Structure−Reactivity Relationships for Associative Displacement Reactions of Penta- and Hexacoordinate Cyclic Oxyphosphoranes with Catechols[1,2]

A. Chandrasekaran, Paul Sood, and Robert R. Holmes*

Department of Chemistry, Box 34510, University of Massachusetts, Amherst, Massachusetts 01003

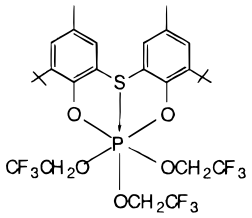
Received July 24, 1997

The reactivity of a series of cyclic pentaoxyphosphoranes containing a sulfonyl group was carried out, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**), $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OPh)_3$ (**2**), $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**), and $O_2S[(t\text{-}Bu)_2C_6H_2O]_2P(OPh)_3$ (**5**). Also included were derivatives containing sulfur, $S[(t\text{-}Bu)MeC_6H_2O]_2P(OPh)_3$ (**6**) and $S[(t\text{-}Bu)_2C_6H_2O]_2P(OPh)_3$ (**8**), and the methylene group, $CH_2[(t\text{-}Bu)MeC_6H_2O]_2P(OPh)_3$ (**7**), in place of the sulfonyl group in the ring-containing component. ^{31}P NMR monitoring of the reactions of the oxyphosphoranes with catechol and 4-nitrocatechol shows the following order of reactivity: **7** > **8** > **6** > **2** > **5** ≫ **1**. It is established that the reactions are associative. An analysis of the products formed is given relative to this mechanistic process. Both **1** and **4** are found to be inert toward nucleophilic displacement by the catechols employed. It is suggested that the looseness of P−O bonds (implied by their increased length) that reside in either octahedral formulations or in axial positions of a trigonal biyramid is the principal factor associated with reactivity for these cyclic oxyphosphoranes. For the hexacoordinated geometries, the order of reactivity parallels the extent of octahedral character: **8** > **6** > **2** > **5**.

Introduction

Although there exists a considerable body of literature dealing with the synthesis, structural aspects, and reactivities of pentacoordinated phosphorus compounds,[3−10] little work is evident concerning reactivities relative to other coordination geometries. In studies concerned with nucleophilic substitution reactions of pentacoordinate phosphorus primarily centering on oxyphosphoranes,[3,7,8,11−21] rate laws and mechanistic considerations suggest the importance of hexacoordinate intermediates (or transition states) as controlling features.

In work in our laboratory, we have employed sulfur atoms to act as donors in promoting hexacoordination in structural studies of cyclic pentaxoyphosphoranes.[1b,22−26] A representative member is **A**[23] which has a P−S distance of 2.362(2) Å.



A[23]

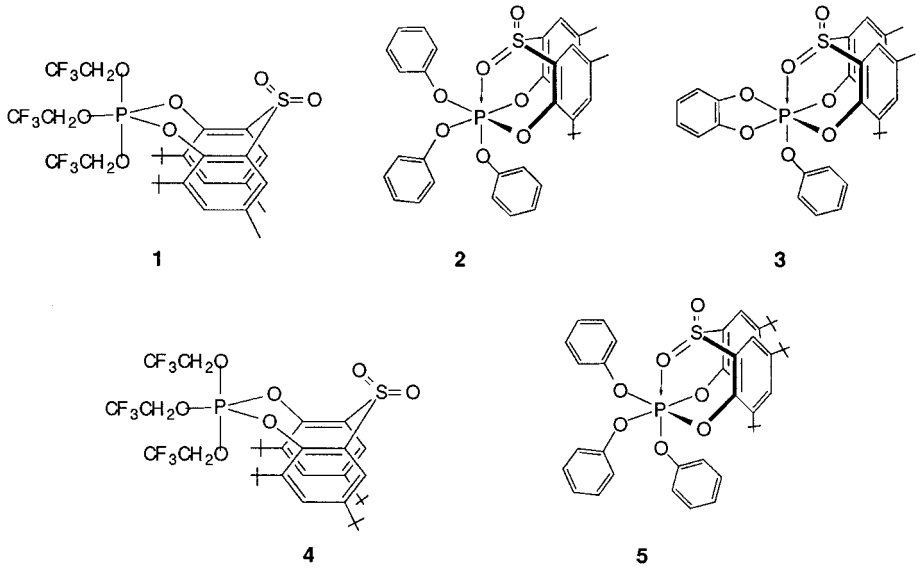
P–S 2.362(2)Å

Recently, Cavell[27] extended this range to 2.33 Å in a related

(1) (a) Pentacoordinated Molecules. 120. (b) Part 119: Sood, P.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5730.
(2) Presented in part at the 211th National Meeting of the American Chemical Society, New Orleans, LA, March 24−28, 1996; INOR 189.
(3) Thatcher, G. R. J.; Kluger, R. *Advances in Physical Organic Chemistry*; Bethell, D., Ed.; Academic Press: New York, 1989; Vol. 25, pp 99−265 and references cited therein.
(4) (a) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70; *Pure Appl. Chem.* **1977**, *49*, 1059. (b) Gerlt, J. A.; Westheimer, F. H.; Sturtevant, J. M. *J. Biol. Chem.* **1975**, *250*, 5059.
(5) Ramirez, F. *Pure Appl. Chem.* **1964**, *9*, 337.
(6) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168.
(7) Holmes, R. R. *Pentacoordinated Phosphorus-Structure and Spectroscopy, Volume I*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; 479 pp.
(8) Holmes, R. R. *Pentacoordinated Phosphorus-Reaction Mechanisms, Volume II*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; 237 pp.
(9) Holmes, R. R.; Day, R. O.; Deiters, J. A.; Kumara Swamy, K. C.; Holmes, J. M.; Hans, J.; Burton, S. D.; Prakasha, T. K. In *Phosphorus Chemistry, Developments in American Science*; Walsh, E. N., Griffiths, E. J., Parry, R. W., Quin, L. D., Eds.; ACS Symposium Series 486; American Chemical Society: Washington, DC, 1992; pp 18−40 and references cited therein.
(10) Holmes, R. R. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1984; Vol. 32, pp 119−235.
(11) (a) Gillespie, P.; Ramirez, F.; Ugi, I.; Marquarding, D. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 91. (b) Hall, C. R.; Inch, T. D. *Tetrahedron* **1980**, *36*, 2059. (c) Hall, C. R.; Inch, T. D.; Peacock, G.; Pottage, C.; Williams, N. E. *J. Chem. Soc., Perkin Trans.* **1984**, *1*, 669.
(12) (a) Schmutzler, R. In *Halogen Chemistry*; Gutmann, V., Ed.; Academic Press: New York, 1967; Vol. 2, pp 31−113. (b) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 63.
(13) Ramirez, F.; Tasaka, K.; Desai, N. B.; Smith, C. P. *J. Am. Chem. Soc.* **1968**, *90*, 751.
(14) Ramirez, F.; Loewengart, G. V.; Tsolis, E. A.; Tasaka, K. *J. Am. Chem. Soc.* **1972**, *94*, 3531.
(15) Bel'skii, V. E.; Khismatullina, L. A.; Bykova, T. G.; Burykina, A. V.; Ivanov, B. E. *J. Gen. Chem. USSR* **1979**, *49*, 298.
(16) Queen, A.; Lemire, A. E.; Janzen, A. F. *Int. J. Chem. Kinet.* **1981**, *13*, 411.
(17) Skowronska, A.; Pakulski, M.; Michalski, J. *J. Am. Chem. Soc.* **1979**, *101*, 7412.
(18) Ramirez, F.; Tasaka, K.; Hershberg, R. *Phosphorus* **1972**, *2*, 61.
(19) Archie, W. C., Jr.; Westheimer, F. H. *J. Am. Chem. Soc.* **1973**, *95*, 5955.
(20) Aksness, G.; Eide, A. I. *Phosphorus* **1974**, *4*, 209.
(21) Chang, B. C.; Denney, D. B.; Powell, R. L.; White, D. W. *Chem. Commun.* **1971**, 1070.
(22) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913.
(23) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360.

