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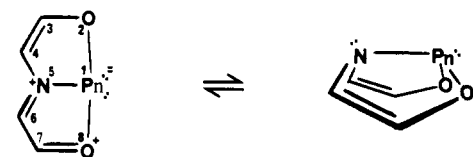
## The Synthesis, Structure, and Chemistry of 10-Pn-3 Systems: Tricoordinate Hypervalent Pnictogen Compounds<sup>†1a</sup>

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**Abstract:** A set of previously unknown tricoordinate hypervalent pnictogen compounds, 10-Pn-3 ADPnO, has been synthesized. The chemistry of these systems has been studied. Reactions with alcohols,  $\alpha$ -dicarbonyl compounds, halogens, transition metals, protic acids, and acetylenes are among the chemistry described. In general, it was found that 10-As-3 ADAsO and 10-Sb-3 ADSbO systems behave similarly and offer different chemistry from that of the 10-P-3 ADPO system. Among these unusual reactions is a novel C-C bond-forming reaction with hexafluoro-2-butyne. The electronic structure of these systems has been considered in light of preliminary *ab initio* molecular orbital calculations. The cyclic voltammetry data on the 10-Pn-3 ADPnO systems have been measured and are in accord with theoretical expectations. X-ray structures on a wide variety of derivatives provide insight into the chemistry of these systems. Phosphorus compounds with coordination numbers ranging from 2 to 6 have been characterized, and a trend is observed for <sup>31</sup>P-<sup>15</sup>N coupling constants and phosphorus coordination number.

Our interest in transargononic<sup>1b</sup> compounds with low coordination number but high electron count has led us to investigate a family of compounds, 10-Pn-3<sup>1c</sup> 5-aza-2,8-dioxo-1-pnictabicyclo[3.3.0]octa-2,4,6-triene (ADPnO) (Pn = pnictogen: N, P, As, Sb, Bi).<sup>2a,3,4</sup> In preliminary reports we have briefly de-



10-Pn-3

ADPnO

8-Pn-3

Pn = Pnictogen (N, P, As, Sb, Bi)

scribed the synthesis and structures of the three central members of this unusual family.<sup>2a,3,4</sup> These ADPnO ring systems afford

a unique opportunity to examine the electromorphism<sup>2a</sup> between the 8-Pn-3 and 10-Pn-3 structures and hence gain new insight into

(1) (a) The terms "pnictogen" and "pnictide" have been used to refer to the main group 5 (group 15) elements (N, P, As, Sb, Bi). These terms are derived from the Greek word *pniktos* (suffocate—the origin of the prefix "pnicto"). See: Brown, R. W. *Composition of Scientific Words*; George W. King Printing Co.: Baltimore, MD, 1954; p 620. The terms "pnigogen" and "pnicogen" have also been used to identify this family of elements (Suchow, L. *Inorg. Chem.* **1978**, *17*, 2041). The latter two terms are somewhat inappropriate since *pnigo* (the source of pnigogen) means "choke" rather than "suffocate" and "pnicogen" does not reflect the proper etymology (the "t" should not be omitted). For the spoken words, the terms "pnictogen" and "pnictide" are clearly and easily enunciated. Thus we prefer the terms derived from "pnicto" (pnictogen and pnictide). (b) The term "transargononic" has been used by Linus Pauling to describe the bonding about some central atom that results in a formal valence electron count at that atom which is greater than the number of valence electrons for the argonon (noble gas) at the end of the period to which the central atom belongs. See: Pauling, L. *General Chemistry*, 3rd ed.; W. H. Freeman: San Francisco, 1970. (c) 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. (d) Because of the number of structurally diverse compounds discussed in this paper we have used acronyms derived from the name of central ring system, 5-aza-2,8-dioxo-1-pnictabicyclo[3.3.0]octa-2,4,6-triene (ADPnO). The acronyms are identified with the drawings in the text. Prefixes are added to indicate substituents in the 3 and 7 positions (e.g., DitBuADPnO). The central pnictogen (if specifically identified) is referred to by its atomic symbol. Products derived from the parent ADPnO systems are identified by adding a suffix to the acronym which identifies the elements or moieties that have been chemically incorporated (e.g., DitBuADPO-2HFB for the adduct of DitBuADPO and two molecules of hexafluoro-2-butyne). The "." used to append the suffix indicates composition but not the nature of the bonds formed. The abbreviations used as suffixes are for simple compounds: HFB for hexafluoro-2-butyne; HFBA for hexafluorobiacetyl; or HOTf for triflic acid.

<sup>†</sup>This paper is dedicated to Professor Linus Pauling on the occasion of his 85th birthday.

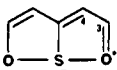
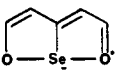
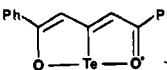
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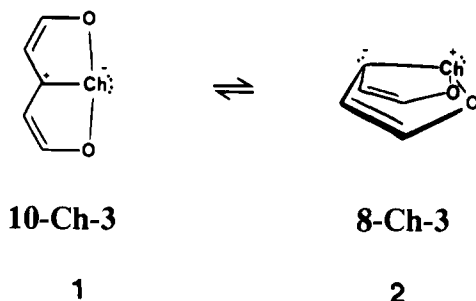
**Table I.** Comparative Spectral Properties between 10-Pn-3- and 10-Ch-3-Containing Molecules

compound	<sup>1</sup> H NMR H <sup>a</sup>	<sup>13</sup> C NMR		UV λ <sub>max</sub> , nm (log ε) <sup>a</sup>
		C3	C4	
DitBuADPO	7.50 <sup>b</sup>	169.9 <sup>b</sup>	111.2 <sup>b</sup>	221 (3.45), 314 (3.20)
	6.90 <sup>c,d</sup>	167.8 <sup>d,e</sup>	104.1 <sup>d,e</sup>	222 (3.38), 257 (3.35), 339 (4.06) <sup>c</sup>
DitBuADAsO	7.90 <sup>b</sup>	174.8 <sup>b</sup>	113.6 <sup>b</sup>	238 (3.9), 362 (4.2)
	7.10 <sup>c,d</sup>			211 (3.26), 288 (3.45), 353 (4.11) <sup>c</sup>
DitBuADSbO	8.46 <sup>b</sup>	176.7 <sup>b</sup>	117.8 <sup>b</sup>	325 (3.74), 407 (3.56), 568 (2.48)
	8.15 <sup>d,f</sup>	181.0 <sup>d,f</sup>	107.7 <sup>d,f</sup>	424 (4.61) <sup>f,g</sup>

<sup>a</sup>In cyclohexane. <sup>b</sup>In CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup>Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkins Trans. 1*, 1975, 775. <sup>d</sup>In CDCl<sub>3</sub>. <sup>e</sup>Jacobsen, J. P.; Hansen, J.; Pedersen, C. T.; Pedersen, T. *J. Chem. Soc., Perkins Trans. 2*, 1979, 1521. <sup>f</sup>Detty, M. R.; Luss, H. R. *J. Org. Chem.*, 1983, 48, 5149. <sup>g</sup>In CH<sub>2</sub>Cl<sub>2</sub>.

hypervalent bonding systems. At present we have observed the ADPnO ring in both bent<sup>5</sup> and planar arrangements which correlates with the electronic demands at the pnictogen center. We now report detailed structural correlations of the ADPnO systems along with extensive multinuclear magnetic resonance studies and the varied chemistry exhibited by these molecules.

The 10-Pn-3 ADPnO family is both structurally and electronically related to the 10-Ch-3 dioxachalcapentalenes (1) (Ch



Ch = Chalcogen (O, S, Se, Te)

= chalcogen: S, Se, Te).<sup>6</sup> The 10-Ch-3 structures can be thought of as arising from a "proton-transfer" reaction in which a proton is moved from the nitrogen nucleus to the heavier pnictogen nucleus in the 10-Pn-3 ADPnO structures. This transforms nitrogen to carbon, pnictogen to chalcogen, and 10-Pn-3 ADPnO into a dioxachalcapentalene (1). The analogy between the 10-Pn-3 ADPnO systems and the dioxachalcapentalenes is manifested in the NMR and UV spectra of these compounds. Table I shows the similarity between the 10-P-3 and 10-S-3 systems.

(2) (a) We previously introduced the term "electromorphism" to describe the relationship between two structures (e.g., planar 10-P-3 ADPO and bent 8-P-3 ADPO) for which the isomerism relating the structures arises from differences in electron distribution and geometry. There is, however, no difference in connectivities or spin states for the structures. See: Culley, S. A.; Arduengo, A. J., III. *J. Am. Chem. Soc.* 1984, 106, 1164. (b) Recently 10-P-3 bonding arrangements have been implicated in other systems. See: Lochschmidt, S.; Schmidpeter, A. *Z. Naturforsch.* 1985, 40b, 765.

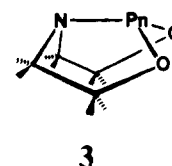
(3) Culley, S. A.; Arduengo, A. J., III. *J. Am. Chem. Soc.* 1985, 107, 1089.

(4) Stewart, C. A.; Harlow, R. L.; Arduengo, A. J., III. *J. Am. Chem. Soc.* 1985, 107, 5543.

(5) Arduengo, A. J., III; Stewart, C. A.; Davidson, F. *J. Am. Chem. Soc.* 1986, 108, 322.

(6) (a) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Chem. Commun.* 1972, 1283. (b) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkin Trans. 1* 1975, 775. (c) Detty, M. R.; Luss, H. R. *J. Org. Chem.* 1983, 48, 5149. (d) Gleiter, R.; Gygax, R. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1976; Vol. 63, p 49.

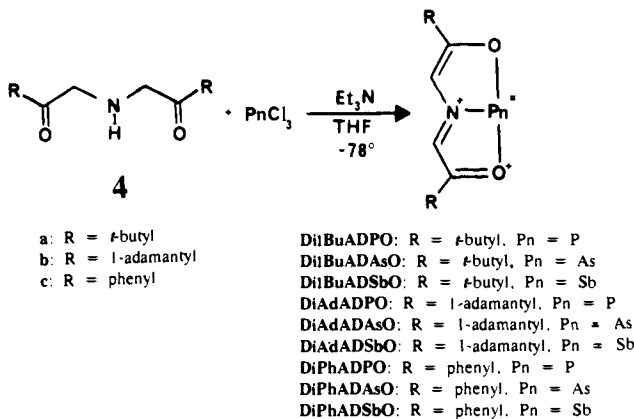
While there exists a structural analogy between the 10-Pn-3 ADPnO systems and the dioxachalcapentalenes, the latter would not be expected to exhibit electromorphism<sup>2</sup> between 8-Ch-3 (2) and 10-Ch-3 (1) states. The substitution in the dioxachalcapentalenes is not desirable for stabilizing the 8-Ch-3 electromorph. Dioxasulfonium ions ((RO)<sub>2</sub>S<sup>+</sup>R) are generally unstable,<sup>7</sup> and there is no substituent stabilization of the carbanion in the angular position. On the other hand the ADPnO ring system is substituted in a manner which should give a fairly stable 8-Pn-3 electromorph. Indeed, saturated analogues (3) of these pnictogen ring systems have been synthesized and exhibit the expected bent geometry.<sup>8</sup>



At the time we began this work the phosphoranediide (10-P-3) functional group was unknown,<sup>2b</sup> and care was taken to include several features in the ADPnO ring system such that the 10-Pn-3 electromorph could be stabilized.<sup>9</sup> These features include five-membered-ring linkage of equatorial and apical sites, electro-negative elements in apical positions, charge compensation for the formally dianionic Pn center, and a 10-π-electron system (potentially aromatic, although aromaticity does not seem to be an important stabilizing feature; vide infra).

## Results and Discussion

In general, the synthesis of the 10-Pn-3 ADPnO systems is easily accomplished by reaction of a diketoamine ligand (4) with the



appropriate pnictogen trihalide and triethylamine. We have synthesized representative ADPnO compounds in which the 3 and 7 positions have been substituted with *tert*-butyl (DitBuADPnO<sup>10</sup>), adamantyl (DiAdADPnO), and phenyl (DiPhADPnO) groups. As would be expected the diadamantyl systems are somewhat more stable than their di-*tert*-butyl analogues. The diphenyl system, however, is only stable enough to allow isolation when the central pnictogen is arsenic. DiPhADPO<sup>10</sup> and DiPhADSbO have both been observed in solution but decompose on attempted isolation.

The structures of the three central (P, As, Sb) ADPnO systems are those of the 10-Pn-3 electromorphs with no evidence for the 8-Pn-3 electromorphs. Figure 1<sup>11</sup> illustrates the solid-state ge-

(7) (a) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* 1977, 99, 4400. (b) Minato, H.; Yamaguchi, K.; Kobayashi, M. *Chem. Lett.* 1975, 307.

(8) (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.

(9) For a general discussion of the stabilization of hypervalent species see: (a) Martin, J. C.; Perozzi, E. F. *Science (Washington, D.C.)* 1976, 191, 154. (b) Martin, J. C. *Science (Washington, D.C.)* 1983, 221, 509.

(10) DiPhADPO was synthesized by S. A. Culley but could not be isolated. See: Culley, S. A. Ph.D. Thesis, University of Illinois, 1984.

Table II. Selected Bond Lengths (pm) and Angles (deg) in 10-Pn-3 ADPnO Systems

compound	Pn-O	Pn-N	C-O	C-N	C-C <sub>ring</sub>	O-Pn-O	N-Pn-O	C-O-Pn	C-N-Pn	C-C-N	C-C-O	C-N-C	Pn <sub>r</sub> radius
DitBuADPO <sup>a</sup>	183.5 (2)	170.3 (2)	133.1 (4)	137.5 (3)	134.2 (4)	167.7 (1)	83.5 (1)	114.3 (2)	118.0 (2)	111.3 (2)	112.8 (2)	125.2 (2)	110
DitBuADAsO	179.2 (2)	183.9 (3)	132.8 (4)	138.2 (3)	133.7 (4)	160.3 (1)	84.2 (1)	115.4 (2)	116.8 (2)	111.3 (3)	112.3 (3)	125.2 (3)	122
DiAdADAsO	199.8 (3)	184.2 (2)	131.0 (4)	137.2 (4)	136.0 (5)	160.6 (1)	80.0 (1)	113.6 (2)	117.2 (2)	113.5 (3)	115.3 (3)	126.1 (3)	122
DitBuADSB <sup>o</sup>	198.0 (2)	206.4 (3)	131.5 (4)	137.5 (4)	135.7 (4)	149.6 (1)	80.3 (1)	114.0 (2)	117.0 (2)	113.8 (3)	114.8 (3)	125.1 (3)	143
DiAdADS <sup>o</sup>	197.3 (2)	214.4 (3)	131.1 (4)	137.6 (4)	135.9 (4)	148.7 (3)	80.3 (1)	114.3 (2)	116.9 (2)	113.6 (3)	116.4 (4)	123.0 (10)	143
	216.5 (3)	204.6 (10)	131.5 (6)	136.2 (6)	137.6 (7)		74.9 (1)	115.0 (3)	117.3 (3)	115.2 (4)	117.9 (4)		
	213.3 (8)		133.0 (15)	138.5 (15)	139.0 (20)		74.6 (4)	115.5 (7)	118.1 (8)	114.0 (10)	117.0 (10)		
	215.7 (8)		130.0 (20)	138.1 (15)	135.0 (20)		74.6 (4)	115.8 (8)	118.4 (8)	114.0 (10)	117.0 (10)		

<sup>a</sup>These data are taken from a second structure determination on this compound more accurate than that reported in ref. 2. See supplementary material. O<sub>r</sub>radius = 73, N<sub>r</sub>radius = 75.

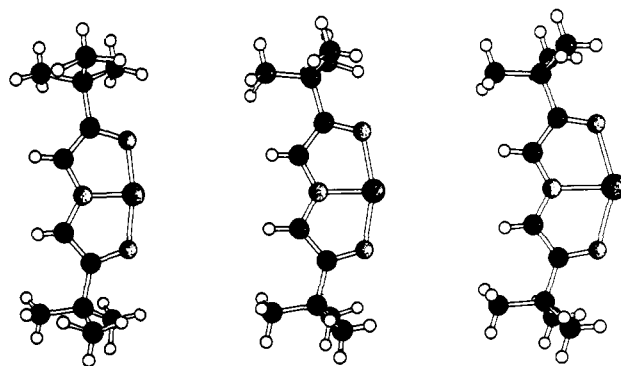


Figure 1. X-ray structures of representative 10-Pn-3 ADPnO systems (left to right, Pn = P, As, Sb).<sup>11</sup>

Table III. Representative Bond Lengths (pm) in 10-Pn-5 Systems

compound	Pn-O	Pn-N
5a, <sup>a</sup> Pn = P, R = H	171.0	164.0
DitBuADPO-2HFB	170.5	161.3
DitBuADPO-(CH <sub>3</sub> ) <sub>2</sub>	174.0	169.2
DitBuADPO-CH <sub>3</sub> /Cl	170.2	167.0
5b, <sup>b</sup> Pn = As, R = phenyl	188.0	180.7

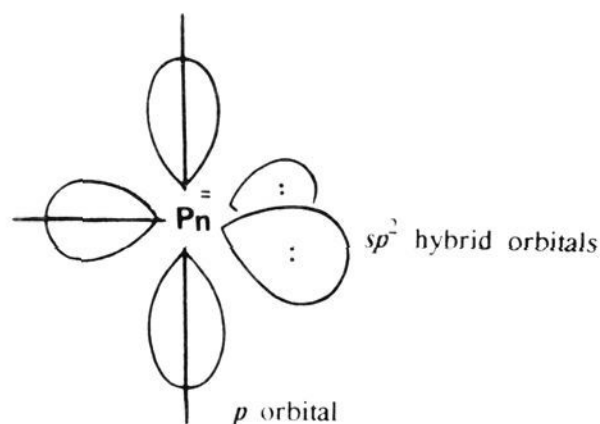
<sup>a</sup>Meunier, P. F.; Day, R. O.; Devillers, J. R.; Holmes, R. R. *Inorg. Chem.* **1978**, *17*, 3270. <sup>b</sup>Day, R. O.; Holmes, J. M.; Sau, A. C.; Devillers, J. R.; Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2127.

ometries observed for the 10-Pn-3 DitBuADPnO (Pn = P, As, Sb) molecules. The structural features designed into the ADPnO ring have clearly resulted in the planar geometries indicative of the 10-electron bonding scheme about the pnictogens (P, As, Sb). Table II gives some selected bond lengths and angles in the 10-Pn-3 ADPnO systems along with the covalent radii of the pnictogen centers.<sup>12</sup> Several structural features are evident from these data. First, these 10-Pn-3 systems show rather long Pn-N and Pn-O bonds. Second, as one moves from phosphorus to antimony the Pn-N bonds lengthen faster than the mean Pn-O bonds. The experimental Pn-O bonds are greater than (or equal to) the sum of the covalent radii whereas the Pn-N bonds are shorter than the sum of the covalent radii. As the size of the pnictogen center increases, the experimental distances approach the sum of the covalent radii. Of course bond length estimates based on covalent radii do not include ionic contributions which would shorten the nominal Pn-X single bonds as shown in Table II. The structure of the ligand backbone is rather invariant. The C-N bonds are longer than that in vinylamine<sup>13a</sup> while the C-C bonds are suggestive of delocalized  $\pi$  systems.<sup>13b</sup> The C-O bonds are intermediate between vinyl ethers and carbonyls.<sup>13b</sup>

(11) The drawings in this paper were made with the KANVAS computer graphics program. This program is based on the program SCHARAL of E. Keller (Kristallographisches Institute der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. When present the planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

(12) (a) For covalent radii see: Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper and Row: New York, 1978; pp 232-233. (b) For van der Waals radii see: Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

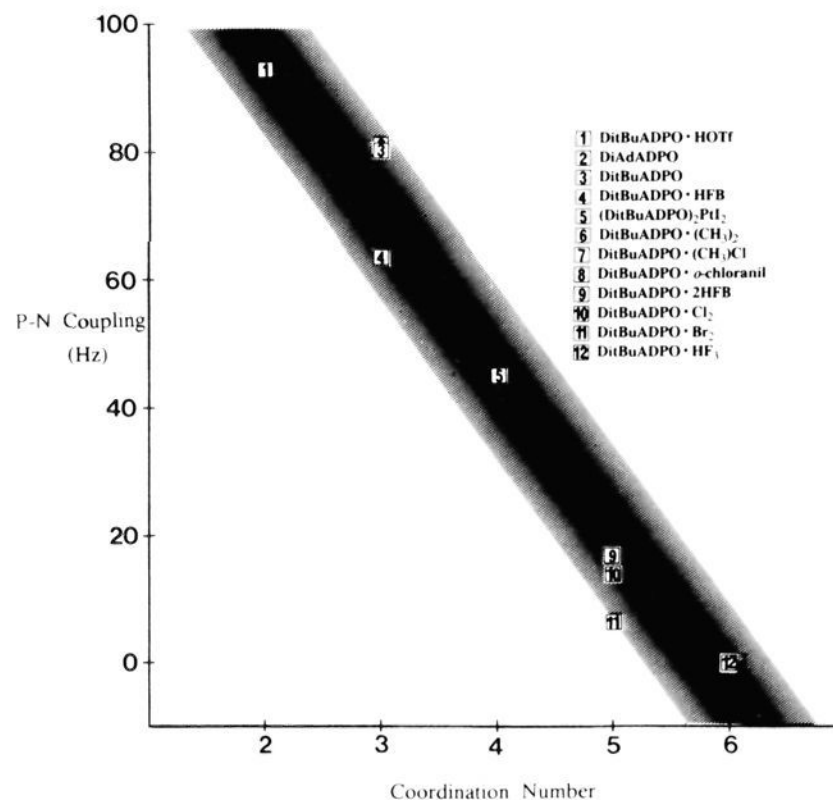
(13) (a) Eades, R. A.; Weil, D. A.; Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A.; Douglass, C. H., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 5372. (b) *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Sutton, C. E., Ed.; The Chemical Society: London, 1958. Special Publications No. 11, and 1965 Special Publications No. 18.



**Figure 2.** Idealized pnictogen hybridization in the 10-Pn-3 bonding scheme.

Long Pn–O bonds would be expected in the 10-Pn-3 ADPnO systems since the oxygens occupy the apical positions of a pseudo-trigonal-bipyramidal structure (nitrogen and two lone pairs occupy the equatorial sites). Interestingly, the Pn–O bonds in 10-Pn-3 ADPnO are long even when compared to apical bonds in representative 10-Pn-5 species (Table III). The long bonds to the pnictogen centers do not suggest a great deal of  $\pi$  interaction between these centers and their neighboring oxygens and nitrogens. If the ADPO systems are considered to contain a +1 or +3 oxidation state phosphorus center, a smaller ionic component to the P–O bond would be expected relative to the compounds in Table III which must be considered as P<sup>V</sup>. This is consistent with the somewhat lengthened hypervalent P–O bonds of ADPO. A weaker ionic component to the Pn–O bonds is also supported by calculated charges relative to 10-Pn-5 systems (vide infra). While some  $\pi$  interaction is evident from the NMR spectra of the compounds, there is no evidence for aromaticity (vide infra).<sup>4</sup> The long Pn–O bonds may result from ring strain since the interior angles in the ligand backbone are all reduced from 120°. However, the P–O and P–N bonds in DitBuADPO are long even when compared to 10-P-5 systems that contain the tridentate ligand (e.g., DitBuADPO·2HFB, DitBuADPO·(CH<sub>3</sub>)<sub>2</sub>, and DitBuADPO·CH<sub>3</sub>/Cl; see Table III). It should be noted that the ligand backbone seems to “relax” only slightly when larger atoms are placed in the ligand mandible. Thus, there may not be a direct relationship between the small interior ligand angles and the long Pn–O bonds. Finally, the length of the Pn–O bond could be influenced by electronic repulsions with the 10-Pn-3 center. These 10-electron tricoordinate pnictogens bear two lone pairs in their equatorial sites (along with a nitrogen). Electron repulsion with the oxygen lone pairs may be responsible, at least in part, for the long Pn–O bonds. The two pnictogen lone pairs should also prefer increased s-orbital character over the sp<sup>2</sup> hybrids in the idealized bonding scheme (Figure 2). Although the hypervalent (three-center, four-electron) bond to the apical sites is usually envisioned as arising from a sole p-orbital on the central element,<sup>14</sup> some s-orbital character would be expected to stabilize (and shorten) the hypervalent bonds. With the strong s-orbital demand of the two pnictogen lone pairs this may not be possible in the 10-Pn-3 ADPnO series.

The s-orbital demand of the pnictogen lone pairs in 10-Pn-3 ADPnO is also consistent with the long Pn–N bonds since this bond should be rich in p-orbital character at the heavier pnictogen center. This effect is also manifested in the small P–H NMR coupling to the ring protons in 10-P-3 ADPO (vide infra). The more rapid lengthening of the Pn–N bond relative to the Pn–O bonds as one moves from phosphorus to antimony in the 10-Pn-3 system also reflects s-orbital character demand by the pnictogen lone pairs. This demand would be more strongly felt in a 10-Sb-3 than in a 10-P-3 system. This demand parallels a reduced ability of the heavy pnictogen to stabilize lone pairs by delocalization onto neighboring second row (N, O) elements. This trend is also evident in the NMR chemical shifts of various nuclei in the



**Figure 3.** <sup>31</sup>P–<sup>15</sup>N couplings vs. coordination number.

10-Pn-3 ADPnO systems (vide infra). Finally, the small variation of the ligand backbone in the 10-Pn-3 ADPnO systems is a natural consequence of the rapidly lengthening Pn–N bond, which displaces the heavier pnictogen center further from the ligand mandible. This displacement thus reduces the O–Pn–O angles such that increases in the Pn–O bond lengths are offset somewhat. The corresponding O–O distances increase from 361 to 390 to 416 pm through the series from phosphorus to antimony, while the covalent radius of the pnictogen increases from 110 to 122 to 143 pm. In summary, long Pn–O bonds in 10-Pn-3 ADPnO systems can be attributed to a combination of a weaker ionic component for these bonds relative to 10-Pn-5 species, s-orbital demand of the pnictogen lone pairs, and lone-pair repulsions between the pnictogen and oxygen centers.

