Table I. Second-Order Rate Constants for the Dimerization of *o*-QDM's 1, 6, and 7 in Acetonitrile[a]

| temp, °C	k_1, L mol^{-1} s^{-1} [b]	k_6, L mol^{-1} s^{-1} [c]	k_7, L mol^{-1} s^{-1} [d]
25	$9.94 \pm 0.32 \times 10^3$	$3.90 \pm 0.15 \times 10^3$	$5.59 \pm 0.21 \times 10^3$
35	$12.1 \pm 0.41 \times 10^3$	$5.24 \pm 0.18 \times 10^3$	$7.89 \pm 0.30 \times 10^3$
45	$15.4 \pm 0.51 \times 10^3$	$6.78 \pm 0.24 \times 10^3$	$10.1 \pm 0.38 \times 10^3$

[a] For all reactions the concentration of TBAF was 5.00×10^{-2} M and the concentration of 1, 6, or 7 was 5.00×10^{-4} M. Rate constants were obtained from an average of at least nine kinetic runs. [b] $\Delta H_1^* = 3.5 \pm 0.13$ kcal mol^{-1}, $\Delta S_1^* = -29 \pm 1.1$ cal mol^{-1} K^{-1}. [c] $\Delta H_6^* = 4.8 \pm 0.17$ kcal mol^{-1}, $\Delta S_6^* = -26 \pm 1.0$ cal mol^{-1} K^{-1}. [d] $\Delta H_7^* = 4.9 \pm 0.20$ kcal mol^{-1}, $\Delta S_7^* = -25 \pm 1.0$ cal mol^{-1} K^{-1}.

zation of 1 and other reactive *o*-QDM's to be measured using the stopped-flow technique. Since the rate of dimerization is a second-order process, measurement of the rate constant requires knowledge of the concentration of 1 and this can be obtained by knowing the ϵ_{max} of 1. Michl estimated the ϵ_{max} of 1 in a frozen matrix to be >3000,[3] and Roth used Michl's estimated value of 3000 in his flash photolysis study.[5] We have determined the ϵ_{max} for 1 in the following manner. Several runs were carried out[10] in which the concentration of 2 was kept constant but the fluoride ion concentration was varied from 5×10^{-3} to 1 M. As the concentration of fluoride ion increased, the maximum absorbance of the intermediate did not continue to increase but leveled off at a fluoride ion concentration of 0.025 M. We assumed that when the fluoride ion concentration was at least 0.025 M, 2 was converted quantitatively to 1 before much of 1 had dimerized. Knowing the concentration of 2, we calculated ϵ_{max} to be 3015.

Rate constants for the dimerization of 1 from 25 to 45 °C were measured and these are reported in Table I. Both the values of the k's and the temperature dependence of the reaction are in good agreement with Roth's data: $k_1 = 9.85 \times 10^3$ L mol^{-1} s^{-1} at 22.3 °C, $\Delta H^* = 5.3$ kcal/mol, and $\Delta S^* = -24.3$ eu.[5]
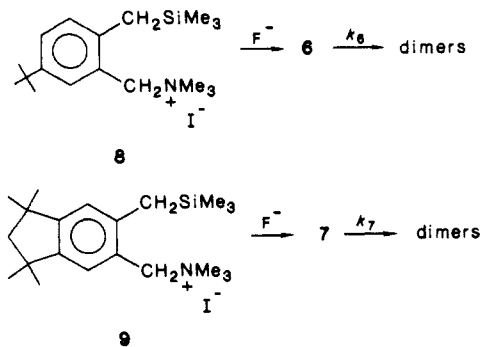
Some previous work in our laboratory on the corresponding 2,3-dimethylene-2,3-dihydrofuran system suggests that *o*-QDM dimerizations proceed via a stepwise mechanism involving a diradical intermediate.[11] It is believed that in forming the diradical intermediate, the *o*-QDM monomers prefer a non-endo approach.[12]

o-QDM's such as 6 and 7 contain alkyl substituents which introduce steric bulk on the ring away from the reactive site without significantly changing the electronic nature of the molecule. If, *o*-QDM monomers prefer an endo approach when