S0020-1669(97)00919-1 CCC: $15.00
Published on Web 01/23/1998

Chart 1

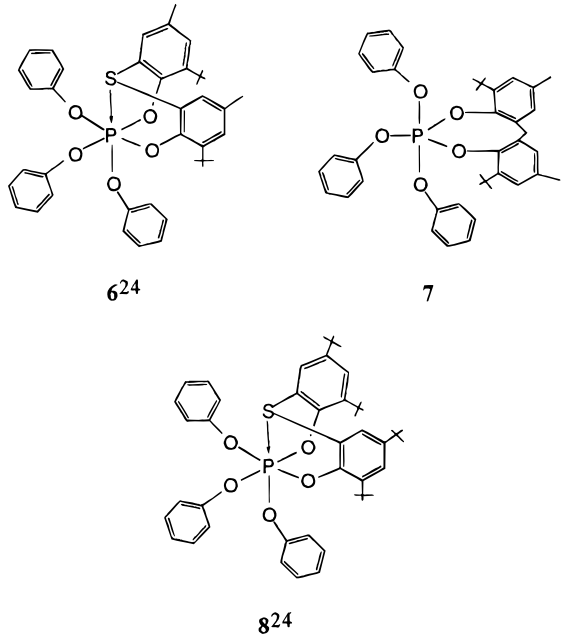


phosphorane having the same type of sulfur ring system but with the use of chlorine ligands in place of OR groups. There also are quite a few X-ray studies identifying hexacoordinated phosphorus formed by oxygen or nitrogen coordination.[28,29]

In work with organosilanes, we have employed the ring system present in **A**, where the donor atom was varied from S,[28,30−34] to SO,[35] to SO_2.[36] Although the sulfinyl group did not exhibit donor action, the sulfur atom[30−34] and sulfonyl group[36] provided a series of structures displaced toward a trigonal bipyramid.

With the use of the sulfonyl group in cyclic oxyphosphoranes, oxygen atom coordination also occurs leading to octahedral geometries as established by X-ray analysis.[37−39] It then becomes of interest to examine their reactivity. In the present work, we address this aspect of hypervalent phosphorus by carrying out nucleophilic displacement reactions of a series of cyclic oxyphosphoranes with catechols. The influence of substituent effects and coordination geometry on reaction rates are examined. The sulfonyl-containing series studied comprises the cyclic pentaoxyphosphoranes **1**−**5** (Chart 1), all of which whose syntheses and X-ray structures were previously reported.[39]

Relative reactivities with catechol and 4-nitrocatechol are followed by ^{31}P NMR spectroscopy. By the use of ^{31}P NMR monitoring, a more detailed study of the course of the reaction of **2** with catechol and with 4-nitrocatechol is delineated. For the reactivity studies, phosphoranes **6** and **8**, whose synthesis



and X-ray structures are available from previous work,[24] and that of **7**, which is newly synthesized, are included. Phosphoranes **6** and **7** differ in composition from **2** only in that the sulfonyl group is replaced by a sulfur atom for **6** and by a methylene group for **7**. Phosphorane **8** has additional *tert*-butyl groups compared to **6**. Thus, the study allows the opportunity to compare relative reactivity on the basis of a change in coordination geometry as well as a change in substituent composition.

(24) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1993**, *115*, 2690.
(25) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1992**, *31*, 3391.
(26) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, Silicon* **1993**, *75*, 249.
(27) Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem*. **1996**, *35*, 325−334.
(28) Holmes, R. R. *Chem. Rev*. **1996**, *96*, 927.
(29) Additional X-ray structures of neutral hexacoordinate phosphorus are found in a recent review: Wong, C. Y.; Kennepohl, D. K.; Cavell, R. G. *Chem. Rev*. **1996**, *96*, 1917.
(30) Day, R. O.; Prakasha, T. K.; Holmes, R. R.; Eckert, H. *Organometallics* **1994**, *13*, 1285.
(31) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, Silicon* **1994**, *87*, 59.
(32) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, Silicon* **1994**, *95*−96, 375.
(33) Prakasha, T. K.; Srinivasan, S.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1995**, *117*, 10003.
(34) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1996**, *35*, 3614.
(35) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3182.
(36) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189.
(37) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1997**, *36*, 2578.
(38) Sherlock, D. J.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.*, in press.
(39) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1997**, *119*, 11434.