### Nuclear Magnetic Resonance Spectra

Multinuclear magnetic resonance spectra provide some interesting data on the 10-Pn-3 ADPnO systems. The solid-state and solution spectra are virtually identical, indicating the 10-Pn-3 electromorph is present in solution as well as in the solid state. The solution spectra (Table IV) show rather smooth downfield shifts for <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N nuclei as the central 10-electron pnictogen is changed from phosphorus to antimony. These downfield shifts are consistent with the importance of a resonance structure which places positive charge in the ligand backbone. Thus the general low-field shift of the ring protons is primarily the result of positive charge delocalization (not ring current or aromaticity).<sup>4</sup> As the 10-electron center is changed from phosphorus to antimony, there is diminution (because of poorer overlap) of the ability of the Pn center to return electron density to the ligand  $\pi$  system. Thus more positive charge is felt by the ligand backbone in 10-Sb-3 ADSbO than 10-As-3 ADAAsO than 10-P-3 ADPO. This charge effect is also observed in the <sup>13</sup>C and <sup>15</sup>N spectra<sup>15</sup> of these systems. The <sup>15</sup>N resonances for the 10-Pn-3 ADPnO molecules (Table IV) show the expected downfield shift as the 10-Pn-3 center becomes heavier. In addition these shifts are typical of pyridinium type nitrogens,<sup>16</sup> again consistent with a high degree of positive charge delocalization over a  $\pi$  system containing a planar tricoordinate nitrogen. As expected, the shifts move substantially upfield as electron density is returned to the

(14) (a) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. (b) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112. (c) Pimentel, C. G. *J. Chem. Phys.* **1951**, *19*, 446. Also see ref 9.

(15) The 30.48-MHz <sup>15</sup>N{<sup>1</sup>H} magnetic resonance spectra were obtained using a DEPT pulse sequence: Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323. MLEV 16 decoupling was used during the acquisition. The final proton pulse was set to a 45° angle and  $\tau(1/2J)$  set between 50 and 125 ms.

(16) (a) *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Levy, G. C., Lichter, R. L., Eds.; Wiley: New York, 1979; p 77. (b) *Nuclear Magnetic Resonance*, Vol. 18, <sup>15</sup>N-NMR Spectroscopy; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1981; p 127.

Table IV. Selected Multinuclear NMR Chemical Shifts<sup>a</sup> and Coupling Constants<sup>b</sup> for ADPnO Derived Systems

compound	<sup>1</sup> H NMR, H <sub>4(6)</sub>	<sup>13</sup> C NMR		<sup>15</sup> N NMR, N <sub>5</sub>	<sup>31</sup> P	<sup>17</sup> O	<sup>3</sup> J <sub>CH<sup>c</sup></sub> C <sub>6(4)</sub> -H <sub>4(6)</sub>
		C <sub>3(7)</sub>	C <sub>4(6)</sub>		NMR, P <sub>1</sub>	NMR, O <sub>2(8)</sub>	
DitBuADPO	7.50 ( <sup>3</sup> J <sub>PH</sub> = 9.6)	169.9 (J <sub>PC</sub> = 0.2)	111.2 (J <sub>PC</sub> = 5.7)	-126.3 ( <sup>1</sup> J <sub>PN</sub> = 80.0)	187.0	324	1.5
DiAdADPO	7.40 ( <sup>3</sup> J <sub>PH</sub> = 9.9)	169.6	111.1 (J <sub>PC</sub> = 5.6)	-126.0 ( <sup>1</sup> J <sub>PN</sub> = 81.0)	185.0		
DitBuADAsO	7.90	174.8	113.6	-96.0		330	1.2
DiAdADAsO	7.88	174.9	113.6	-96.1			2.0
DiPhADAsO	8.64	162.6	115.4	-95.5			
DitBuADSbO	8.46	176.7	117.8	-90.9		305	3.1
DiAdADSbO	8.35	176.6	117.7	-94.5			3.0
DitBuADPO·HOTf	5.84 ( <sup>3</sup> J <sub>PH</sub> = 7.8)	215.8 (J <sub>PC</sub> = 3.17)	61.3 (J <sub>PC</sub> = 10.8)	-152.6 ( <sup>1</sup> J <sub>PN</sub> = 93.4)	234.2		1.8
	7.81 ( <sup>3</sup> J <sub>PH</sub> = 6.4)	171.2 (J <sub>PC</sub> = 3.4)	122.5 (J <sub>PC</sub> = 4.9)				
DitBuADAsO·HOTf	6.07	219.5	62.6	-121.0			
	8.03	177.0	125.9				
DitBuADPO·o-chloranil	6.25 ( <sup>3</sup> J <sub>PH</sub> = 32.0)	195.4	108.9 (J <sub>PC</sub> = 15.9)	-275.9 ( <sup>1</sup> J <sub>PN</sub> = 16.8)	-10.2		1.0
DitBuADAsO·o-chloranil	7.56	190.8	126.2	-48.6			6.2
DitBuADSbO·o-chloranil	7.80	196.1	123.4				5.0
DitBuADPO·HFBA	5.44 ( <sup>3</sup> J <sub>PH</sub> = 10.8)	210.3 (J <sub>PC</sub> = 1.1)	73.0 (J <sub>PC</sub> = 7.6)		159.0		
	5.71 ( <sup>3</sup> J <sub>PH</sub> = 12.0)	155.4 (J <sub>PC</sub> = 11.7)	112.4 (J <sub>PC</sub> = 4.4)				
DitBuADAsO·HFBA	7.47	191.0	125.8	-42 ( <sup>14</sup> N)			
DitBuADSbO·HFBA	7.73	196.2	123.0				
DitBuADSbO·2HFBA	7.29	197.0	123.4				
DitBuADPO·HFB	5.64 ( <sup>3</sup> J <sub>PH</sub> = 4.2)	207.2 (J <sub>PC</sub> = 4.7)	75.1 (J <sub>PC</sub> = 15.2)	-289.6 ( <sup>1</sup> J <sub>PN</sub> = 64.0)	163.6		4.4
	5.53 ( <sup>3</sup> J <sub>PH</sub> = 12.2)	154.2 (J <sub>PC</sub> = 10.4)	113.8 (J <sub>PC</sub> = 6.3)				1.0
DitBuADPO·2HFB	6.01 ( <sup>3</sup> J <sub>PH</sub> = 36.8)	141.7 (J <sub>PC</sub> = 4.9)	102.8 (J <sub>PC</sub> = 18.4)	-285.1 ( <sup>1</sup> J <sub>PN</sub> = 16.0)	-21.8		1.0
DitBuADAsO·2HFB	5.76	208.1	80.6				
DitBuADSbO·2HFB	6.17	211.6	79.7	-318.7			4.8
DitBuADPO·Cl <sub>2</sub>	6.15 ( <sup>3</sup> J <sub>PH</sub> = 35.8)	152.5 (J <sub>PC</sub> = 8.1)	102.3 (J <sub>PC</sub> = 23.0)	-262.4 ( <sup>1</sup> J <sub>PN</sub> = 13.7)	-24.9		
DitBuADPO·Br <sub>2</sub>	6.20 ( <sup>3</sup> J <sub>PH</sub> = 35.9)	154.5 (J <sub>PC</sub> = 10.7)	102.9 (J <sub>PC</sub> = 23.3)	-256.8 ( <sup>1</sup> J <sub>PN</sub> = 6.2)	-90.7		
DitBuADAsO·Cl <sub>2</sub>	7.70	196.7	121.2				
DitBuADSbO·Cl <sub>2</sub>	7.94	202.9	119.3				
DitBuADPO·CH <sub>3</sub> /Cl	5.99 ( <sup>3</sup> J <sub>PH</sub> = 35.6)	151.2 (J <sub>PC</sub> = 5.7)	102.0 (J <sub>PC</sub> = 13.9)	-271.0 ( <sup>1</sup> J <sub>PN</sub> = 16.9)	-0.8		
DitBuADPO·(CH <sub>3</sub> ) <sub>2</sub>	5.31 ( <sup>3</sup> J <sub>PH</sub> = 31.2)	150.0 (J <sub>PC</sub> = 3.8)	99.8 (J <sub>PC</sub> = 15.5)	-303.0 ( <sup>1</sup> J <sub>PN</sub> = 17.4)	-9.1		0.9
(DitBuADPO) <sub>2</sub> PtI <sub>2</sub>	5.95 ( <sup>3</sup> J <sub>PH</sub> = 29.0)	156.0	113.9	-276.0 ( <sup>1</sup> J <sub>PN</sub> = 44.8)	126.5		0.8
(DitBuADSbO) <sub>2</sub> PtI <sub>2</sub>	8.38	195.2	123.3				
(DitBuADSbO)Pt(PPh <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> <sup>+</sup>	8.72	195.6	123.9				

<sup>a</sup> Chemical shifts are given in ppm with positive values downfield of the reference; see Experimental Section. <sup>b</sup> Coupling constants are given in Hz. <sup>c</sup> For derivatives in which pyramidalization of a single carbon attached to nitrogen has occurred that center is identified as C(4).

nitrogen center and a pyramidal geometry is assumed (e.g., DitBuADPO·o-chloranil and (DitBuADPO)<sub>2</sub>PtI<sub>2</sub>; vide infra).

It is interesting to note that there is a general trend for the <sup>31</sup>P-<sup>15</sup>N coupling constant in these systems to decrease in magnitude with increasing coordination number at phosphorus (Figure 3). Similar trends have been noted in other systems and are believed to arise from changes in the Fermi contact between the nuclei.<sup>17</sup> Changes in the hybridization at nitrogen are clearly partially responsible for the differences in P-N couplings. A planar sp<sup>2</sup>-hybridized nitrogen (e.g., 10-P-3 ADPO) contributes more s-orbital character to the P-N bond than a pyramidal sp<sup>3</sup>-hybridized nitrogen (e.g., (DitBuADPO)<sub>2</sub>PtI<sub>2</sub>, DitBuADPO·Cl<sub>2</sub>, and DitBuADPO·HFB). Hence, the P-N coupling constant in 10-P-3 ADPO is larger than those observed in the folded systems that contain a pyramidal nitrogen. When the hybridization of the phosphorus orbital directed toward nitrogen is changed in such a way as to decrease the phosphorus s-orbital contribution, the P-N coupling constant also decreases in some cases. The trend between phosphorus coordination number and P-N coupling does show some aberration depending upon the site occupied by nitrogen. DitBuADPO·Cl<sub>2</sub>, with a coordination number of 5, shows a P-N coupling of 13.7 Hz whereas DitBuADPO·o-chloranil, which is also 5-coordinate, has a P-N coupling of 16.8 Hz. This change is small when the overall range of almost 100 Hz is considered, but it is interesting to note that the smaller of these two numbers (13.7 for DitBuADPO·Cl<sub>2</sub>) is in a system whose

solid-state structure places nitrogen in an equatorial position about phosphorus whereas the larger coupling is found for a system in which nitrogen is in an apical position. Consideration of the phosphorus hybridizations would have led to the opposite predictions. Time-averaged solution structures may account for some of the slight variations in P-N couplings over what might be expected based on solid-state structures. The greatest deviation of the expected P-N coupling is found for DitBuADPO·Br<sub>2</sub> with <sup>1</sup>J<sub>PN</sub> = 6.2 Hz. This could actually indicate a 6-coordinate phosphorus (the <sup>31</sup>P NMR resonance is -90 ppm). Such a structure would be possible with bridging bromines, but we have no direct evidence of this behavior and a solid-state structure determination has not been possible. It is also possible that the anomalous <sup>31</sup>P chemical shift (and P-N coupling constant) of DitBuADPO·Br<sub>2</sub> is the result of a heavy atom effect from the bromines.<sup>18</sup>

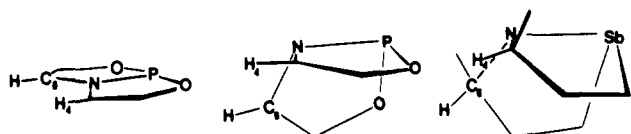
The natural abundance <sup>17</sup>O NMR spectra of the 10-Pn-3 ADPnO systems do not show the same smooth variation in shifts as do the <sup>13</sup>C, <sup>15</sup>N, and <sup>1</sup>H nuclei. It is important, however, to note that the "out of place" 10-As-3 ADAsO <sup>17</sup>O resonance is close to that of 10-P-3 ADPO so that a slight variation would have brought the chemical shifts into a consecutive order. Undoubtedly paramagnetic contributions to the <sup>17</sup>O shielding tensors interfere with smooth changes in the diamagnetic tensors. The <sup>17</sup>O chemical shifts are far upfield of normal carbonyl oxygens (e.g., +540 ppm in **4a**). This chemical shift range is consistent with divalent oxygen adjacent a positively charged center (protonated carbonyls are in this chemical shift range).<sup>19</sup>

(17) (a) Reference 16a, p 135. (b) Reference 16b, p 198. (c) Some P-N systems have been considered specifically in terms of nitrogen hybridization, but recall that in our systems DitBuADPO·HOTf and DitBuADPO·HF<sub>3</sub> have similar nitrogen centers (chemical shifts of δ -152.6 and -124.0, respectively) but differ by over 90 Hz in P-N coupling constant. See: Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Chialang, H.; Liu, L.-T.; Tseng, K.-S. *Phosphorus Sulfur* **1983**, *15*, 281. (d) Gouesnard, J. P.; Dorie, J. J. *Mol. Struct.* **1980**, *67*, 297. (e) Gouesnard, J. P.; Dorie, J.; Martin, G. J.; *Can. J. Chem.* **1980**, *58*, 1295.

(18) Webb, G. A. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 1, Chapter 4, p 94.

(19) (a) Kintzinger, J. P. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 2, Chapter 4, p 82. (b) *The Multinuclear Approach to NMR Spectroscopy*; Lambert, J. B., Riddell, F. G., Eds.; Deidel, Boston, 1982; Chapter 11, p 250.

The vicinal proton-carbon couplings also provide an indication of planarity or folding in the ligand backbone. For the planar systems, the vicinal proton-carbon couplings  $^3J_{C_6(4),H_4(6)}$  are in the range between 1.0 and 6.2 Hz, which is consistent with the  $0^\circ$  dihedral angle between the hydrogen and carbon centers. As the ring is folded and the nitrogen and phosphorus are pyramidalized, this coupling falls with the increasing dihedral angle (H-C-N-C). For the folded systems DITBuADPO-*o*-chloranil and (DITBuADPO) $_2$ PtI $_2$  this coupling falls below 1 Hz (vide infra). However, since this coupling depends on the dihedral angle between  $C_{6(4)}$  and  $H_{4(6)}$ , the relationship to the ring folding can be disrupted if the carbons attached to nitrogen are not  $sp^2$  hybridized. If the  $C_{4(6)}$  center is also pyramidalized such that  $H_{4(6)}$  moves into the endo side of the fold (e.g., DITBuADSbO-2HFB and DITBuADPO-HFB), the dihedral angle between  $H_{4(6)}$  and  $C_{6(4)}$  remains close to  $0^\circ$  and the coupling remains large.

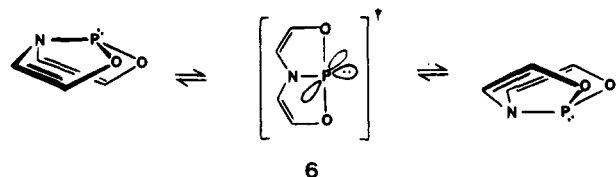


The  $^{14}\text{N}$  NMR spectra of the ADPnO derived systems also provide information concerning the planarity of nitrogen and hence the folding about the Pn-N bond. For the planar systems in which nitrogen remains in a fairly symmetrical environment the  $^{14}\text{N}$  resonances are easily observed and consistent with the  $^{15}\text{N}$  spectra (e.g., DITBuADPO  $\delta$  -127; DITBuADPO-2HFB  $\delta$  -281). For the severely bent systems in which the nitrogen is in a  $C_2$  environment the  $^{14}\text{N}$  resonances were too broad to be observed (e.g., DITBuADPO-HFB and (DITBuADPO) $_2$ PtI $_2$ ).

One final note should be made of the  $^{31}\text{P}$  NMR chemical shift in 10-P-3 DITBuADPO (+187 ppm). This shift is what could be expected for a tricoordinate phosphorus bearing a nitrogen and two oxygens $^{20}$  and indicates the consideration of no-bond resonance contributors for the 10-Pn-3 ADPnO systems is inappropriate. The P-N coupling constants for the ADPO systems also indicate a 3-coordinate phosphorus (vide supra).

### Electronic Structure of 10-Pn-3 Systems

One of the most fascinating aspects of the ADPnO systems is the preference of these molecules (Pn = P, As, Sb) for the planar 10-Pn-3 geometry rather than the pyramidal (bent) 8-Pn-3 geometry. We have previously outlined the structural features of the ADPnO ring system which may lead to a preference for the planar electromorph. $^2$  Numerous saturated analogues of the ADPO and ADAsO systems have been prepared, $^8$  and these compounds possess the structure of the more classical 8-Pn-3 electromorph. Thus, the geometric preference in our systems has been changed merely by the introduction of C-C unsaturation in the ligand backbone. One obvious explanation for this change would be angle strain; however, we have observed our ADPO system in a bent (8-P-4) geometry when complexed to platinum. $^5$  It is most instructive to envision planar 10-P-3 ADPO as intermediate (6) between two inverted 8-P-3 electromorphs. This



interconversion takes place through a T-shaped intermediate $^{21}$  rather than the classical " $D_{3h}$ " trigonal-planar transition state (or intermediate) normally associated with amine and phosphine inversions. As the T-shaped geometry is approached the oxygens move into the apical positions of a hypervalent bonding ar-

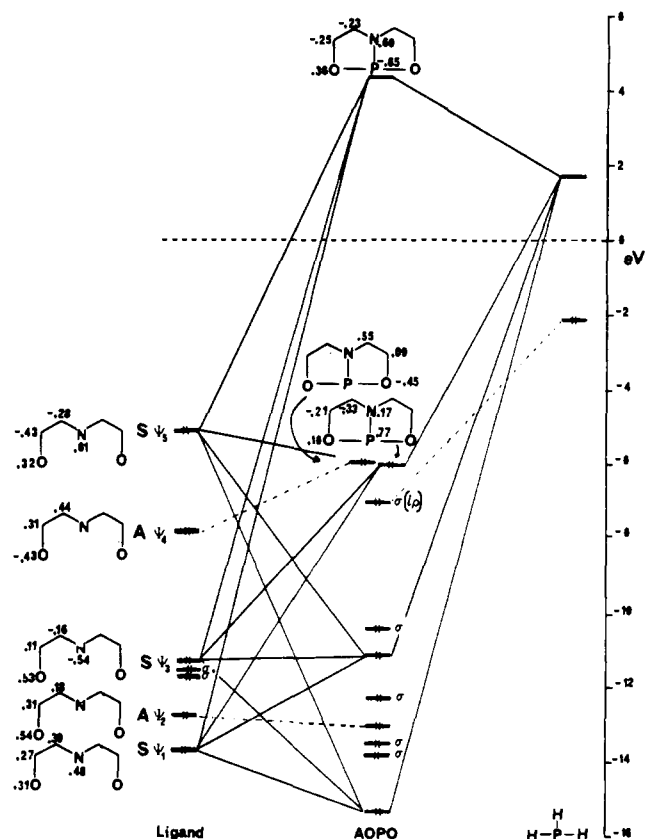


Figure 4. Correlation diagram for the construction of the  $\pi$  molecular orbitals of ADPO system. Orbital energies are given in eV and since a symmetry plane is present about nitrogen orbital coefficients are labeled on one side only with the symmetry indicated (symmetric or antisymmetric).

angement with the central pnictogen. The original pnictogen lone pair of the pyramidal (8-Pn-3) structure, which has high  $s$  character, can correlate with an orbital on the pnictogen (opposite nitrogen) that retains (or augments) the high  $s$  character. This would leave a vacant  $p$ -orbital on the pnictogen perpendicular to the plane of the three attached atoms. Alternatively, the original pyramidal pnictogen lone pair (large  $s$  character) could have correlated with the developing out-of-plane vacant  $p$ -orbital on the pnictogen and become a  $p$  type lone pair as is usual for planar-trigonal inversions (vertex inversion). The decreasing strength of bonds to the pnictogen center as one moves down the family results in placement of lone pairs in orbitals with high  $s$  character at the heavier elements (P, As, Sb, Bi). $^{22}$  Thus, this hypothetical intermediate can be represented as structure 6.

The vacant  $p$ -orbital on the pnictogen center in 6 would normally not be compatible with the hypervalent bonding arrangement (four electron pairs in the plane) to which it is orthogonal. Ordinarily one would expect a change in geometry to give two two-center two-electron Pn-O bonds (e.g., the pyramidal 8-Pn-3 structures) rather than the three-center four-electron hypervalent O-Pn-O bond and vacant  $p$ -orbital of structure 6. In structure 6, however, the ligand backbone places three excellent lone-pair donors adjacent to the vacant pnictogen  $p$ -orbital. In this manner structure 6 can be stabilized. In the case of the ADPnO systems further electronic stabilization results from the C-C unsaturation. This unsaturation provides a better  $\pi$  donation of proper symmetry to interact with the out-of-plane  $p$ -orbital.

If the isolated ligand backbone in the ADPnO systems is considered, its donor properties are evident. The highest occupied molecular orbital ( $\Psi_5$ ) for the  $\pi$  backbone contains four nodes

(20) The saturated 8-P-3 systems like 3 show  $^{31}\text{P}$  NMR resonances in this range. See ref 8a,c,d.

(21) (a) Dixon, D. A.; Arduengo, A. J., III; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 2461. (b) Arduengo, A. J., III; Dixon, D. A.; Roe, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 6821.

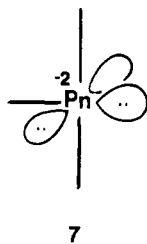
(22) There has been much discussion of the reluctance of heavier main group elements to form hydrid bonds and to maintain lone pairs in orbitals of high  $s$ -orbital character. See: *Inorganic Chemistry* 2nd ed.; Huheey, J. E.; Harper and Row: New York, 1978; pp 723-725 and references therein.

and is symmetric about nitrogen. The structure of this orbital from an *ab initio* molecular orbital calculation<sup>23a</sup> determined with an STO-3G basis set<sup>23b</sup> is depicted on the correlation diagram in Figure 4.<sup>24</sup> Interaction of the ligand HOMO with the vacant pnictogen p-orbital provides excellent stabilization. Two other  $\pi$  orbitals of the ligand ( $\Psi_2$  and  $\Psi_1$ ) also have the proper symmetry to mix with the pnictogen p-orbital. They are, however, of too low an energy for significant mixing with the pnictogen p-orbital. The HOMO in this calculation on the ADPO system is actually a  $\Psi_4$  derived level and shows the expected structure (Figure 4). Almost degenerate with the HOMO is an orbital derived from the vacant phosphorus p-orbital and  $\Psi_5$  of the ligand. The major contribution to this near HOMO is the previously vacant phosphorus p-orbital (coeff = 0.77), and thus this level is best characterized as a p type phosphorus lone pair (although delocalized). Effectively two electrons have been removed from the ligand backbone to become a delocalized second lone pair at the phosphorus center in the T-shaped species. This representation thus suggests that a resonance structure with two positive charges in the ligand backbone and a formal -2 charge at the pnictogen provides a reasonable valence bond description of the system.

A brief discussion should also be made of calculated charge distribution in the 10-Pn-3 ADPnO systems. While the best valence bond structure indicates a formal -2 charge at the pnictogen center, the pnictogen center is hypervalent and thus loses electron density in the  $\sigma$ -framework to the apical oxygens. The electron distribution in hypervalent systems places considerable density on the apical substituents at the expense of the central atom. Indeed, calculations on various hypervalent species generally show quite significant positive charge at the hypervalent center.<sup>25</sup> In our model ADPO system, the calculated charge at phosphorus is +0.63 e. This is less positive than has been calculated for 10-P-5 systems<sup>26</sup> or the phosphorus of T-shaped  $\text{PH}_3$  with an in-plane  $sp^n$  lone pair ( $q_p = +0.91$  e). This charge is consistent with electron shuttle from the  $\pi$  framework through phosphorus to the apical oxygens via the hypervalent bond in the  $\sigma$  framework.

Two basic factors are necessary for the T-shaped 10-Pn-3 electromorph to be stable with respect to the more classical 8-Pn-3 electromorph. First, the pnictogen center must bear at least two electronegative substituents which can assume the apical positions in the hypervalent bonding scheme and withdraw electrons in the  $\sigma$ -framework. Second, there must be sufficient  $\pi$  donation from the ligands to stabilize the "vacant" pnictogen p-orbital (which effectively becomes a new lone pair).

