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Dihalo Derivatives of 3-Coordinate Hypervalent Phosphorus Compounds

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ABSTRACT

The preparation of 1,1-difluoro-3,7-di-tert-butyl-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-3,6-diene (DitBuADPO · F_2) from hexafluoropropylene oxide (HFPO) and 3,7-di-tert-butyl-2,8-dioxa-1-phosphabicyclo-[3.3.0]octa-2,4,6-triene (DitBuADPO) is described. The solid state structure of DitBuADPO · F_2 shows an unusual square pyramidal geometry. The structural and spectroscopic properties of DitBuADPO · F_2 are compared with other oxidized derivatives of DitBuADPO that contain 5-coordinate phosphorus.

INTRODUCTION

In previous reports, we have described considerable chemistry of 3,7-di-*tert*-butyl-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (DitBuADPO)[1–12]. Oxidative additions of halogen, *o*-chloranil, or hexafluoro-2-butyne (HFB) to DitBuADPO occur smoothly at the phosphorus center of DitBuADPO to produce structures which appear to be best described as trigonal bipyramidal (Scheme 1) [3].

The DitBuADPO · X_2 adduct is reactive toward nucleophiles in a manner typical for 5-coordinate phosphorus halides. It is possible to substitute one or both of the halogens by methyl group(s). This alkylation reaction afforded the methyl(chloro) and dimethyl adducts of DitBuADPO according to Scheme 2 [3].

The geometries of these products of oxidative addition to DitBuADPO are all believed to possess trigonal bipyramidal geometries. The DitBuADPO · Cl_2, DitBuADPO · Br_2, DitBuADPO · $(CH_3)Cl$, and DitBuADPO · $(CH_3)_2$ adducts have very similar NMR spectra, indicating similar structures in solution [3]. Both DitBuADPO · $(CH_3)Cl$ and DitBuADPO · $(CH_3)_2$ have had solid state structures determined by X-ray crystallography, and indeed these two compounds are best described by trigonal bipyramidal geometries similar to the depictions in Scheme 2 [3]. In these geometries, the tridentate ligand spans the two apical sites with its oxygens while the ligand nitrogen occupies one of the equatorial sites.

Although DitBuADPO · Cl_2 and DitBuADPO · Br_2 have been synthesized [3], DitBuADPO · F_2 has not been available for structural and spectroscopic comparisons. During an investigation of the reactivity of ADPO with fluorocarbon systems, we discovered the reactions shown in Scheme 3 that provide a route to DitBuADPO · F_2.

RESULTS AND DISCUSSION

When DitBuADPO was allowed to react with hexafluoropropylene oxide (HFPO) in tetrahydrofuran (thf) at room temperature, a 1:1 adduct (DitBuADPO · HFPO) was formed (Scheme 3). The ^{31}P NMR chemical shift of δ −32.6 for DitBuADPO · HFPO (Table 1) supports a 5-coordinate phosphorus structure similar to DitBuADPO · Cl_2, DitBuADPO · Br_2, and the related compounds. A fluorine-phosphorus coupling constant of 1021.1 Hz indicates that there is a single fluorine attached di-

Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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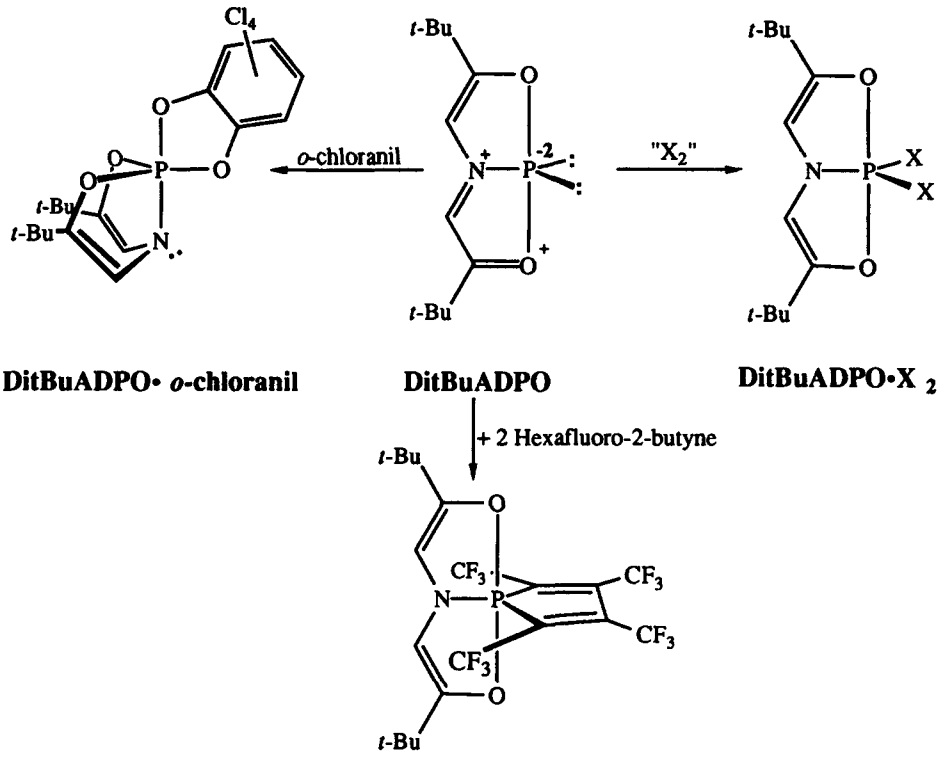

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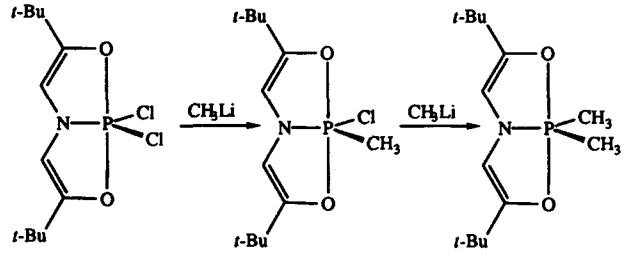

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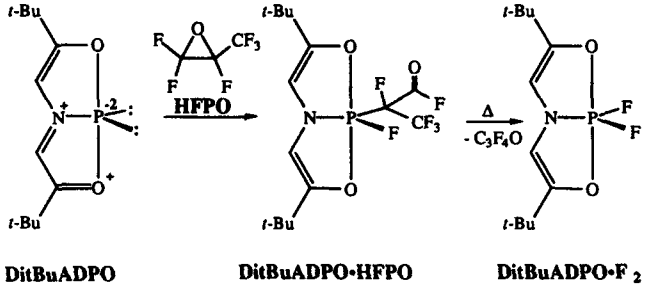


SCHEME 3

rectly to the phosphorus. The ^{13}C and ^{1}H NMR spectra show upfield shifts for every center in the original tridentate organic ligand on DitBuADPO. This shift pattern has been seen previously and indicates the tridentate ligand is intact but present in a reduced form [3,6]. The ^{15}N NMR chemical shift of −266.8 also supports a reduced tridentate organic ligand, and the $^{1}J_{PN}$ value of 28.2 Hz further supports a 5-coordinate phosphorus center [3]. The ^{19}F NMR spectrum reveals the identity of the remaining fluorocarbon fragment. There is a ^{19}F resonance at δ 31.00, which indicates an acid fluoride functionality. The presence of the acid fluoride is further supported by the ^{13}C resonance at δ 154.0, with $^{1}J_{FC}$ = 367.1 Hz. There is another ^{19}F resonance at δ −70.67 and a corresponding ^{13}C resonance at δ 121.0 ($^{1}J_{FC}$ = 367.1 Hz), which indicate the presence of a trifluoromethyl group. The ^{19}F resonance for the fluorine attached directly to phosphorus is at δ −52.99, with the expected large $^{1}J_{PF}$ (1021.1 Hz). The final ^{19}F resonance occurs at δ −172.79 and can be assigned to a fluoromethine center attached directly to phosphorus. This fluoromethine center shows a ^{13}C resonance at δ 95.3. This latter carbon resonance is very interesting in that the largest coupling to this center appears as a triplet pattern with $J_{(apparent)}$ = 219.6 Hz, with su-