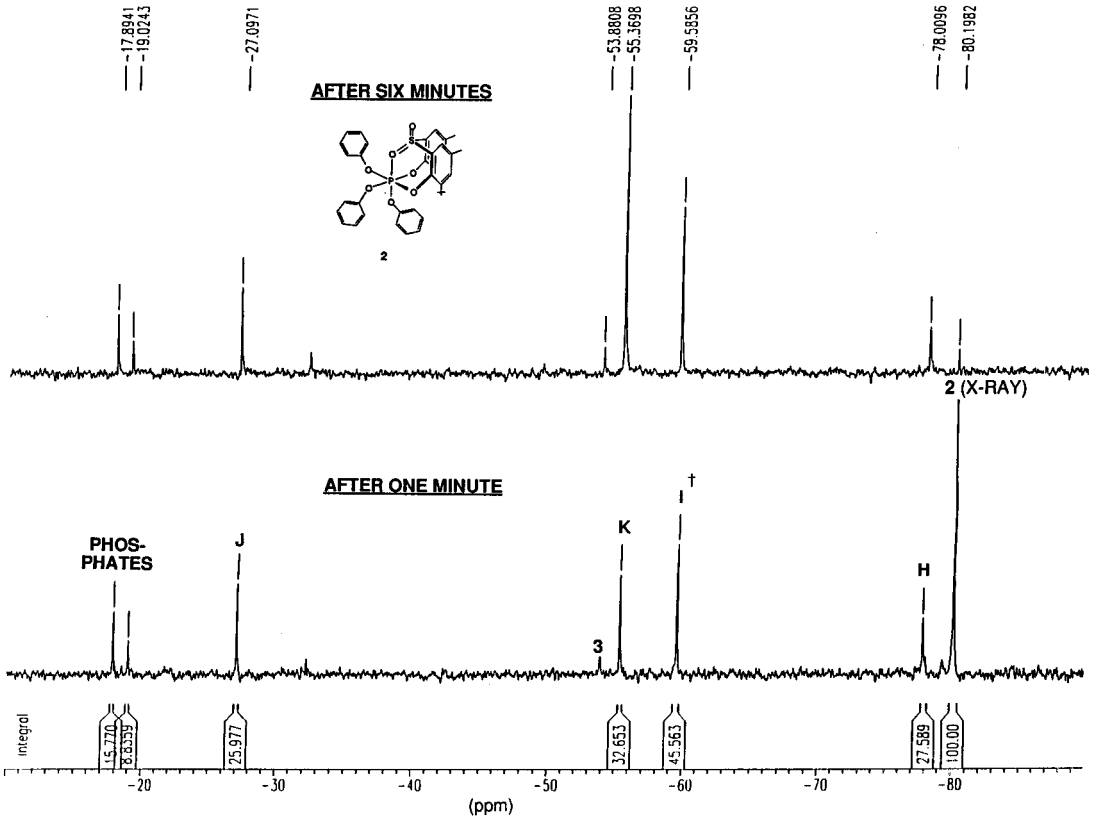


Figure 1. ^{31}P NMR monitoring of the reaction of hexacoordinated phosphorane **2** with 4-nitrocatechol in a 1:2 ratio in toluene-d_8 at 90 °C after 1 min (lower spectrum) and after 6 min (upper spectrum). Spectra were recorded at 20 °C. The solution contains 0.086 mmol of each reactant in 2.4 mL of toluene-d_8. The dagger indicates the signal for **I** was independently verified.

Experimental Section

Triphenyl phosphite (Eastman) was used as supplied. Methylenebis-(4-methyl-6-*tert*-butylphenol)[40] and *N*-chlorodiisopropylamine[37,41] were synthesized according to literature methods. Solvents were purified according to the standard procedures.[42] All the reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. Phosphorus-31 NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All the spectra were recorded in $CDCl_3$ unless otherwise mentioned. Some of the ^{31}P NMR spectra (including the reaction monitoring) were recorded in $C_6H_5CH_3$ in the sweep-off mode. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane for ^{1}H NMR or 85% H_3PO_4 for ^{31}P NMR. All NMR spectra were recorded at 23 °C unless otherwise mentioned. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Synthesis and Reactions. [Methylenebis(4-methyl-6-*tert*-butylphenoxy)]triphenoxyphosphorane, $CH_2[(t\text{-Bu})MeC_6H_2O]_2P(OPh)_3$ (7). To a solution of methylenebis(4-methyl-6-*tert*-butylphenol) (1.30 g, 3.82 mmol) and $P(OPh)_3$ (1.00 mL, 3.82 mmol) in ether (200 mL) was added an excess of Pr^i_2NCl (0.700 mL, 4.76 mmol) with constant stirring at about 23 °C for 1 min. The resultant mixture was stirred for a further period of 24 h and filtered. Hexane (50 mL) was added to the filtrate and the solution left under a nitrogen flow to give a mixture of crystals and brown oil. The oil was washed off with Skelly-F and the crystals dried under vacuum. Yield: 1.1 g (44%). Mp: 240−245 °C. ^{1}H NMR: 1.42 (s, 18 H, *t*-Bu), 2.31 (s, 6 H, aryl-*Me*), 3.16 (dd, 1 H, CH_2, 14 Hz, 3 Hz), 3.87 (dd, 1 H, CH_2, 14 Hz, 1 Hz), 6.7−7.4 (m, 19 H, aryl). ^{31}P NMR: −83.5. Anal. Calcd for $C_{41}H_{45}O_5P$: C, 75.90; H, 6.99. Found: C, 76.22; H, 7.01.

Attempted Reaction of 1 with Catechol. A solution of phosphorane **1** (0.27 g) and catechol (0.045 g) in toluene (30 mL) was heated under reflux for 48 h. The ^{31}P NMR spectrum of the solution showed only the two isomers of phosphorane **1**. Thus, there was no reaction or hydrolysis. The solvent was removed under vacuum. The residue was dissolved in 1,2-dichlorobenzene (10 mL) and heated at 150 °C for 2 h. After removal of the solvent, the ^{31}P NMR of the residue showed the presence of two phosphates (at −8.52 and −20.21 ppm corresponding to 12% and 51%, respectively) and the unreacted phosphorane (37%). No catechol substituted product was found.

^{31}P NMR Monitoring of the Reaction of Phosphorane 2 with Catechols. With the use of a Schlenk flask, phosphorane **2** (60 mg) and catechol or 4-nitrocatechol in a 1:1 or 1:2 ratio were placed in an NMR tube and the contents evacuated. The tube was filled with nitrogen, and heptane was added to the Schlenk flask. $C_6D_5CD_3$ (2.4 mL) was added to the NMR tube using a syringe. The NMR tube was capped, sealed with Teflon tape, and removed from the Schlenk flask. The Schlenk flask was immersed in a preheated oil bath to the solvent level and the flask kept under a nitrogen flow. After the boiling point was reached, the NMR tube was kept inside the flask (the first time, the cap was removed to avoid the developing pressure) for the required time. Then the NMR tube was removed and taken to the NMR instrument, and the ^{31}P NMR spectrum was recorded. Afterward, an NMR tube with toluene was placed in the Schlenk tube along with a thermometer and the temperature was measured. The ^{31}P spectra of **2** was recorded as a function of reaction time and as a function of temperature. It was found that the ^{31}P spectra recorded at 90 °C and that recorded at 20 °C, for example upon heating the phosphorane **2**−catechol reaction mixture for 3 h, showed neither any changes in chemical shifts for the products formed nor any significant changes in spectral intensities. Hence, for convenience, ^{31}P monitoring spectra were recorded at room temperature for some of the heating cycles.