The above description is also consistent with a derivation of the T-shaped 10-Pn-3 electromorph beginning with the "pnictandiide" moiety 7.<sup>27</sup> In this approach the pnictogen p-orbital



7

(23) (a) GRADSCF is an *ab initio* program system designed and written by A. Kormonicki at Polyatomic Research and supported on grants through NASA-Ames Research Center. (b) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(24) The geometry of the ligand was optimized in the all-trans (extended  $C_{2v}$  symmetry) structure with protons added in the plane at nitrogen and the oxygens to satisfy valence requirements. The geometry of ADPO is from a large basis set optimization and is the same as the symmetrized experimental structure. The energy of the phosphorus vacant p orbital is obtained from a calculation on T-shaped  $\text{PH}_3$  with the lone pair in an in-plane  $sp^n$  hybrid orbital. The geometry for planar T-shaped  $\text{PH}_3$  is from ref 21.

(25) For some phosphorus systems see: (a) Rauk, A.; Allen, L. C.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 3055. (b) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047 and references therein.

(26) We calculated a charge of +0.81e for  $D_{3h}$   $\text{PH}_3$ . This is in accord with previous reports (ref 25). It should be noted that the ADPO system bears elements more electronegative than hydrogen at the phosphorus center. As such the charge of +0.63e in ADPO is quite remarkable.

Table V. Cyclic Voltammetry Data on 10-Pn-3 ADPnO Systems<sup>a</sup>

compound	$E^1_{pa}$	$E^2_{pa}$	$E^1_{pc}$
DitBuADPO <sup>b</sup>	1.13	2.03	-2.09
DitBuADAsO <sup>b</sup>	1.04	2.07	-1.84/-1.75 <sup>c</sup>
DitBuADSbO <sup>b</sup>	0.54	1.85	-1.71 <sup>d</sup>
DiPhADAsO <sup>b</sup>	0.69	1.95	-1.54/-1.43 <sup>e,f</sup>
DiAdADPO <sup>g</sup>	1.39 <sup>g</sup>	1.64 <sup>g</sup>	-1.94
DiAdADAsO <sup>g</sup>	1.04	1.32 <sup>g,h</sup>	-1.67
DiAdADSbO <sup>g</sup>	0.98	2.23	-1.54

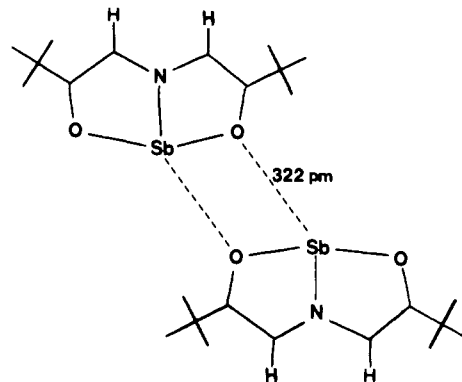
<sup>a</sup> Voltammograms were recorded on glassy carbon at 100 mV/s sweep rate. All peak potentials are quoted in volts vs. Ag/AgCl reference electrode. <sup>b</sup> In acetonitrile, 0.1 M tetrabutylammonium tetrafluoroborate (TBAF). <sup>c</sup> A comparison with ferrocene-ferrocenium couple points to a  $1e^-$  redox couple, assuming similar diffusion coefficients. <sup>d</sup> Becomes quasi-reversible at 500 mV/s: -1.73/-1.60. <sup>e</sup> A second reduction wave is observed at -2.28 V. <sup>f</sup> In methylene chloride, 0.1 M TBAF. These compounds are only slightly soluble in acetonitrile. <sup>g</sup> A broad wave. There are other smaller ill-defined waves. <sup>h</sup> A third oxidation wave is observed at 2.18 V.

would begin as a p type lone pair and be stabilized by the vacant orbital  $\Psi_5$  from the ligand dication. These two approaches thereby give rise to the same final structure.

We have recorded cyclic voltammetry data on the 10-Pn-3 ADPnO series, and the oxidation and reduction potentials are in accord with the above theoretical description of the systems. As expected the antimony systems are the easiest to oxidize and reduce followed by the arsenic and finally the phosphorus systems. For the DiPhADAsO and DitBuADAsO systems the diphenyl system is more easily oxidized (and reduced) than the di-*tert*-butyl system. Phenyl substitution has a similar effect on the oxidation potential and the reduction potentials (Table V). The second oxidation potentials of these systems are fairly constant and may reflect ionization from an orbital to which the 10-Pn-3 center does not contribute.

#### Bismuth and Nitrogen Systems

Our success with the synthesis of a stable 10-Sb-3 system led us to speculate on the synthesis of a 10-Bi-3 system. The bismuth compound could be expected to be substantially more reactive than the corresponding antimony system due to the increased strain and the large exposed surface area at bismuth. The solid-state structure of DitBuADSbO system shows a long-range intermolecular Sb-O interaction as illustrated below. The dimer pair



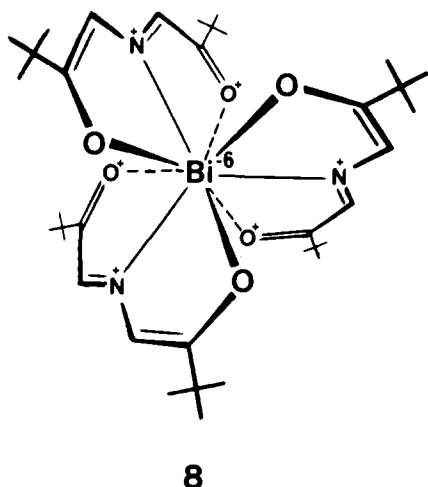
is completely planar with intermolecular Sb-O distances (322 pm) within the sum of the van der Waals radii (360 am).

A related interaction has been observed by Martin and Nguyen in the solid-state structures of 10-Br-3 and 10-I-3 systems.<sup>28</sup> This

(27) Structure 7 and that depicted in Figure 2 are equivalent representations of the pnictandiide moiety differing only in lone pair mixing. A related set of structures can be written for  $\text{H}_2\text{O}$  in which the lone pairs may be placed in a set of approximate  $sp^3$  hybrid orbitals (localized) or one lone pair in a p orbital and the second in an approximate  $sp^2$  hybrid orbital (canonical). While the former structure (two equivalent lone pairs) is convenient for representing structure and chemistry (e.g., the structure of ice) the latter provides a better model for IR spectra. See: *The Organic Chemist's Book of Orbitals*, Jorgensen, W. L., Salem, L., Academic: New York, 1973; p 42.

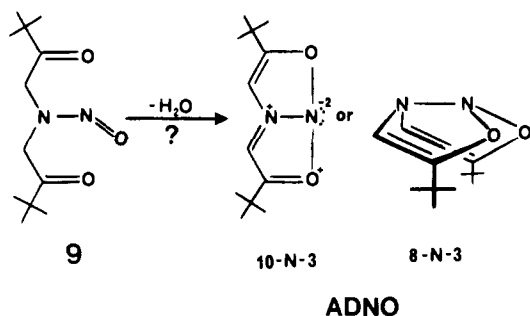
(28) (a) Nguyen, T. T.; Martin, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7382. (b) Nguyen, T. T.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3803.

interaction suggests that if the size and reactivity of the pnictogen center become sufficiently great, a mechanism may be available for disproportionation and ligand migration. These factors combined with the reduction potential of bismuth(III) and the tendency of bismuth to accept high coordination environments led to the formation of a 20-Bi-9 system (**8**)<sup>29</sup> from a synthetic route identical



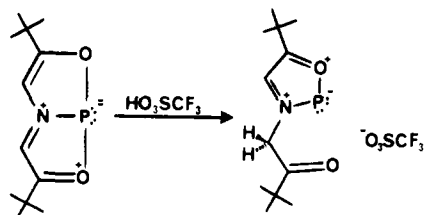
with those used for the lighter 10-Pn-3 ADPnO systems. Even when the steric bulk of the ligand is increased by substituting adamantyl for *tert*-butyl, the 10-Bi-3 system could not be observed.

Attempts to synthesize a 10-N-3 or 8-N-3 ADNO system have thus far been unsuccessful. We have prepared the *N*-nitroso derivative **9**<sup>30</sup> of the ligand system **4a**. Attempts to dehydrate **9** with a variety of reagents have given no evidence for the formation of an ADNO system.



#### Protonation of the ADPnO Systems

If DitBuADPO is treated with triflic acid in dichloromethane, a transient yellow color is observed followed by a complete loss of color. The transient yellow color may be due to a phosphorus



DitBuADPO

DitBuADPO·HOTf

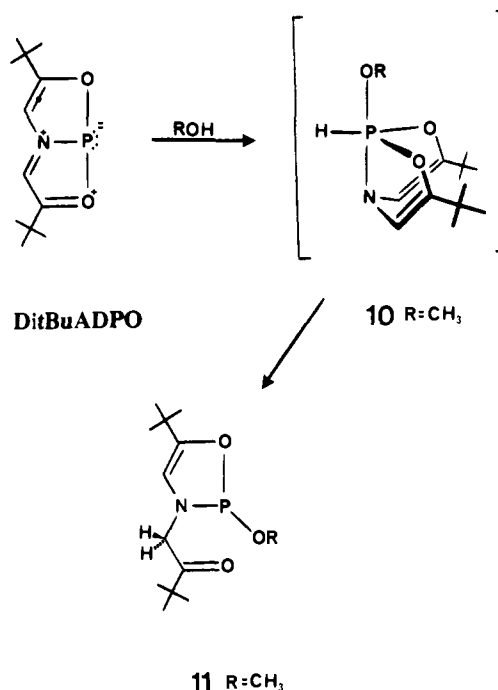
protonated species in accord with the reactions observed with alcohols (vide infra). The NMR data on the ultimate protonated ADPO species indicate the new proton resides on C-4 (essentially the reverse of the reaction used to make DitBuADPO). The <sup>31</sup>P chemical shift of +234 ppm is suggestive of a 2-coordinate phosphorus compound. The <sup>15</sup>N NMR chemical shift at -153

ppm indicates that electron density has increased at the nitrogen center relative to 10-P-3 ADPO but is less than that in the compounds containing pyramidal nitrogen (e.g., (DitBuADPO)<sub>2</sub>PtI<sub>2</sub>). The <sup>1</sup>H NMR clearly shows the methylene resonance at  $\delta$  5.84 (<sup>3</sup>*J*<sub>PH</sub> = 7.8 Hz) and the vinyl proton at 7.81 (<sup>3</sup>*J*<sub>PH</sub> = 6.4 Hz). The vicinal coupling between the vinyl proton and the methylene carbon of 1.8 Hz indicates a planar nitrogen center such that there may be a slight bonding interaction between phosphorus and the oxygen of the carbonyl adjacent the methylene.

The <sup>13</sup>C NMR spectrum shows resonances at  $\delta$  215.8 (*J*<sub>PC</sub> = 3.17 Hz) and 171.2 (*J*<sub>PC</sub> = 3.36 Hz) for the carbons attached to oxygens. This further indicates that one of the oxygens is tightly bound to phosphorus while the second is a carbonyl which is loosely coordinated to the phosphorus center. This structural arrangement is also supported by an IR absorption at 1695 cm<sup>-1</sup> for the "free" carbonyl. The regiochemistry of this protonation is similar to that which has been previously reported for dioxachalcapentalenes.<sup>31</sup> DitBuADAsO gives a similar result upon protonation by triflic acid.

#### Oxidative Addition of Alcohols

DitBuADPO undergoes a rapid addition of alcohols (e.g., CH<sub>3</sub>OH, (CH<sub>3</sub>)<sub>2</sub>HCOH, and *p*-cresol). This reaction amounts to oxidative insertion of phosphorus into the O-H bond. The first formed intermediate in this reaction is a 10-P-5 phosphorane (**10**) which rearranges to the 8-P-3 species **11**.



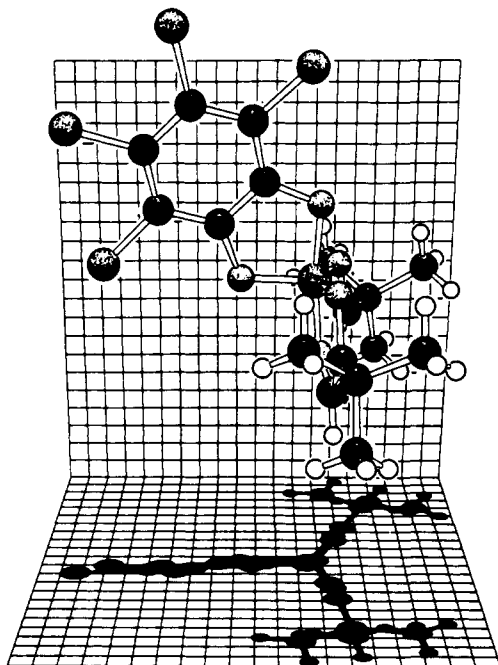
The structure of **10** is verified by the chemical shift and P-H coupling constant of the proton directly bound to phosphorus ( $\delta$  8.04 (<sup>1</sup>*J*<sub>PH</sub> = 877 Hz)). The protons of the methoxy group also show the expected phosphorus coupling (<sup>3</sup>*J*<sub>PH</sub> = 14.2 Hz). The *tert*-butyl groups and vinyl protons of **10** indicate the bicyclic ring structure remains symmetric but that electron density has been returned to the ligand backbone from phosphorus. Attempts to isolate **10** were unsuccessful due to the facile rearrangement to **11**. Compound **11** is a stable crystalline solid whose NMR spectral properties are consistent with the 8-P-3 structure. The proton which had been directly attached to phosphorus is no longer evident in the <sup>1</sup>H NMR spectrum, and a methylene is obvious at +4.3 ppm. The <sup>31</sup>P NMR resonance at +122 ppm is supportive of the 8-P-3 center. We saw no evidence for similar oxidative insertions with DitBuADAsO or DitBuADSbO. Dimethylamine failed to give an adduct with DitBuADPO.

(29) Stewart, C. A.; Calabrese, J. C.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1985**, *107*, 3397.

(30) The preparation of this compound by M. B. Mizen is described in a Bachelor of Science Thesis, University of Illinois, 1984.

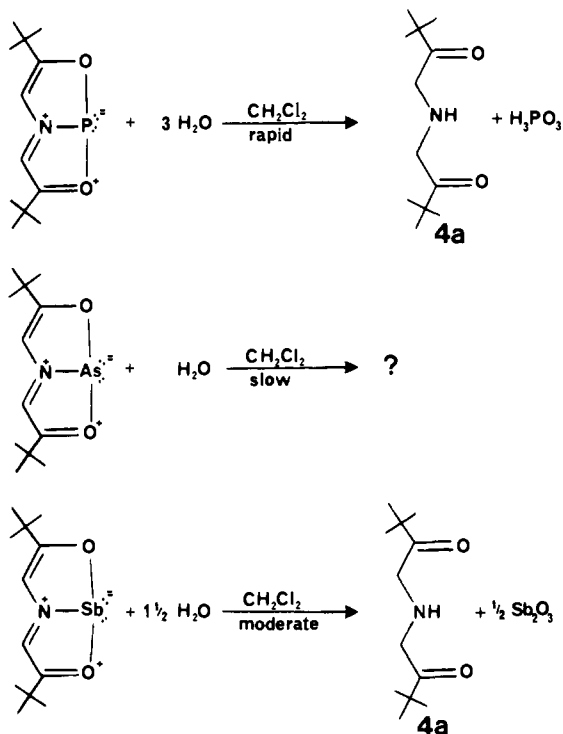
(31) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkin Trans 1* **1975**, 2097.




 Figure 5. X-ray structure of DitBuADPO·*o*-chloranil.

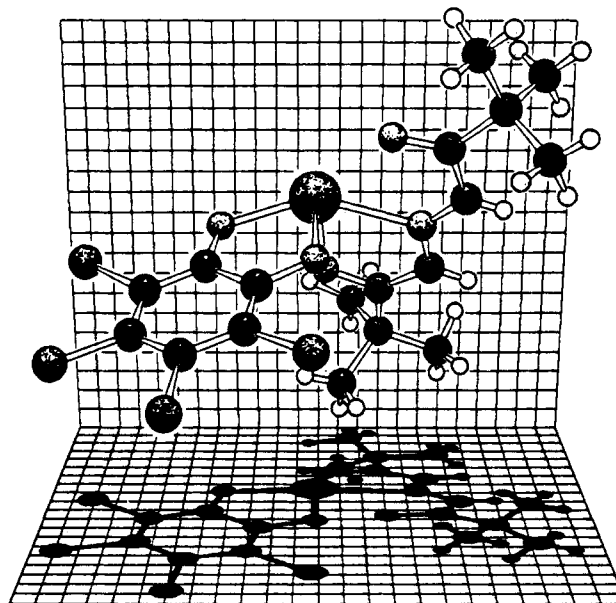
#### Hydrolysis of ADPnO Systems

In a reaction which is probably related to the reaction with alcohols, the ADPnO systems undergo hydrolysis with varying ease. DitBuADPO is rapidly hydrolyzed in moist  $\text{CH}_2\text{Cl}_2$  at room temperature in a matter of minutes to yield the phosphorous acid salt of the diketo amine ligand **4a**.<sup>32</sup> Under the same conditions



>90% DitBuADAsO can be recovered after 2 days (very prolonged exposure (weeks) to moisture did lead to decomposition).

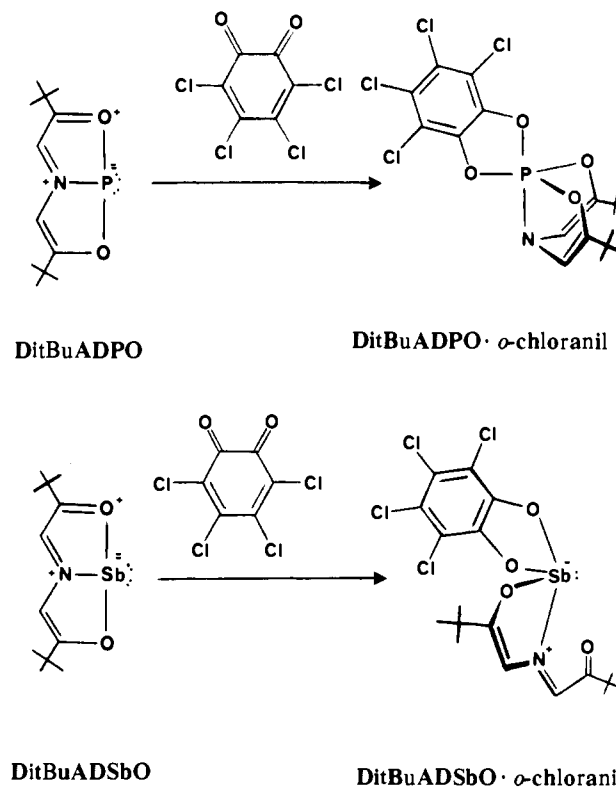
(32) In a typical hydrolysis reaction 0.05 g of DitBuADPO is dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$  under nitrogen. Two to three drops of water are added through an 18-gauge needle and the mixture is stirred at room temperature. After 10 min the precipitated solids are collected by filtration and dried in vacuo. The phosphorous acid salt of **4a** decomposes at 237 °C with melting and gives  $^1\text{H}$  NMR (75%  $\text{CD}_3\text{OD}/25\% \text{D}_2\text{O}$ )  $\delta$  1.2 (s, 18 H,  $\text{CH}_3$ ), 4.29 (s, 4 H,  $\text{CH}_2$ ), 6.82 (d,  $^1J_{\text{PH}} = 617$  Hz, 1 H, PH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75%  $\text{CD}_3\text{OD}/25\% \text{D}_2\text{O}$ )  $\delta$  26.0 (s,  $\text{CH}_3$ ), 44.1 (s,  $\text{CC}_4$ ), 52.0 (s, CN), 210.3 (s, CO);  $^{31}\text{P}\{^1\text{H}\}$  NMR (75%  $\text{CD}_3\text{OD}/25\% \text{D}_2\text{O}$ )  $\delta$  3.5 (s);  $^{31}\text{P}$  NMR gated  $\delta$  3.5 (d,  $^1J_{\text{HP}} = 612$  Hz).


 Figure 6. X-ray structure of DitBuADSbO·*o*-chloranil.

DitBuADSbO is hydrolyzed in moist  $\text{CH}_2\text{Cl}_2$  at room temperature over a 2-day period to yield the free diketo amine ligand **4a** and  $\text{Sb}_2\text{O}_3$ .

#### Reactions with $\alpha$ -Dicarbonyl Compounds

We have previously reported adduct formation between DitBuADPO and *o*-chloranil and between DitBuADSbO and hexafluorobiacyl<sup>4</sup> (HFBA). Similar adducts of HFBA or *o*-chloranil and all members of the DitBuADPnO series have since been synthesized. The structures of these six adducts have been determined by X-ray crystallography. Here we make a point of the difference in reactivity between ADPO and the heavier members of the ADPnO series. This difference is illustrated in the structures of DitBuADPO·*o*-chloranil<sup>33</sup> and DitBuADSbO·*o*-chloranil (Figures 5 and 6).



(33) This adduct was reported by Culley (ref 10), but its instability precluded complete characterization at that time.

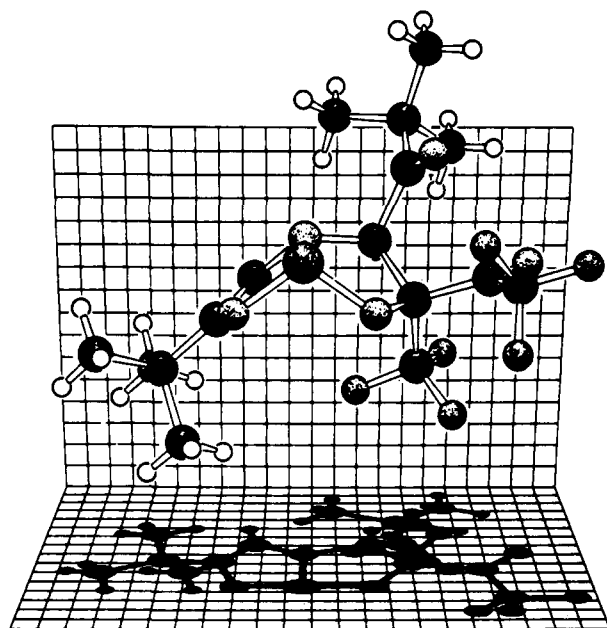


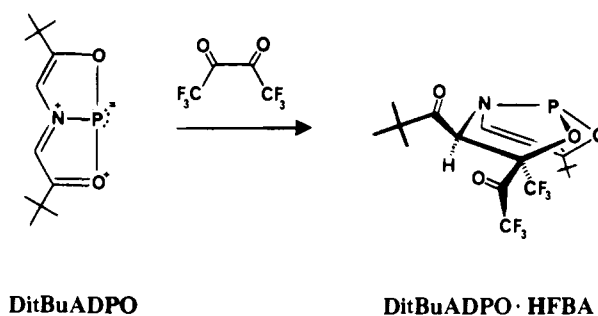
Figure 7. Structure of DitBuADPO·HFBA.

After reaction with *o*-chloranil, the phosphorus of the adduct maintains a 10-electron hypervalent bonding system by returning two electrons to the ligand backbone while forming two new P–O bonds. The ligand backbone in the DitBuADPO·*o*-chloranil adduct maintains the planarity of each of the two original five-membered rings, but there is a fold about the P–N bond so that the angle between these two rings is now 146°; the nitrogen of this adduct is noticeably pyramidal. The <sup>15</sup>N NMR chemical shift of –275.9 ppm (<sup>1</sup>J<sub>PN</sub> = 17 Hz) is also consistent with the pyramidal (8-N-3) nature of the nitrogen.<sup>16</sup> The phosphorus is in a typical 10-P-5 bonding arrangement (midway between a trigonal-bipyramidal (TBP) and square-pyramidal (SP) geometry). The <sup>31</sup>P NMR chemical shift of –10.2 ppm is consistent with the 10-P-5 structure. The best TBP description places the nitrogen and one oxygen of the *o*-chloranil in apical positions such that there are three five-membered ring apical–equatorial linkages with three equatorial oxygens. The closest fit to a SP structure places the two oxygens and nitrogen from the original ligand system and one *o*-chloranil oxygen in the basal positions. The O–P–O angle in the eight-membered ring is 141.8°. The N–P–O angle between the TBP apical positions is 172.0°. The <sup>1</sup>H NMR shows a ring proton shift of δ 6.25 (<sup>3</sup>J<sub>PH</sub> = 32 Hz), consistent with the uncharged ligand backbone. The solution <sup>13</sup>C NMR indicates the *o*-chloranil unit is equilibrating its two oxygens between the apical and equatorial positions. This motion can occur via a Berry pseudorotation<sup>34</sup> analogous to that considered for α-dicarbonyl derivatives of saturated systems of the type 3.<sup>35</sup>

In contrast, the DitBuADSbO·*o*-chloranil adduct shows a solid state geometry similar to the previously reported DitBuADSbO·HFBA adduct.<sup>4</sup> The original ligand backbone remains essentially planar, but the antimony is much closer to one of the oxygens (this lateral distortion is somewhat reminiscent of 1-oxa-6,6a-dithiapentalene type distortions<sup>6d</sup>). The DitBuADSbO·*o*-chloranil adduct can thus be regarded as containing a stiborane (10-Sb-4) center with an additional loosely coordinated oxygen (275 pm). The best ψ-TBP structure places nitrogen and one *o*-chloranil oxygen apical with the equatorial sites occupied by the second *o*-chloranil oxygen, the closest oxygen from the tridentate ligand and a lone pair. The apical N–Sb–O angle is 148.7° and the equatorial O–Sb–O angle is 90.5°. The most distant oxygen in the solid state (275 pm) is inside the sum of the van der Waals radii<sup>12</sup> (360 pm) but outside the sum of the covalent radii<sup>12</sup> (216

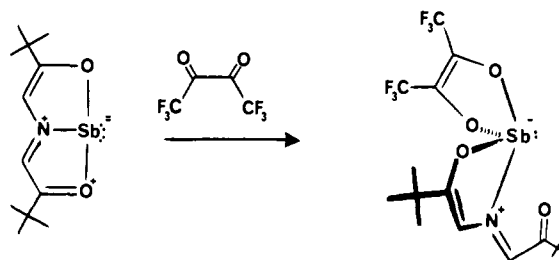
pm). In solution the DitBuADSbO·*o*-chloranil adduct shows only single resonances for the vinyl and *tert*-butyl protons, suggesting a rapidly equilibrating structure. The vinyl proton resonance at δ 7.80 suggests positive charge delocalization in the ligand backbone similar to that in the initial DitBuADSbO system.

