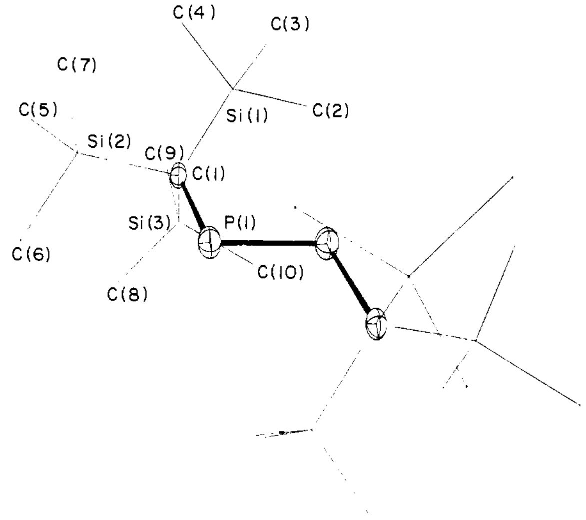

Figure 1. View of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**1**) showing the atom numbering scheme. Pertinent metric parameters for molecule A: P(1)-P(1)′ 2.014 (6), P(1)-C(1) 1.85 (1) Å; ∠P(1)′-P(1)-C(1) 108.2 (4)°. For molecule B: P(1)-P(1)′ 2.004 (6), P(1)-C(1) 1.87 (1) Å; ∠P(1)′-P(1)-C(1) 108.9 (4)°.

in **2**, presumably as a result of the larger size of $(Me_3Si)_3C$ over $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$. We suggest that this difference in ligand size is responsible for the stability of the HCl addition product **3** and the absence of a corresponding product from the reaction of **2** with HCl.

Acknowledgment. Generous financial support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page.

Vinyl Hydrogen Activation in Mono- and Dinuclear (η^5-Cyclopentadienyl)(hexatriene)cobalt Complexes. Thermal and Photochemical Hydrogen Shifts of Complementary Stereochemistry

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The activation of C–H bonds in hydrocarbons by soluble transition-metal complexes has been the focus of intensive recent research.[1] Its vinyl variant has been relatively unexplored,[2] having frequently been restricted to low-yielding complex cluster reactions.[3] It also suffers from little mechanistic understanding. This is surprising, considering the ready availability of alkenes such

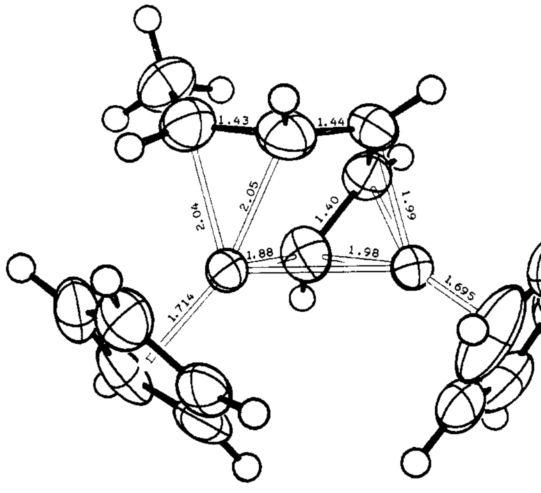
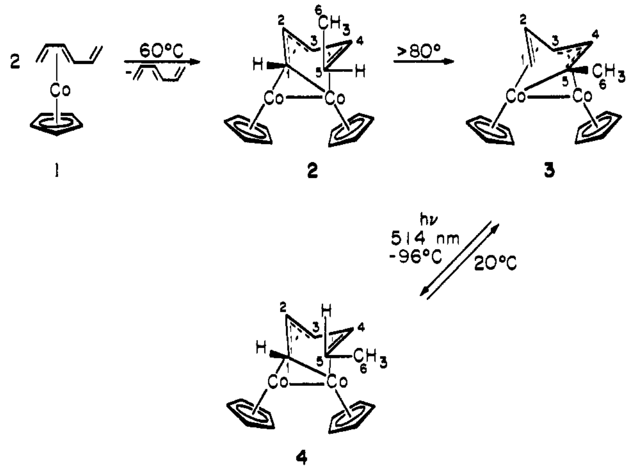


Figure 1. ORTEP drawing of **2** including selected bond lengths (angstroms). Ellipsoids are scaled to represent 50% probability surface. The hydrogen positions shown are those calculated on the basis of idealized geometry following their locations on the difference Fourier electron density map.

