First Characterization of a 10-P-5 Spirophosphorane with an Apical Carbon−Equatorial Oxygen Ring. Kinetic Studies on Pseudorotation of Stereoisomers

Satoshi Kojima, Kazumasa Kajiyama,[†]
Masaaki Nakamoto, and Kin-ya Akiba*

Department of Chemistry, Faculty of Science
Hiroshima University, 1-3-1 Kagamiyama
Higashi-Hiroshima 739, Japan

Received June 25, 1996
Revised Manuscript Received October 29, 1996

10-P-5[1] phosphoranes usually assume trigonal bipyramidal structures in the ground state, in which there are two distinctive sites, the apical and the equatorial positions.[2] It is well-known that a phosphorane bearing oxygen and carbon substituents preferentially has oxygen atoms in the apical positions as the most stable stereoisomer according to the apicophilicity of the elements.[2,3] Quite recently, it was reported that a specially designed tetraoxyphosphorane in which a carbon substituent occupies the apical position due to steric hindrance could be isolated as the only detectable isomer.[4] Here, we report on the first isolation and characterization of a spirophosphorane having an apical carbon−equatorial oxygen five-membered ring and its thermodynamically more stable apical oxygen−equatorial carbon isomer and discuss the relative thermal stability of these stereoisomers on the basis of kinetic studies.

When P−H (equatorial) spirophosphorane **1** [^{31}P NMR ($CDCl_3$) δ −45.8 ($^1J_{PH}$ = 729 Hz)][5,6] was treated with more than 2 equiv of *n*-BuLi in ether and carefully treated with dilute hydrochloric acid, we obtained monocyclic P−H (apical) phosphorane **2**[7] [90%; mp 119 °C; ^{31}P NMR ($CDCl_3$) δ −34.4 ($^1J_{PH}$ = 273 Hz); ^{19}F NMR ($CDCl_3$) δ −72.9 (br s, 3F), −76.3 (q, $^4J_{FF}$ = 9.2 Hz, 3F), −76.8 (q, $^4J_{FF}$ = 8.2 Hz, 3F), −77.0 (qq, $^4J_{FF}$ = 9.2 Hz, $^9J_{FF}$ = 4.9 Hz, 3F)] and spirophosphorane **3** bearing a butyl group [9%; mp 109 °C; ^{31}P NMR ($CDCl_3$) δ −18.8; ^{19}F NMR ($CDCl_3$) δ −75.1 (q, $^4J_{FF}$ = 9.3 Hz, 6F), −75.4 (q, $^4J_{FF}$ = 9.3 Hz, 6F)] (Scheme 1).

Thermal reactions of **2** in refluxing toluene afforded **3**, quantitatively (Scheme 2). However, when **2** was treated with 2 equiv of pyridine in tetrahydrofuran at 60 °C for 20 min, a new species (**4**) [71%; mp 115 °C; ^{31}P NMR ($CDCl_3$) δ −3.5] was obtained along with **3** (29%) after separation by TLC (hexane/CH_2Cl_2 2:1; SiO_2). X-ray structural analysis of **3**[8] and

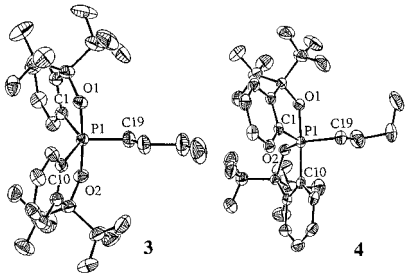
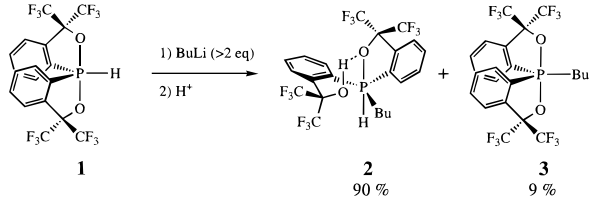
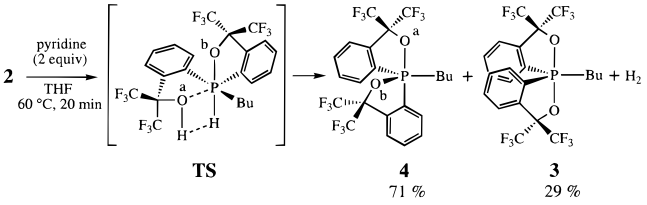