The adduct of DitBuADSbO and hexafluoroacetyl (HFBA) is very similar in structure to DitBuADSbO·*o*-chloranil. The



DitBuADPO

DitBuADPO·HFBA



DitBuADSbO

DitBuADSbO·HFBA

reaction of HFBA and DitBuADPO provides an example of yet another mode of addition for α-diketones. Effectively, only one carbonyl unit participates in this reaction, resulting in carbonyl addition across phosphorus and the ring carbon attached to nitrogen (C4). This reaction is similar to the addition of hexafluoro-2-butyne (vide infra). The ring system in the DitBuADPO·HFBA adduct is bent as would be expected producing a pyramidal nitrogen and phosphorus. In the solid state the trifluoroacetyl and pivaloyl substituents are on the exo face of the saturated five-membered ring (Figure 7).

It is interesting to recall that in the *o*-chloranil adducts it is the larger pnictogen that adopts the lower coordination number (at least in the solid state). The addition of HFBA proceeds as would be expected with DitBuADSbO (and DitBuADAsO), in contrast to the rather unusual structure with DitBuADPO.

While the HFBA and *o*-chloranil adducts of DitBuADAsO and DitBuADSbO show 10-Pn-4 geometries in the solid state, their solution structures represent averaged 12-Pn-5 type structures. Not only does the tridentate ligand appear symmetric, but the α-dicarbonyl units appear to possess a mirror plane perpendicular to and bisecting the O–C–C–O plane. For adducts derived from DitBuADAsO, the dynamic behavior can be halted at low temperatures. The coalescence temperature for the <sup>13</sup>C and <sup>19</sup>F NMR spectra of DitBuADAsO·HFBA is about –25 °C. At –70 °C in CD<sub>2</sub>Cl<sub>2</sub> the <sup>19</sup>F NMR spectrum of DitBuADAsO·HFBA shows two quartets at δ –84.60 and –84.97 (*J*<sub>FF</sub> = 9.7 Hz). At this same temperature the <sup>13</sup>C NMR spectrum reveals two resonances for the carbons attached to oxygen in the tridentate ligand (δ 201.5 and 179.5). Clearly one loosely coordinated carbonyl group is indicated. The temperature-dependent <sup>13</sup>C NMR spectra of DitBuADAsO also indicate the motions of the tridentate ligand and the α-dicarbonyl unit are linked.

It is interesting to note the barriers to the dynamic behavior in the DitBuADSbO adducts with α-dicarbonyl compounds are

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

(35) Denney, D. B.; Denney, D. Z.; Gavrilovic, D. M.; Hammond, P. J.; Huang, C.; Tseng, K.-S. *J. Am. Chem. Soc.* **1980**, *102*, 7072.

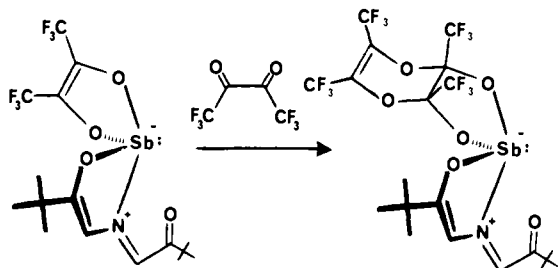
lower than the arsenic derived systems. The rapid equilibration of D<sub>it</sub>BuADSbO·HFBA was not halted at temperatures above -90 °C in solution. We previously reported the adduct of D<sub>it</sub>BuADAsO and 3,4-bis(trifluoromethyl)dithiete and suggested a 10-As-5 structure for this adduct.<sup>3</sup> With consideration of the present  $\alpha$ -dicarbonyl adducts, the dithiete adduct most likely has a rapidly equilibrating 10-As-4 structure.

A dissociative mechanism for these equilibrations is discounted by the observation of independent resonances at room temperature for D<sub>it</sub>BuADAsO and D<sub>it</sub>BuADAsO·HFBA in solutions where the two compounds are mixed. Further investigation is necessary to identify the mechanism of the dynamic behavior of these systems.

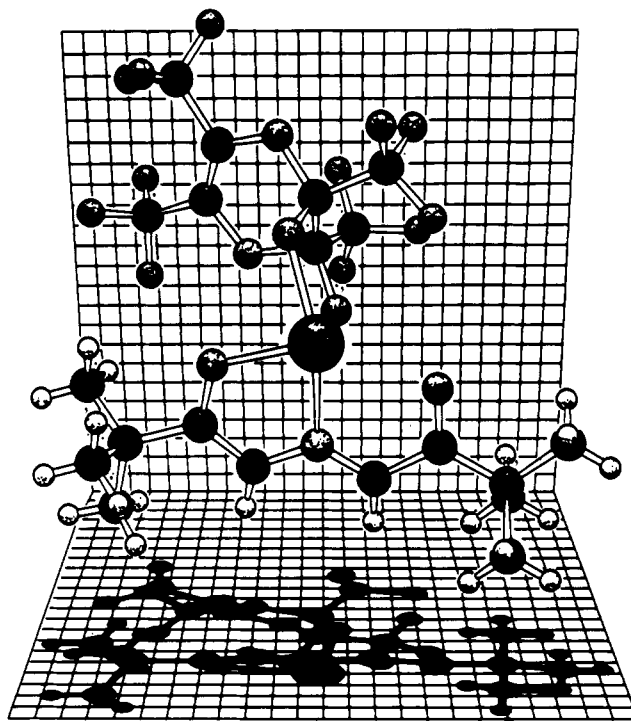
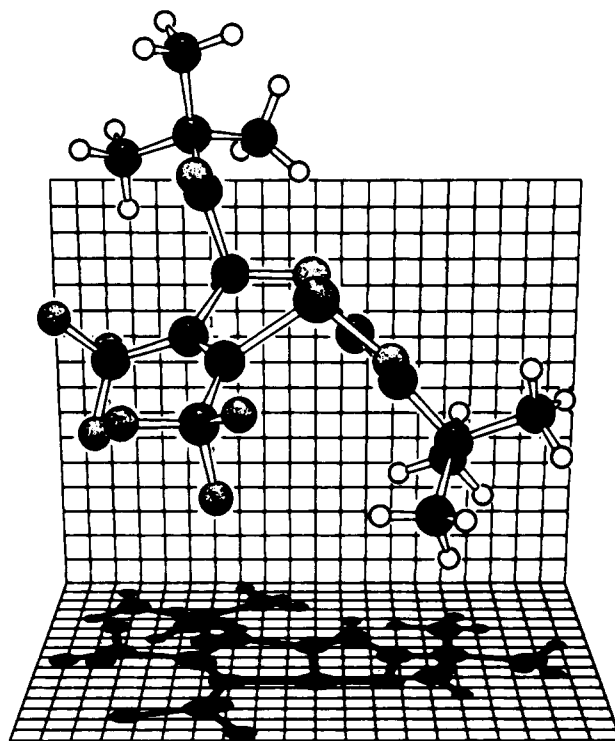
While  $\alpha$ -dicarbonyl units are not rapidly transferred between pnictogen centers of ADPnO moieties on the NMR time scale, a reaction does occur which allows this transfer along certain pathways. Samples of D<sub>it</sub>BuADPnO and D<sub>it</sub>BuADPn'O-*o*-chloranil were mixed in CD<sub>2</sub>Cl<sub>2</sub>. The exchange reactions to form D<sub>it</sub>BuADPnO-*o*-chloranil and D<sub>it</sub>BuADPn'O were followed by NMR spectroscopy. There is no tendency for D<sub>it</sub>BuADPO-*o*-chloranil to transfer the *o*-chloranil group to D<sub>it</sub>BuADAsO or D<sub>it</sub>BuADSbO. D<sub>it</sub>BuADAsO-*o*-chloranil will transfer the *o*-chloranil unit to both D<sub>it</sub>BuADPO and D<sub>it</sub>BuADSbO with the latter reaction proceeding at a faster rate. After 2 h at room temperature the reaction between D<sub>it</sub>BuADAsO-*o*-chloranil and D<sub>it</sub>BuADSbO is essentially complete whereas 4 days is required to transfer the *o*-chloranil unit from arsenic to phosphorus. D<sub>it</sub>BuADSbO-*o*-chloranil will transfer the *o*-chloranil unit to D<sub>it</sub>BuADPO (a slow reaction, complete in about 1 month) but not to D<sub>it</sub>BuADAsO. Similar results were obtained for transfers of the HFBA unit except that the very slow reaction between D<sub>it</sub>BuADSbO·HFBA and D<sub>it</sub>BuADPO gives an exchanged product different from the previously prepared D<sub>it</sub>BuADPO·HFBA (8-P-3). The phosphorus adduct from the exchange reaction seems to have a 10-P-5 arrangement about phosphorus similar to D<sub>it</sub>BuADPO-*o*-chloranil. This second adduct of D<sub>it</sub>BuADPO and HFBA shows a doublet at  $\delta$  6.18 ( $J_{HP} = 32$  Hz). The isolation of this second adduct has been hindered by the slow progress of the exchange and the sensitivity of the product.

Transfer of *o*-chloranil between ADPnO systems and "normal" 8-Pn-3 triphenyl pnictogens was also briefly investigated. There was no evidence of transfer of an *o*-chloranil unit from ADPnO-*o*-chloranil to the corresponding triphenylpnictogen at room temperature after a few weeks. Reactions between mixed pnictogens were not investigated. Triphenylphosphine tetrachlorocatecholates also failed to transfer its *o*-chloranil unit to D<sub>it</sub>BuADPO. Both triphenylarsine tetrachlorocatecholates and triphenylstibine tetrachlorocatecholates will transfer their *o*-chloranil units to the corresponding D<sub>it</sub>BuADPnO systems.

Since a lone pair remains at the antimony center in D<sub>it</sub>BuADSbO·HFBA, we were curious to see if the oxidative addition of a second molecule of HFBA would occur at antimony to give a 7-coordinate antimony compound. At room temperature a second mole of HFBA does add to the 1:1 adduct to give a 1:2 compound (D<sub>it</sub>BuADSbO·2HFBA). This 1:2 adduct shows only

D<sub>it</sub>BuADSbO·HFBAD<sub>it</sub>BuADSbO·2HFBA

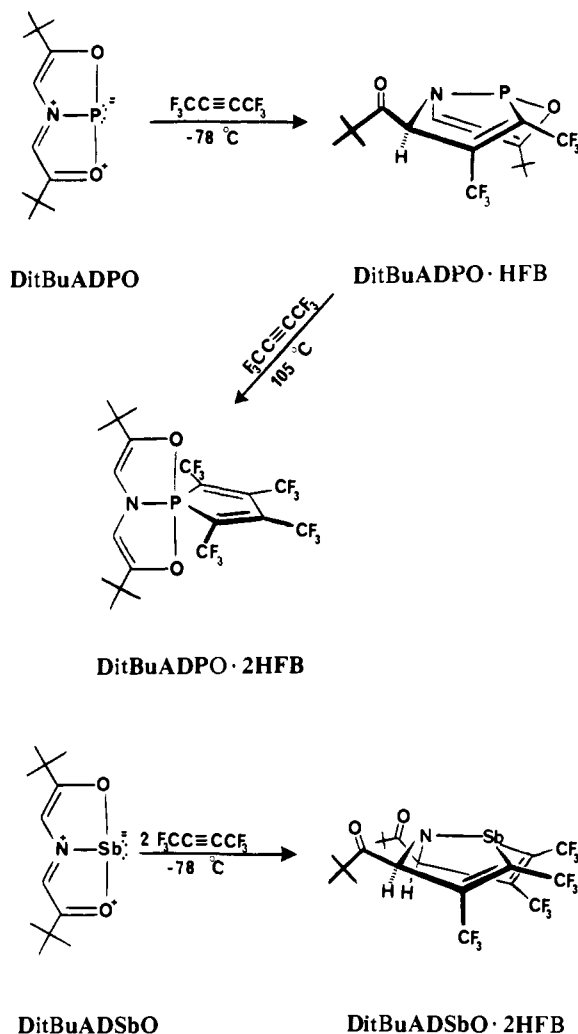
single *tert*-butyl and vinyl proton resonances in the <sup>1</sup>H NMR at room temperature. The <sup>19</sup>F NMR shows two trifluoromethyl

Figure 8. X-ray structure of D<sub>it</sub>BuADSbO·2HFBA.Figure 9. X-ray structure of D<sub>it</sub>BuADPO·HFBA.

environments. Single-crystal X-ray structure analysis (Figure 8) shows D<sub>it</sub>BuADSbO·2HFBA is formed by the addition of the second molecule of HFBA in a 2 + 4 fashion across the C=C function of the first HFBA unit. This results in maintenance of the 10-Sb-4 center with similar dynamic behavior to the 1:1 adduct (*vide supra*). Under similar conditions we were unable to add a third molecule of HFBA.

#### Addition of Hexafluoro-2-butyne

The addition of hexafluoro-2-butyne (HFB) to ADPnO systems illustrates yet more differences in reactivity among these pnictogen compounds. All the 10-Pn-3 ADPnO systems undergo a facile reaction with HFB. In the case of D<sub>it</sub>BuADPO a 1:1 adduct is formed at temperatures below 105 °C. The structure of this



adduct is illustrated in Figure 9. It is similar in structure to the previously mentioned DitBuADPO·HFB adduct. The structure of DitBuADPO·HFB is also consistent with the observed  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{31}\text{P}$ , and  $^{19}\text{F}$  NMR spectra. As would be expected the folded ring structure places the free pivaloyl group on the exo face. A similar 1:1 adduct may be formed between DitBuADSbO and HFB; however in this case the addition of a second mole of HFB proceeds rapidly to give a 1:2 adduct so that the 1:1 adduct is not observed. This DitBuADSbO·2HFB adduct has two new rings formed by incorporation of the HFB unit. Each of the rings is analogous to the new ring formed in DitBuADPO·HFB.

Interestingly, when DitBuADPO·HFB is forced to add a second equivalent of HFB a remarkable rearrangement occurs to give a  $\lambda^5$ -phosphole (10-P-5). The DitBuADPO·2HFB adduct gives solution NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ) consistent with two planar orthogonal ring systems. This structure (Figure 10) was verified by single-crystal X-ray structure analysis. A substantial rearrangement is necessary to form the DitBuADPO·2HFB adduct. This and the relatively high temperatures ( $105^\circ\text{C}$ ) necessary for reaction lead us to believe this process proceeds in a stepwise fashion. Initial P–O bond cleavage in DitBuADPO·HFB assisted by the nitrogen lone pair would form phosphide (8-P-2) and iminium centers. Addition of the second HFB unit could then proceed in a 2 + 3 cycloaddition across phosphorus and the  $\pi$  system from the initial HFB unit. Finally, the necessary C–C bond cleavage and P–O bond formation would lead to DitBuADPO·2HFB. The much milder conditions employed in the synthesis of DitBuADSbO·2HFB (and DitBuADAsO·2HFB) do not allow the rearrangement of the initial adduct. Attempts to rearrange DitBuADSbO·2HFB to a DitBuADPO·2HFB type structure led only to decomposition of the adduct.

Mention should also be made of the rather intense blue color of the DitBuADPO·2HFB adduct. Such color might not be

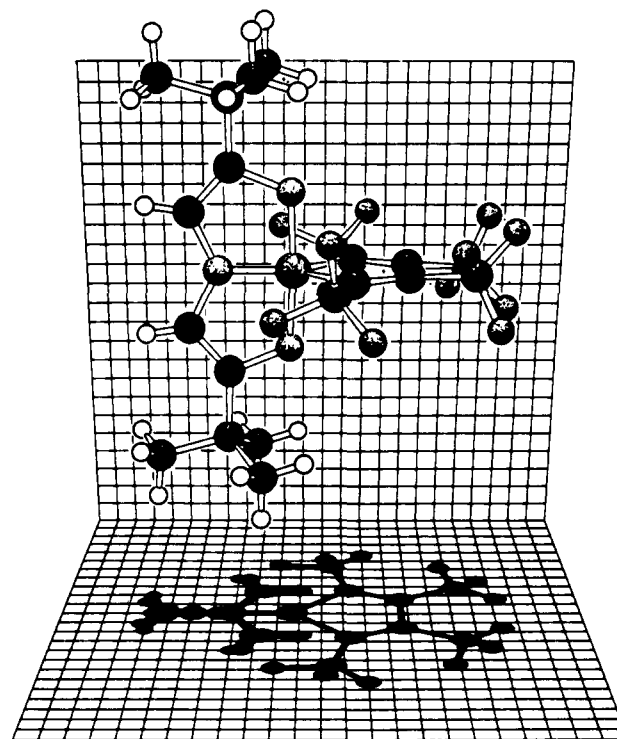


Figure 10. X-ray structure of DitBuADPO·2HFB.

expected for a molecule which incorporates the 10- $\pi$  tridentate ligand backbone (DitBuADPO·Cl<sub>2</sub>, DitBuADPO·(CH<sub>3</sub>)<sub>2</sub>, and DitBuADPO·CH<sub>3</sub>/Cl are colorless) and a  $\lambda^5$ -phosphole (generally  $\lambda^5$ -phospholes are yellow<sup>36a</sup> to orange<sup>36b</sup> if they bear conjugating substituents). It should be noted, however, that DitBuADPO·2HFB is bis(ipso)aromatic<sup>37</sup> and potentially spiroconjugated.<sup>38</sup>

#### Dihalo Derivatives

Members of the 10-Pn-3 ADPnO series can also be oxidized to a series of ADPnO·X<sub>2</sub> compounds. The two new halogen bonds are formed with the pnictogen center. There are two basic routes to these dihalo derivatives. The first approach involves addition of the elements of X<sub>2</sub> to ADPnO. PnX<sub>5</sub>, X<sub>2</sub>, and SO<sub>2</sub>Cl<sub>2</sub> are among the suitable halogenation agents. The second general method is to directly introduce the 5-coordinate pnictogen into the diketo amine ligand 4.

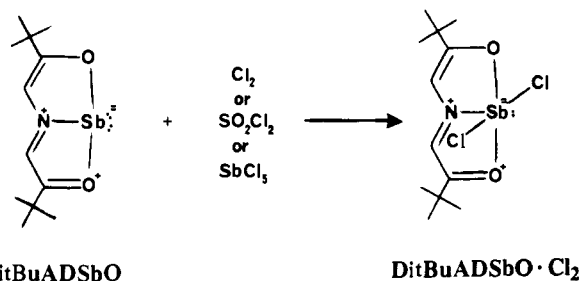
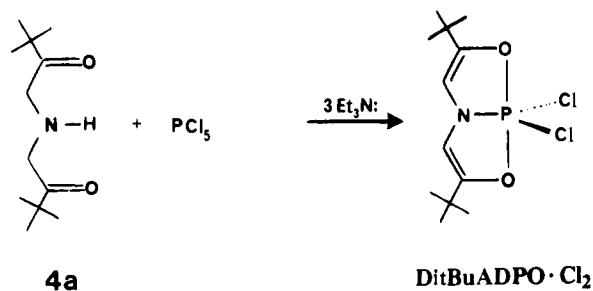
DitBuADPO·Cl<sub>2</sub> is most conveniently prepared by reaction of the diketoamine ligand 4a with PCl<sub>5</sub> (DitBuADPO·Br<sub>2</sub> is similarly prepared). We have not been able to obtain crystals of DitBuADPO·Cl<sub>2</sub> (or DitBuADPO·Br<sub>2</sub>) suitable for X-ray structure analysis. However, this structural analysis is obviated by extensive multinuclear NMR data. The  $^{31}\text{P}$  chemical shift of  $-24.9$  ppm is indicative of a 10-P-5 bonding system. The ring proton resonance of  $\delta$  6.15 ( $^3J_{\text{PH}} = 36$  Hz) and  $^{15}\text{N}$  resonance of  $-262$  ppm ( $^1J_{\text{PN}} = 14$  Hz) indicate a neutral ligand backbone free from the positive charges in the initial ADPO system. The  $^{13}\text{C}$  NMR further supports an approximately planar ligand backbone without positive charge (similar to DitBuADPO·CH<sub>3</sub>/Cl and DitBuADPO·(CH<sub>3</sub>)<sub>2</sub>; vide infra). This places the phosphorus in a TBP environment with apical oxygens and equatorial chlorines and nitrogen.

In contrast, DitBuADSbO·Cl<sub>2</sub> shows a 12-Sb-5 bonding system and thus a pseudooctahedral geometry about antimony. The ligand backbone in DitBuADSbO·Cl<sub>2</sub> still shows the evidence of positive charge necessary to form the remaining antimony lone pair. The ring proton resonance of  $\delta$  7.94 is similar to the 10-Pn-3

(36) (a) Hendrickson, J. B.; Spenger, R. E.; Sims, J. J. *Tetrahedron* **1963**, *19*, 707. (b) Reddy, G. S.; Weis, C. D. *J. Org. Chem.* **1963**, *28*, 1822.

(37) The term bis(ipso)aromatic was introduced by Forbus, T. R., Jr.; Martin, J. C., *J. Am. Chem. Soc.* **1979**, *101*, 5057.

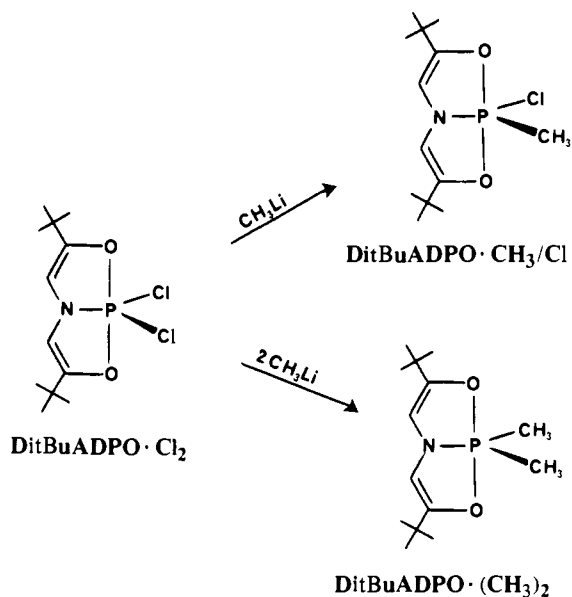
(38) (a) Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208. (b) Gordon, M. D.; Fukunaga, T.; Simmons, H. E. *J. Am. Chem. Soc.* **1976**, *98*, 8401.



ADPnO systems. The  $^{13}\text{C}$  NMR spectrum also suggests a similarly structured ligand backbone. The X-ray structure of DitBuADSbO·Cl<sub>2</sub> reveals the pseudooctahedral geometry about antimony (Figure 11). The chlorines are bent back away from the remaining antimony lone pair to give a Cl–Sb–Cl angle of 160°. The O–Sb–O angle of 146° is about 4° smaller than in DitBuADSbO. On the basis of very similar NMR data a pseudooctahedral geometry can be assigned to DitBuADAsO·Cl<sub>2</sub>. Halogenation of the 10-Te-3 compound studied by Detty and Luss also gives 12-Te-5 systems analogous to DitBuADSbO·Cl<sub>2</sub>.<sup>6c</sup>

Interestingly, again the phosphorus systems behave differently from the arsenic and antimony analogues. This is in contrast to the usual alternation in periodicity which suggests that phosphorus and antimony should behave similarly, but differently from arsenic and bismuth (and nitrogen).<sup>39</sup>

The chlorine substituents of DitBuADPO·Cl<sub>2</sub> can be replaced by nucleophiles. With this reaction both DitBuADPO·CH<sub>3</sub>/Cl and DitBuADPO·(CH<sub>3</sub>)<sub>2</sub> can be prepared by the action of 1 or 2 equiv of methyllithium on DitBuADPO·Cl<sub>2</sub>. These methylated



derivatives both show solution NMR spectra similar to DitBuADPO·Cl<sub>2</sub> and both are nicely crystalline. X-ray structure analyses of DitBuADPO·CH<sub>3</sub>/Cl and DitBuADPO·(CH<sub>3</sub>)<sub>2</sub> (Figures 12 and 13) reveal TBP geometries about a 10-P-5 center

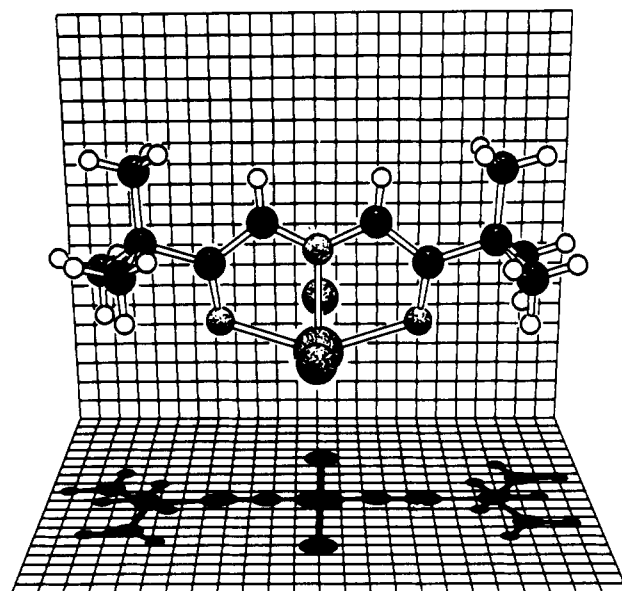


Figure 11. Structure of DitBuADSbO·Cl<sub>2</sub>.