(40) (a) Davis, A. R.; Sullivan, A. V. U.S. Patent 2,538,355, 1951. (b) Davis, A. R.; Sullivan, A. V. *Chem. Abstr*. **1951**, *45*, 4086b.e.
(41) Bock, H.; Kompa, K. L. *Chem. Ber*. **1966**, *99*, 1347.
(42) (a) Riddick, J. A.; Bunger, W. B., Eds. Organic Solvents. In *Physical Methods in Organic Chemistry*; Weissberger, Ed.; Wily Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

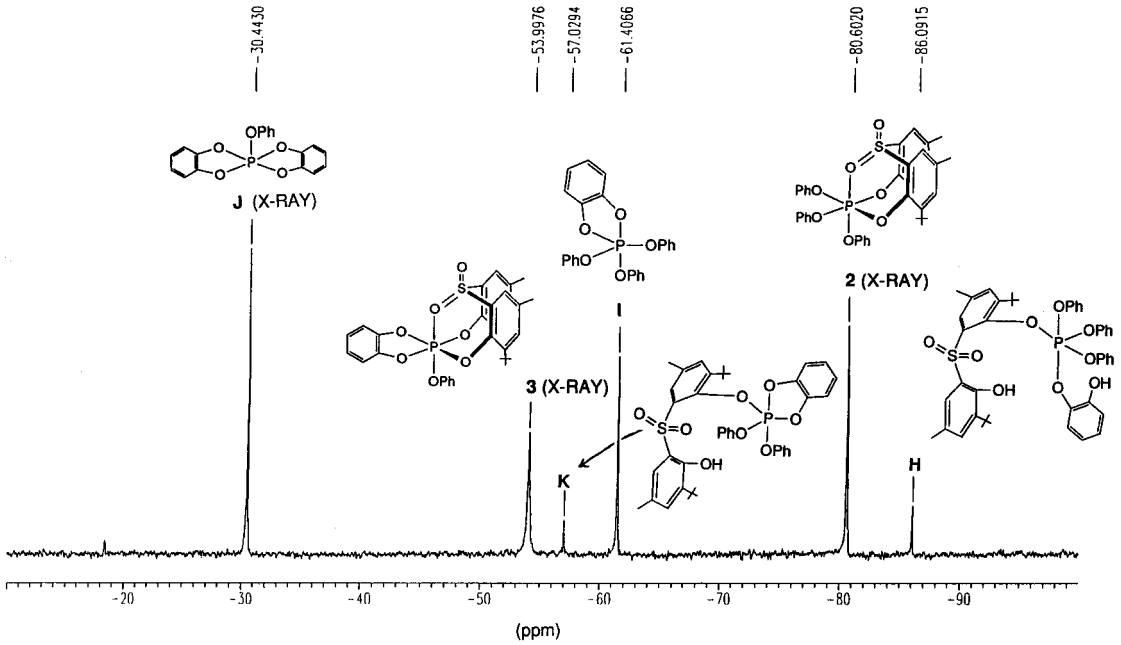


Figure 2. ^{31}P NMR spectrum of the reaction products of hexacoordinated phosphorane **2** with catechol in a 1:1 ratio in toluene-d_8 at 90 °C after 3 h. The spectrum was recorded at 20 °C. The solution contains 0.72 mmol of each reactant in 2.4 mL of toluene-d_8. The chemical shifts displayed on the upper part of the graph are the printed values recorded by the spectrometer. The ^{31}P shifts are recorded to their proper significance in Figure 3.

The percentage of the phosphorane relative to the total phosphorus containing species was measured from each spectrum by means of the integrated signals. The results may not be accurate enough to determine the rate constants (due to sparingly soluble nature of catechols and the inaccuracies encountered during the heating cycles relative to the time required to record the ^{31}P spectrum). The sample at room temperature has to be placed in a hot solvent bath which will not allow the reaction to proceed immediately at the rate expected for 90 °C. Thus, the error will be greater for short intervals. However, the results are accurate enough to show the correlation between the relative reaction rates and concentration changes or with the variation in the catechol employed.

The reactions of phosphoranes **5**, **6**, and **8** (100 mg each) and phosphorane **7** (56 mg) also were monitored similarly but in nondeuterated toluene (2.4 mL).

Results and Discussion

In reactivity toward catechol, trigonal bipyramidal **1** and **4** containing trifluoroethoxy ligands are much less reactive than the octahedral forms for **2** and **5**, which contain phenoxy ligands. Phosphorane **1** does not react or decompose upon heating with 1 molar equiv of catechol in boiling toluene (110 °C) for 48 h as shown by ^{31}P NMR spectra. Even after being heated for 2 h at 150 °C in 1,2-dichlorobenzene, **1** did not react with catechol. Two ^{31}P signals at −8.5 ppm (12%) and at −20.2 ppm (51%) appeared in the phosphate region. Also no decomposition or hydrolysis was observed when **1** or **4** was heated in a mixture of toluene and water for 24 h. This suggests that C−O cleavage occurs to yield the phosphate products. In contrast, 50% of **2** reacts with catechol in just 1 h at 90° giving catechol-substituted products including **3** and some phosphate.

With 4-nitrocatechol, a more rapid reaction occurred. Figure 1 displays the ^{31}P signals associated with the products formed when **2** was heated with 4-nitrocatechol in a 1:2 ratio in a toluene-d_8 solution at 90 °C for 1 min and for 6 min. The spectrum was recorded at 20 °C. After 6 min, most of the initial phosphorane **2** had reacted. The products formed are of the same type that resulted from the reaction of **2** with catechol conducted in a 1:1 ratio in toluene-d_8 at 90 °C. For the latter reaction, a ^{31}P spectrum recorded at 20 °C was obtained after 3 h. It is presented in Figure 2. It was found that recording the ^{31}P NMR spectrum at 90 °C did not give any significant differences in line intensities or chemical shifts relative to recording the spectrum at 20 °C. The formulations associated with each of the ^{31}P signals in Figure 2 are consistent with chemical shifts for known compounds in the case of **I** and **J**. Compounds **H** and **K** are postulated on the basis of our proposed mechanism for this reaction sequence as shown in Figure 3.

On the basis of reactivity studies which show the importance of the attacking nucleophile, an associative mechanism is indicated. This is illustrated for phosphorane **5** in toluene solution in Figure 4. It is apparent that the rate of reaction increases with an increase in catechol concentration or with the use of 4-nitrocatechol in place of catechol as a reactant. A similar dependence of reaction rate on the nature of the incoming nucleophile is found with **2**, **6**, and **7**.