6   7
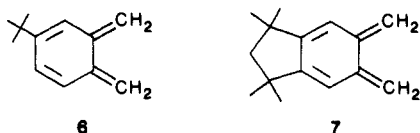
undergoing dimerization, the bulky substituents on 6 and 7 would be expected to repel one another, resulting in significantly reduced rates of dimerization for these *o*-QDM's. Alternatively, if a non-endo approach is preferred, one would expect similar rates of dimerization for 1, 6, and 7. When iodides[13] 8 and 9 were treated with fluoride ion in acetonitrile, *o*-QDM's 6 and 7,[16]

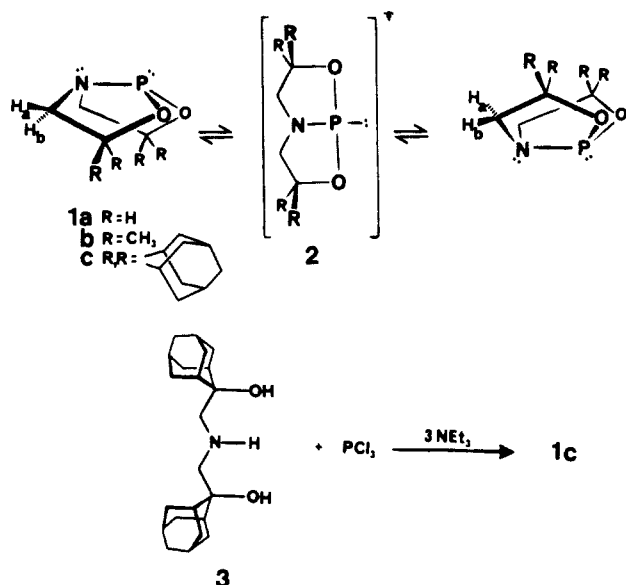(9) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

(10) The progress of the reactions was monitored with use of a Canterbury SF-3A stopped-flow spectrophotometer and OLIS Model 3820 computer.

(11) Chou, C.-H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 1438.

(12) Chou, C.-H. Ph.D. Dissertation, Iowa State University, Ames, IA, 1985.

(13) Iodide 8[14] was prepared from [*p-tert*-butylbenzyl]trimethylammonium bromide in a manner analogous to that used for the parent system.[4] Iodide 9[15] was prepared as follows: Sommelet–Hauser rearrangement of [3,4-(1,1,3,3-tetramethyltrimethylene)benzyl]trimethylammonium chloride produced a mixture of two isomeric (pentamethylindanyl)dimethylamines which were separated on silica gel. Conversion of the appropriate amine to 9 was analogous to the sequence used for the parent system.[4]

(14) 8: mp 205–206 °C; IR (KBr) 2940, 1470, 1240 cm^{-1}; ^{1}H NMR (CD$_3$CN; Me$_4$Si as an external reference) δ -0.05 (s, 9 H), 1.33 (s, 9 H), 2.30 (s, 2 H), 3.06 (s, 9 H), 4.43 (s, 2 H), 7.2–7.6 (m, 3 H). Anal. Calcd for C$_{18}$H$_{34}$INS: C, 51.54; H, 8.17, N, 3.34. Found: C, 51.62; H, 8.22; N, 3.27.

respectively, were generated. Rate constants for the dimerization

8

9

of 6 and 7 are listed in Table I. Clearly the differences in rate constants for the dimerization of 1, 6, and 7 are small and this supports the non-endo approach of monomers.

The 1,4-elimination from [*o*-[α-(trimethylsilyl)alkyl]benzyl]-trimethylammonium halides seems well suited for generating *o*-QDM's for the purpose of spectroscopic investigation. This method makes it possible to study many substituted *o*-QDM's, the precursors of which are readily prepared from simple starting materials.

(15) 9: mp 204–205 °C; IR (KBr) 2940, 1484, 1460, 1240 cm^{-1}; ^{1}H NMR (CD$_3$CN, Me$_4$Si as an external reference) δ -0.03 (s, 9 H), 1.31 (s, 12 H), 1.91 (s, 2 H), 2.31 (s, 2 H), 3.04 (s, 9 H), 4.40 (s, 2 H), 6.96 (s, 1 H), 7.20 (s, 1 H). Anal. Calcd for C$_{21}$H$_{38}$INS: C, 54.88; H, 8.33; N, 3.05. Found: C, 54.81; H, 8.35; N, 3.01.

(16) Uv–visible data: 6, $\lambda_{max} = 381$ nm, $\epsilon_{max} = 2120$; 7, $\lambda_{max} = 378$ nm, $\epsilon_{max} = 2390$.