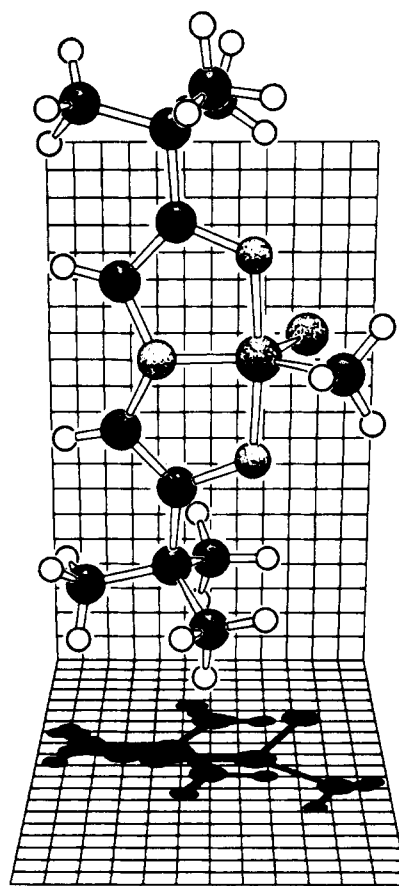
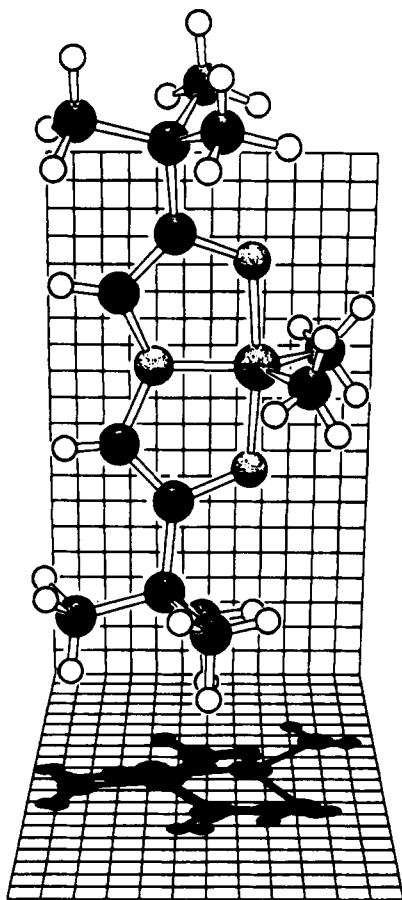


Figure 12. X-ray structure of DitBuADPO·CH<sub>3</sub>/Cl.

(DitBuADPO·CH<sub>3</sub>/Cl is slightly distorted to a square-pyramidal geometry). The tridentate ligand is not completely planar in these derivatives (showing some pyramidalization of the nitrogen). Related 10-P-5 structures bearing a tridentate ligand substituted in the 3 and 4 positions by phenyls and having benzo fusion at positions 6 and 7 have been synthesized by a different route.<sup>40</sup> These 10-P-5 systems containing an asymmetric ligand backbone show similar (though asymmetric) geometries.<sup>40b</sup>

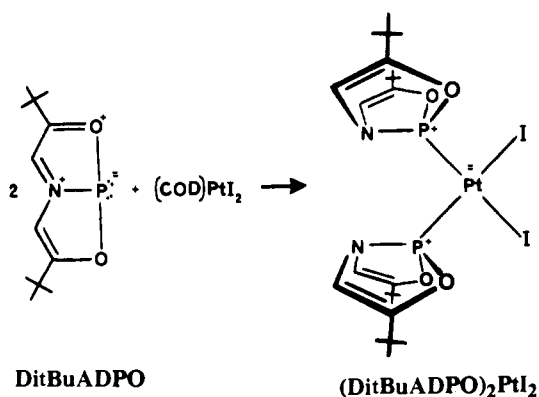
(40) (a) Schmidpeter, A.; Weinmaier, J. H. *Chem. Ber.* **1978**, *111*, 2086. (b) Schmidpeter, A.; Weinmaier, J. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 489. (c) Sheldrick, W. S.; Schmidpeter, A.; Weinmaier, J. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 490.

(39) For a discussion of alternations in periodicity see ref 22, pp 721–723.

Figure 13. X-ray structure of DitBuADPO·(CH<sub>3</sub>)<sub>2</sub>.

### Transition-Metal Complexes

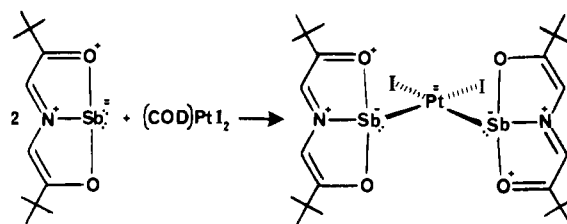
If one views the 10-Pn-3 ADPnO systems as containing two sets of lone pairs at the pnictogen center, they would be expected to behave as Lewis bases toward transition metals. Potentially, the pnictogen could act as a two- or four-electron donor. Behavior as a two-electron donor could be accompanied by a geometrical rearrangement of the ADPnO ring system as we have previously reported for the bis(DitBuADPO) adduct of platinum diiodide ((DitBuADPO)<sub>2</sub>PtI<sub>2</sub>).<sup>5</sup>



DitBuADPO

(DitBuADPO)<sub>2</sub>PtI<sub>2</sub>

The bending of the phosphorus ligand backbones in (DitBuADPO)<sub>2</sub>PtI<sub>2</sub> allows for steric relaxation and better electronic features of the lone pairs used for complexation as we have previously described.<sup>5</sup> In contrast, the ADSbO transition-metal adducts form geometrically different complexes. Reaction of 2 equiv of DitBuADSbO with (cyclooctadiene)platinum diiodide ([COD]PtI<sub>2</sub>) affords the 2:1 complex (DitBuADSbO)<sub>2</sub>PtI<sub>2</sub>. The proton ring resonance for this complex at  $\delta$  8.38 represents only a small upfield shift (0.08 ppm) relative to DitBuADSbO. The carbonyl resonance exhibits an 18.7 ppm shift downfield upon coordination to platinum ((DitBuADSbO)<sub>2</sub>PtI<sub>2</sub>, +195.2 ppm).

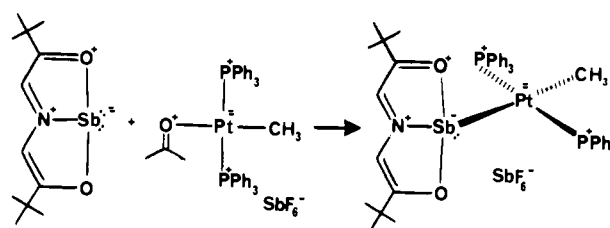


DitBuADSbO

(DitBuADSbO)<sub>2</sub>PtI<sub>2</sub>

These NMR data suggest that there is no major rehybridization at the heavier pnictogen center. The deshielding of the carbonyls does indicate a slight reduction in electron density in the ligand backbone but no significant change in geometry. DitBuADAsO also appears to follow DitBuADSbO in terms of maintaining the planar geometry upon coordination to transition metals.<sup>41</sup>

After numerous unsuccessful attempts at crystallization of (DitBuADSbO)<sub>2</sub>PtI<sub>2</sub> for X-ray quality crystals, we chose a different platinum derived system, the acetone adduct of *trans*-bis(triphenylphosphine)methylplatinum hexafluoroantimonate, [(CH<sub>3</sub>)<sub>2</sub>C=O](Ph<sub>3</sub>P)<sub>2</sub>PtCH<sub>3</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup>. One equivalent of DitBuADSbO reacts with the platinum complex to afford the dark-red 10-Sb-4 platinum adduct.<sup>42</sup> The ring proton resonance



DitBuADSbO

(DitBuADSbO)Pt(PPh<sub>3</sub>)<sub>2</sub>CH<sub>3</sub><sup>+</sup>  
SbF<sub>6</sub><sup>-</sup>

of the ADSbO moiety in the complex is at  $\delta$  8.72. This is actually a slight downfield shift of 0.26 ppm. This strongly suggests the presence of a delocalized positive charge still residing in the ligand backbone. The room temperature <sup>31</sup>P NMR indicates the presence of two nonequivalent triphenyl phosphine ligands at the platinum center. The <sup>1</sup>H NMR resonance of the platinum methyl, which is a triplet ( $\delta$  -0.74, <sup>3</sup>J<sub>HP</sub> = 6.6 Hz), initially rules out *trans* to *cis* isomerization of the triphenylphosphines. Since there was no *trans* to *cis* isomerization of the triphenylphosphines at the platinum center during the course of the reaction, the nonequivalent phosphorus resonances indicate the presence of a stereoactive lone pair of electrons at the antimony. The nonequivalence of the phosphines is not sufficient to be seen in coupling constants to the platinum methyl hydrogens. The solid-state structure (Figure 14) study confirms the planarity of the ADSbO substituent and the presence of a stereoactive lone pair at antimony.

The differences between ADPO and ADSbO upon complexation can be explained by the relative sizes of the pnictogen center and the s-orbital that contains the lone pair of electrons in the 10-Pn-3 ADPnO molecule. In 10-P-3 ADPO the lone pair electrons reside in a nondirectional s-orbital. Upon complexation the phosphorus rehybridizes from sp (or sp<sup>2</sup>) to a more directional sp<sup>3</sup>-orbital. One pair of electrons is put back into the ligand backbone. The remaining lone pair of electrons is now in a more

(41) For example, DitBuADAsO reacts with dichlorobis(benzonitrile)-palladium(II) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature to yield the 1:1 dimer complex (DitBuADAsO)<sub>2</sub>PdCl<sub>2</sub>. The brick red complex gives consistent elemental analyses (CHN) and melts at 148–149 °C. The planarity of the ADAsO moiety in the complex is evident from the <sup>1</sup>H and <sup>13</sup>C NMR spectra: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.43 (s, 18 H, CH<sub>3</sub>), 8.42 (s, 2 H, CH); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  27.4 (s, CH<sub>3</sub>), 40.4 (s, CCA), 121.7 (s, NC), 195.0 (s, CO); <sup>13</sup>C NMR gated (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  121.7 (dd, <sup>1</sup>J<sub>CH</sub> = 186.1 Hz, <sup>3</sup>J<sub>CH</sub> = 1.8 Hz, NC).

(42) Stewart, C. A.; Arduengo, A. J., III. *Inorg. Chem.* **1986**, *25*, 3847.

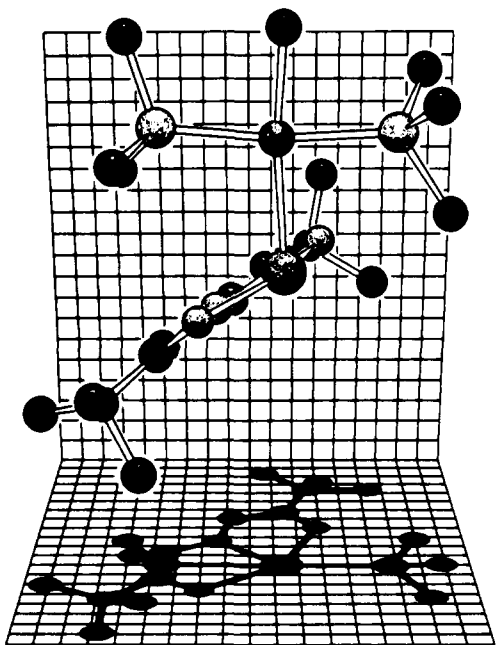
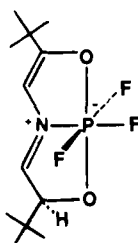


Figure 14. X-ray structure of  $(\text{DitBuADSbO})\text{Pt}(\text{PPh}_3)_2\text{CH}_3^+$ . Hydrogens and phenyls (except ipso carbons) have been omitted for clarity.

directional  $\text{sp}^3$  orbital and is able to achieve better overlap with the platinum. In contrast the heavier pnictogens, arsenic and antimony, do not need to rehybridize to overlap sufficiently with palladium or platinum. Therefore, they retain their original electronic configuration and geometry. More details on related transition-metal complexes will be discussed in a subsequent publication.

#### Six-Coordinate Phosphorus System

The chlorides of  $\text{DitBuADPO}\cdot\text{Cl}_2$  can be replaced with fluorides by treatment with tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF). However, in the presence of tris(dimethylamino)sulfonium bifluoride ( $\text{TAS}^+\text{FHF}^-$ ) HF quickly adds to the  $\text{DitBuADPO}\cdot\text{F}_2$  moiety. The result is the addition of another mole of fluoride to the phosphorus and protonation of a *tert*-butyl bearing carbon ( $\text{DitBuADPO}\cdot\text{HF}_3$ ).



$\text{DitBuADPO}\cdot\text{HF}_3$

The  $^{31}\text{P}$  NMR is consistent with a hexacoordinate phosphorus anion ( $\delta -113$ ). The detection of an  $^{14}\text{N}$  resonance with chemical shift at  $\delta -123$  indicates a positively charged, essentially planar nitrogen. Another noteworthy point is the  $<1$  Hz  $^{31}\text{P}$ - $^{15}\text{N}$  coupling constant. This coupling constant is consistent with our observed trend of decreasing P-N coupling constants with increasing phosphorus coordination number (Figure 3).

#### Conclusions

The 10-Pn-3, hypervalent tricoordinate pnictogen, bonding system can be a stable bonding arrangement if care is taken to supplement the stability of the pnictandiide structure (7). Four basic stabilizing features have been used. First, the ligand system for 7 should be designed to compensate for the rather large formal charge buildup at the pnictogen center. Pi interactions are somewhat important in this regard (see NMR data and ab initio calculations above). Second, the equatorial position is linked to

the apical sites via 5-membered rings which help support the necessary  $\psi$ -TBP geometry. Third, electronegative substituents should be placed in the apical position to stabilize the hypervalent bonding arrangement. Fourth, and finally, some steric bulk may be necessary to provide a kinetic barrier to the inherent reactivity of the molecules (this is not so important for 10-As-3 systems as the stability of  $\text{DiPhADAsO}$  suggests). Consideration of these factors led to our choice of the ligand system derived from 4 and the synthesis of the 10-Pn-3 ADPnO compounds. Saturated analogues of our ADPnO systems are known to exist solely as the bent 8-Pn-3 electromorph, and we have observed complexes of  $\text{DitBuADPO}$  in bent 8-electron environments. However, the parent ADPnO systems are sufficiently stabilized that there is no evidence for the presence of an 8-Pn-3 electromorph for any of the molecules we have investigated thus far. The 10-Pn-3 ADPnO structures represent the ultimate stabilization of the transition state involved in the recently recognized edge inversion process for trivalent pnictogens.<sup>2a,21</sup>

Charge distributions from ab initio calculations on ADPO show the expected positive charge at the phosphorus center consistent with the hypervalent bonding arrangement. However, this charge is less positive than has been previously recognized for other hypervalent (10-P-5) centers. This is consistent with the phosphorus center receiving electron density from the  $\pi$  system of the tridentate ligand and losing electron density to the apical oxygens of the 3-center 4-electron bond. The simple valence bond representation of the 10-Pn-3 ADPnO systems which has a formal -2 charge at the pnictogen center is thus somewhat exaggerated but provides a convenient chemically and structurally accurate representation of these systems while providing insight into the bonding scheme. Furthermore, the  $^{15}\text{N}$  and  $^{17}\text{O}$  NMR spectra suggest the identity of the nitrogen and oxygen centers is iminium and protonated carbonyl-like, respectively, so that the conventional representation of these centers is also satisfied.

The well-known dioxachalcapentalenes (1) are close structural and electronic analogues of the 10-Pn-3 ADPnO molecules. There are remarkable similarities in the spectral properties of these two classes of compounds. The chemistry of the chalcogen and pnictogen derived systems shows some common features (e.g., protonation and halogenation). In general the ADPnO molecules show a wealth of chemistry at the 10-Pn-3 center compared to the reported chemistry of 1.

Whereas the ligand backbone in the ADPnO system is able to stabilize hypervalent bonding at 3-coordinate phosphorus, the 4-coordinate phosphorus systems prefer a tetrahedral structure in accord with the octet rule. The 5-coordinate phosphorus systems derived from 10-P-3 ADPO exhibit only 10-electron hypervalent bonding systems in which no extra electrons are donated to the phosphorus from the ligand backbone. This tendency toward lower electron counts at phosphorus is dramatically contrasted by the 10-Pn-4 and 12-Pn-5 systems which are formed by metal complexation and halogenation of 10-Pn-3 ADPnO molecules when the central pnictogen is arsenic or antimony. This results in unique chemistry for the phosphorus-derived systems while a second mode of reactivity is followed by both arsenic and antimony. The chemistry of our 10-Pn-3 ADPnO thus falls into two general categories (one for phosphorus and one for arsenic and antimony).

Although the phosphorus, arsenic, and antimony systems generally fall into two groups, the bismuth system is quite unique, forming a very high coordinate 20-Bi-9 system (8). Thus the parent 10-Bi-3 system has not been observed. No definite statement can be made about possible nitrogen derived systems since attempts to prepare ADNO systems have been unsuccessful.

NMR spectroscopic investigation of the variety of phosphorus compounds available from this work reveals an interesting correlation between the coordination number at phosphorus and the one-bond  $^{31}\text{P}$ - $^{15}\text{N}$  coupling constant. This relationship holds well throughout these systems since much of the ligation at phosphorus is kept constant. The correlation is very useful in making reasonable predictions for molecular structures of ADPO derived systems. Further structural information is readily available from  $^1\text{H}$ ,  $^{13}\text{C}$  [ $^1\text{H}$ ],  $^{14}\text{N}$ ,  $^{15}\text{N}$ , and proton-coupled  $^{13}\text{C}$  NMR spectra as

to the electron distribution and geometry of the tridentate ligand in the ADPnO systems.

The reactions and exchanges with  $\alpha$ -dicarbonyl derivatives of the ADPnO systems indicate that chemical oxidation occurs more easily at phosphorus followed by antimony and then arsenic. That is to say that the phosphorus-centered adducts form the ultimate thermodynamic sink for chemical oxidants. This is in contrast to the cyclic voltammetric results which indicate that electrochemical oxidation occurs most easily at antimony followed by arsenic and then phosphorus. The difference in these oxidation orderings is probably the result of the stronger bonds formed to the lighter pnictogen centers upon chemical oxidation.

## Experimental Section

**General Methods.** All solvents were freshly distilled and dried before use according to established procedures.<sup>43</sup> Melting points were measured on a Thomas-Hoover capillary apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on a General Electric QE-300 spectrometer. <sup>13</sup>C, <sup>15</sup>N, <sup>14</sup>N, <sup>31</sup>P, <sup>195</sup>Pt, and <sup>17</sup>O NMR spectra were recorded on a Nicolet NT-300WB spectrometer. Fluorine NMR spectra were obtained on a Nicolet NT-200 spectrometer. Solid-state <sup>13</sup>C CP-MAS spectra were recorded on a GE S-100 spectrometer. All NMR spectra are reported in ppm  $\delta$  (positive shifts downfield of the reference). NMR references are (<sup>1</sup>H) Me<sub>4</sub>Si, (<sup>13</sup>C) Me<sub>4</sub>Si, (<sup>15</sup>N) NH<sub>4</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup> (D<sub>2</sub>O), (<sup>14</sup>N) NH<sub>4</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup> (D<sub>2</sub>O), (<sup>31</sup>P) 85% H<sub>3</sub>PO<sub>4</sub>, (<sup>195</sup>Pt) K<sub>2</sub>PtCl<sub>4</sub> (D<sub>2</sub>O), (<sup>17</sup>O) H<sub>2</sub>O, (<sup>19</sup>F) CFCl<sub>3</sub>.

Mass spectra were obtained on a VGMM 7070 double-focusing high-resolution mass spectrometer. UV spectra were recorded on a Varian Cary 2300. Infrared spectra were obtained on a Perkin-Elmer 983G spectrophotometer.

Manipulations of air-sensitive samples were performed in a Vacuum Atmospheres drybox under nitrogen. Reactions involving gaseous reagents (except hydrogen) were conducted by metering the gas into a vacuum manifold of known volume and condensing the gas into the reaction vessel with liquid nitrogen. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, Oneida Research Services, Whitesboro, NY, and J. Nemeth, University of Illinois, Urbana, IL, and are within 0.4% of theoretical values unless otherwise indicated. Single-crystal X-ray structure determinations were performed by Molecular Structure Corporation, College Station, TX, and Oneida Research Services.

**5-Aza-5-benzyl-2,2,8,8-tetramethylnonane-3,7-dione Hydrobromide.** A 12-L three-neck flask fitted with a mechanical stirrer and a condenser was charged with 8 L of benzene and 1-bromo-3,3-dimethyl-2-butanone (1.278 kg, 7.144 mol). The flask was purged with nitrogen and benzylamine (765.1 g, 7.144 mol) was added as a single portion. The mixture was heated at reflux for 2 days and then allowed to cool to room temperature. The solids were collected by filtration and washed with water (2  $\times$  1 L) to give 850 g of the desired crude product. The solid was recrystallized from ethanol to yield 780 g (57%): mp 214–215 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.14 (s, CH<sub>3</sub>, 18 H), 4.63 (d, COCH<sub>2</sub>, 4 H), 4.67 (d, PhCH<sub>2</sub>, 2 H), 7.47 (m, Ar, 3 H), 7.67 (m, Ar, 2 H).

**5-Aza-2,2,8,8-tetramethylnonane-3,7-dione Hydrobromide.** A 10-L polyethylene vessel equipped with a mechanical stirrer was charged with 8 L of methanol and 664 g (1.68 mol) of 5-aza-5-benzyl-2,2,8,8-tetramethylnonane-3,7-dione hydrobromide. The mixture was purged with nitrogen for 10 min and 10 g of 5% Pd on charcoal was added as a single portion. Hydrogen was bubbled through the mixture for 18 h. The Pd/C was removed by filtration and the solvent removed in vacuo. The residue was recrystallized from ethanol to give 466 g (91%) of the desired amine hydrobromide: mp 240–242 °C; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  1.10 (s, 18 H, CH<sub>3</sub>), 3.20 (s, 2 H, NH), 4.20 (s, 4 H, COCH<sub>2</sub>). Anal. (C<sub>12</sub>H<sub>24</sub>NO<sub>2</sub>Br): C, H, N, Br.

**5-Aza-2,2,8,8-tetramethylnonane-3,7-dione (4a).** A 1-L three-neck flask was charged with 250 mL of H<sub>2</sub>O, 150 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 14.7 g (50 mmol) of 5-aza-2,2,8,8-tetramethylnonane-3,7-dione hydrobromide. The mixture was purged with nitrogen for 5 min and cooled with an ice bath. A solution of 22.8 g (60 mmol) of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O in 150 mL of H<sub>2</sub>O was added dropwise to the stirred solution over 1 h. The mixture was stirred for an additional 2 h at 5 °C. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated. The aqueous layer was washed (3  $\times$  20 mL) with CH<sub>2</sub>Cl<sub>2</sub>. The combined CH<sub>2</sub>Cl<sub>2</sub> layers were washed (3  $\times$  20 mL of H<sub>2</sub>O), dried, and evaporated. The residue was sublimed in vacuo to yield 9.7 g (91%) of the desired amine: mp 61–62 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.15 (s, 18 H, CH<sub>3</sub>), 2.44 (s, 1 H, NH), 3.61 (s, 4 H, COCH<sub>2</sub>); IR (CsI) 3390, 2966,

2872, 1714, 1480, 1459, 1368 cm<sup>-1</sup>. Anal. (C<sub>12</sub>H<sub>23</sub>NO<sub>2</sub>): C, H, N.

**3-Aza-3-benzyl-1,5-di-1-adamantylpentane-1,5-dione Hydrobromide.** A 3-L three-neck flask fitted with a condenser and mechanical stirrer was charged with 1-adamantyl bromomethyl ketone (77.1 g, 0.3 mol) and 2 L of dry benzene. Benzylamine (32.5 g, 0.3 mol) was added as a single portion. The flask was purged with nitrogen and heated to reflux. The reflux was continued for 48 h. The suspended solids were collected by filtration and washed with 500 mL of benzene. The solids were thoroughly washed with 1 L of water in a blender and dried in vacuo. Additional product was obtained by the evaporation of the benzene filtrate. Recrystallization from EtOH yielded 30.0 g (37%) of the desired amine hydrobromide: mp 218–220 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.69 (m, 12 H, CH), 1.77 (s, 12 H, CH<sub>2</sub>), 2.04 (s, 6 H, C<sub>3</sub>CH), 4.69 (dd, 4 H, COCH<sub>2</sub>), 4.70 (d, 2 H, PhCH<sub>2</sub>), 7.45 (m, 3 H, Ar), 7.68 (m, 2 H, Ar).

**3-Aza-1,5-di-1-adamantylpentane-1,5-dione Hydrobromide.** A 1-L heavy-walled Erlenmeyer flask was charged with 3-aza-3-benzyl-1,5-di-1-adamantylpentane-1,5-dione hydrobromide (37.7 g, 69.8 mmol) and 800 mL of methanol. The methanol suspension was purged with nitrogen for 10 min and 0.66 g of 5% Pd on charcoal was added as a single portion. Hydrogen was bubbled through the suspension for 18 h. The Pd/C was removed by filtration and the filtrate evaporated to yield 23.1 g (74%) of the desired amine hydrobromide: mp 282–284 °C; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  1.68 (m, 6 H, CH<sub>2</sub>), 1.76 (m, 6 H, CH<sub>2</sub>), 2.00 (m, 3 H, C<sub>3</sub>CH), 4.20 (s, 2 H, COCH<sub>2</sub>).