Associative Mechanism. An initial proposed activated state is shown in Figure 3 as a heptacoordinated formulation resulting from an associative process in the reaction of **2** with either catechol or 4-nitrocatechol in toluene solution at 90 °C. The fact that 4-nitrocatechol is a poorer nucleophile than catechol but results in a rate acceleration may be associated with this first step. If this is considered the slow step, the cleavage of the catechol O−H bond may assist in the formation of the initial intermediate. Thus, the faster reaction of 4-nitrocatechol that predominates over catechol in this series of oxyphosphoranes may be due to the stronger acidity of the former and accompanying ease of cleavage of the O−H bond as the hydrogen is transferred to the departing oxygen in forming **H**.[43] Subsequent decomposition to the pentacoordinate intermediate **H** seems reasonable. **H** would result from cleavage of the P−O ring bond *trans* to the incoming catechol unit and accompanied by cleavage of the P−O donor interaction from the sulfonyl group. This formulation provides the route to **I** and **J**, both

(43) The initial step need not involve a seven-coordinated intermediate if the reaction is concerted with the displacement of the sulfonyl oxygen atom as the P−O bond forms from the incoming catecholate.

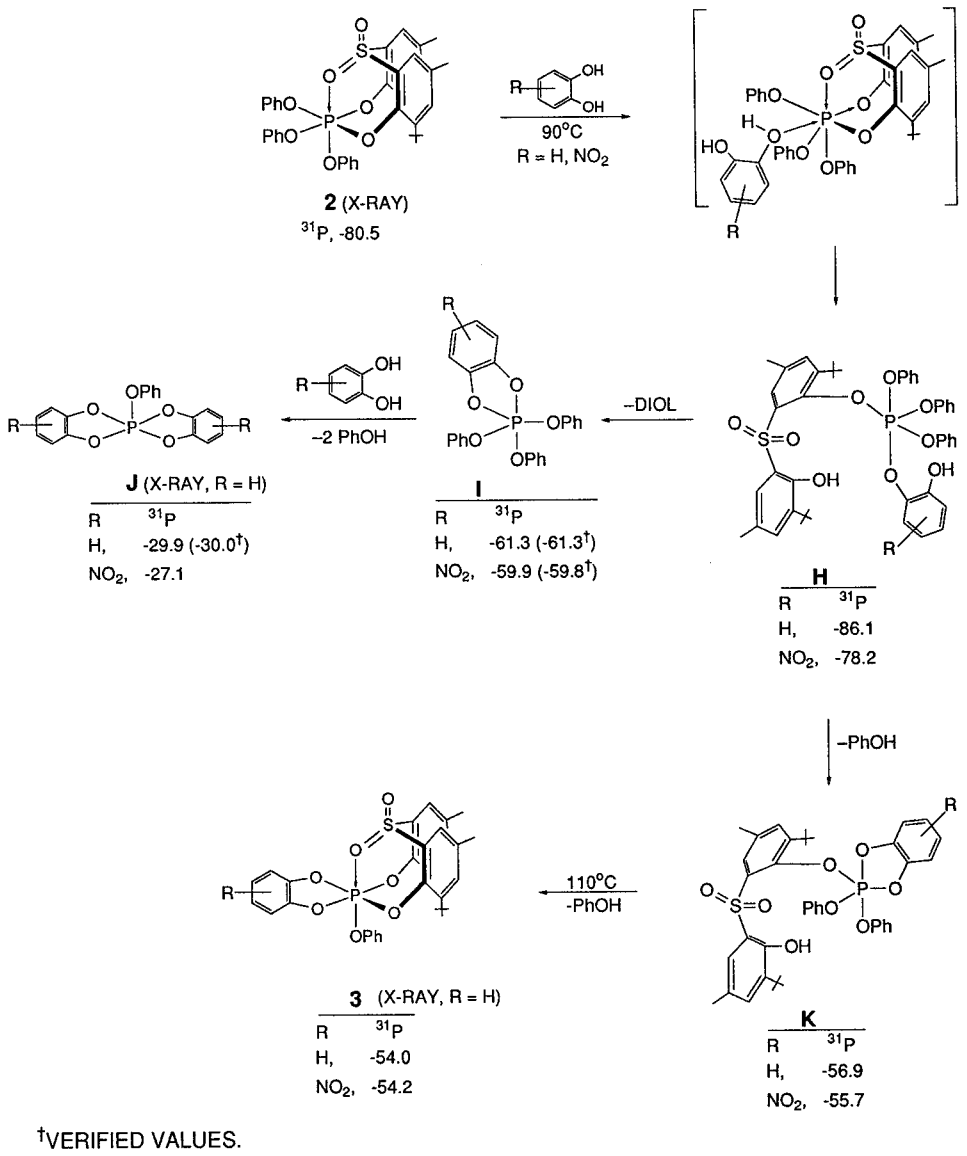
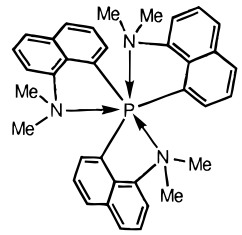


Figure 3. Association mechanism for the nucleophilic displacement reaction of phosphorane **2** with either catechol or 4-nitrocatechol in toluene solution at 90 °C.

indentifiable products, and the route to **K** and **3**. Like **3**, **J**[44] has been identified from an X-ray study. In the formation of **I**, the unreacted hydroxy oxygen of the catechol moiety must serve as the nucleophile that is envisioned to produce a hexacoordinated activated state from which P−O bond cleavage occurs to liberate the sulfonyl containing diol. In the formation of **K**, an additional hexacoordinate state is envisioned to accommodate passage to **K**, which requires cleavage of a phenoxy group. In the final step, the reaction temperature is elevated to 110 °C, in order to form **3**, another product identified by ^{31}P NMR and an X-ray study of its molecular structure.[39] In this process, the unattached sulfonyl-containing ring hydroxyl group serves as the nucleophile in an assumed hexacoordinate state to displace an additional phenoxy group.