Scheme I



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[1] See, for example: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (b) Parshall, G. W. *Acc. Chem. Res.* **1975**, *4*, 113-117. (c) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97-143. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240-4242. (e) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *Ibid.* **1982**, *104*, 6994-7001. (f) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1982**, *104*, 352-354. (g) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243-1244 and the references therein.

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[3] See, for example: (a) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2017-2020. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 1190-1191. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *Ibid.* **1980**, 547-549. (d) Bhaduri, S.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Raithby, P. R.; Rehani, S.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1979**, 562-568. (e) Ferrari, R. P., Vaglio, G. A. *J. Organomet. Chem.* **1979**, *182*, 245-249. (f) Pierpont, C. G.; Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 616-618. (g) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *J. Organomet. Chem.* **1976**, *113*, C42-C44. (h) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614-1620. (i) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29-C31. (j) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415-1419.

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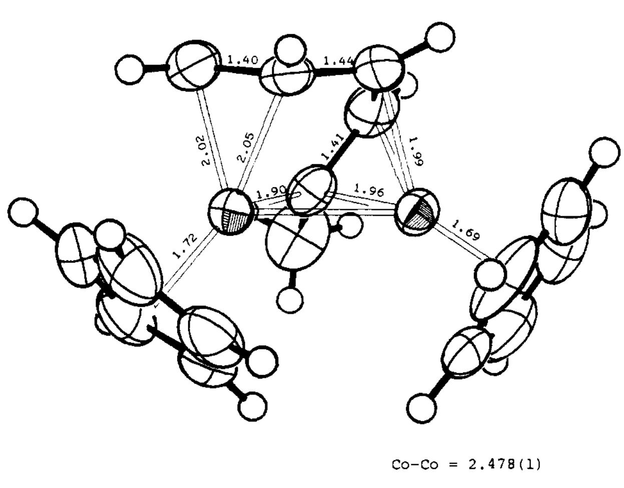

Figure 2. ORTEP drawing of **3**.

as ethylene and 1,3-butadiene, the catalytic conversion of which to functionalized molecules by such a mechanism would be of substantial interest. We report an unprecedented series of thermal vinyl hydrogen shifts in a complexed hydrocarbon ligand, including a thermally reversible photochemical migration to a dinuclear carbene center exhibiting complementary stereochemistry. This work demonstrates novel pathways for ligand rearrangements on dinuclear metal systems, which may also be regarded as homogeneous models for hydrocarbon rearrangement and C–H exchange processes on surfaces.[4]

We have found that *trans*-(η^4-1,3,5-hexatriene)(η^5-cyclopentadienyl)cobalt (**1**, Scheme I),[5,6] in stark contrast to its isostructural rhodium[7a] and very stable isoelectronic iron tricarbonyl counterparts,[7b–e] dimerizes in 24 h at 60 °C (C_6H_6) accompanied by the clean extrusion of one molecule of intact triene ligand. The product of this transformation is the flyover carbene **2**,[6] derived from a novel 1,6-hydrogen transfer in quantitative yield. In **2** the ligand functions as a six-electron donor, the carbene carbon 1 being bound to one cobalt atom in σ-fashion and to the other as part of an η^3-allyl unit involving C_{1-3} (Figure 1). One notes that trans–cis isomerization is necessary in order to attain the product stereochemistry at $C_{3,4}$. We envisage this to occur through the intermediacy of $(CpCo)_2(\mu\text{-}\eta^6\text{-}C_6H_8)$, in which the ligand adopts a bis(η^3-allyl) configuration.[8,9] The kinetics of disappearance of **1** are complicated. At high dilution (0.001 M) the rate of reaction is concentration dependent; in more concentrated solutions (0.35 M) it initially follows first order. Added excess ligand retards the rate of formation of **2**. These preliminary data imply that the identity of the rate-determining step may be a function of the reaction conditions. A more detailed kinetic investigation is the subject of continuing efforts. Thermolysis of **1**-*6,6*-d_2[10] gave **2** with C_1 enriched in label (k_H/k_D = 4.95 ± 0.14 at 90 °C), suggesting an essentially irreversible proton shift.