**3-Aza-1,5-di-1-adamantylpentane-1,5-dione (4b).** A 1-L three-neck flask was charged with 200 mL of H<sub>2</sub>O, 150 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 14.4 g (31.6 mmol) of 3-aza-1,5-di-1-adamantylpentane-1,5-dione hydrobromide. The mixture was purged with nitrogen for 15 min and cooled in an ice bath. A solution of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O (18.0 g, 47.0 mmol) in 150 mL of H<sub>2</sub>O was added to the stirred solution over 15 min. The mixture was stirred at 0 °C for an additional 2.5 h. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated, washed (3  $\times$  50 mL of H<sub>2</sub>O), and dried over MgSO<sub>4</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated and the residue recrystallized from cyclohexane to yield 11.0 g (93%) of the desired amine: mp 134–136 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.74 (m, 12 H, CH<sub>2</sub>), 1.81 (m, 12 H, CH<sub>2</sub>), 2.04 (m, 6 H, C<sub>3</sub>CH), 2.18 (s, 1 H, NH), 3.57 (s, 4 H, COCH<sub>2</sub>). Anal. (C<sub>24</sub>H<sub>35</sub>NO<sub>2</sub>): C, H, N.

**3-Aza-3-benzyl-1,5-diphenylpentane-1,5-dione Hydrobromide.**<sup>44</sup> A 3-L three-neck flask fitted with a condenser and mechanical stirrer was charged with  $\alpha$ -bromoacetophenone (199.0 g, 1.0 mol) and 2 L of dry benzene. Benzylamine (107.2 g, 1.0 mol) was added as a single portion. The flask was purged with nitrogen and heated to reflux. The reflux was continued for 48 h. The suspended solids were collected by filtration and washed with 500 mL of benzene. The solids were washed thoroughly with 1 L of water and dried in vacuo. Recrystallization from CH<sub>3</sub>CN yielded 127.0 g (60%) of the desired amine hydrobromide: mp 198–204 °C; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  4.56 (s, CH<sub>2</sub>Ph, 2 H), 5.13 (s, CH<sub>2</sub>CO, 2 H), 7.34 (m, *m,p*-PhCH<sub>2</sub>, 3 H), 7.57 (t, *m*-PhCO, 4 H), 7.64 (m, *o*-PhCH<sub>2</sub>, 2 H), 7.72 (t, *p*-PhCO, 2 H), 7.88 (d, *o*-PhCO, 4 H). Anal. (C<sub>23</sub>H<sub>22</sub>NO<sub>2</sub>Br): C, H, N, Br.

**3-Aza-1,5-diphenylpentane-1,5-dione Hydrobromide.** A 1-L flask was charged with 3-aza-3-benzyl-1,5-diphenylpentane-1,5-dione hydrobromide (24.82 g, 58.5 mmol) and 750 mL of methanol. The mixture was degassed with nitrogen, and 5% Pd on charcoal (0.75 g) was added as a single portion. Hydrogen gas was bubbled through the suspension for 4 h, during which time all the solids dissolved. The uptake of hydrogen still continued at this point. The methanol solution was filtered through Celite, reduced to one-half volume on a rotovap, and placed in a freezer at -25 °C overnight. The solution deposited crystals which were collected by filtration to give 4.4 g (23% yield) of 3-aza-1,5-diphenylpentane-1,5-dione hydrobromide, mp 232–238 °C; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  4.88 (s, 4 H, COCH<sub>2</sub>), 7.61 (m, 4 H, *m*-Ph), 7.73 (m, 2 H, *p*-Ph), 8.00 (m, 4 H, *o*-Ph), 9.58 (s, 2 H, NH<sub>2</sub>).

**3-Aza-1,5-diphenylpentane-1,5-dione**<sup>45</sup> (4c). A 500-mL three-neck flask was charged with 100 mL of H<sub>2</sub>O, 75 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 5.78 g (17.0 mmol) of 3-aza-1,5-diphenylpentane-1,5-dione hydrobromide. The mixture was purged with nitrogen for 15 min and cooled in an ice bath. A solution of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O (7.81 g, 21.0 mmol) in 75 mL of H<sub>2</sub>O was added to the stirred solution over 15 min. The mixture was stirred at 5 °C for 1 h. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated, washed (3  $\times$  50 mL of H<sub>2</sub>O), and dried over MgSO<sub>4</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated and the residue recrystallized from toluene to yield 2.6 g (60%) of the desired amine: mp 82–85 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  2.69 (br, NH, 1 H), 4.26 (s, COCH<sub>2</sub>, 4 H), 7.51 (m, *m*-Ph, 4 H), 7.62 (m, *p*-Ph, 2 H), 7.97 (m, *o*-Ph, 4 H). Anal. (C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>): C, H, N.

**5-Aza-2,8-dioxo-3,7-di-*tert*-butyl-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (DitBuADPO).** To a stirred solution of PCl<sub>3</sub> (2.2 g, 16.0 mmol)

(43) *Purification of Laboratory Chemicals*, 2nd ed.; Perrin, D. D., Armarego, W. L. F., Perrin, D. R.; Pergamon: New York, 1985.

(44) Mason, A. T.; Winder, G. R. *J. Chem. Soc.* **1893**, D63, 1355.

(45) Gabriel, S. *Ber.* **1908**, *41*, 1127.



in 100 mL of THF held at  $-78^{\circ}\text{C}$  was added dropwise 5-aza-2,2,8,8-tetramethylnona-3,7-dione (**4a**) (3.41 g, 16.0 mmol) in 30 mL of THF. When the addition was complete, triethylamine (6.8 mL, 48.7 mmol) in 30 mL of THF was added dropwise. After several hours the reaction mixture was allowed to warm slowly to room temperature. The THF was removed under reduced pressure. The white solid was washed with pentane to give a slightly yellow solution. The pentane was removed under reduced pressure, leaving 3.3 g (80 %) of crude DiBuADPO. DiBuADPO was recrystallized from pentane at  $-25^{\circ}\text{C}$  to give a white crystalline solid: mp  $138\text{--}140^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.31 (s, 18 H), 7.50 (d,  $^3J_{\text{PH}} = 9.6$  Hz, 2 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  28.1 ( $\text{CH}_3$ , d,  $^3J_{\text{PC}} = 0.9$  Hz), 34.3 ( $\text{C}(\text{CH}_3)_3$ , d,  $^3J_{\text{PC}} = 7.1$  Hz), 111.2 (CN, d,  $J_{\text{PC}} = 5.7$  Hz), 169.9 (CO, d,  $J_{\text{PC}} = 0.2$  Hz);  $^{13}\text{C}$  gated  $\delta$  111.2 ( $^1J_{\text{CH}} = 189.9$  Hz,  $^3J_{\text{CH}} = 1.5$  Hz);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-126.3$  (d,  $^1J_{\text{PN}} = 80$  Hz);  $^{17}\text{O NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  324;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  187; IR (CsI) 3132, 2969, 1717, 1557, 1478, 1459, 1392, 1363, 1312, 1222, 1214, 1144, 1113, 948, 937, 806, 762  $\text{cm}^{-1}$ ; solid-state  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  27, 33, 111, 170; EI mass spectrum (70 eV),  $m/z$  241. Anal. ( $\text{C}_{12}\text{H}_{20}\text{NO}_2\text{P}$ ): C, H, N, P.

**5-Aza-2,8-dioxo-3,7-di-tert-butyl-1-arsabicyclo[3.3.0]octa-2,4,6-triene (DiBuADAsO).** Under nitrogen, 3-aza-2,2,8,8-tetramethylnona-3,7-dione (**4a**) (3.41 g, 16.0 mmol) in 30 mL of THF was added dropwise to a stirred solution of  $\text{AsCl}_3$  (2.90 g, 16.0 mmol) in 100 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (6.8 mL, 48.7 mmol) in 30 mL of THF was added dropwise. After 3 h the reaction mixture was allowed to warm to room temperature. Upon warming, the solution turned to a pale yellow. The THF was removed in vacuo. The light yellow solid was washed with pentane to afford a solid (crude triethylamine hydrochloride) and a yellow-green solution. The volume of the pentane was reduced in vacuo to induce crystallization. DiBuADAsO was recrystallized from pentane at  $-25^{\circ}\text{C}$  to give light green crystals, 3.7 g (80 % yield): mp  $124\text{--}126^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.31 (s, 18 H), 7.90 (s, 2 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  28.3 ( $\text{CH}_3$ ), 36.3 ( $\text{C}(\text{CH}_3)_3$ ), 113.6 (CN), 174.8 (CO);  $^{13}\text{C}$  gated  $\delta$  113.6 ( $^1J_{\text{CH}} = 185.6$  Hz,  $^3J_{\text{CH}} = 1.2$  Hz);  $^{15}\text{N NMR}$   $\delta$   $-96$ ;  $^{17}\text{O NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  330. IR (CsI) 3130, 3098, 2486, 1701, 1497, 1462, 1427, 1391, 1358, 1345, 1305, 1219  $\text{cm}^{-1}$ ; solid-state  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  27, 35, 114, 174; EI mass spectrum (70 eV),  $m/z$  285. Anal. ( $\text{C}_{12}\text{H}_{20}\text{NO}_2\text{As}$ ): C, H, N.

**5-Aza-2,8-dioxo-3,7-di-tert-butyl-1-stibabicyclo[3.3.0]octa-2,4,6-triene (DiBuADSbO).** Under nitrogen, 3-aza-2,2,8,8-tetramethylnona-3,7-dione (**4a**) (3.41 g, 16.0 mmol) in 30 mL of THF was added dropwise to a stirred solution of  $\text{SbCl}_3$  (3.65 g, 16.0 mmol) in 100 mL of THF held at  $-78^{\circ}\text{C}$ . After the addition was complete, triethylamine (6.8 mL, 48.7 mmol) in 30 mL of THF was added dropwise. After 3 h the reaction mixture was allowed to warm to room temperature where it gradually turned from green to dark red-brown. The THF was removed in vacuo. The dark yellow solid was washed with pentane to give a light yellow solid (crude triethylamine hydrochloride) and a dark red-brown solution. The volume of pentane was reduced in vacuo to induce crystallization. DiBuADSbO was recrystallized from pentane at  $-25^{\circ}\text{C}$  to give a yellow-green solid 3.7 g (70 % yield): mp  $116^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.39 (s, 18 H), 8.46 (s, 2 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  28.8 ( $\text{CH}_3$ ), 38.0 ( $\text{C}(\text{CH}_3)_3$ ), 117.8 (CN), 176.7 (CO);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-90.9$ ;  $^{17}\text{O NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  305;  $^{13}\text{C}$  gated  $\delta$  117.7 ( $^1J_{\text{CH}} = 181.0$  Hz,  $^3J_{\text{CH}} = 3.1$  Hz); IR (CsI) 3101, 2965, 3177, 1685, 1583, 1552, 1497  $\text{cm}^{-1}$ ; solid-state  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  28, 37, 118, 176; EI mass spectrum (70 eV),  $m/z$  331. Anal. ( $\text{C}_{12}\text{H}_{20}\text{NO}_2\text{Sb}$ ): C, H, N.

**5-Aza-2,8-dioxo-3,7-di-1-adamantyl-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (DiAdADPO).** Under nitrogen, 3-aza-1,5-di-1-adamantylpentane-1,5-dione (**4b**) (0.530 g, 1.43 mmol) in 10 mL of THF was added dropwise to a stirred solution of  $\text{PCl}_3$  (0.194 g, 1.43 mmol) in 50 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (0.442 g, 4.3 mmol) in 15 mL of THF was added dropwise to the cold mixture over 0.5 h. The mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h and then allowed to warm to room temperature. The mixture was filtered and the THF mother liquor evaporated to yield 0.165 g of crude product. The solid was recrystallized from hot toluene to afford DiAdADPO: mp  $315\text{--}319^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.76 (m, 6 H,  $\text{CH}_2$ ), 1.89 (m, 6 H,  $\text{CH}_2$ ), 2.05 (m, 3 H,  $\text{C}_3\text{CH}$ ), 7.40 (d,  $^3J_{\text{PH}} = 9.9$  Hz, 1 H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  28.8, 37.2, 40.1 ( $\text{C}_4\text{C}$ ), 40.8, 111.1 (CN, d,  $J_{\text{PC}} = 5.6$  Hz), 169.6 (CO);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-126.0$  ( $^1J_{\text{PN}} = 81$  Hz);  $^{14}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-126$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  185. Anal. ( $\text{C}_{24}\text{H}_{32}\text{NO}_2\text{P}$ ): C, H, N.

**5-Aza-2,8-dioxo-3,7-di-1-adamantyl-1-arsabicyclo[3.3.0]octa-2,4,6-triene (DiAdADAsO).** Under nitrogen, 3-aza-1,5-di-1-adamantylpentane-1,5-dione (**4b**) (1.85 g, 5.0 mmol) in 20 mL of THF was added dropwise to a stirred solution of  $\text{AsCl}_3$  (0.91 g, 5.0 mmol) in 70 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (1.52 g, 15.0 mmol) in 15 mL of THF was added dropwise to the cold mixture over 0.5 h. The mixture was stirred at  $-78^{\circ}\text{C}$  for 2.5 h and then

allowed to warm to room temperature. The mixture was filtered and the THF mother liquor evaporated to yield 1.37 g of a yellow solid. The original solids from filtration were washed with 50 mL of water (to remove triethylamine hydrochloride). After a methanol rinse these solids (0.3 g) were dried in vacuo. The combined solids were recrystallized from toluene to yield 1.4 g (63 %) of DiAdADAsO: mp  $289\text{--}295^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.78 (m, 6 H,  $\text{CH}_2$ ), 1.94 (m, 6 H,  $\text{CH}_2$ ), 2.06 (m, 3 H,  $\text{C}_3\text{CH}$ ), 7.88 (s, 1 H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  28.8, 37.1, 38.4 ( $\text{C}_4\text{C}$ ), 40.6, 113.6 (CN), 174.9 (CO);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-96.1$ ;  $^{13}\text{C}$  gated  $\delta$  113.6 (dd,  $^1J_{\text{CH}} 185$  Hz,  $^3J_{\text{CH}} = 2$  Hz). Anal. ( $\text{C}_{24}\text{H}_{32}\text{NO}_2\text{As}$ ): C, H, N.

**5-Aza-2,8-dioxo-3,7-di-1-adamantyl-1-stibabicyclo[3.3.0]octa-3,6-diene (DiAdADSbO).** Under nitrogen, 3-aza-1,5-di-1-adamantylpentane-1,5-dione (**4b**) (2.01 g, 5.45 mmol) in 20 mL of THF was added dropwise to a stirred solution of  $\text{SbCl}_3$  (1.24 g, 5.44 mmol) in 70 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (1.65 g, 16.34 mmol) in 15 mL of THF was added dropwise to the cold mixture over 0.5 h. The mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h and then allowed to warm to room temperature. The THF was removed in vacuo and the resulting yellow solid extracted with  $\text{CH}_2\text{Cl}_2$  (100 mL). The  $\text{CH}_2\text{Cl}_2$  was removed in vacuo and the residue recrystallized from toluene to yield 1.7 g (64 %) of DiAdADSbO: mp  $263\text{--}278^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.71 (m, 6 H,  $\text{CH}_2$ ), 1.96 (m, 6 H,  $\text{CH}_2$ ), 2.09 (m, 3 H,  $\text{C}_3\text{CH}$ ), 8.35 (s, 1 H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  29.0, 37.3, 39.8 ( $\text{C}_4\text{C}$ ), 40.9, 117.7 (CN), 176.6 (CO);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-94.5$ ;  $^{13}\text{C}$  gated  $\delta$  117.7 (dd,  $^1J_{\text{CH}} = 182$  Hz,  $^3J_{\text{CH}} = 3$  Hz). Anal. ( $\text{C}_{24}\text{H}_{32}\text{NO}_2\text{Sb}$ ): C, H, N.

**5-Aza-2,8-dioxo-3,7-diphenyl-1-arsabicyclo[3.3.0]octa-2,4,6-triene (DiPhADAsO).** Under nitrogen, 3-aza-1,5-diphenylpentane-1,5-dione (**4c**) (1.23 g, 5.0 mmol) in 20 mL of THF was added dropwise to a stirred solution of  $\text{AsCl}_3$  (0.91 g, 5.0 mmol) in 70 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (1.52 g, 15.0 mmol) in 15 mL of THF was added dropwise to the cold mixture over 0.5 h. The mixture was stirred at  $-78^{\circ}\text{C}$  for 2.5 h and then allowed to warm to room temperature. The mixture was filtered and the THF mother liquor evaporated to yield a red-brown residue. This residue was recrystallized from  $\text{CH}_2\text{Cl}_2$  to yield 0.75 g (46 %) of DiPhADAsO: mp  $192\text{--}193^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.39 (t, 1 H,  $J = 6.7$  Hz,  $p$ -Ph), 7.48 (dd, 2 H,  $J = 6.7$  and 8.1 Hz,  $m$ -Ph), 7.88 (d, 2 H,  $J = 8.1$  Hz,  $o$ -Ph), 8.64 (s, 1 H, NCH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  115.4 (CN), 125.8 ( $o$ -C), 129.2 ( $m$ -C), 129.7 ( $p$ -C), 134.5 ( $\text{C}_3\text{C}$ ), 162.6 (CO);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-95.5$ . Anal. ( $\text{C}_{16}\text{H}_{12}\text{NO}_2\text{As}$ ): C, H, N.

**Attempted Preparation of DiPhADSbO.** Under nitrogen, a solution of 3-aza-1,5-diphenylpentane-1,5-dione (**4c**) (0.47 g, 1.9 mmol) in 10 mL of THF was added dropwise to a stirred solution of  $\text{SbCl}_3$  (0.41 g, 1.9 mmol) in 50 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (0.91 mL, 6.7 mmol) in 5 mL of THF was added dropwise to the cold mixture over a period of 0.5 h. The mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h and then allowed to warm to room temperature. Removal of the THF in vacuo left a dark brown residue. The residue was washed with several portions of pentane to give a light yellow solution. The pentane was removed in vacuo and the yellow-brown residue isolated. The  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ) showed numerous resonances. The instability of the product precluded further characterization.

**Preparation of the 20-Bi-9 System [Tris(4-aza-1,7-dioxo-2,6-di-tert-butylhepta-2,5-diene-1,4,7-triyl)bismuth] (8).** Under nitrogen, 5-aza-2,2,8,8-tetramethylnona-3,7-dione (**4a**) (1.707 g, 8.0 mmol) in 20 mL of THF was added dropwise to a stirring solution of  $\text{BiCl}_3$  (2.52 g, 8.0 mmol) in 30 mL of THF held at  $-78^{\circ}\text{C}$ . When the addition was complete, triethylamine (4.5 mL, 32.0 mmol) in 20 mL of THF was added dropwise to the cooled mixture over 0.5 h. The dark brown mixture was allowed to gradually warm to room temperature while stirring. The stirring was continued for 12 h. Removal of the THF under vacuo left a dark red-brown solid. The solid was washed with pentane to give a dark-red solution and a black solid. The solid was washed with 250 mL of methanol to afford black bismuth powder (1.2 g, theory; 1.1 g). The methanol mother liquors contained triethylamine hydrochloride (2.96 g, theory; 3.3 g). The pentane solution containing the 20-Bi-9 system (**8**) were evaporated and the dark-red product recrystallized from isopropyl alcohol to give 0.67 g (30 % yield) of **8**; mp  $202^{\circ}\text{C}$  dec under nitrogen;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.18 (s, 18 H), 8.13 (s, 2 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  27.4 ( $\text{CH}_3$ ), 41.0 ( $\text{C}(\text{CH}_3)_3$ ), 122.6 (CN), 197.6 (CO);  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$   $-52$ ;  $^{17}\text{O NMR}$  ( $\text{CD}_2\text{Cl}_2$ ) not observed; UV-vis (cyclohexane),  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 268 (4.14), 456 (4.52); solid-state  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  28, 41, 121, 198. Anal. ( $\text{C}_{36}\text{H}_{60}\text{N}_3\text{O}_6\text{Bi}$ ): C, H, N.

**N-Nitroso-5-aza-2,2,8,8-tetramethylnona-3,7-dione (9).** Under nitrogen, acetic anhydride (20 mL, 0.212 mol) was added dropwise to nitric acid (90 %, 12.50 g, 0.198 mol) held at  $0^{\circ}\text{C}$ . After the addition was complete zinc chloride (0.10 g, 0.0007 mol) and urea (0.1 g, 0.0017 mol) were added to the cooled, stirring solution. After this addition was complete, 5-aza-2,2,8,8-tetramethylnona-3,7-dione hydrobromide (4.0 g,

0.014 mol) was added and the mixture stirred for 10 min at 0 °C. During this time the solution turned a dark yellow. The solution was neutralized with sodium carbonate and the aqueous solution extracted with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was removed by vacuum pumping to afford *N*-nitroso-5-aza-2,2,8,8-tetramethylnona-3,7-dione (1.16 g, 32 %). The product was recrystallized from ethanol to give 0.8 g of white needles, mp 133–134 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.22 (s, 9 H), 1.28 (s, 9 H), 4.58 (s, 2 H), 5.32 (s, 2 H); IR (KBr), 1720 cm<sup>-1</sup> (C=O), 1440 cm<sup>-1</sup> (NN=O). Anal. (C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>): C, H, N.

**Reaction of DitBuADPO with Trifluoromethanesulfonic Acid.** Under nitrogen, trifluoromethanesulfonic acid (0.15 g, 1.0 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to DitBuADPO (0.241 g, 1.0 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture turned a light yellow and then colorless. The mixture was stirred at room temperature for 12 h. Removal of the CH<sub>2</sub>Cl<sub>2</sub> and volatiles under vacuo left a yellow solid. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> at -32 °C to give DitBuADPO-HOTf (0.31 g, 80 %): mp 170–175 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.37 (s, 18 H), 5.84 (d, <sup>3</sup>J<sub>PH</sub> = 7.83 Hz, 2 H), 7.81 (d, <sup>3</sup>J<sub>PH</sub> = 6.42 Hz, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.5 (CH<sub>3</sub>), 27.8 (CH<sub>3</sub>), 34.6 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 3.3 Hz), 43.2 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 0.81 Hz), 61.3 (CH<sub>2</sub>, d, <sup>1</sup>J<sub>PC</sub> = 10.8 Hz), 122.5 (CN, d, <sup>1</sup>J<sub>PC</sub> = 4.9 Hz), 171.2 (CO, d, <sup>1</sup>J<sub>PC</sub> = 3.36 Hz), 215.8 (CO, d, <sup>1</sup>J<sub>PC</sub> = 3.17 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -152.6 (d, <sup>1</sup>J<sub>PN</sub> = 93.4 Hz); <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -156; <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 234.2; <sup>13</sup>C gated δ 60.8 (ddt, <sup>1</sup>J<sub>PC</sub> = 10.8 Hz, <sup>1</sup>J<sub>CH</sub> = 136.0 Hz, <sup>3</sup>J<sub>CH</sub> = 1.80 Hz); IR (CsI) 3125, 2976, 1719, 1695, 1481, 1463, 1370, 1255, 1166 cm<sup>-1</sup>. Anal. (C<sub>12</sub>H<sub>21</sub>NO<sub>2</sub>PSO<sub>3</sub>CF<sub>3</sub>): C, H, N.

**Reaction of DitBuADAsO with Trifluoromethanesulfonic Acid.** Under nitrogen, trifluoromethanesulfonic acid (0.15 g, 1.0 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a stirred solution of DitBuADAsO (0.285 g, 1.0 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture turned yellow. The mixture was stirred at room temperature for 12 h. Removal of the CH<sub>2</sub>Cl<sub>2</sub> and volatiles in vacuo left a yellow solid. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> at -32 °C to give 0.146 g (33 %) of DitBuADAsO-HOTf: mp 201–205 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.39 (s, 9 H), 1.42 (s, 9 H), 6.07 (s, 2 H), 8.30 (s, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.6 (CH<sub>3</sub>), 28.1 (CH<sub>3</sub>), 36.9 (C(CH<sub>3</sub>)<sub>3</sub>), 43.6 (C(CH<sub>3</sub>)<sub>3</sub>), 62.6 (CH<sub>2</sub>), 125.9 (CN), 177.0 (CO), 219.5 (CO); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -121; <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -122; IR (CsI): 3132, 2975, 1724, 1680, 1559, 1480, 1467, 1368, 1262 cm<sup>-1</sup>. Anal. (C<sub>12</sub>H<sub>21</sub>NO<sub>2</sub>AsSO<sub>3</sub>CF<sub>3</sub>): C, H, N.

**DitBuADPO Adduct with MeOH (10).** Under nitrogen, methanol (0.016 g, 0.50 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to DitBuADPO (0.121 g, 0.50 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. There was no visible color change upon addition. The mixture was stirred for 0.5 h. The volatiles were removed by vacuum pumping. The remaining colorless oil was dissolved in CD<sub>2</sub>Cl<sub>2</sub> for <sup>1</sup>H NMR and exhibited the following resonances: δ 1.14 (s, 18 H), 3.47 (d, <sup>3</sup>J<sub>PH</sub> = 14.2 Hz, 3 H), 5.97 (d, <sup>3</sup>J<sub>PH</sub> = 33.8 Hz, 2 H), 8.04 (d, <sup>1</sup>J<sub>PH</sub> = 877 Hz, 1 H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -34.4. Methanol-*d*<sub>4</sub> can also be used to oxidatively add to ADPO. In this case the <sup>31</sup>P spectrum shows a triplet at -34.8 <sup>1</sup>J<sub>PD</sub> = 133.7 Hz.