TABLE 1 Selected NMR Chemical Shifts in ADPO and ADPO · X_2

Compound	^1H NMR H4(6)	^{13}C NMR C3(7)	^{13}C NMR C4(6)	^{15}N NMR N5	^{31}P NMR P_t	^{17}O NMR O2(8)	Reference
DitBuADPO	7.50 ($^3J_{PH}$ = 9.6)	169.9 (J_{PC} = 0.2)	111.2 (J_{PC} = 5.7)	−126.3 ($^1J_{PN}$ = 80.0)	187.0	324	3
DiAdADPO	7.40 ($^3J_{PH}$ = 9.9)	169.6	111.1 (J_{PC} = 5.6)	−126.0 ($^1J_{PN}$ = 81.0)	185.0	—	3
DiCumylADPO	7.41 ($^3J_{PH}$ = 9.6)	168.5	113.1 (J_{PC} = 6.0)	−128.1 (^{14}N)	188.3	—	this work
DitBuADPO · F_2	6.15 ($^3J_{PH}$ = 33.7)	148.4 (J_{PC} = 1.2)	103.1 (J_{PC} = 20.1)	−270.2 ($^1J_{PN}$ = 30.0)	−34.0	151	this work
DitBuADPO · Cl_2	6.15 ($^3J_{PH}$ = 35.8)	152.5 (J_{PC} = 8.1)	102.3 (J_{PC} = 23.0)	−262.4 ($^1J_{PN}$ = 13.7)	−24.9	224	3
DitBuADPO · Br_2	6.20 ($^3J_{PH}$ = 35.9)	154.5 (J_{PC} = 10.7)	102.9 (J_{PC} = 23.3)	−256.8 ($^1J_{PN}$ = 6.2)	−90.7	—	3
DitBuADPO · $(CH_3)Cl$	5.99 ($^3J_{PH}$ = 35.6)	151.2 (J_{PC} = 5.7)	102.0 (J_{PC} = 13.9)	−271.0 ($^1J_{PN}$ = 16.9)	−0.8	—	3
DitBuADPO · $(CH_3)_2$	5.31 ($^3J_{PH}$ = 31.2)	150.0 (J_{PC} = 3.8)	99.8 (J_{PC} = 15.5)	−303.0 ($^1J_{PN}$ = 17.4)	−9.1	171	3
DitBuADPO · 2HFB	6.01 ($^3J_{PH}$ = 36.8)	141.7 (J_{PC} = 4.9)	102.8 (J_{PC} = 18.4)	−285.1 ($^1J_{PN}$ = 16.0)	−21.8	—	3
DitBuADPO · *o*-chloranil	6.25 ($^3J_{PH}$ = 32.0)	195.4	108.9 (J_{PC} = 15.9)	−275.9 ($^1J_{PN}$ = 16.8)	−10.2	—	3
DitBuADPO · HFPO	6.24 ($^3J_{PH}$ = 35.4)	150.4 (J_{PC} = 4.8)	104.1 (J_{PC} = 19.6)	−266.8($^1J_{PN}$ = 28.2)	−32.6	—	this work

perimposed smaller couplings. This triplet pattern arises because $^1J_{PC}$ is approximately equal to $^1J_{FC}$. These NMR data indicate that the structure of the DitBuADPO · HFPO adduct is as depicted in Scheme 3. One final aspect of the structure of DitBuADPO · HFPO is the chiral carbon from the fluorocarbon moiety which is attached to the phosphorus. This renders the 5-membered rings in the tridentate organic ligand backbone diastereotopic. The very slight differences in these rings are evident from what is actually an ABMX splitting pattern for the ring proton (A,B = H; M = P; X = F). The very slight doublet observed for the *t*-butyl resonances could arise from either phosphorus coupling or, more likely, different chemical shift values.