Significantly, **2** is not the endpoint of the thermal chemistry of **1** but quantitatively isomerizes to **3**[5] (Figure 2) at higher temperatures, following first-order kinetics (E_a = 29.1 ± 0.4 kcal mol^{-1}, log A = 11.6 ± 0.6). The stereochemistry of this unprecedented 1,5-hydrogen shift was probed with the above **2**-d_2 (enriched at C_1). It revealed the emergence of the transferred hydrogen *exclusively endo* (i.e., pointing toward the carbene carbon), possibly indicating initial oxidative addition to the bound cobalt, followed by stereospecific reductive elimination involving C_1.

In light of these results, the photochemistry of **3** is also truly remarkable. Irradiation in toluene at −96 °C for 1 h using an argon ion laser (514 nm) generates **4** (a stereoisomer of **2**)[6] in a time-invariant (and therefore presumed) photostationary ratio of **4**:**3** = 63:37. This complex is the result of a 1,5-hydrogen shift exhibiting stereochemistry *opposite* to that encountered in the thermal generation of **3** from **2**. To our knowledge this constitutes the first observation of such stereochemical complementarity (common in organic chemistry) in an organometallic system of this type. In contrast, **2** is photoinert at this wavelength (possibly due to its relatively smaller extinction coefficient[6]). At room temperature **4** rapidly and unimolecularly reverts to **3** (E_a = 19.4 ± 0.9 kcal mol^{-1}, log A = 10.0 ± 1.3). The data rule out **2** as an intermediate in either process; however, it is possible that **4** is an intermediate in the thermal conversion of **2** to **3**. This photochemical energy-storage cycle has been repeated more than 20 times without visible deterioration. Although currently impractical, this system is novel and suggests future experimentation, aimed at improving efficiency and slowing the rate of thermal reversal by exploiting the enormous "fine-tuning" potential of organometallic systems.

Further labeling and thermochemical experiments are being initiated to elucidate additional mechanistic details and thermodynamic aspects. In light of the above results, it will be intriguing to elucidate the stereochemistry of the **3** ⇄ **4** cycle at C_1: will

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(4) (a) Gault, F. G. *Adv. Catal.* **1981**, *30*, 1–95; (b) *Gazz. Chim. Ital.* **1979**, *109*, 255–269. (c) Ledoux, M.; Gault, F. G.; Masini, J.-J.; Roussy, G. *J. Chem. Soc., Chem. Commun.* **1975**, 153–154. (d) Touroude, R.; Gault, F. G. *Ibid.* **1975**, 154–155. (e) Iwasawa, Y.; Hamamura, H. *Ibid.* **1983**, 130–132.

(5) Prepared[6] by irradiation of $CpCo(CO)_2$ and *trans*-1,3,5-hexatriene, 4 °C, 4.5 h, and reverse-phase HPLC, 65%.