**Rearrangement of 10 to 11.** The phosphorane will rearrange to a phosphite over a period of 0.5 day at room temperature. The <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> consists of the following resonances: δ 1.19 (s, 9 H), 1.21 (s, 9 H), 3.30 (d, <sup>3</sup>J<sub>PH</sub> = 7.2 Hz, 3 H), 4.20 (dd, <sup>2</sup>J<sub>HH</sub> = 18.6 Hz, <sup>3</sup>J<sub>HP</sub> = 10.8 Hz, 1 H), 4.33 (dd, <sup>2</sup>J<sub>HH</sub> = 18.6 Hz, <sup>3</sup>J<sub>HP</sub> = 7.4 Hz, 1 H), 5.64 (d, <sup>3</sup>J<sub>PH</sub> = 6.1 Hz, 1 H). <sup>31</sup>P{<sup>1</sup>H} in (CD<sub>2</sub>Cl<sub>2</sub>) δ 122.4 (s). The deuterated phosphorane also rearranges to exhibit a singlet at 122.4 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra.

**DitBuADPO-*o*-Chloranil.** Under nitrogen, a 200 mL round bottom flask was charged with DitBuADPO (0.490 g, 2.03 mmol) and 100 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was cooled to -78 °C and a solution of *o*-chloranil (0.493 g, 2.01 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The *o*-chloranil color was discharged as the addition proceeded resulting in a pale yellow solution. The mixture was warmed to room temperature, at which point it developed a slight lavender color. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The solid residues were recrystallized from toluene/hexamethylidisiloxane to give DitBuADPO-*o*-chloranil (0.70 g, 71 % yield), mp 235–237 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.15 (s, 18 H), 6.25 (d, <sup>3</sup>J<sub>PH</sub> = 32 Hz, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.9 (CH<sub>3</sub>, s) 31.2 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 9.6 Hz), 108.9 (CN, d, <sup>1</sup>J<sub>PC</sub> = 15.9 Hz), 114.8 (OCCCl, d, <sup>1</sup>J<sub>PC</sub> = 17.6 Hz), 124.7 (OCCCl, s), 141.0 (OCCCl, d, <sup>1</sup>J<sub>PC</sub> = 7.0 Hz), 195.4 (OCCN, s); <sup>13</sup>C gated δ 123.4 (<sup>1</sup>J<sub>CH</sub> = 191.0 Hz, <sup>3</sup>J<sub>CH</sub> = 1.0 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -10.2; <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -275.9 (d, <sup>1</sup>J<sub>PN</sub> = 16.8 Hz). Anal. (C<sub>18</sub>H<sub>20</sub>NO<sub>4</sub>PCl<sub>4</sub>): C, H, N.

**DitBuADAsO-*o*-Chloranil.** Under nitrogen, a 200-mL round-bottom flask was charged with DitBuADAsO (0.570 g, 2.0 mmol) and cooled to -78 °C. A solution of *o*-chloranil (0.50 g, 2.03 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the cooled, stirring solution. As the addition proceeded the solution turned orange. The mixture was warmed to room temperature and the CH<sub>2</sub>Cl<sub>2</sub> removed in vacuo. The residue was recrystallized from toluene/hexamethylidisiloxane to give DitBuADAs-

*o*-chloranil (0.750 g, 70 % yield), mp 164–165 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.22 (s, 18 H), 7.56 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.8 (CH<sub>3</sub>, s), 40.2 (C(CH<sub>3</sub>)<sub>3</sub>, s), 116.6 (OCCCl, s), 122.4 (OCCCl, s), 126.2 (CH, s), 147.5 (OCCCl, s), 190.8 (CO, S); <sup>13</sup>C gated δ 126.2 (<sup>1</sup>J<sub>CH</sub> = 176.2 Hz, <sup>3</sup>J<sub>CH</sub> = 6.2 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -48.6. Anal. (C<sub>18</sub>H<sub>20</sub>NO<sub>4</sub>AsCl<sub>4</sub>): C, H, N, Cl, As.

**DitBuADSbO-*o*-Chloranil.** Under nitrogen, a 200-mL round-bottom flask was charged with DitBuADSbO (0.160 g, 0.50 mmol) and 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. A solution of *o*-chloranil (0.120 g, 0.50 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the stirred solution. After 30 min the CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo and the residue recrystallized from benzene/hexamethylidisiloxane to give DitBuADSbO-*o*-chloranil (0.208 g, 74 % yield), mp 257–259 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.27 (s, 18 H), 7.80 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.6 (CH<sub>3</sub>, s), 40.5 (C(CH<sub>3</sub>)<sub>3</sub>, s), 117.6 (OCCCl, s), 120.3 (OCCCl, s), 123.4 (CN, s), 149.2 (OCCCl, s), 196.1 (OCCN, s); <sup>13</sup>C gated δ 123.4 (<sup>1</sup>J<sub>CH</sub> = 178.7 Hz, <sup>3</sup>J<sub>CH</sub> = 5.0 Hz). IR (CsI) 2967, 1649, 1582, 1439, 1381, 1361, 1339, 1251, 1228, 1140, 1065, 1000, 978 cm<sup>-1</sup>. Anal. (C<sub>18</sub>H<sub>20</sub>NO<sub>4</sub>SbCl<sub>4</sub>): C, H, N, Cl.

**DitBuADPO-HFBA.** Under nitrogen, a heavy walled glass ampule with a screw valve (Teflon fluorocarbon resin) was charged with DitBuADPO (0.241 g, 1.0 mmol) in 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was degassed by the freeze-pump-thaw method (3 times) and cooled to -196 °C. Hexafluorobiacetyl (HFBA) (1.0 mmol) was condensed into the ampule and the valve closed. The mixture was warmed to -78 °C; mixing was accomplished by gentle shaking. The solution was allowed to warm slowly to room temperature with periodic shaking. After several hours at room temperature all of the volatiles were removed by vacuum pumping leaving a colorless solid, crude DitBuADPO-HFBA. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (-35 °C) to give 0.34 g (80%), mp 85 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.17 (s, 9 H), 1.30 (s, 9 H), 5.44 (d, <sup>3</sup>J<sub>PH</sub> = 10.8 Hz, 1 H), 5.71 (d, <sup>3</sup>J<sub>PH</sub> = 12.0 Hz, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.2 (CH<sub>3</sub>), 27.6 (CH<sub>3</sub>), 32.4 (C(CH<sub>3</sub>)<sub>3</sub>), 44.7 (C(CH<sub>3</sub>)<sub>3</sub>), 73.0 (CN, d, <sup>1</sup>J<sub>PC</sub> = 7.6 Hz), 81.7 (POC(CF<sub>3</sub>)<sub>2</sub>, qd, <sup>2</sup>J<sub>PC</sub> = 8.0 Hz, <sup>2</sup>J<sub>CF</sub> = 30.1 Hz), 112.4 (CN, dq, <sup>1</sup>J<sub>PC</sub> = 4.4 Hz, <sup>1</sup>J<sub>CF</sub> = 0.8 Hz), 115.9 (CF<sub>3</sub>, dq, <sup>1</sup>J<sub>PC</sub> = 0.9 Hz, <sup>1</sup>J<sub>CF</sub> = 291.8 Hz), 122.6 (CF<sub>3</sub>, dq, <sup>1</sup>J<sub>PC</sub> = 1.8 Hz, <sup>1</sup>J<sub>CF</sub> = 287.9 Hz), 155.4 (*t*-BuCO, dq, <sup>2</sup>J<sub>PC</sub> = 11.7 Hz, <sup>1</sup>J<sub>CF</sub> = 1.2 Hz), 187.4 (F<sub>3</sub>CC=O, dq, <sup>2</sup>J<sub>PC</sub> = 5.4 Hz, <sup>2</sup>J<sub>CF</sub> = 36.3 Hz), 210.3 (*t*-BuC=O, d, <sup>1</sup>J<sub>PC</sub> = 1.1 Hz); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -72.5 (m, 3 F), -37.6 (m, 3 F); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 159.3 (q, <sup>4</sup>J<sub>PF</sub> = 4.8 Hz); HRMS for (C<sub>16</sub>H<sub>20</sub>NO<sub>4</sub>F<sub>6</sub>P), *m/z* calcd, 435.1034; found, 435.1039. Anal. (C<sub>16</sub>H<sub>20</sub>NO<sub>4</sub>PF<sub>6</sub>): C, H, N.

**DitBuADAsO-HFBA.** Under nitrogen, a heavy-walled ampule with a screw valve was charged with DitBuADAsO (0.290 g, 1.02 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was degassed by the freeze-pump-thaw method (3 times) and finally cooled to -196 °C. HFBA (1.0 mmol) was condensed into the ampule, the valve closed, and the mixture warmed to -78 °C. When the mixture had melted, mixing was accomplished by gentle shaking. The mixture was allowed to sit at room temperature overnight. Removal of the volatiles in vacuo left crude DitBuADAsO-HFBA, which was recrystallized from pentane (-35 °C) to give 0.225 g (47%); mp 128–131 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.22 (s, 18 H), 7.47 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.7 (CH<sub>3</sub>), 40.2 (C(CH<sub>3</sub>)<sub>3</sub>), 121.0 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 271.0 Hz), 125.8 (CN), 132.4 (CCF<sub>3</sub>, m), 191.0 (CO); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -63.9; <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -42 (br). Anal. (C<sub>16</sub>H<sub>20</sub>NO<sub>4</sub>AsF<sub>6</sub>): C, H, N.

**DitBuADSbO-HFBA.** Under nitrogen, a heavy-walled glass ampule with a screw valve was charged with DitBuADSbO (0.332 g, 1.0 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was degassed by the freeze-pump-thaw method (3 times) and finally cooled to -196 °C. HFBA (1.0 mmol) was condensed into the ampule and the valve closed. The mixture was warmed to -78 °C. When the mixture had melted, mixing was accomplished by gentle shaking. At this point a green color was observed which soon vanished to give a dark red solution. The mixture was allowed to warm to room temperature with periodic shaking. All of the volatiles were removed by vacuum pumping and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (-35 °C) to give 0.4 g (80 % yield) of DitBuADSbO-HFBA as a yellow-orange solid: mp 132–134 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.27 (s, 18 H), 7.73 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.6 (CH<sub>3</sub>), 40.5 (C(CH<sub>3</sub>)<sub>3</sub>), 122.7 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 270.0 Hz), 123.0 (CN), 133.6 (CCF<sub>3</sub>, q, <sup>2</sup>J<sub>CF</sub> = 44.5 Hz), 196.2 (CO); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -63.9; MS EI (70 eV) M<sup>+</sup>, *m/z* 526. Anal. (C<sub>16</sub>H<sub>20</sub>NO<sub>4</sub>SbF<sub>6</sub>): C, H, N.

**DitBuADSbO-2HFBA.** Under nitrogen, a heavy-walled glass ampule with a screw valve was charged with DitBuADSbO (0.340 g, 1.02 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was degassed by the freeze-pump-thaw method (3 times) using liquid nitrogen as the coolant and then cooled to -196 °C. HFBA (2.04 mmol) was condensed into the ampule and the valve closed. The mixture was warmed to -78 °C. When the mixture had melted, mixing was accomplished by gentle shaking. At this point the solution turned from a dark red to green then to a light yellow. The ampule was allowed to remain at room temperature for 3 h. Removal

of the volatiles in vacuo left crude DitBuADSbO·2HFBA. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give 0.21 g (30 % yield) as a light yellow solid: mp 105–108 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.23 (s, 18 H), 7.29 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.9 (CH<sub>3</sub>), 40.9 (C(CH<sub>3</sub>)<sub>3</sub>), 79 (CCF<sub>3</sub>, m), 97 (CCF<sub>3</sub>, m), 119.4 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 272.7 Hz), 122.2 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 287.9 Hz), 123.4 (CN, s), 197.0 (CO); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -79.1 (s, 6 F), -65.2 (s, 6 F); MS EI (70 eV), (M<sup>+</sup> - *t*-Bu), *m/z* 663. Anal. (C<sub>20</sub>H<sub>20</sub>NO<sub>6</sub>SbF<sub>12</sub>): C, H, N.

**Triphenylphosphine Tetrachlorocatecholate.**<sup>46</sup> Under nitrogen, a 100-mL Schlenk flask was charged with 20 mL of dry CH<sub>2</sub>Cl<sub>2</sub> and triphenylphosphine (2.62 g, 10.0 mmol). The solution was stirred, and *o*-chloranil (2.46 g, 10.0 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise over a period of 10 m at which point a brown precipitate was formed. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from benzene/hexamethyldisiloxane to yield 3.5 g (70 %) of triphenylphosphine tetrachlorocatecholate: mp 220–224 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.44 (m, 3 H), 7.68 (m, 2 H).

**Triphenylarsine Tetrachlorocatecholate.** Under nitrogen, a 100-mL Schlenk flask was charged with 30 mL of dry CH<sub>2</sub>Cl<sub>2</sub> and triphenylarsine (3.06 g, 10.0 mmol). The solution was stirred and *o*-chloranil (2.46 g, 10.0 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise over a period of 10 min, at which point the solution became dark green. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from toluene/hexamethyldisiloxane to yield 3.7 g (67 %) of the yellow crystalline triphenylarsine tetrachlorocatecholate: mp 192–194 °C (lit.<sup>47</sup> 193–195 °C from benzene/petroleum ether); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.50 (m, 3 H), 7.75 (m, 2 H). Anal. (C<sub>24</sub>H<sub>15</sub>AsO<sub>2</sub>Cl<sub>4</sub>): C, H.

**Triphenylantimony Tetrachlorocatecholate.** Under nitrogen, a 100-mL Schlenk flask was charged with 20 mL of dry CH<sub>2</sub>Cl<sub>2</sub> and triphenylantimony (3.5 g, 10.0 mmol). The solution was stirred and *o*-chloranil (2.46 g, 10.0 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise over a period of 10 m. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from toluene/hexamethyldisiloxane to yield 4.0 g (67 %) of triphenylstibine tetrachlorocatecholate: mp 183–185 °C (lit.<sup>45</sup> 185 °C); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.59 (m, 3 H), 7.80 (m, 2 H). Anal. (C<sub>24</sub>H<sub>15</sub>SbO<sub>2</sub>Cl<sub>4</sub>): C, H, Sb, Cl.

**DitBuADPO-HFB.** Under nitrogen, a 40-mL thick-walled glass bomb with a valve (Teflon fluorocarbon resin) was charged with DitBuADPO (0.723 g, 3.00 mmol) and 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was degassed on a vacuum line by three successive freeze–thaw cycles using liquid nitrogen. Hexafluoro-2-butyne (HFB) (3.10 mmol) was condensed into the bomb at -196 °C. The valve was closed and the mixture was slowly warmed to room temperature with periodic shaking. The solution gradually turned a light yellow. The solution was kept at room temperature for 12 h. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from pentane to give DitBuADPO-HFB (0.870 g, 68 % yield): mp 96–97 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.12 (s, 9 H), 1.30 (s, 9 H), 5.53 (d, 1 H, vinyl H, <sup>3</sup>J<sub>PH</sub> = 12.2 Hz), 5.64 (dm, 1 H, <sup>3</sup>J<sub>PH</sub> = 4.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.1 (CH<sub>3</sub>), 27.6 (CH<sub>3</sub>), 32.3 (C(CH<sub>3</sub>)<sub>3</sub>, s), 45.1 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>CP</sub> = 2.4 Hz), 75.1 (NCC<sub>2</sub>, d, <sup>1</sup>J<sub>PC</sub> = 15.2 Hz), 113.8 (NCH olefinic, d, <sup>1</sup>J<sub>PC</sub> = 6.3 Hz), 121.6 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 274.8 Hz), 122.2 (CF<sub>3</sub>, dq, <sup>1</sup>J<sub>CF</sub> = 272.6 Hz, <sup>1</sup>J<sub>PC</sub> = 13.2 Hz), 140.0 (PCCF<sub>3</sub>, dq, <sup>1</sup>J<sub>PC</sub> = 23.6 Hz, <sup>2</sup>J<sub>CF</sub> = 35.6 Hz, <sup>3</sup>J<sub>CF</sub> = 5.2 Hz), 146.5 (PCCF<sub>3</sub>, dq, <sup>1</sup>J<sub>PC</sub> = 83.6 Hz, <sup>2</sup>J<sub>CF</sub> = 35.2 Hz, <sup>3</sup>J<sub>CF</sub> = 2.0 Hz), 154.2 (CCOP, d, <sup>1</sup>J<sub>PC</sub> = 10.4 Hz), 207.2 (C=O, d, <sup>1</sup>J<sub>PC</sub> = 4.7 Hz); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -56.2 (m, 3 F), -60.6 (dq, 3 F, <sup>1</sup>J<sub>FF</sub> = 9.0 Hz, <sup>1</sup>J<sub>PF</sub> = 3.0 Hz); <sup>13</sup>C gated δ 75.1 (ddd, <sup>1</sup>J<sub>HC</sub> = 148.0 Hz, <sup>3</sup>J<sub>HC</sub> = 1.0 Hz, <sup>1</sup>J<sub>PC</sub> = 15.2 Hz), 113.8 (ddd, <sup>1</sup>J<sub>HC</sub> = 189.3 Hz, <sup>3</sup>J<sub>HC</sub> = 4.4 Hz, <sup>1</sup>J<sub>PC</sub> = 6.3 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 163.6 (br s); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -289.6 (d, <sup>1</sup>J<sub>PN</sub> = 64.0 Hz). Anal. (C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>F<sub>6</sub>P): C, H, N, P.

**DitBuADPO-2HFB.** Under nitrogen, a 40-mL glass bomb with a screw valve was charged with DitBuADPO-HFB (0.350 g, 0.87 mmol) and 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. On a vacuum line the solution was degassed by three successive freeze–thaw cycles. HFB (2.64 mmol) was condensed into the bomb with liquid nitrogen as the coolant. The valve was closed. The solution was warmed to -78 °C and mixed by shaking prior to warming to room temperature. The bomb was heated at 105 °C for 8 days. The contents of the bomb were cooled to room temperature and the CH<sub>2</sub>Cl<sub>2</sub> removed in vacuo. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give DitBuADPO-2HFB (0.230 g, 47 % yield): mp 125–126 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.10 (s, 18 H), 6.01 (d, 2 H, <sup>3</sup>J<sub>PH</sub> = 36.8 Hz); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -57.4 (m, 6 F), -59.1 (m, 6 F); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -285.1 (d, <sup>1</sup>J<sub>PN</sub> = 16.0 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -21.8 (sept., <sup>1</sup>J<sub>PF</sub> = 7.4 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 27.1 (CH<sub>3</sub>, s), 32.6 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 3.8 Hz), 102.8 (CN, d, <sup>1</sup>J<sub>PC</sub> = 18.4 Hz), 120.7

(CF<sub>3</sub>, dq, <sup>1</sup>J<sub>FC</sub> = 277.0 Hz, <sup>1</sup>J<sub>PC</sub> = 31.4 Hz), 121.1 (CF<sub>3</sub>, dq, <sup>1</sup>J<sub>FC</sub> = 272.7 Hz, <sup>1</sup>J<sub>PC</sub> = 11.3 Hz), 144.4 (PCCF<sub>3</sub>, dq, <sup>2</sup>J<sub>FC</sub> = 39.5 Hz, <sup>1</sup>J<sub>PC</sub> = 159.4 Hz), 141.7 (COP, d, <sup>3</sup>J<sub>PC</sub> = 4.9 Hz); <sup>13</sup>C gated δ 102.8 (ddd, <sup>1</sup>J<sub>HC</sub> = 192.5 Hz, <sup>2</sup>J<sub>PC</sub> = 18.4 Hz, <sup>3</sup>J<sub>HC</sub> = 1.1 Hz); UV-vis (cyclohexane), λ<sub>max</sub> (log ε) 225 (4.11), 552 (1.85) nm. Anal. (C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub>PF<sub>12</sub>): C, H, N, P, F.

**DitBuADSbO-2HFB.** Under nitrogen, a 40-mL glass bomb with a threaded valve was charged with DitBuADSbO (0.370 g, 1.11 mmol) and 15 mL of CH<sub>2</sub>Cl<sub>2</sub>. On a vacuum line the solution was degassed by three successive freeze–thaw cycles at liquid nitrogen temperatures. HFB (2.30 mmol) was condensed into the bomb and the valve was closed. The bomb was warmed to -78 °C and mixed (with periodic shaking), at which time the dark color of DitBuADSbO disappeared. The bomb was warmed to room temperature and allowed to stand for 12 h. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo and the residue recrystallized from pentane to give DitBuADSbO-2HFB (0.520 g, 71 % yield): mp 110–112 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.22 (s, 18 H), 6.17 (s, 2 H); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -52.2 (q, 6 F, <sup>1</sup>J<sub>FF</sub> = 9.6 Hz), -59.6 (q, 6 F, <sup>1</sup>J<sub>FF</sub> = 9.6 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -318.7; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 27.1 (CH<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 1.1 Hz) 44.5 (C(CH<sub>3</sub>)<sub>3</sub>, s), 79.7 (NCH, s br), 121.8 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 277.3 Hz), 124.9 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 272.1 Hz), 145.3 (CCF<sub>3</sub>, qq, <sup>2</sup>J<sub>CF</sub> = 33.1 Hz, <sup>3</sup>J<sub>CF</sub> = 6.4 Hz), 161.2 (CCF<sub>3</sub>, qm, <sup>2</sup>J<sub>CF</sub> = 39.3 Hz), 211.6 (CO, s); <sup>13</sup>C gated δ 79.7 (dd, <sup>1</sup>J<sub>CH</sub> = 146.9, <sup>3</sup>J<sub>CH</sub> = 4.8 Hz). Anal. (C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub>SbF<sub>12</sub>): C, H, N, Sb.

**Preparation of DitBuADAsO-2HFB.** Under nitrogen, a 40-mL glass bomb with a threaded valve was charged with DitBuADAsO (0.571 g, 2.00 mmol) and 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was degassed on a vacuum line by three successive freeze–thaw cycles using liquid nitrogen. HFB (6.00 mmol) was condensed into the bomb using liquid nitrogen as the coolant. The bomb was warmed to -78 °C and mixed by shaking. The bomb was warmed to room temperature and kept for 12 h. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give DitBuADAsO-2HFB (0.623 g, 51 % yield): mp 105–108 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.23 (s, 18 H), 5.76 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.7 (CH<sub>3</sub>), 44.3 (C(CH<sub>3</sub>)<sub>3</sub>), 80.6 (NCH, q, <sup>1</sup>J<sub>CF</sub> = 1.0 Hz), 120.2 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 276.3 Hz), 122.0 (CF<sub>3</sub>, q, <sup>1</sup>J<sub>CF</sub> = 273.3 Hz), 141.8 (CCF<sub>3</sub>, qq, <sup>2</sup>J<sub>CF</sub> = 34.5 Hz, <sup>3</sup>J<sub>CF</sub> = 5.2 Hz), 152.0 (CCF<sub>3</sub>, qm, <sup>2</sup>J<sub>CF</sub> = 40.3 Hz), 208.1 (CO, s); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -54.0 (q, 6 F, <sup>1</sup>J<sub>FF</sub> = 9.0 Hz), -59.0 (q, 6 F, <sup>1</sup>J<sub>FF</sub> = 9.0 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -244.1. Anal. (C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub>AsF<sub>12</sub>): C, H, N, F, As.

**DitBuADPO-Cl<sub>2</sub>.** Under nitrogen, a solution of 5-aza-2,2,8,8-tetramethylnona-3,7-dione (**4a**) (2.56 g, 12.0 mmol) in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to phosphorus pentachloride (2.50 g, 12.0 mmol) in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> held at -78 °C. When the addition was complete, triethylamine (5.0 mL, 36.0 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise, the solution turned dark purple. The mixture was warmed slowly to room temperature and stirred for 12 h. Removal of the volatiles in vacuo left a dark purple solid. The purple solid was extracted with pentane to give a dark purple solution containing DitBuADPO-Cl<sub>2</sub> and a light purple solid (crude triethylamine hydrochloride). The pentane filtrates were evaporated to yield a purple solid (2.83 g, 76 %, crude DitBuADPO-Cl<sub>2</sub>). The product was sublimed (0.005 torr, 70 °C) to give 2.4 g (65 % yield) of light yellow-green crystals: mp 105 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.17 (s, 18 H), 6.15 (d, <sup>3</sup>J<sub>PH</sub> = 35.8 Hz, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 27.5 (CH<sub>3</sub>, s), 32.2 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 6.8 Hz), 102.3 (CN, d, <sup>1</sup>J<sub>PC</sub> = 23.0 Hz), 152.5 (CO, d, <sup>1</sup>J<sub>PC</sub> = 8.1 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -262.4 (d, <sup>1</sup>J<sub>PN</sub> = 13.7 Hz); <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -267; <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -24.9; HRMS for (C<sub>12</sub>H<sub>20</sub>NCl<sub>2</sub>PO<sub>2</sub>) *m/z* calcd, 311.0609; found, 311.0590. UV-vis, (cyclohexane) λ<sub>max</sub> (log ε) 302 (4.95), 230 (4.48) nm. Anal. (C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>PCL<sub>2</sub>): C, H, N.