It might be argued that, due to the lack of evidence for the existence of heptacoordinated phosphorus, the initial activated state in Figure 3 may prove fallacious. Pseudo-heptacoordination has been proposed for the tricoordinated phosphane **L**[45] and the tris(dithiacarbamato) complex of phosphorus(III),

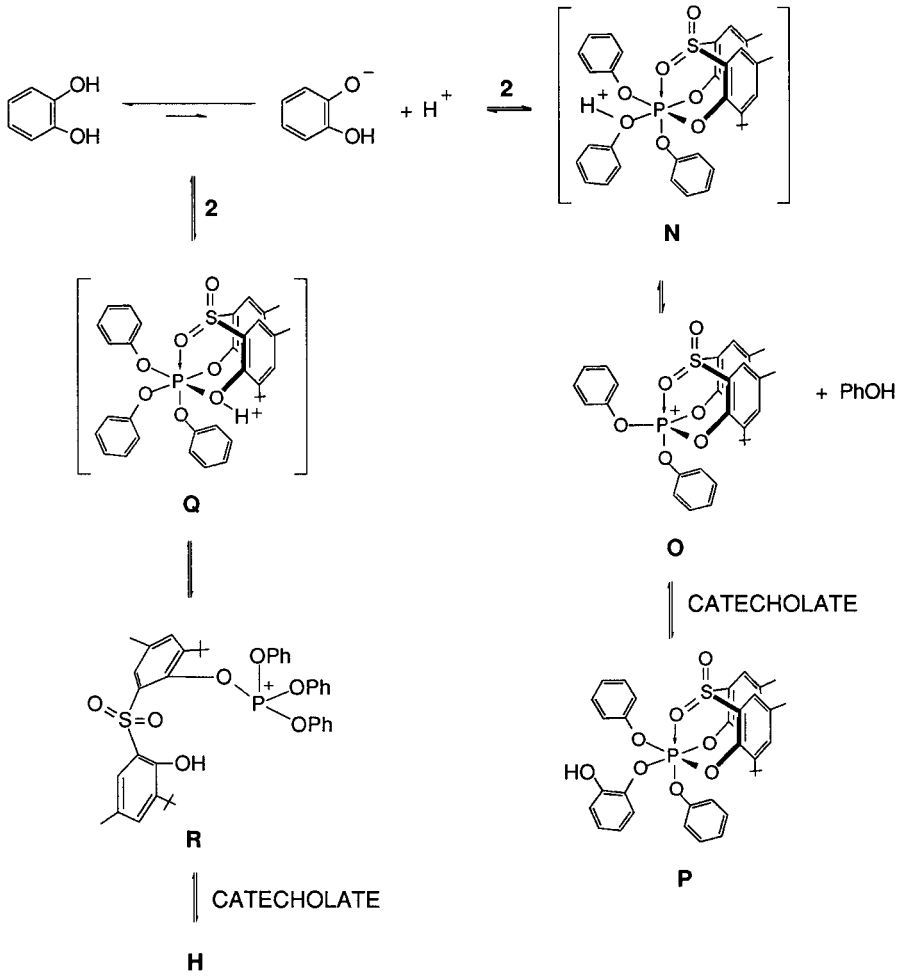


L [45]

$P[S_2CNMe_2]_3$ (**M**).[46] For both of these compounds, the pyramidal structure is retained at phosphorus for the phosphane ligands in **L** and for a PS_3 unit in **M**. For the latter, of the six sulfur atoms attached to phosphorus, three are short (2.18−2.20 Å) and three are long (2.87−3.02 Å).[46] For **L**, the three P−N distances (2.805, 2.844, and 2.853 Å) are long[45] but shorter than the van der Waals' sum (3.4 Å[47]). Also a lone electron pair in each accounts for the seventh coordination position. In

(44) Sarma, R.; Ramirez, F.; Marecek, J. F. *J. Org. Chem.* **1976**, *41*, 473.
(45) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reyé, C.; Declercq, J. P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430.
(46) Light, R. W.; Hutchins, L. D.; Paine, R. T.; Campana, C. F. *Inorg. Chem.* **1980**, *19*, 3597.
(47) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Scheme 1



view of the coordination geometry of these two compounds, the proposed seven-coordinate activated state in Figure 3 may be more reasonable if we consider that the incoming catechol oxygen *trans* to the departing ring oxygen atom are weakly coordinated as well as that of the sulfonyl oxygen atom attached to phosphorus. In this sense, donor action assists the nucleophilic attack of the incoming catechol unit in a concerted manner such that the donor interaction decreases as the phosphorus-ring oxygen bond is cleaved and the catechol P−O linkage is formed.

Alternatively, the associative mechanism may be subjected to acid catalysis via dissociation of the catechol reactant (Scheme 1). Two processes are envisioned. In one process, a phenoxy group of the hexacoordinated reactant **2** is protonated to give **N** which suffers the loss of phenol to yield the pentacoordinated phosphonium intermediate **O**. Attack of the latter by the catecholate unit leads to the hexacoordinate phosphorane **P** with accompanying ring opening and reaction with phenol to give **H** in Figure 3. In another, protonation by the catechol at one of the ring oxygens of **2** to give **Q** is followed by ring opening to give the phosphonium intermediate **R**. Attack of the latter by the catecholate leads to **H** in Figure 3. The latter process suffers due to the presence of ring oxygen atoms that are sterically protected by *tert*-butyl groups in all cases. However, this mechanism[48] is favored by not requiring the addition of a phenol group in forming **H** from **P** as presented in the alternate scheme, **N** → **O** → **P** → **H**.

Comparative Reactivities. Comparative reaction rates for **7**, **2**, and **5** as measured by ^{31}P monitoring of the decay of the phosphorane signal for a 1:1 mixture of reactants in toluene at 90 °C are displayed in Figure 5. For the reaction of **5** with catechol conducted at 90 °C, only two signals are present in the ^{31}P spectrum in addition to that for the reactant phosphorane.

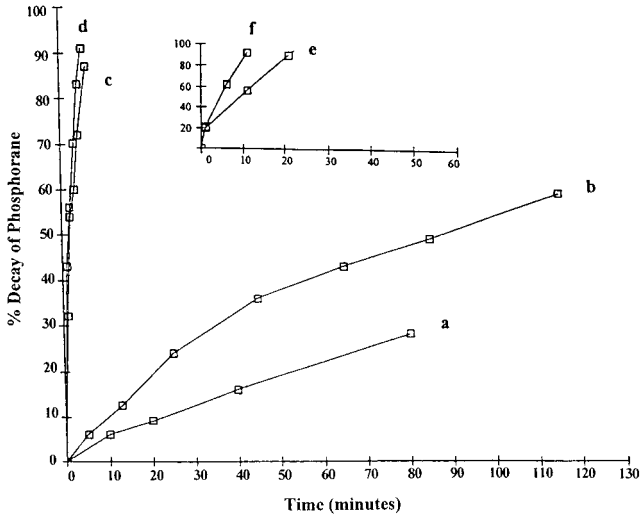


Figure 4. ^{31}P NMR monitoring of the reaction of hexacoordinated phosphorane **5** with catechols in toluene at 90 °C: (a) phosphorane + catechol in a 1:1 ratio; (b) phosphorane + catechol in a 1:2 ratio; (c) phosphorane + 4-nitrocatechol in a 1:1 ratio; (d) phosphorane + 4-nitrocatechol in a 1:2 ratio. Inset: Reaction monitoring of 4-nitrocatechol in (e) a 1:1 ratio and (f) in a 1:2 ratio, in toluene at 70 °C.