The mechanism for the formation of DitBuADPO · HFPO is uncertain, but a direct ring opening of the epoxide ring followed by transfer of fluoride from the perfluoroalkoxide center to phosphorus seems likely. Nucleophilic ring opening of HFPO and related unsymmetrical fluoroepoxides generally proceed with attachment of the nucleophile at the more substituted carbon [13,14].

Although DitBuADPO · HFPO forms nicely shaped crystals from a variety of solvents, it was not possible to complete an X-ray crystallographic structure determination. Structure refinement yielded reasonable positions for the atoms of the tridentate organic ligand and the phosphorus (similar to those in DitBuADPO · $(CH_3)Cl$), but there was an extremely large amount of disorder in the fluoroalkyl group, which prevented satisfactory refinement.

When DitBuADPO · HFPO was heated above 100 °C, the fluorocarbon substituent was replaced by an additional fluorine to form DitBuADPO · F_2 (Scheme 3). The identity of the fluorocarbon which was eliminated is unknown. No DitBuADPO was isolated from the reaction mixture, which suggests that HFPO behaved as a donor of two fluorines. The structure of the DitBuADPO · F_2 adduct was apparent from the multinuclear magnetic resonance spectra (Table 1). The ^{31}P resonance at δ −34.0 is a triplet (875.7 Hz) due to coupling to the two directly attached fluorines. The ^{15}N NMR spectrum indicates, by the high field chemical shift value (δ −270.2), that the tridentate organic ligand is in a reduced oxidation state. The ^{31}P-^{15}N coupling constant of 30 Hz supports a 5-coordinate phosphorus center [3]. The high field ^{17}O chemical shift (δ 151) provides further support for a reduced ligand backbone. As with DitBuADPO · HFPO, the ^1H and ^{13}C NMR spectra indicate an intact reduced tridentate organic ligand backbone (see above).

The precise solid state structure of DitBuADPO · F_2 was determined by X-ray crystallography and is depicted by the KANVAS [15] drawing in Figure 1. The solid state structure of DitBuADPO · F_2 contained two crystallographically unique

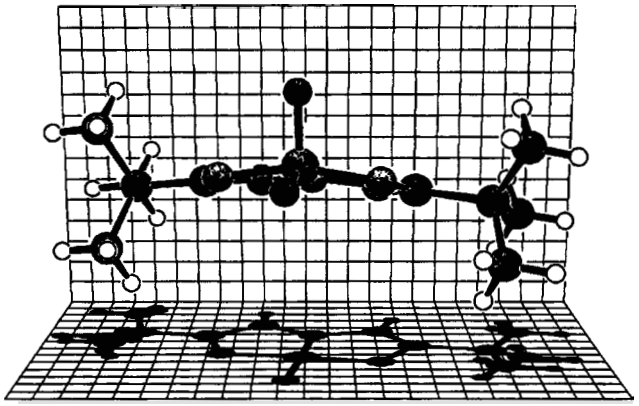


FIGURE 1 KANVAS drawing of DitBuADPO · F_2.

molecules whose structures were very similar. The average data from the two structures are presented in Table 2. The DitBuADPO · F_2 structure shows bond lengths in the tridentate organic ligand backbone, which suggest the ligand backbone is in a reduced oxidation state. As in the other 5-coordinate phosphorus derivatives of ADPO that contain a reduced ligand backbone (DitBuADPO · $(CH_3)_2$, DitBuADPO · $(CH_3)Cl$, DitBuADPO · *o*-chloranil, DitBuADPO · 2HFB), the C–O and C–N bonds are lengthened relative to the oxidized ligand backbones found in the parent ADPO molecules (DitBuADPO and DiCumylADPO) and the 5-coordinate silver complex (DitBuADPO · Ag_2) [11]. On the other hand, the C–C_{ring} bond in the ligand shortens in the reduced form of the ligand relative to the oxidized form. These data suggest a localization of multibonding character between the ring carbons at the expense of the C–O and C–N bonds (in accord with the resonance structures depicted in Schemes 1 and 3). The P–O and P–N bonds also tend to be shorter when the ligand backbone is reduced. Even though the magnitude of these changes is not large, they are consistently repeated throughout the ADPO series. One detail of the structure of DitBuADPO · F_2 which is most interesting is the geometry around the phosphorus center.

