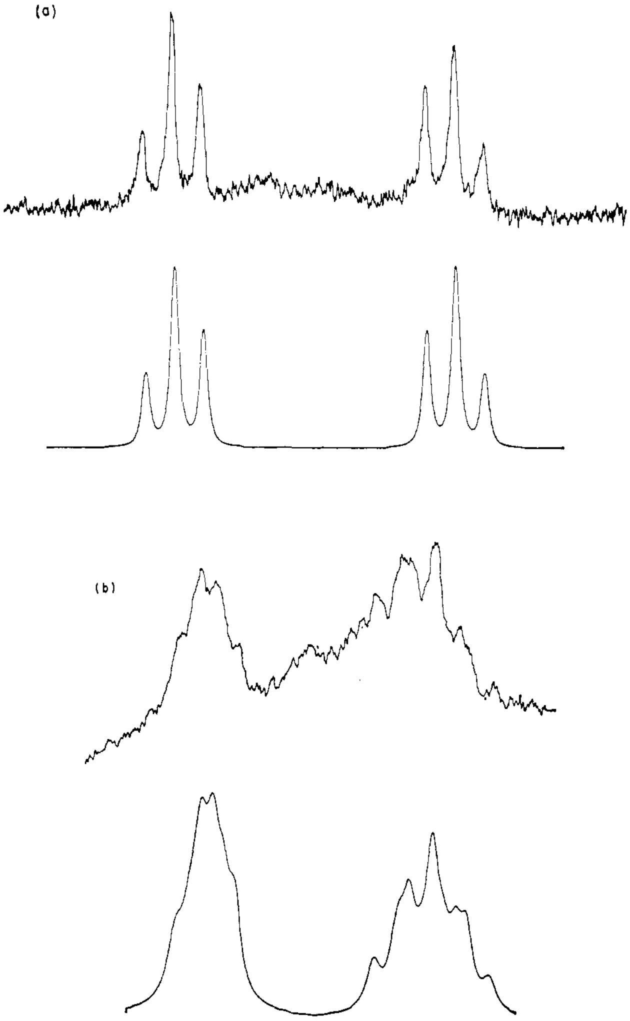

Figure 2. Observed and simulated 40.5-MHz ^{31}P nmr spectra of complex **2** (a) with proton noise decoupling (−40°) and (b) without proton noise decoupling (−50°). The broad central absorptions in the two experimental spectra are assigned to the *trans* isomer.

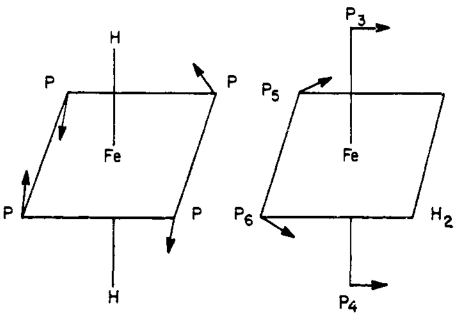

Figure 3. Structures of H_2FeL_4 complexes. Arrows indicate probable distortions from idealized geometries. The numbering in the *cis* structure is used to designate the coupling constants in Table I.

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(3) Trigonal prismatic forms are considered less likely because of unfavorable steric-electronic factors and because accidental degeneracies must be invoked to give an A_2B_2 pattern. The three possible trigonal prismatic isomers have AA′BB′, AA′A″A‴, and AA′BC phosphorus spin systems.

The ^{31}P resonance of the *trans* form of **2** appears to show line broadening effects even when the *cis* isomer is in the slow-exchange limit (Figure 2). It is probable that the energy minimum for the *trans* molecule corresponds to the distorted structure indicated in Figure 3a and that the inequivalent phosphorus ligands are undergoing rapid intramolecular exchange.

The passage of the *cis* and *trans* ^{1}H resonances in **2** to a simple quintet with increasing temperature shows that *cis–trans* isomerization *via* a polytopal[1,4] rearrangement is operative here. The analysis of the hydride spectrum for compound **1** is the same as for **2** except that only the *cis* isomer was detected.

The distortions in the *cis* and *trans* isomers indicated in Figure 3 suggest a polytopal rearrangement alternative to the trigonal or "Bailar" twist.[5] The distortion modes could, in highly excited vibrational states, approach a tetrahedral disposition of phosphorus nuclei about the iron nucleus; hydrogen traverse (tunneling or classical) of trigonal faces would then complete the nuclear permutation process. This alternative is more attractive on steric grounds because of the obvious steric relief in the transition state. We cannot now rigorously distinguish between these two possible rearrangements, but detailed analysis of nmr transitional line shapes using the density matrix approach and analogous studies of other L_4MH_2 complexes now in progress may provide a definitive answer. Full details of spectral assignments and mechanistic studies will be published shortly.