Direct Determination of the Barrier to Edge Inversion at Trivalent Phosphorus: Verification of the Edge Inversion Mechanism

Anthony J. Arduengo, III,* David A. Dixon, and D. Christopher Roe

Contribution No. 4118
E. I. du Pont de Nemours & Company
Central Research & Development Department
Experimental Station, Wilmington, Delaware 19898

We now report the direct determination of the barrier to edge inversion at a trivalent 8-electron phosphorus center (8-P-3).[1] The experimentally determined ΔH^* of 23.4 kcal/mol for 1c is in excellent agreement with a large basis set ab initio calculation of a barrier height of 28.1 kcal/mol for 1a. These results verify the operation of the recently recognized edge inversion process proceeding through transition state 2 at suitably substituted 8-P-3 centers.[2]

In a previous report we presented evidence that the classical vertex inversion process, e.g., NH$_3$ inversion, should not be expected for the inversions of all 8-Pn-3 (Pn = pnictogen P, As, Sb, Bi) centers.[2] Substitution of the pnictogen center by electronegative groups (σ-acceptors) and π-donors can lead to a pref-

(1) The *N-X-L* nomenclature system has previously been described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). *N* Valence electrons about a central atom X, with *L* ligands.

(2) Dixon, D. A.; Arduengo, A. J., III; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 2461.

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Communications to the Editor

1a R=H
b R=CH₃
c R,R=

2

3

erence for the edge inversion process. While the stereochemical outcomes of edge and vertex inversion processes are the same, the pnictogen lone pair is not inverted by the edge inversion process and the geometric requirements of the two transition states are markedly different. These considerations led us to choose a bicyclo[3.3.0]octane ring system **1** to verify the new edge inversion process. Systems related to **1** but containing delocalized π frameworks have been shown to have a T-shaped geometry about phosphorus in their ground states.[3] The saturated systems **1** are known to exhibit a folded structure containing both a pyramidal phosphorus and pyramidal nitrogen.[4] Additionally, **1** offers two sites where diastereotopic substituents are interchanged by the ring fold inversion (on the carbons attached to oxygen and nitrogen). Thus we chose system **1c** in which spiro fusion of the adamantyl substituent in the 3- and 7-positions can effectively block oligomerization which can be a problem in these systems.[4]

Compound **1c** was synthesized by the reaction of the amine diol **3** with PCl₃ in the presence of triethylamine. Compound **1c** is a stable microcrystalline material melting 197–202 °C. If the melt is heated to 270 °C it resolidifies and does not remelt until 350–355 °C. This melting behavior may be due to oligomerization under extreme conditions. Consistent ¹H, ¹³C, ³¹P, ¹⁷O, and ¹⁵N NMR spectra and elemental analysis were obtained for **1c**.[5] As expected the methylene attached to nitrogen showed an ABX pattern in the ¹H NMR spectra. Because of the larger separation in H_a and H_b resonances[6] and the wide liquid temperature range, toluene was the solvent of choice for variable-temperature NMR