Figure 1. The ORTEP drawings of **3** and **4** showing the thermal ellipsoids at the 30% probability level. All hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (deg): **3** P1−O1, 1.765(2); P1−O2, 1.753(2); P1−C1, 1.818(2); P1−C10, 1.820(2); P1−C19, 1.818(2); O1−P1−O2, 175.79(6); O1−P1−C1, 87.32(8); O2−P1−C10, 87.30(8); C1−P1−C10, 126.84(8), C10−P1−C19, 116.6(1); C1−P1−C19, 116.6(1); **4** P1−O1, 1.768(3); P1−O2, 1.659(2); P1−C1, 1.813(4); P1−C10, 1.863(4); P1−C19, 1.835(5); O1−P1−C10, 170.6(1); O1−P1−C1, 87.1(2); O2−P1−C10, 87.8(1); O2−P1−C1, 119.9(2), O2−P1−C19, 124.0(2); C1−P1−C19, 114.8(2).

Scheme 1



Scheme 2



4[9] revealed that these compounds were stereoisomers with trigonal bipyramidal structure, as shown in Figure 1. It is clearly shown that the apical bonds of **4** are longer than the corresponding equatorial bonds (i.e., P1−O1(ap) 1.768 > P1−O2(eq) 1.659 Å and P1−C10(ap) 1.863 > P1−C1(eq) 1.813 Å. On the other hand, the pairs of bonds of **3** are almost equal (i.e., P−O(ap) 1.753, 1.765 Å and P−C(aryl; eq) 1.818, 1.820 Å.

The observation at room temperature (rt) that the $^1J_{C(aryl)P}$ for **3** (160 Hz) and **4** (88 Hz)[10] are quite different while the $^1J_{C(alkyl)P}$ are essentially the same (116 and 114 Hz, respectively) indicates that the solution structures of these compounds are also trigonal bipyramids.

^{19}F NMR spectra of compound **4** at rt showed only a pair of quartets [^{19}F NMR ($CDCl_3$, 293 K) δ −74.9 (q, $^4J_{FF}$ = 8.5 Hz, 6F), −76.2 (q, $^4J_{FF}$ = 8.5 Hz, 6F)] for the four anisochronous CF_3 groups. At low temperatures, the CF_3 groups decoalesced into four signals [^{19}F NMR (toluene-d_8, 193 K) δ −74.3 (brs, 3F), −74.5 (brs, 3F), −75.5 (brs, 3F), −76.0 (brs, 3F)], whereas a sole ^{31}P signal [^{31}P NMR (toluene-d_8, 219 K) δ −3.6] could be observed for the compound throughout the temperature range. This can only be rationalized as due to interconversion between

[†] Research Fellow of the Japan Society for the Promotion of Science.

(1) For N-X-L designation, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(2) Holmes, R. R. *Pentacoordinated Phosphorus - Structure and Spectroscopy*; ACS Monograph 175, 176; American Chemical Society: Washington, DC, 1980; Vols. I, II.

(3) (a) Trippett, S. *Phosphorus Sulfur* **1976**, *1*, 89. (b) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849. (c) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55. (d) Thatcher, G. R. J.; Campbell, A. S. *J. Org. Chem.* **1993**, *58*, 2272.

(4) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 4525.

(5) (a) Kojima, S.; Kajiyama, K.; Akiba, K.-y. *Tetrahedron Lett.* **1994**, *35*, 7037. (b) Kojima, S.; Kajiyama, K.; Akiba, K.-y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1785. (c) Kojima, S.; Nakamoto, M.; Kajiyama, K.; Akiba, K.-y. *Tetrahedron Lett.* **1995**, *36*, 2261.