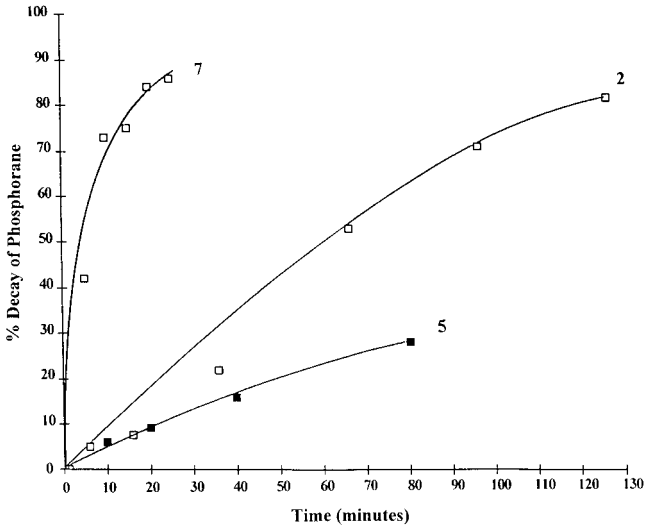


Figure 5. ^{31}P NMR monitoring of the reaction of phosphoranes X[(*t*-Bu)$RC_6H_2O]_2P(OPh)_3$ with catechol in a 1:1 ratio in toluene at 90 °C: **5**, X = SO_2, R = *t*-Bu; **2**, X = SO_2, R = Me; **7**, X = CH_2, R = Me.

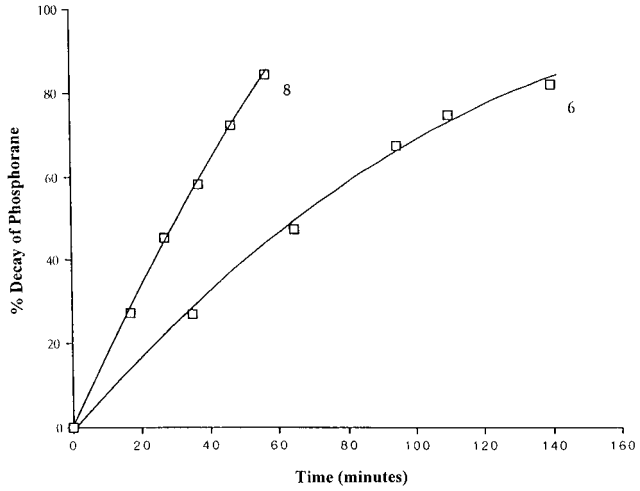


Figure 6. ^{31}P NMR monitoring of the reaction of S[(*t*-Bu)$RC_6H_2O]_2P$-$(OPh)_3$ with catechol in a 1:1 ratio in toluene at 70 °C: **6**, R = Me; **8**, R = *t*-Bu.

These signals at −30.4 and −56.9 ppm correspond to the final reaction products depicted in Figure 3, **J** and **K**, respectively.

^{31}P monitoring of the reaction of **7** with catechol was conducted in 1:1 and 1:2 ratios, respectively, at both 70 and 90 °C in toluene solution. Approximately equal amounts of phosphate, identified at −17.3 ppm, and most likely **3**, corresponding to a signal at −58.4 ppm, appeared in the ^{31}P spectra at 70 °C. When the reaction was monitored at 90 °C, the same two signals were present in addition to the ^{31}P signal for **7** (−83.5 ppm). However, formation of phosphate was much reduced in the faster catechol reaction at this temperature. For a 1:1 ratio of **7** to catechol, the ratio of phosphate to **3** was ∼1:7. For the acceleration in rate by increasing the catechol concentration to a 1:2 ratio, the phosphate ratio to **3** was ∼1:10, respectively.

A ^{31}P monitoring study of the relative reactivity of **6** and **8** with catechol was carried out under similar conditions (Figure 6). When these data are combined with that reported in this study, the order of reactivity with catechol shown in Chart 2 is obtained. Relative half-lives ($t_{1/2}$) are listed in parentheses. It is of interest that pentacoordinate **7** is the most reactive member (although not much different in rate compared to **8**) while pentacoordinate **1** is the least reactive in this series. The inertness of **4** approximates that of **1**. Considering the difficulty in controlling the amount of phosphate formed in each of the reactions, the difference between the reactivity of **7** and **8** with catechol is not significant. The three phosphoranes, **7**, **6**, and **2**, have the same aryl groups and phenoxy ligands. They vary in the type of bridging group, CH_2, S, and SO_2, respectively, with the latter two allowing the formation of hexacoordinate geometries. It would appear that this additional coordination relative to the pentacoordinate state for **7**, which lacks donor action, serves to hinder the approach of the catechol nucleophiles. Although the specific steric effect cannot be assigned, catechol attack giving the initial seven-coordinate activated complex following the associative reaction in Figure 3 from either **2** or **6** would encounter increased steric inhibition compared to the formation of a six-coordinate complex from **7**. A similar rationale applies to the associative mechanism described in Scheme 1, where interaction of a catechol unit with the phosphonium intermediate **O** to give **P** would experience increased steric effects for **2** and **6** compared to that for **7**. The same holds true if the route in Scheme 1 from **Q** to **R** is followed.