(3) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 1089.
(4) The bicyclo[3.3.0] ring structure of **1** can be expected to discourage the fold inversion by the classical vertex mechanism at phosphorus due to inordinate strain at the transition state. Generally barriers to vertex inversion at phosphorus substituted with electronegative groups are high and can be greater than the bond dissociation energies! (a) Bonningue, C.; Houraid, D.; Sanchez, M.; Wolf, R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 19. (b) Sommer, V. K.; Lauer, W.; Becke-Goehring, M. *Z. Anorg. Allg. Chem.* **1970**, *379*, 48. (c) Houlla, D.; Osman, F. H.; Sanchez, M.; Wolf, R. *Tetrahedron Lett.* **1977**, *35*, 3041. (d) Bonningue, C.; Houlla, D.; Wolf, R. *J. Chem. Soc., Perkin Trans 2* **1983**, 773.
(5) A sample of **1c** recrystallized from toluene gave mp 197–202 °C. Anal. (C₂₂H₃₂NO₂P) C, H, N. ¹H NMR (CD₂Cl₂) δ 1.70 (m, 24 H), 2.20 (dm, 2 H, *J* = 11.5 Hz), 2.28 (dm, 2 H, *J* = 11.0 Hz), 3.14 (dd, 2 H, ²*J*ₕₕ = 11.80, ³*J*ₚₕ = 9.00 Hz), 3.25 (dd, 2 H, ²*J*ₕₕ = 11.80, ³*J*ₚₕ = 8.59 Hz). ¹³C{¹H} NMR (toluene-d₈) δ 27.3 (s, CH), 27.4 (s, CH), 33.7 (s, CH₂), 33.9 (s, CH₂), 35.5 (s, CH₂), 36.4 (s, CH₂), 37.9 (s, CH₂), 38.3 (s, HCCO), 40.0 (d, HCCO, ³*J*ₚ = 3.0 Hz), 61.7 (d, *J*ₚ = 3.8 Hz), 88.5 (d, CO, *J*ₚ = 10.7 Hz). ³¹P{¹H} NMR (toluene-d₈) δ 158.0. ¹⁵N{¹H} NMR (toluene-d₈) δ –313.5 (d, ¹*J*ₙₚ = 53.8 Hz) (reference NH₄ ¹⁵NO₃). ¹⁷O NMR (toluene-d₈) δ 128.4 (d, ¹*J*ₒₚ = 185.2 Hz) (reference H₂¹⁷O).
(6) The separation between resonances for H_a and H_b are solvent-dependent: (CD₂Cl₂) δ H_a 3.14, H_b 3.25, ³*J*ₚₕ = 8.59 Hz, ³*J*ₚₕ = 9.00 Hz, ²*J*ₕₕ = 11.80 Hz; pyridine-d₅ δ H_a 3.25, H_b 3.33, ³*J*ₚₕ = 8.80 Hz, ³*J*ₚₕ = 9.00 Hz, ²*J*ₕₕ = 11.99 Hz; toluene-d₈ δ H_a 2.94, H_b 3.15, ³*J*ₚₕ = 8.38 Hz, ³*J*ₚₕ = 8.75 Hz, ²*J*ₕₕ = 11.74 Hz.
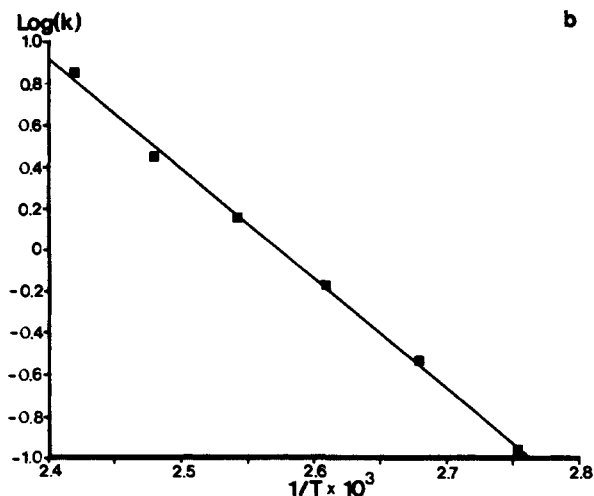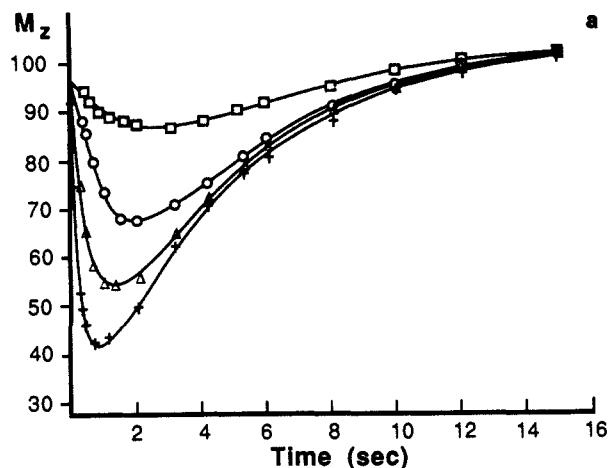

Figure 1. (a) response of H_a intensity to selective inversion of H_b at 90 (□), 100 (○), 110 (△), and 120 °C(+). Data obtained at 130 and 140 °C are omitted for clarity. Best-fitting theoretical curves (—) provided the rate constants used. (b) Fit of rate data to the Arrhenius equation.

studies. Over a temperature range from –10 to +180 °C there was insufficient change in the ¹H NMR spectrum of **1c** (toluene-d₈) to allow line-shape analysis (i.e., slow exchange). However, the site exchange of the H_a and H_b positions is evident from magnetization transfer experiments.