(6) All new compounds (except **4**) gave satisfactory analytical and spectral data. In particular, the connectivity in the hydrocarbon ligands of **1–4** was assigned by complete decoupling experiments and further corroborated by inspection of models; see ref 9 and the following: Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 219–222. **1** (red oil): ^{1}H NMR (all at 250 MHz in C_6D_6) δ −0.05 (ddd, J = 9.1, 1.8, 0.9 Hz, 1 H), 1.13 (ddd, J = 9.3, 8.2, 0.9 Hz, 1 H), 1.88 (ddd, J = 6.4, 1.8, 0.9 Hz, 1 H), 4.58 (s, 5 H), 4.82 (ddd, J = 9.1, 6.4, 4.5 Hz, 1 H), 4.96 (ddd, J = 8.2, 4.5, 0.9 Hz, 1 H), 5.63 (ddd, J = 15.8, 9.4, 9.3 Hz, 1 H), 5.08 (dd, J = 9.4, 2.1 Hz, 1 H), 5.25 (dd, J = 15.8, 2.1 Hz, 1 H); ^{13}C NMR (all at 63 MHz, in C_6D_6) δ 143.4, 108.6, 79.9, 78.9, 75.7, 50.7, 30.4. **2** (green-black prisms): mp 145–146 °C; ^{1}H NMR (assignments for **2–4** follow the numbering in **2**) δ 0.94 (d, J = 6.4 Hz, 3 H, H_6), 2.68 (dq, J = 8.2, 6.4 Hz, 1 H, H_5), 3.56 (ddd, J = 8.2, 3.2, 0.8 Hz, 1 H, H_4), 4.02 (ddd, J = 4.9, 3.2, 0.8 Hz, 1 H, H_2), 4.56 (ddd, J = 3.2, 3.2, 1.3 Hz, 1 H, H_3), 4.72 (s, 10 H), 7.71 (dd, J = 4.9, 1.3 Hz, 1 H, H_1); ^{13}C NMR δ 207.7, 82.7, 79.8, 78.5, 66.2, 56.4, 50.3, 18.5; UV λ_{max} (hexane) 265 nm (log ϵ = 3.90), 294 (sh, 3.86), 372 (sh, 3.79), 390 (sh, 3.60), $\epsilon_{514} \approx$ 340. X-ray: crystal size 0.13 × 0.31 × 0.43 mm; monoclinic Laue symmetry; space group $P2_1/n$; a = 5.9689 (7) Å, b = 26.434 (5) Å, c = 8.5044 (14) Å, β = 98.478 (13)°; V = 1327.0 (6) Å^3 at 25 °C; Z = 4; μ_{calcd} = 25.7 cm^{-1}; d_{calcd} = 1.65 g cm^{-3}; radiation = graphite monochromatized Mo Kα (λ 0.71073 Å); scan range 1.5° ≤ 2θ ≤ 45°; reflections collected = 1793, 1559 unique with $F^2 > 3\sigma(F^2)$, R = 0.0296, R_w = 0.0458. **3** (green-black crystals): mp 104–106 °C; ^{1}H NMR δ 0.08 (dd, J = 10.2, 0.9 Hz, 1 H, H_1 endo), 1.75 (dd, J = 6.9, 0.9 Hz, 1 H, H_1 exo), 2.68 (s, 3 H, H_6), 3.24 (dd, 2.4, 1.4 Hz, 1 H, H_4), 3.34 (dddd, J = 10.2, 6.9, 1.6, 1.4 Hz, 1 H, H_2), 4.65 (s, 5 H), 4.80 (s, 5 H), 4.82 (dd, J = 2.4, 1.6 Hz, 1 H, H_3); ^{13}C NMR δ 83.6, 79.3, 73.72, 53.1, 52.5, 32.9, 27.5 (the carbene carbon peak could not be located); UV λ_{max} (hexane) 277 nm (log ϵ = 4.14), 343 (sh, 3.66), 474 (sh, 3.29), $\epsilon_{514} \approx$ 1500. X-ray: crystal size 0.16 × 0.26 × 0.30 nm; orthorhombic Laue symmetry; space group *Pbca*; a = 8.444 (1) Å, b = 13.270 (3) Å, c = 23.782 (2) Å; V = 2665 (1) Å^3 at 25 °C; Z = 8; μ_{calcd} = 25.6 cm^{-1}, d_{calcd} = 1.636 g cm^{-3}; radiation = graphite monochromatized MoKα (λ 0.71073 Å); scan range = 3° ≤ 2θ ≤ 45°; reflections collected = 2029, 1377 unique with $F^2 > 3\sigma(F^2)$, R = 0.0392, R_w = 0.0575. **4**: ^{1}H NMR (toluene-d_8) δ 0.73 (dq, J = 8.7, 6.4 Hz, 1 H, H_5), 1.15 (d, J = 6.4 Hz, 3 H, H_6), 2.96 (ddd, J = 8.7, 3.2, 0.8 Hz, 1 H, H_4), 3.58 (ddd, J = 5.1, 3.1, 0.8 Hz, 1 H, H_2), 4.58 (ddd, J = 3.2, 3.1, 2.6 Hz, 1 H, H_3), 4.58 (s, 5 H), 4.60 (s, 5 H), 7.95 (dd, J = 5.1, 2.6 Hz, 1 H, H_1). Due to its thermal sensitivity this compound has not yet been isolated.