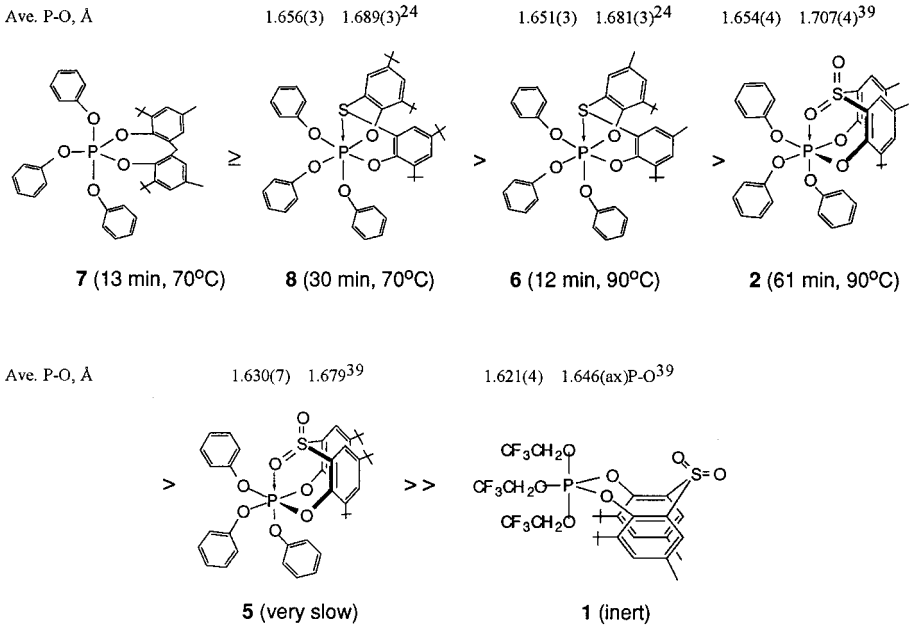
However, an increase in coordination usually results in a bond lengthening effect which would indicate weaker bonds and perhaps a more facile associative type reaction. This phenomena is well-known in silicon chemistry, where five-coordinate silicon exhibits enhanced reactivity compared to tetracoordinated silicon.[28,49−51] An analogy can be made between these two systems of geometrical changes. In the case of the silicon comparison, the geometrical change involves a tetrahedron compared to a trigonal bipyramid. There is a substantial increase in the axial bond distances of the TBP geometry relative to that for the tetrahedron. Presumably, there is an accompanying bond weakening. *Ab initio* calculations have emphasized the importance of the lower bond strength for axial bonds of trigonal bipyramidal geometries in accounting for the enhanced reactivity of five- vs four-coordinate silicon.[50,52] For the pentaoxyphosphoranes under consideration here, comparisons of P−O bond distances are revealing. Above each formulation in the preceding reactivity series (Chart 2) are listed the average P−O bond distance (excluding that with the donor atom) and the longest P−O distance.[24,39] In all hexacoordinate structures, the latter distance involves the P−O distance to a diol. For the pentacoordinate geometry **1**, this distance is an axial P−O value. Unfortunately, **7** was not amenable to an X-ray study. The average P−O bond distances for the more reactive oxyphosphoranes **8**, **6**, and **2** are similar. However, they are considerably lower for **5** and **1** in agreement with their lower reactivity.

Within the series of hexacoordinated oxyphosphoranes, we note that the degree of reactivity with catechol parallels the extent of octahedral character. This order is **8** > **6** > **2** > **5**, as measured by the structural displacement toward an octahedron,

(48) This process also is favored on the basis of X-ray data[39] that shows longer distances for the diol P−O linkages relative to the other P−O bonds in monocyclic hexacoordinate pentaoxyphosphoranes formed by donor action. For example, the diol P−O bonds (excluding the one with the donor group) for **2** and **5** average 1.676(5) Å compared to 1.620(5) Å for the other P−O bond distances. The lengthening of 0.056 Å may imply a more ready cleavage of a diol P−O bond in forming **R** relative to cleavage of a phenol P−O bond in forming **O**.

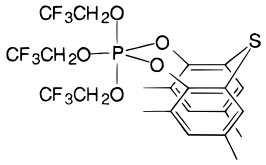
(49) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17 and references cited therein.
(50) Deiters, J. A.; Holmes, R. R. *Organometallics* **1996**, *15*, 3944.
(51) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371 and references cited therein.
(52) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 7197.

Chart 2



60.8% (**8**), 56.8% (**6**), 44.5% (**2**), and 39.6% (**5**), respectively.[39] Further, it is noted that, in this closely related series having the same ligands other than the bridging donor group, oxyphosphoranes **6** and **8** exhibit increased hexacoordination as a result of sulfur donor action relative to **2** and **5** which contain sulfonyl donor groups.

The inertness of **1** and **4** (which contain trifluoroethoxy ligands with TBP geometries) toward catechol may partially be a result of a decreased electrophilic character at phosphorus due to the presence of trifluoroethoxy ligands in place of phenoxy groups. In either Figure 3 or Scheme 1, this effect would render the phosphorus atom less susceptible to nucleophilic attack by catechol in the formation of the initial intermediate and that of **P**, respectively. Related work indicates that when a sulfonyl group is replaced by a sulfur atom, as in the TBP phosphorane **9**,[53] a slow reaction with catechol is



9 [53]

observed at 90 °C in toluene solution. This compares with the lack of any reaction under these conditions for **1** or **4**. However, for the most part, the trifluoroethoxy group acts as a poorer leaving group relative to the phenoxy ligand, particularly when the reactivity of **9** is compared to the much higher reactivity of the related phosphoranes, pentacoordinated **7** and hexacoordinated **8**.

Summary and Conclusions

Pentaoxyphosphoranes **1** and **4** which are trigonal bipyramidal and have trifluoroethoxy ligands are unreactive with catechols, whereas **2** and **5** which are octahedral as a result of sulfonyl donor action and possess phenoxy ligands undergo associative reactions with catechols via postulated hypervalent activated states. In comparison with a cyclic oxyphosphorane with a TBP geometry that lacks donor coordination but possesses phenoxy ligands (**7**), reactivity with catechol is high and comparable to that of hexacoordinated **8**. It is not known to what extent steric effects control the observed order of reactivity with catechol. The order of reactivity for the hexacoordinated members, including analogous members that have a sulfur atom in place of a sulfonyl group in the ring component (**6** and **8**), parallels the degree to which the members have achieved octahedral character (**8** > **6** > **2** > **5**). Also the average P−O bond lengths (excluding the P−O donor bond) for the more reactive members **8**, **6**, and **2** are considerably longer than those for the less reactive members **1** and **5**. This observation suggests that the looseness of P−O bonds (implied by their increased length) is a principal factor associated with reactivity for these cyclic oxyphosphoranes.

The inertness of trigonal bipyramidal **1** and **4** may be associated with the fact that the trifluoroethoxy group is inherently a poorer leaving group compared to the phenoxy group. Thus, accelerated reactions for pentaoxyphosphoranes subjected to donor coordination depend on sufficient electrophilicity supplied by electronegative ligands that are good leaving groups and which allows phosphorus to accommodate oxygen-containing nucleophiles in a possible expansion of its coordination sphere. Such conditions may exist at active sites of cAMP and phosphoryl transfer enzymes.

Acknowledgment. The support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The authors express appreciation to Professor C. Dennis Hall for suggesting acid catalysis as discussed in Scheme 1.

Supporting Information Available: A listing of rate data for the reactions of **2**, **5**, and **7** with catechol and for the reactions of **2** and **5** with 4-nitrocatechol (2 pages). Ordering information is given on any current masthead page.

IC970919S

(53) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. Unpublished work.