There is a rather dramatic difference between the structures of DitBuADPO · F_2 and DitBuADPO · $(CH_3)_2$. DitBuADPO · $(CH_3)_2$ represents the 5-coordinate ADPO derivative, with a reduced ligand backbone that most closely fits an idealized trigonal bipyramidal (TBP) geometry. DitBuADPO · F_2 is close to the "strainless" geometry of a square pyramid (SP) described by Holmes *et al.* [16,17]. The average deviations of the angles around phosphorus from these idealized geometries are listed in Table 2. DitBuADPO · $(CH_3)_2$ and DitBuADPO · $(CH_3)Cl$ both fit closely to a TBP structure. DitBuADPO · F_2 deviates more from the ideal-

TABLE 2 Selected Bond Lengths (pm) and Angles in DitBuADPO · X_2 and Related Molecules

Property	*DitBuADPO*	*DiCumylADPO*	*DitBuADPO · F_2*[a]	*DitBuADPO · o-chloranil*	*DitBuADPO · 2HFB*	*DitBuADPO · $(CH_3)Cl$*	*DitBuADPO · $(CH_3)_2$*	*DitBuADPO · Ag_2*[b]
P–O	183.5(2)	181.3(2)	166.4	161.8(5)	170.5(6)	170.1(8)	174.1(3)	177.5(12)
	179.2(2)	179.5(2)	164.4	162.3(4)		170.2(8)	173.8(3)	183.9(13)
P–N	170.3(2)	170.2(2)	169.2	169.6(5)	161.3(10)	167.0(10)	169.2(3)	172.8(14)
C–O	133.1(4)	133.7(3)	141.0	142.1(7)	140.6(10)	138.0(10)	137.5(4)	134.2(20)
	132.8(4)	133.7(3)	141.5	140.6(7)		139.0(10)	136.8(4)	132.2(21)
C–N	137.5(3)	138.5(3)	134.5	140.3(8)	140.8(10)	139.0(10)	140.9(5)	135.1(18)
	138.2(3)	139.0(3)	142.0	139.6(8)		140.0(10)	139.5(5)	129.3(21)
C–C	134.2(4)	134.3(3)	136.5	130.5(9)	128.8(11)	135.0(2)	130.6(5)	137.1(22)
	133.7(4)	134.1(3)	131.0	131.4(9)		133.0(1)	132.5(5)	134.7(23)
P–X	—	—	159.1[f]	171.7(4)[g]	183.4(9)	211.1(4)Cl	178.1(6)	243.4(5)
	—	—	153.2[g]	163.8(5)[h]		177.0(10)CH_3	179.9(5)	257.4(5)
O–P–O	167.7(1)	167.72(7)	162.8	141.8(3)	176.6(5)	173.5(5)	171.7(1)	167.7(6)
N–P–O	83.5(1)	83.58(9)	87.3	90.8(3)	88.3(3)	87.3(5)	86.5(1)	84.7(6)
	84.2(1)	84.22(9)	89.7	89.9(3)		86.8(5)	86.5(1)	83.0(6)
X–P–O	—	—	87.0, 87.8[f]	87.5(2), 86.7(2)[g]	91.8(3)	92.2(3), 92.8(3)Cl	93.9(2), 93.4(2)	95.1(5), 94.4(4)
	—	—	97.3, 99.8[g]	106.8(2), 111.1(3)[h]		91.4(5), 91.0(5)CH_3	90.6(2), 90.2(2)	90.4(4), 90.2(5)
X–P–N	—	—	151.8[f]	172.0(3)[g]	134.7(4)	115.5(4)Cl	119.3(2)	118.3(5)
	—	—	109.7[g]	95.4(3)[h]		136.6(5)CH_3	128.2(2)	109.9(5)
X–P–X	—	—	98.4	92.6(2)	90.7(7)	107.9(4)	112.5(3)	131.5(2)
ΣN^{oc}	360.0	360.0	360.0	352.0	360.1	355.1	353.4	359.8
Δ-TBP[d]	—	—	13	7	7	5	4	6
Δ-SP[e]	—	—	4	8	14	11	12	12