(6) Ross, M. R.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1234.

(7) See Supporting Information for the ORTEP figure and crystallographic data.

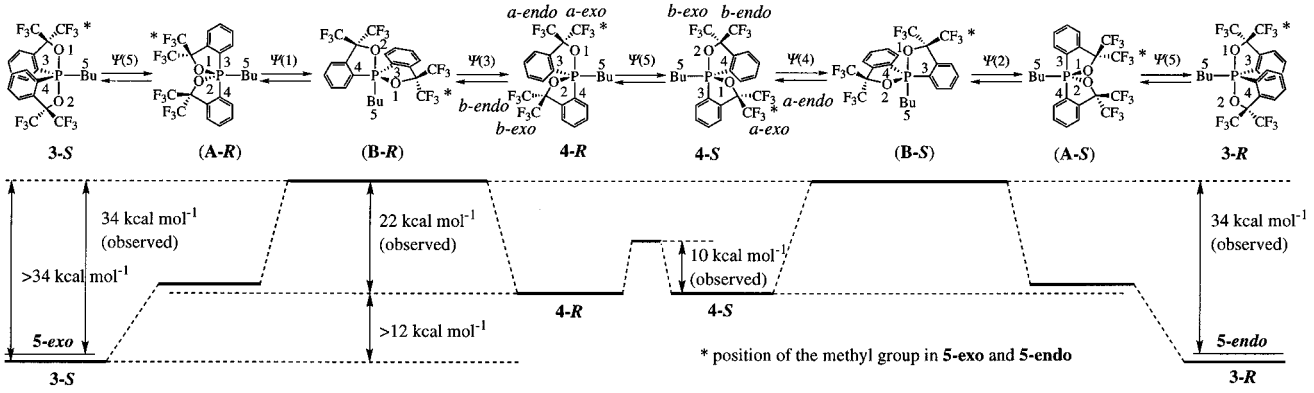
(8) Crystal data for **3**: monoclinic, $P2_1/a$, colorless, a = 19.522(4) Å, b = 11.819(2) Å, c = 10.596(2) Å, β = 103.50(2)°, V = 2377.4(8) Å^3, Z = 4, R = 0.045, R_w = 0.081, GOF = 2.70.

(9) Crystal data for **4**: monoclinic, $P2_1/n$, colorless, a = 12.041(2) Å, b = 16.936(3) Å, c = 11.401(2) Å, β = 96.05(1)°, V = 2311.9(6) Å^3, Z = 4, R = 0.066, R_w = 0.093, GOF = 2.67.

(10) Low temperature (to 203 K) ^{13}C NMR spectra were broad and did not give well-resolved signals for the two inequivalent Martin ligand carbons in **4**. If we assume that the equatorial $^1J_{C(aryl)P}$ is 160 Hz as in **3**, then the axial $^1J_{C(aryl)P}$ = 16 Hz.

S0002-7863(96)02140-3 CCC: $12.00

Scheme 3. Energy Diagram for Berry Pseudorotation of **3**−**5**



enantiomers **4-*R*** and **4-*S***, in which exchange between fluorines, *a-endo* and *b-endo*, and *a-exo* and *b-exo*, occurs, respectively, by a single-step pseudorotation[11] with the *n*-Bu group as the pivot. Line shape analysis of the ^{19}F NMR spectra (temperature range of 223−243 K; $T_c = 235$ K) of one of the pairs of signals gave the activation parameters $\Delta H^{\ddagger} = 10.0 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.4 \pm 1.0$ eu.

Rates of pseudorotation of **4** to **3**, an apparently irreversible process, were measured by monitoring ^{19}F NMR in toluene (temperature range of 302−328 K) and were found to obey first-order kinetics.[12] The Eyring plot of the rates gave the activation parameters $\Delta H^{\ddagger} = 21.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.0 \pm 1.2$ eu.