**DitBuADPO-Br<sub>2</sub>.** Under nitrogen, a solution of 5-aza-2,2,8,8-tetramethylnona-3,7-dione (**4a**) (2.56 g, 12.0 mmol) in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to phosphorus pentabromide (5.16 g, 12.0 mmol) in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> held at -78 °C. When the addition was complete, triethylamine (5.0 mL, 36.0 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise, the solution turned dark purple. The mixture was warmed slowly to room temperature and stirred for 12 h. Removal of the volatiles in vacuo left a dark purple solid. The dark purple solid was extracted with pentane to give an orange-brown solution containing DitBuADPO-Br<sub>2</sub> and a purple solid (crude triethylamine hydrochloride). The mother liquors were evaporated to yield a brown solid 2.8 g (60 % yield). Crude DitBuADPO-Br<sub>2</sub> was sublimed (0.005 torr, 70 °C) to give an orange crystalline solid: mp 138–140 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.18 (s, 18 H), 6.20 (d, <sup>3</sup>J<sub>PH</sub> = 35.9 Hz, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 27.5 (CH<sub>3</sub>, s), 32.4 (C(CH<sub>3</sub>)<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 5.6 Hz), 102.9 (CN, d, <sup>1</sup>J<sub>PC</sub> = 23.3 Hz), 154.5 (CO, d, <sup>1</sup>J<sub>PC</sub> = 10.7 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -256.8 (d, <sup>1</sup>J<sub>PN</sub> = 6.22 Hz); <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -257; <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -90.7; HRMS for (C<sub>12</sub>H<sub>20</sub>NBr<sub>2</sub>PO<sub>2</sub>) *m/z* calcd 398.9598; measured 398.9595; UV-vis (cyclohexane), λ<sub>max</sub> (log ε) 360 (3.15), 234 (3.53) nm. Anal. (C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>PBr<sub>2</sub>): C, H, N.

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**DitBuADSbO-Cl<sub>2</sub> from SbCl<sub>5</sub> and 5-Aza-2,2,8,8-tetramethyl-nona-3,7-dione (4a).** Under nitrogen, a 250-mL flask was charged with 5-aza-2,2,8,8-tetramethyl-nona-3,7-dione (**4a**) (0.427 g, 2.00 mmol) and 100 mL of CH<sub>2</sub>Cl<sub>2</sub>. The ligand solution was cooled to -78 °C, and a solution of SbCl<sub>5</sub> (0.598 g, 2.00 mmol) in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise over 30 min. The reaction mixture became a bright yellow. After the addition was complete a solution of triethylamine (0.610 g, 6.00 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The reaction mixture turned a dark orange color which upon warming to room temperature became red. The solution was filtered and the CH<sub>2</sub>Cl<sub>2</sub> removed from the mother liquors in vacuo. The residue was recrystallized from pentane/CH<sub>2</sub>Cl<sub>2</sub> to give DitBuADSbO-Cl<sub>2</sub> (0.60 g, 75% yield): mp 181–183 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.38 (s, 18 H), 7.94 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 27.0 (CH<sub>3</sub>, s), 41.0 (C(CH<sub>3</sub>)<sub>3</sub>, s), 119.3 (NCH, s), 202.9 (CO, s). Anal. (C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>SbCl<sub>2</sub>): C, H, N, Cl.

**DitBuADSbO-Cl<sub>2</sub> from DitBuADSbO and SbCl<sub>5</sub>.** Under nitrogen, a 250-mL flask was charged with DitBuADSbO (0.340 g, 1.02 mmol) and 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. This solution was cooled to -78 °C, and a solution of SbCl<sub>5</sub> (0.330 g, 1.10 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The reaction mixture became a bright orange with some precipitate. After the addition was complete and the mixture was warmed to room temperature, at which point the precipitate dissolved. The CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give orange crystals of DitBuADSbO-Cl<sub>2</sub>·(SbCl<sub>5</sub>) (0.592 g, 75% yield): mp 130–132 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.39 (s, 18 H), 7.94 (s, 2 H). Anal. (C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>Sb<sub>2</sub>Cl<sub>3</sub>): C, H, N, Cl, Sb.

**DitBuADSbO-Cl<sub>2</sub> from DitBuADSbO and Cl<sub>2</sub>.** A 5-mm NMR tube was charged with DitBuADSbO (0.035 g, 0.11 mmol) and 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub>. On a vacuum line the solution was degassed by three successive freeze-thaw cycles with liquid nitrogen. Chlorine gas (0.12 mmol) was condensed into the tube using liquid nitrogen as the coolant. The tube was sealed and warmed to -78 °C. The solution was bright orange at -78 °C and the color deepened slightly as the mixture was warmed to room temperature. The NMR spectra indicated the presence of DitBuADSbO-Cl<sub>2</sub> in >70% yield with resonances at δ 1.38 (s, 18 H), 7.95 (s, 2 H). There were numerous other resonances in the spectra in the *tert*-butyl region. Under nitrogen the tube was broken open and the CD<sub>2</sub>Cl<sub>2</sub> removed in vacuo. The residue was recrystallized from benzene/hexamethyldisiloxane and then CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane to give orange crystals of DitBuADSbO-Cl<sub>2</sub>·1/2SbCl<sub>5</sub> (0.020 g); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.38 (s, 18 H), 7.95 (s, 2 H). Anal. for (C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>SbCl<sub>2</sub>)<sub>1/2</sub>·SbCl<sub>5</sub>: Calcd: C, 27.86; H, 3.87; N, 2.70; Cl, 24.01. Found: C, 28.65; H, 4.05; N, 2.57; Cl, 22.8.

**DitBuADAsO-Cl<sub>2</sub>.** Under nitrogen, a 100-mL flask was charged with DitBuADAsO (0.500 g, 1.75 mmol) and 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was cooled to -78 °C and a solution of SO<sub>2</sub>Cl<sub>2</sub> (0.242 g, 1.79 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring. The solution turned deep red and after 30 min was allowed to warm to -35 °C, at which temperature the CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give DitBuADAsO-Cl<sub>2</sub> (0.546 g, 88% yield): mp 65–74 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.35 (s, 18 H), 7.70 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.6 (CH<sub>3</sub>, s), 40.3 (C(CH<sub>3</sub>)<sub>3</sub>, s), 121.2 (NCH, s), 196.7 (CO, s). The instability of the sample precluded accurate elemental analysis. A sample shipped at -78 °C for analysis gave the following. Anal. Calcd for (C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>AsCl<sub>2</sub>): C, 40.48; H, 5.66; N, 3.93. Found C, 37.71; H, 5.35; N, 3.57.

**DitBuADPO-CH<sub>3</sub>/Cl.** Under nitrogen, a solution of MeLi (1.2 mL of a 1.7 M solution in Et<sub>2</sub>O, 2.0 mmol) was added to a stirred solution of DitBuADPO-Cl<sub>2</sub> (0.624 g, 2.0 mmol) in 50 mL of Et<sub>2</sub>O at room temperature. A white precipitate (LiCl) resulted upon addition. The mixture was stirred for 3 h. The LiCl was removed by filtration and the clear, slightly pinkish, solution was concentrated by removing some of the Et<sub>2</sub>O in vacuo. The solution was placed in the freezer at -35 °C. Small cubelike crystals were grown overnight (0.35 g, 60% yield): mp 109–111 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.12 (s, 18 H), 2.38 (d, <sup>2</sup>J<sub>PH</sub> = 18.8 Hz, 3 H), 5.99 (d, <sup>3</sup>J<sub>PH</sub> = 35.6 Hz, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 27.2 (PCH<sub>3</sub>, d, 2.00 Hz), 27.4 (CH<sub>3</sub>, s), 32.2 (C(CH<sub>3</sub>)<sub>3</sub>, d, J<sub>PC</sub> = 2.2 Hz), 102.0 (d, J<sub>PC</sub> = 13.9 Hz), 151.2 (d, J<sub>PC</sub> = 5.7 Hz); <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -0.8; <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -271, (d, <sup>1</sup>J<sub>PN</sub> = 16.9 Hz); <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -272; HRMS for (C<sub>13</sub>H<sub>23</sub>NO<sub>2</sub>PCL), *m/z* calcd 291.1154; found, 291.1152. Anal. (C<sub>13</sub>H<sub>23</sub>NO<sub>2</sub>PCL): C, H, N.

**DitBuADPO-(CH<sub>3</sub>)<sub>2</sub>.** Under nitrogen, MeLi (8.4 mL of a 1.7 M solution in Et<sub>2</sub>O, 4.0 mmol) was added to a stirred solution of DitBuADPO-Cl<sub>2</sub> (0.624 g, 2.0 mmol) in 50 mL of Et<sub>2</sub>O at room temperature. The addition resulted in a white precipitate (LiCl) and a slightly pink solution. The mixture was stirred for 3 h. The LiCl was removed by filtration. All of the volatiles were removed by vacuum pumping whereupon a light pink solid remained, crude DitBuADPO-(CH<sub>3</sub>)<sub>2</sub> (0.48 g, 90% yield). The product was recrystallized from Et<sub>2</sub>O at -35 °C to give clear yellow needles: mp 69–70 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.12 (s,

18 H), 1.57 (d, <sup>2</sup>J<sub>PH</sub> = 14.8 Hz, 6 H), 5.31 (d, <sup>3</sup>J<sub>PH</sub> = 31.2 Hz, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 20.9 (CH<sub>3</sub>, d, <sup>1</sup>J<sub>PC</sub> = 126.9 Hz), 27.3 (C(CH<sub>3</sub>)<sub>3</sub>, s), 31.7 (C(CH<sub>3</sub>)<sub>3</sub>, d, J<sub>PC</sub> = 1.7 Hz), 99.8 (CN, d, J<sub>PC</sub> = 15.5 Hz), 150.0 (CO, d, J<sub>PC</sub> = 3.8 Hz); <sup>13</sup>C gated δ 99.8 (<sup>3</sup>J<sub>CH</sub> = 0.9 Hz, <sup>1</sup>J<sub>CH</sub> = 186.6 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -9.1; <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -303 (d, <sup>1</sup>J<sub>PN</sub> = 17.4 Hz); <sup>14</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -306; HRMS for (C<sub>14</sub>H<sub>26</sub>NO<sub>2</sub>P), *m/z* calcd 271.1701; found, 271.1687. Anal. (C<sub>14</sub>H<sub>26</sub>NO<sub>2</sub>P): C, H, N.

**(DitBuADPO)<sub>2</sub>PtI<sub>2</sub>.** Under nitrogen, a solution of DitBuADPO (0.241 g, 1.0 mmol) in 3 mL of toluene was added dropwise to (1,5-cyclooctadiene)platinum(II) iodide (0.279 g, 0.50 mmol) suspended in 20 mL of toluene. After the addition was complete the mixture turned a clear golden yellow. The solution was stirred at room temperature for several hours. The toluene was removed by vacuum pumping to induce crystallization at which point the mixture was placed in the freezer at -35 °C. After 3 days 0.394 g of yellow crystalline (DitBuADPO)<sub>2</sub>PtI<sub>2</sub> was isolated as the toluene adduct (80% yield): mp 245–247 °C dec (loses solvent at 100 °C). (DitBuADPO)<sub>2</sub>PtI<sub>2</sub> was recrystallized from hot benzene at room temperature: mp 245–247 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.20 (s, 18 H), 5.95 (dd, <sup>3</sup>J<sub>PH</sub> = 29.0 Hz, <sup>4</sup>J<sub>PH</sub> = 16.7 Hz, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 26.7 (CH<sub>3</sub>), 32.1 (C(CH<sub>3</sub>)<sub>3</sub>), 113.9 (CN), 156.0 (CO); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -276 (dd, <sup>1</sup>J<sub>PN</sub> = 44.8 Hz, <sup>2</sup>J<sub>PN</sub> = 108 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 126.5 (d, <sup>1</sup>J<sub>PP</sub> = 5.622 Hz), <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -3487 (t, <sup>1</sup>J<sub>PPt</sub> = 5.622). Anal. (C<sub>24</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>PtI<sub>2</sub>·1/4C<sub>6</sub>H<sub>6</sub>): C, H, N.

**(DitBuADSbO)<sub>2</sub>PtI<sub>2</sub>.** Under nitrogen, a solution of DitBuADSbO (0.332 g, 1.0 mmol) in 5 mL of toluene was added dropwise to (1,5-cyclooctadiene)platinum(II) iodide (0.279 g, 0.50 mmol) in 10 mL of toluene. After the first three drops of the DitBuADSbO solution the mixture turned very dark. After the addition was complete the mixture was stirred at room temperature, at which time a black precipitate became evident. The mixture was stirred for 12 h at room temperature. The solution was filtered to yield 0.457 g of (DitBuADSbO)<sub>2</sub>PtI<sub>2</sub> (80%): mp 166 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.24 (s, 18 H), 8.38 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 28.2 (CH<sub>3</sub>), 41.1 (C(CH<sub>3</sub>)<sub>3</sub>), 123.3 (CN), 195.2 (CO); <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -3405. Anal. (C<sub>24</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>Sb<sub>2</sub>PtI<sub>2</sub>): C, H, N.

**[(DitBuADSbO)Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup>.** Under nitrogen, DitBuADSbO (0.033 g, 0.10 mmol) in 5 mL of ether was added dropwise to a slurry of [(CH<sub>3</sub>)<sub>2</sub>C=O](Ph<sub>3</sub>P)<sub>2</sub>Pt(CH<sub>3</sub>)<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (0.110 g, 0.10 mmol) in 10 mL of Et<sub>2</sub>O. Upon addition of the first drop a light red suspension became evident. After the addition was complete the mixture turned a dark red. The mixture was stirred for 12 h at room temperature. The ether was removed by vacuum pumping and the dark red solid dissolved in CH<sub>2</sub>Cl<sub>2</sub>/hexamethyldisiloxane. Small red crystals of [(DitBuADSbO)Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexamethyldisiloxane at -35 °C over a period of several weeks (0.04 g, 30%): mp 221 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -0.74 (t, <sup>3</sup>J<sub>PH</sub> = 6.6 Hz, 3 H), 1.43 (s, 18 H), 7.41 (m, 30 H), 8.72 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 3.4 (PtCH<sub>3</sub>, dd), 27.9 (CH<sub>3</sub>, s), 41.1 (C(CH<sub>3</sub>)<sub>3</sub>, s), 123.9 (CN, s), 128 (Ph, mult), 131 (Ph, mult), 134 (Ph, mult), 195.6 (CO, s); <sup>31</sup>P{<sup>1</sup>H} NMR δ 19.4 (apparent dt due to <sup>195</sup>Pt satellites, <sup>2</sup>J<sub>PP</sub> = 15.5 Hz, <sup>1</sup>J<sub>PPt</sub> = 2066 Hz), 37.3 (apparent dt due to <sup>195</sup>Pt satellites, <sup>2</sup>J<sub>PP</sub> = 15.5 Hz, <sup>1</sup>J<sub>PPt</sub> = 3041 Hz); <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 3174 (dd, <sup>1</sup>J<sub>PPt</sub> = 3041 Hz, <sup>1</sup>J<sub>PPt</sub> = 2066 Hz).

**Reaction of DitBuADPO-Cl<sub>2</sub> with Tris(dimethylamino)sulfur Difluorotrimethylsiliconate (TASF) and Tris(dimethylamino)sulfur Bifluoride.** Under nitrogen, a solution of TASF and TASF<sup>+</sup>FHF<sup>-</sup> (3:7) in 5 mL of THF was added dropwise to DitBuADPO-Cl<sub>2</sub> (0.312 g, 1.0 mmol) in 50 mL of THF. After the addition was complete an intense pink solution appeared. The mixture was stirred overnight at room temperature. The solution was filtered to give a red-pink solution and a white precipitate (TASCl). Removal of the THF in vacuo left a cream-colored solid (0.1 g, 33% yield). The light colored solid was dissolved in dichloromethane and placed in the freezer (-35 °C). After several days, micro-fine colorless, crystals appeared: mp 180–181 °C; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.06 (s, 9 H), 1.23 (s, 9 H), 4.52 (m, 1 H), 6.5 (ddd, <sup>3</sup>J<sub>PH</sub> = 23.3 Hz, <sup>4</sup>J<sub>FH</sub> = 1.6 Hz, 1 H), 7.85 (dd, <sup>3</sup>J<sub>PH</sub> = 36.0 Hz, <sup>4</sup>J<sub>FH</sub> = 0.9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 24.9 (CH<sub>3</sub>, d, J<sub>PC</sub> = 1.0 Hz), 25.9 (CH<sub>3</sub>, s), 33.1 (C(CH<sub>3</sub>)<sub>3</sub>, d, J<sub>PC</sub> = 10.4 Hz), 35.2 (C(CH<sub>3</sub>)<sub>3</sub>, dd, J<sub>PC</sub> = 6.9 Hz, J<sub>FC</sub> = 4.2 Hz), 92.7 (OCH, dq, J<sub>PC</sub> = 4.8 Hz, J<sub>FC</sub> = 2.4 Hz), 97.8 (CN, d, J<sub>PC</sub> = 22.5 Hz), 148.8 (CN, d of mult, J<sub>PC</sub> = 27.1 Hz), 171.7 (C=CCO, mult); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -112.8 (q, <sup>1</sup>J<sub>FP</sub> = 782 Hz); <sup>19</sup>F{<sup>1</sup>H} δ -46.1 (ddd, <sup>1</sup>J<sub>PF</sub> = 782 Hz, <sup>2</sup>J<sub>FF</sub> = 42.5 Hz), -55.2 (dd, <sup>1</sup>J<sub>PF</sub> = 782 Hz, <sup>2</sup>J<sub>FF</sub> = 45.7 Hz), -80.4 (ddd, <sup>1</sup>J<sub>PF</sub> = 782 Hz, <sup>2</sup>J<sub>PF</sub> = 45.5 Hz, <sup>2</sup>J<sub>PF</sub> = 42.7 Hz); <sup>15</sup>N NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -124 (mult); HRMS for (C<sub>12</sub>H<sub>21</sub>NO<sub>2</sub>PF<sub>3</sub>), *m/z* calcd, 299.1260; found, 299.1259.

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Registry No. **4a**, 88686-46-8; **4a**·HBr, 105858-01-3; **4b**, 105858-04-6; **4b**·HBr, 105858-03-5; **4c**, 105858-06-8; **4c**·HBr, 105858-05-7; **8**, 96412-32-7; **9**, 105881-93-4; **10**, 105858-17-1; **11**, 105881-94-5; DiBuADPO, 88686-45-7; DiBuADAsO, 93684-26-5; DiBuADSbO, 105858-07-9; DiAdADPO, 105858-08-0; DiAdADAsO, 105858-09-1; DiAdADSbO, 105858-10-4; DiPhADAsO, 105858-11-5; DiPhADSbO, 105858-12-6; DiBuADPO·HOTf, 105858-14-7; DiBuADAsO·HOTf, 105858-16-0; DiBuADPO·*o*-Chloranil, 105858-18-2; DiBuADAsO·*o*-Chloranil, 105858-29-5; DiBuADSbO·*o*-Chloranil, 105858-30-8; DiBuADPO·HFBA, 105881-95-6; DiBuADPO·HFB, 105858-19-3; DiBuADPO·2HFB, 105858-20-6; DiBuADAsO·HFBA, 105858-31-9; DiBuADAsO·2HFB, 105899-58-9; DiBuADSbO·HFBA, 97921-06-7; DiBuADSbO·2HFB, 105858-33-1; DiBuADSbO·2HFB, 105858-21-7; DiBuADPO·Cl<sub>2</sub>, 105858-22-8; DiBuADPO·Br<sub>2</sub>, 105858-23-9; DiBuADSbO·Cl<sub>2</sub>, 105858-24-0; DiBuADPO·CH<sub>3</sub>/Cl, 105858-26-2; DiBuADPO·(CH<sub>3</sub>)<sub>2</sub>, 105858-27-3; DiBuADAsO·Cl<sub>2</sub>, 105858-25-1; DiBuADPO·HF<sub>3</sub>, 105858-34-2; HFBA, 685-24-5; HFB, 692-50-2; TASF, 105858-28-4; [(DiBuADSbO)Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, 104130-28-1;

(DiBuADPO)<sub>2</sub>PtI<sub>2</sub>, 99688-40-1; (DiBuADSbO)<sub>2</sub>PtI<sub>2</sub>, 104130-26-9; [((CH<sub>3</sub>)<sub>2</sub>C=O)(PPh<sub>3</sub>)<sub>2</sub>PtCH<sub>3</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, 104130-30-5; 1-bromo-3,3-dimethyl-2-butanone, 5469-26-1; 5-aza-5-benzyl-2,2,8,8-tetramethyl-3,7-dione hydrobromide, 105858-00-2; benzylamine, 100-46-9; 1-adamantylbromomethyl ketone, 5122-82-7; 3-aza-3-benzyl-1,5-di-1-adamantylpentane-1,5-dione hydrobromide, 105858-02-4;  $\alpha$ -bromoacetophenone, 70-11-1; 3-aza-3-benzyl-1,5-diphenylpentane-1,5-dione hydrobromide, 31410-17-0; *o*-chloranil, 2435-53-2; triphenylphosphine, 603-35-0; triphenylarsine, 603-32-7; triphenylantimony, 603-36-1; triphenylphosphine tetrachlorocatecholate, 62475-98-3; triphenylarsine tetrachlorocatecholate, 86780-28-1; triphenylantimony tetrachlorocatecholate, 86780-29-2; (1,5-cyclooctadiene)platinum(II) iodide, 12266-72-7.

**Supplementary Material Available:** A complete description of the X-ray crystallographic structure determinations, including experimental procedures, tables of data, and stereodrawings (297 pages). Ordering information is given on any current masthead page.

## Carbon Scrambling and <sup>13</sup>C-<sup>13</sup>C Coupling Constants in <sup>13</sup>C NMR Spectra of 2-Norbornyl Chloride

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**Abstract:** 2-Norbornyl-2,3-<sup>13</sup>C<sub>2</sub> chloride undergoes carbon scrambling in nitrobenzene induced by a catalytic amount of SnCl<sub>4</sub>, evidently by reversible ionization. <sup>13</sup>C NMR spectra show approach to equilibrium, in days, at 5 °C. The order of isomer appearance is completely explained through the Wagner-Meerwein, 6-2 hydride, and 3-2 hydride shifts. A possible rearrangement via the norpinyl cation was shown to be at least 20 times slower than the 3-2 hydride shift at room temperature. <sup>13</sup>C-<sup>13</sup>C coupling was measured, using standard <sup>13</sup>C NMR, for all pairs of carbon atoms in the scrambled 2-norbornyl chloride. A single di-<sup>13</sup>C-labeled precursor thus generated all of the dilabeled isomers in a controlled fashion, yielding both mechanistic information concerning the rearrangement and all the <sup>13</sup>C-<sup>13</sup>C coupling constants.

<sup>13</sup>C-<sup>13</sup>C coupling constants are of interest for several reasons. They may be empirically correlated with bonding in the case of adjacent atoms or with molecular geometry in the case of non-adjacent atoms or compared with theoretically calculated values. Although, NMR pulse sequences exist for obtaining <sup>13</sup>C-<sup>13</sup>C coupling constants from compounds without enrichment above natural abundance,<sup>1</sup> the signal-to-noise ratio is usually extremely poor and/or the time of acquisition extremely long. <sup>13</sup>C-<sup>13</sup>C coupling constants have also been obtained from monolabeled substances,<sup>2</sup> but one still must observe the unenriched signal in the <sup>13</sup>C NMR and the <sup>13</sup>C still needs to be synthetically introduced. In many cases it is no more difficult to incorporate a second <sup>13</sup>C. In fact, for the norbornyl system, it is easier to make the dilabeled material. As a result of the scrambling processes which occur readily in the norbornyl system, it is possible to observe all of the di-<sup>13</sup>C-labeled isomers and thus measure all of the coupling constants starting with a single initial isomer, directly observing signals from the enriched carbons in the <sup>13</sup>C NMR. *J*<sub>12</sub> for both *endo*- and *exo*-2-norbornyl-2,3-<sup>13</sup>C<sub>2</sub> acetate and 2-norbornyl-2,3-<sup>13</sup>C<sub>2</sub> alcohol were obtained in the course of the synthesis of 2-norbornyl-2,3-<sup>13</sup>C<sub>2</sub> chloride.

Table I. <sup>13</sup>C NMR Chemical Shifts in 2-Norbornyl Chloride<sup>a</sup>

carbon	exo $\delta$ , <sup>b</sup> ppm	endo $\delta$ , <sup>b</sup> ppm
1	46.7	44.3
2	63.1	62.0
3	43.9	41.3
4	37.2	37.8
5	28.5	30.0
6	27.0	22.7
7	35.4	38.3

<sup>a</sup><sup>13</sup>C NMR at 62.8 MHz, with 0.116 Hz/pt, at 35 °C. <sup>b</sup>In nitrobenzene-*d*<sub>5</sub> (downfield most peak set to 149.5 ppm, from Me<sub>4</sub>Si).

### Results and Discussion

To obtain mechanistic information on rearrangements which scramble carbon atoms and to measure a complete array of <sup>13</sup>C-<sup>13</sup>C coupling constants in a 2-norbornyl system, the following experiment was performed. 2-Norbornyl-2,3-<sup>13</sup>C<sub>2</sub> chloride was placed in dimethyl-*d*<sub>6</sub> sulfoxide (Figure 1a) and heated. At 150 °C, coupled signals corresponding to C<sub>1</sub> and C<sub>7</sub> simultaneously appeared (assignments taken from literature,<sup>3</sup> Table I), indicating effective Wagner-Meerwein rearrangement, presumably via ionization to the nonclassical cation and return of chloride. Elimination had also begun to take place, creating di-<sup>13</sup>C-labeled nortricyclane (<sup>13</sup>C-<sup>13</sup>C coupling = 43.0 Hz for cyclopropane

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