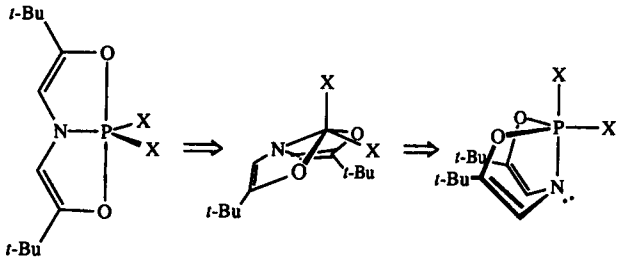
[a]Average of the two unique molecules in the unit cell. [b]Data for the DitBuADPO · Ag_2 unit from a polymeric structure (Ref. [11]). [c]Sum of the angles around the nitrogen. [d]Average deviation of the angles around phosphorus from an ideal trigonal bipyramid. [e]Average deviation of the angles around phosphorus from an ideal square pyramid. [f]X in basal position. [g]X in apical position. [h]X in equatorial position.

ized TBP in favor of a SP geometry, and DitBuADPO · *o*-chloranil is intermediate.

A structural flexibility available to the reduced ligand system that is not readily available to the oxidized ligand backbone is a folding about the P–N bond. This folding plays an important role in many metal complexes of ADPO derivatives [2,7–9]. Although the compounds with a reduced ligand backbone tend to be nonplanar [18], DitBuADPO · *o*-chloranil is the most folded (145.8° between the 2 5-membered rings). DitBuADPO · F_2 has a fold of 168.1°. The tendency to pyramidalize at nitrogen reflects this folding flexibility, and the sums of valence angles about nitrogens are listed in Table 2 as indicators. A second component to this folding is a decrease in the O-P-O angle.

The unusual structures of DitBuADPO · F_2 and DitBuADPO · *o*-chloranil can be considered in terms of stress on the more normal type of TBP structures observed for DitBuADPO · $(CH_3)_2$, DitBuADPO · $(CH_3)Cl$, DitBuADPO · 2HFB, DitBuADPO · Ag_2, and some metal adducts of the ADSbO and ADAsO molecules [8]. In the case of DitBuADPO · F_2, the stress results from an effect of the electronegative fluorines that prefer to occupy the apical sites of TBP structures. In the case of DitBuADPO · *o*-chloranil, the stress arises because the *o*-chloranil ligand forms a 5-membered ring with the phosphorus center. The 5-membered ring would best span an apical and an equatorial site rather than the diequatorial linkage that the usual arrangement of the tridentate organic ligand in ADPnO systems would demand.

The tridentate organic ligand backbone can only span an apical-equatorial-apical (O-N-O) linkage of a "normal" TBP structure (*e.g.*, DitBuADPO · X_2 in Scheme 1) when planar regardless of the ligand oxidation state of the ligand. This leaves the two equatorial sites to be occupied by the remaining substituent(s) at phosphorus. If the tridentate organic ligand is in a reduced form, it can fold, as indicated previously. This folding of the tridentate organic ligand makes it possible to span equatorial-apical-equatorial (O-N-O) sites of an "alternative" TBP structure (*e.g.*, DitBuADPO · *o*-chloranil in Scheme 1), thus leaving an equatorial and an apical site for the remaining substituent(s). It is this latter alternative TBP structure that best describes DitBuADPO · *o*-chloranil. In this alternative TBP arrangement, each equatorial site is linked to an apical site by a 5-membered ring and a diequatorial linkage by the *o*-chloranil unit is avoided. The only negative feature of this alternative arrangement is the placement of nitrogen in an apical position about phosphorus when there are more electronegative oxygens available. The difference between apical nitrogen and oxygen is not sufficient to drive the structure of DitBuADPO · *o*-chloranil to a different minimum. The structure of DitBuADPO · 2HFB deserves some