Selective inversion of the H_b multiplet in the ¹H NMR spectrum leads to a characteristic decrease in intensity for the H_a resonance and indicates that exchange is occurring at a rate comparable to that for spin–lattice relaxation (see Figure 1a). Superimposed on this slow exchange effect is a transient oscillation which dies away quickly and which arises from selective population transfer effects in coupled spin systems. It was found that these early time points could safely be ignored in the analysis, and that the rate constants determined from the remaining points were in agreement with one from the corresponding ¹³C experiment (at 100 °C, $k(^1H)$ = 0.29 ± 0.01 s⁻¹ while the $k(^{13}C)$ = 0.42 ± 0.24 s⁻¹). These results were confirmed by 2-D NMR experiments designed to remove effects arising from *J* coupling. It was also found that substantially increasing the dielectric constant of the solvent led to only a modest increase in the exchange rate (in *o*-dichlorobenzene-d₄ at 100 °C, $k(^1H)$ = 0.98 ± 0.06 s⁻¹).

The rate data from the ¹H NMR experiments are plotted in Arrhenius form in Figure 1b, and from a nonlinear-least-squares fit to the Eyring equation,[7] we obtain $\Delta H^{\ddagger}$ = 23.4 ± 1.6 kcal/mol and $\Delta S^{\ddagger}$ = 1.2 ± 4.2 eu. The value for $\Delta H^{\ddagger}$ is clearly less than the vertex inversion barrier of 34.4 kcal/mol found for PH₃.[8] An

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(8) Marynick, D. S.; Dixon, D. A. *J. Phys. Chem.* **1982**, *86*, 914.

increase in the vertex inversion barrier height over that for PH_3 would have been expected due to the presence of the electronegative ligands in **1**.[2] The significant decrease in the barrier height for **1c** argues strongly that we are indeed observing edge inversion. The low value for $\Delta S^{\ddagger}$ is consistent with a unimolecular process as would be expected for simple inversion. Thus, it is unlikely that a bimolecular process is leading to the low value for the inversion barrier observed for **1c**.

In order to gain insight into the experimental results, we have performed high-level ab initio molecular orbital calculations on the edge inversion process. The geometries for the pyramidal **1a** (C_s symmetry) and planar T-shaped **2a** (C_{2v} symmetry) forms were gradient optimized[9,10] at the self-consistent field (SCF) level with a double-ζ basis set[11] augmented by sets of d polarization functions on P, O, and N.

The most important structural features are the bonding parameters at phosphorus. The P–O bond distances are 1.634 Å, and the P–N bond distance is 1.749 Å for pyramidal **1a**. The OPN bond angles are 93.6°, consistent with normal bond angles at tricoordinate phosphorus,[8] while the O–P–O bond angle is opened up to 106.0°. The lengths of the bonds to phosphorus reverse in planar **2a**. The P–O bond distances have lengthened to 1.718 Å while the P–N bond distance has decreased to 1.660 Å, consistent with our previous calculations on PF_3.[2] As would be expected for a T-shaped planar structure, the OPO group is approximately linear with an OPO bond angle of 172.7° (the OPN bond angles are 86.4°). At this level of calculation, the inversion barrier is 43.0 kcal/mol.

From the optimized geometries for **1a** and **2a**, the energies were recalculated[12] with a slightly larger basis set[13] both at the SCF level and including correlation effects at the MP2-level.[14] The energy difference at the SCF level is 43.5 kcal/mol, in excellent agreement with the SCF value given above. Inclusion of the MP-2 correction lowers the inversion barrier to 28.1 kcal/mol. The large correlation correction of 15.4 kcal/mol is typical of edge inversion processes[15] while vertex inversion usually involves only a small correlation correction;[16] for example, the correlation correction to the vertex inversion barrier in PH_3 is 2 kcal/mol.[8]

The calculated inversion barrier for **1a** is 4.7 kcal/mol higher than the measured inversion barrier for **1c**. This difference may be due to a number of factors. There is considerable difference between adamantyl and hydrogen as a substituent especially in terms of steric bulk. The steric bulk of the adamantyl group could cause the five-membered ring to adopt a higher energy configuration in the pyramidal form thus lowering the inversion barrier.