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(8) Substituted derivatives have been prepared from the reaction of $CpCo(C_6H_5C_2C_6H_5)[P(C_6H_5)_3]$ with diazoacetates, which also furnishes complexes of the type **2**: Hong, P.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *150*, 279–293. For structural analogues, see: Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350–1360. Rudler, H.; Rose, F.; Rudler, M.; Alvarez, C. *J. Mol. Catal.* **1982**, *15*, 81–92. Aumann, R.; Averbeck, H.; Krüger, C. *Chem. Ber.* **1975**, *108*, 3336–3348.

(9) A highly sensitive and incompletely characterized dimer is obtained in small amounts (HPLC) when neat **1** is heated. This dimer furnishes **2** on further heating. Similarly, μ-(η^4-syn-1,3,5-hexatriene)-μ-carbonyl(η^5-cyclopentadienyl)cobalt, prepared as in King, J. A., Jr.; Vollhardt, K. P. C. *Organometallics* **1983**, *2*, 684, cleanly rearranges to **3** at 144 °C.

(10) Prepared from CpCo(η^4-pentadienal) and $CD_2{=}[P(C_6H_5)_3]$ (72%).

the photoinduced and thermal shifts switch the positions of the two methylene protons?

Acknowledgment. This work was supported by NSF (CHE 82-00049). The Directors, Office of Energy Research, Office of Basic Energy Sciences and Fossil Fuels Technology, U.S. Department of Energy under Contract DE-AC03-76SF00098, are thanked for HPLC equipment funds. The crystal structure analyses were performed by Dr. F. J. Hollander, UC Berkeley X-ray Crystallographic Facility. We acknowledge the expert help of Drs. A. H. Kung and T. C. C. Ling, San Francisco Laser Center, UC Berkeley, supported by NSF CHE 79-16250. K. P.C.V. is a Camille and Henry Dreyfus Teacher-Scholar (1978-1983).

Registry No. 1, 86088-72-4; **2**, 86088-74-6; **3**, 86088-73-5; **4**, 86101-35-1; Co, 7440-48-4.

Supplementary Material Available: Listings of positional and thermal parameters and tables of bond lengths and angles derived from crystallographic analysis of **2** and **3** (6 pages). Ordering information is given on any current masthead page.

^{31}P Shielding Tensor of Deoxycytidine 5′-Monophosphate

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The use of ^{31}P NMR in oriented fibers to test structural models of nucleic acids requires a knowledge of the orientation of the eigenvectors of the ^{31}P shielding tensor with respect to the local phosphate skeleton.[1] Previous work along those lines from this laboratory used barium diethyl phosphate[2] (BDEP) and 2-aminoethyl phosphate[3] (AEP) as model compounds: these were the only two for which the orientation of the shielding tensors had been determined. Terao et al. have studied several nucleic acids and nucleotides as powders.[4] Here, we report a single-crystal ^{31}P study of deoxycytidine 5′-monophosphate in the free acid form (5′-dCMP) intended to test the generality of the eigenvector orientations used previously and in a structure perhaps more closely related to that found in nucleic acids.

Single crystals of 5′-dCMP were grown by slow evaporation from an aqueous solution. One crystal with dimensions 4 × 4 × 3 mm was mounted on a NMR goniometer head previously described.[5] The experiment was done on a home-built double-resonance spectrometer operating at 68.4 MHz for ^{31}P and 168.9 MHz for ^{1}H. Cross-polarization conditions were established with a 6-μs ^{1}H 90° pulse, a 3-ms contact and a 10-15-s delay between successive acquisitions. Typically, 100-150 accumulations were collected for each orientation of the crystal, which was rotated in steps of 9° for a total of 20 data points per axis of rotation. The crystal belongs to the $P_{2_12_12_1}$ space group with four molecules per unit cell,[6] and Figure 1 shows the rotation patterns of the four observed ^{31}P resonances.