normal TBP **SP** **alternative TBP**

SCHEME 4

comment at this point since it too contains an additional 5-membered ring that is formed by the "new" substituents at phosphorus. For DitBuADPO · 2HFB, the additional 5-membered ring does manage to span the two equatorial sites required by the normal apical-equatorial-apical position of the tridentate organic ligand. The reason for this geometry in DitBuADPO · 2HFB may be that the new substituents are carbons whose electronegativity relative to oxygen requires that they occupy equatorial sites.

The structure of DitBuADPO · F_2 is greatly influenced by the high electronegativity of the fluorine substituents at phosphorus. Although the alternative TBP structure observed with DitBuADPO · *o*-chloranil would allow one fluorine to be apical, the second fluorine is forced to remain equatorial while the nitrogen assumes the other apical position. This awkward placement of substituents allows DitBuADPO · F_2 to adopt a different geometry altogether. The unusual SP geometry found for DitBuADPO · F_2 is actually intermediate on the pseudorotation surface that connects the normal TBP structure of compounds like DitBuADPO · $(CH_3)_2$ with the alternative TBP structure of DitBuADPO · *o*-chloranil. This is illustrated in Scheme 4.

Finally, it should be recognized that the structures observed for the compounds reported in Table 2 are in the solid state and do not necessarily hold for the solution structures. It is also difficult to establish the role of any crystal packing forces which may give rise to special geometric features. Other than establishing the coordination number of phosphorus, the oxidation state of the tridentate organic ligand, and a slight indication of the pyramidalization at nitrogen (through the ease with which ^{14}N spectra can be obtained and $^3J_{CH}$ couplings in the ring [3]), there is little indication of the finer details of the geometries at the phosphorus centers from the solution NMR spectra given in Table 1. The only possible indication for a square pyramidal geometry preference in solution might be the somewhat higher $^1J_{PN}$ value of 30 Hz found for DitBuADPO · F_2. This remains only a single point

at this time, and more data are necessary to determine if this datum has any special structural correlation.

CONCLUSIONS

As has been recognized at main group hypervalent centers, both electronic and steric effects can play important roles in determining the geometry observed at a central atom. For ADPO derived molecules, the more common TBP arrangement, in which the tridentate organic ligand spans apical-equatorial-apical sites, can be changed to an alternative TBP structure, in which the tridentate organic ligand spans equatorial-apical-equatorial sites or even a square pyramidal geometry under the influence of ligand effects in the other two sites. The square pyramidal geometry of DitBuADPO · F_2, which is unusual for compounds containing this tridentate organic ligand, is largely the result of an electronic effect of the highly electronegative fluorines. The alternative TBP geometry observed for DitBuADPO · *o*-chloranil appears to be the result of both steric and electronic factors. These solid state geometries may be considerably more flexible in solution.

EXPERIMENTAL SECTION

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres dry box or using standard Schlenk techniques. Solvents were dried (using standard procedures), [19] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. The ^{1}H (300.75 MHz), ^{13}C (75.629 MHz), ^{31}P (121.745 MHz), ^{19}F (282.987 MHz), ^{14}N (21.725 MHz), ^{15}N (30.484 MHz), and ^{17}O (40.772 MHz) NMR spectra were recorded on a GE Omega 300WB spectrometer. The NMR references are as follows: $(CH_3)_4Si$ (^{1}H, ^{13}C); 85% H_3PO_4 (^{31}P); $CFCl_3$ (^{19}F); $NH_4^+NO_3^-$ (^{14}N, ^{15}N); and H_2O (^{17}O). The ^{15}N DEPT experiments were run using the standard NT DEPT sequence, assuming $J_{HN} \approx 7$ Hz and $J_{FN} \approx 28$ Hz with a θ pulse of 45°. Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. The X-ray structural study of DitBuADPO · F_2 was performed by Oneida Research Services, and the crystal structure of DiCumylADPO was performed by D. Staley (DuPont Central Research).