Another reason for the difference is that our calculated value is an upper limit at this level of calculation. The force fields for **1a** and **2a** were determined analytically. Structure **1a** has no imaginary frequencies and is thus a minimum on the potential energy surface. If planar **2a** were a transition state, it would have a single imaginary frequency. For the structure with all of the heavy atoms in a plane, three imaginary frequencies are found

and thus our structure is slightly higher in energy than the actual transition state. The largest imaginary frequency ($188i$ cm^{-1}) is the measure of curvature for the inversion mode. The two smaller imaginary frequencies ($84i$ and $30i$ cm^{-1}) are very low (the sum of the latter two frequencies is 0.33 kcal/mol) and correspond to torsions about the C–C bonds. Since the CH_2 groups are in an eclipsed conformation, this leads to an increase in the energy. Furthermore, the MP2 correction may not be recovering all of the correlation energy difference between the planar and pyramidal forms. All of these arguments are consistent with the observed difference between theory and experiment.

Synthetic Methodology for Polyoxocyclopentadienyltitanium Complexes: Synthesis and Structure of $L_6Ti_6O_{8-n}Cl_n$ ($L = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4CH_3$; $n = 4, 2, 0$)

Alan Roth,[†] Carlo Floriani,*[†] Angiola Chiesi-Villa,[‡] and Carlo Guastini[‡]

Chemistry Department, Columbia University
New York, New York 10027
Istituto di Strutturistica Chimica, Centro di
Studio per la Strutturistica Diffrattometrica del CNR
Università di Parma, 43100 Parma, Italy

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Polyoxo- and polyoxochloro organometallic aggregates which do not contain weak metal–metal bonds have several attractive properties. Some of them have been masterly brought into focus by a review from Klemperer and Day on polyoxoanions.[1] In particular, the aggregates may display interesting magnetic properties, cooperative chemical behavior, and geometrical proximity of reactive sites. Synthetically, we became interested in electron-rich and functionalizable aggregates which are not accessible by the common methodologies,[1] including the controlled oxidation of metal cyclopentadienyl derivatives recently devised by Bottomley.[2] We report a synthetic procedure, based on the use of reducing agents, for transforming cyclopentadienyloxochloro complexes of titanium(IV) into the building block of aggregates having the formula $[cp_6Ti_6O_{8-n}Cl_n]$ and $[cp'_6Ti_6O_{8-n}Cl_n]$ ($cp = \eta^5\text{-}C_5H_5$ and $cp' = \eta^5\text{-}MeC_5H_4$; $n = 4, 2, 0$). One member of the two series, $cp_6Ti_6O_8$, has already been reported.[3]

We carried out the reduction of $[cpTiCl(\mu\text{-}O)]_4$,[4] $[cp'TiCl(\mu\text{-}O)]_4$,[5] and $[cpTiCl_2]_2(\mu\text{-}O)$ as shown in eq 1 and following the

1,3,5: L = cp = η^5-C$_5$H$_5$
2,4,6: L = cp' = η^5-MeC$_5$H$_4$

(1)
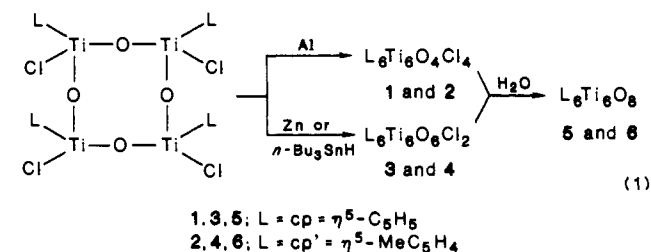
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(11) Dunning, T. H, Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*, Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 1. 3d ζ(p) = 0.50. The basis set is (11s7p1d/9s5p1d/9s5p1d/9s5p/4s)/ [6s4p1d/3s2p1d/3s2p1d/3s2p/2s] in the order P, O, N, C, H.

(12) GRADSCF is an ab initio gradient system designed and written by A. Komornicki at Polyatomics Research and supported on grants through NASA-Ames Research Center.

(13) The basis set is (13s9p1d/9s5p1d/9s5p1d/9s5p/4s)/[6s4p1d/4s2p1d/ 4s2p1d/4s2p/2s]. The s and p orbital coefficients and exponents for C, N, O, and H are from: Dunning, T. H., Jr. *J. Chem. Phys.* **1970,** *53,* 2823. Those for P are from: McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980,** *72,* 5639. The exponents for the polarization functions are those given in ref 12.

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