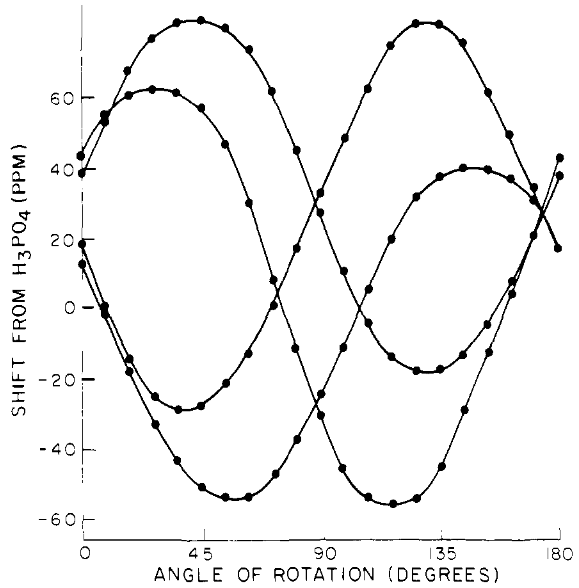

Figure 1. Dependence of NMR line positions as a function of rotation of the single crystal about the *y* axis of the goniometer.

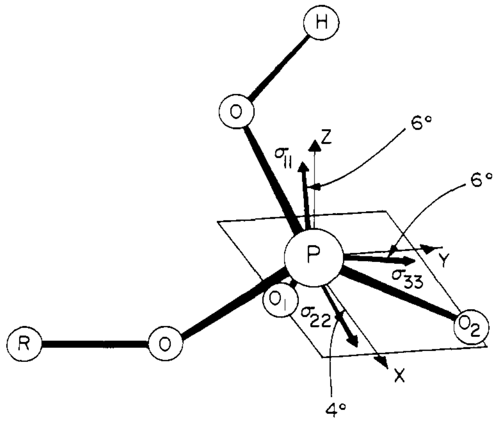

Figure 2. Orientation of the ^{31}P shielding tensor relative to the molecule fixed frame introduced by Herzfeld and co-workers. The frame is defined as follows: The *z* axis is perpendicular to the O_1-P-O_2 plane. The *x* axis bisects the O_1-P-O_2 plane. The *y* axis is chosen as to yield a right-handed system.

Table I. ^{31}P Shielding Tensor Principal Values Relative to H_3PO_4 and Direction Cosines Relative to the Molecule Fixed Frame[a]

$\sigma_{11} = 84.5$	−0.053 74	−0.061 53	0.995 0
$\sigma_{22} = -5.8$	0.997 0	−0.042 12	0.049 07
$\sigma_{33} = -71.2$	0.039 55	0.994 9	−0.068 95
$\bar{\sigma} = 2.5$			

[a] All values given in ppm with ±2 ppm error. Our results are, within experimental error, in agreement with the values determined by Terao et al. in their powder study of 5′-dCMP.[4]

Table I summarizes the data for the ^{31}P shielding tensor of 5′-dCMP along with the corresponding eigenvectors expressed as their direction cosines in a molecule fixed frame. Since the unit cell contains four crystallographically related molecules, a fourfold ambiguity exists in the choice of the orientation of the shielding tensor relative to the molecular frame. Fortunately, only one choice (given in Table I) shows good correlation with the 5′-dCMP molecule as discussed below. Incidentally, the molecule fixed frame shown in Figure 2 corresponds to the one defined by Herzfeld et al. in their study of BDEP[2] and used by Nall et al. in their work on oriented DNA fibers.[1]

As in the case of AEP and BDEP, the principal elements of the shielding tensor in 5′-dCMP show a good correlation with the electron distribution around the ^{31}P atom (cf. Figure 2). The most shielded direction (σ_{33}) lies essentially in the O_1-P-O_2 plane where a multiple-bond character is expected[7] and is substantiated by the

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