(4) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).
(5) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

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The Isolation and Structure of Daphnetoxin, the Poisonous Principle of *Daphne* Species[1]

Sir:

Daphne mezereum L. and other species of the thymelaeaceous genus *Daphne* have been recognized since at least the 11th century[2] as virulent poisons, and more recent cases have confirmed the toxicity, doses of a few berries or a few grams of bark being reported fatal to man, dog, or horse.[3–6] Despite the striking toxicity[7] and the widespread occurrence of the genus both wild and cultivated in Europe and North America, no modern chemical studies of the principle have been made and the activity has been variously ascribed to the coumarin glycosides,[3,4] which are well known constituents of the bark,[8] or to an ill-defined mezerinic acid or mezerinic anhydride.[5,6,9]

Fractionation of CH_2Cl_2 extracts of *D. mezereum* bark or commercial "mezeron" bark (*D. mezereum*, *D. laureola*, and *D. gnidium*) by partitioning between hexane–CH_2Cl_2 and aqueous methanol, removal of phenolic materials by careful base washings, countercurrent fractionation, and finally crystallization from cold ethanol led in approximately 0.02% yield to a crystalline product, daphnetoxin.[10] The isolation procedure was devised on the basis of toxicity tests using goldfish[11] and appears to yield the major toxic component.[12]

Daphnetoxin, mp 194–196°, $[\alpha]_D$ +63°, $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 243 (8950), 337 (84) nm, $C_{27}H_{30}O_8$, suffers degradation to complex mixtures of products in either acid or base but yields with acetic anhydride–pyridine a diacetate, mp 122–124°, $C_{31}H_{34}O_{10}$. Basic hydrolysis affords benzoic acid and suggested the molecule to be the benzoate ester of a diterpene alcohol, a result supported by nmr signals corresponding to five aromatic protons and by an intense peak for $C_6H_5CO^+$ in the mass spectrum of the acetate. The formation of another intense ion corresponding to $C_6H_5C_2O_3^+$, and the ready reduction of daphnetoxin by $NaBH_4$ to products showing typical alkyl benzene fine structure in the uv, however, indicated additional complications.

The parent molecule and a number of derivatives were examined for possible crystallographic study but all proved unsuitable until the bisbromoacetate was found to crystallize in part in hexagonal plates, mp 228–229°, space group $P3_121$ (or $P3_221$) with one molecule in the asymmetric unit, $a = 12.458$, $c = 34.441$ Å.

Intensity data collected on a Picker automatic diffractometer using Cu Kα radiation yielded 2660 reflections of $2\theta \leq 120°$. After correction for absorption ($\mu = 41.5\ \mathrm{cm}^{-1}$) these yielded a Patterson synthesis showing the location of one bromine. A series of structure factor and Fourier calculations revealed in stages the remaining atoms and culminated in the structure **1a**.[13] Because extensive crystal degradation occurred during data collection (average intensity loss *ca.* 25%), the data were remeasured using three separate crystals and discarding these when the intensity losses reached 10%. Refinement on the new data has yielded an R of 8.4% and is continuing, but the presence of

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(1) A portion of the work described here was reported at an intermediate stage as paper D1 at the meeting of the American Crystallographic Association, Seattle, Wash., March 25, 1969. The abstract shows the molecule in what is now known to be the incorrect absolute configuration, and, owing to an error in drawing, with the wrong relative configuration at C-5.

(2) Avicenna (A.D. 980–1037), as cited by Rufinus (*ca.* 1287); *cf.* "The Herbal of Rufinus," L. Thorndyke, Ed., University of Chicago Press, Chicago, Ill., 1946, pp 189–190. The toxicity is also mentioned, although in less vigorous terms, by Dioscorides (1st century A.D.).

(3) J. M. Kingsbury, "Poisonous Plants of the United States and Canada," Prentice-Hall, Englewood Cliffs, N. J., 1964, pp 386–388.

(4) W. C. Muenscher, "Poisonous Plants of the United States," Macmillan, New York, N. Y., 1951, pp 168–171.

(5) O. Gessner, "Die Gift - und Arzneipflanzen von Mitteleuropa," Carl Winter, Universitatsverlag, Heidelberg, 1953, pp 548–551.

(6) A. A. Forsyth, "British Poisonous Plants," Bulletin 161, HMSO, London, 1954, pp 64–66.

(7) These properties are apparently widespread in the family, many genera of which have been popularly recognized as having strong irritant properites (*e.g.*, "burn nose bark" for *Daphnopsis* sp. of Jamaica), and at least one of which (*Schoenobiblus*) has been used as the basis of a Peruvian arrow poison (Dr. H. V. Pinkley, personal communication).

(8) *Cf.* W. Karrer, "Konstitution und Vorkommen der Organischen Pflanzenstoffe," Birkhauser Verlag, Basel, 1958, compounds 1320, 1334, 1449.

(9) Buchheim, *Arch. Path.*, 1 (1872), cited in C. Wehmer, "Die Pflanzenstoffe," Vol. II, Gustav Fischer, Verlag, Jena, 1929, p 814.

(10) W. J. Balkenhol, Ph.D. Thesis, University of Washington, Seattle, Wash., 1967.

(11) W. A. Gersdorff, *J. Amer. Chem. Soc.*, **52**, 3440 (1930).

(12) Daphnetoxin in mice shows LD_{50} *ca.* 275 μg/kg, *i.e.*, approximately half that of strychnine. Goldfish tests indicate that about one-third the total toxicity of the crude extracts is isolated as crystalline product.

(13) The numbering system indicated follows that of Hecker, *et al.*, for phorbol,[14] since this accommodates more reasonably than that of Crombie[15b] the cyclopropyl opening which constitutes the formal distinction between the two skeletons.