The pseudorotation between enantiomers **3-*R*** and **3-*S*** was found to be too slow to measure by NMR techniques such as saturation transfer. Therefore, diastereomers **5-*exo*** [^{31}P NMR ($CDCl_3$) δ −22.2; ^{19}F NMR ($CDCl_3$) δ −75.4 (m, 6F), −79.7 (s, 3F)] and **5-*endo*** [^{31}P NMR ($CDCl_3$) δ −22.7; ^{19}F NMR ($CDCl_3$) δ −74.9 (q, $^4J_{FF} = 9.3$ Hz, 3F), −75.4 (q, $^4J_{FF} = 9.3$ Hz, 3F), −80.1 (s, 3F)], differing from **3** only by having a CH_3 group in the place of one of the CF_3 groups (Scheme 3), were synthesized by alkylation of their corresponding P−H (equatorial) diastereomers **6-*exo*** [^{31}P NMR ($CDCl_3$) δ −49.4] and **6-*endo*** [^{31}P NMR ($CDCl_3$) δ −47.8], which proceeded with full retention of configuration at phosphorus.[5c,13] The pseudorotation between the diastereomers was examined by monitoring the singlet signals of ^{19}F NMR in 4-*tert*-butyltoluene (temperature range of 443−463 K). The averaged activation parameters obtained for the **5**-*exo* to **5**-*endo* and **5**-*endo* to **5**-*exo* processes were $\Delta H^{\ddagger} = 33.7 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.8 \pm 1.9$ eu.

Phosphoranes **5** should be only slightly less stable than **3**, and therefore the activation enthalpy obtained for pseudorotation between **5**-*exo* and **5**-*endo* should differ from that between **3-*R*** and **3-*S*** by only a very small amount. Hence, it is reasonable to use the values to evaluate the permutation process of **3**. Thus, **4** is concluded to be less stable than **3** by at least ca. 12 (=34−22) kcal mol^{-1}.

The shortest series of Berry pseudorotation processes of lowest energy for the inversion of **3** is shown as Scheme 3. The isomer of highest energy must be **B** which has an equatorial five-membered ring, and the next highest must be **A** which has two equatorial oxygens.[14]

Theoretical calculations on PH_5[15] and even cyclic oxyphosphoranes[16] predict the activation energy of Berry pseudorotation to be very low. Thus, the present results exemplify the successful isolation of stereoisomers on the same Berry pseudorotation coordinate utilizing the great ability of the so-called Martin ligand to stabilize hypervalent molecules.

Acknowledgment. The authors are grateful to Central Glass Co., Ltd., for a generous gift of hexafluorocumyl alcohol. Partial support of this work through Grant-in-Aid for Scientific Research (nos. 06740488 and 07740501) provided by the Ministry of Education, Science, Culture, and Sports, Japan, is heartily acknowledged.

Supporting Information Available: X-ray crystallographic data of compounds **2**−**4**, NMR data of compounds **2**−**5**, and rates (simulated and measured) of the three stereomutation processes (34 pages). See any current masthead page for ordering and Internet access instructions.

JA9621408

(11) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(12) Rates at 313 K were 4.03×10^{-5} s^{-1} (in toluene), 4.36×10^{-5} s^{-1} (in pyridine), and 3.44×10^{-5} s^{-1} (in ethanol). The fact that the solvent effect was very small allows the dismissal of alternative mechanisms such as heterolysis.

(13) Kojima, S.; Doi, Y.; Okuda, M.; Akiba, K.-y. *Organometallics* **1995**, *14*, 1928.

(14) The exact structure of the global transition state is not known and does not necessarily correspond to the given trigonal bipyramidal structure. However, it can be assumed to be this or a square pyramidal structure on either side of this on the coordinate.

(15) Moc, J.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 11790 and references cited therein.

(16) (a) Wasada, H.; Hirao, K. *J. Am. Chem. Soc.* **1992**, *114*, 16. (b) Uchimaru, T.; Uebayashi, M.; Hirose, T.; Tsuzuki, S.; Yliniemelä, A.; Tanabe, K.; Taira, K. *J. Org. Chem.* **1996**, *61*, 1599.