DiCumylADPO

A solution of 350 mg (1.04 mmol) of 5-aza-2,8-dimethyl-2,8-diphenylnonane-3,7-dione in 10 mL of thf was added dropwise to a solution of 142 mg (1.04 mmol) of phosphorus trichloride in 10 mL of thf at −78 °C under a dry nitrogen atmosphere. When the addition was complete, a solution of 348 mg (3.11 mmol) of DABCO (diazabicyclo-[2.2.2]octane) in 10 mL of thf was added to the cold reaction mixture in a dropwise fashion. Three hours after the second addition was complete, the mixture was allowed to warm slowly to room temperature and stirred for 1 additional hour. The thf was evaporated in vacuo, and the solid residue was extracted with pentane. The pentane extract was evaporated to dryness and the solid residue recrystallized from diethyl ether to afford 140 mg (37%) DiCumylADPO as an off-white solid: mp 132 °C. [Compared to DitBuADPO, the synthesis of DiCumylADPO seemed more resistant to eliminate the third equivalent of HCl. An attempted synthesis of DiCumylADPO using triethylamine as the base led to the loss of only 2 equivalents of HCl. This intermediate (DiCumylADPO · HCl) gave a ^{31}P resonance at δ 171 in CD_2Cl_2 and ^{1}H NMR (CD_2Cl_2) δ 1.52 (s, CC*H*$_3$, 6H), 1.58 (s, CC*H*$_3$, 6H), 4.20 (d, NC*H*$_2$, 2H), 5.81 (d, NC*H*, 1H), 7.34 (m, Ph*H*, 5H). These data suggest a structure similar to compound **11** of ref. [3]. The third equivalent of HCl could be removed by subsequent treatment with 1 equiv. DABCO.] A sample of DiCumylADPO gave the following data. NMR spectra (CD_2Cl_2): ^{1}H, δ 1.63 (s, CC*H*$_3$, 12 H), 7.16–7.28 (m, Ph*H*, 5H), 7.41 (d, J_{PH} = 9.6 Hz, NC*H*, 2H); ^{13}C {^{1}H}, δ 27.537 (s, *C*CH$_3$), 41.85 (d, J_{PC} = 7.0 Hz, *C*(CH$_3$)$_2$), 113.14 (d, $^{2}J_{PC}$ = 6.0 Hz, *H*CN), 128.54 (s, 2,6-Ph), 126.66 (s, 4-Ph), 126.57 (s, 3,5-Ph), 146.85 (d, J_{PC} = 1.0 Hz, 1-Ph), 168.5 (s, *C*OP); ^{31}P {^{1}H}, δ 188.34; ^{14}N δ −128.1 (brs). Mass spectrum (CI-CH_4^+) 366 (M^++1, 100%), 119 ($C_6H_5C^+(CH_3)_2$, 43%). Elemental analysis: Calcd C, 72.31; H, 6.62; N, 3.83; Found C, 72.22; H, 6.80; N, 3.72.

DitBuADPO · HFPO

A 20 mL heavy walled glass bomb with 6 mm Teflon™ screw valve was charged under N_2 with 3.00 g (12.4 mmol) DitBuADPO, 5 mL CH_2Cl_2, and a stir bar. The solution was degassed under vacuum with three freeze-thaw cycles. Hexafluoropropylene oxide (14.7 mmol) was condensed into the bomb while cooling with liquid N_2. The bomb was allowed to warm slowly to room temperature and was then stirred for 24 hours. The solution became slightly pink and was heated at 50 °C for 72 hours. The solution became a darker red and was heated at 70 °C for 72 hours. The dark red solution was cooled to room temperature and approximately 3 mL of volatiles allowed to distill from the bomb into a trap held at −35 °C. The colorless volatile liquids formed two layers in the collection trap. The residual red solution in the bomb was cooled to −25 °C for 72 hours and colorless crystals formed which were collected by filtration: 377 mg, mp 63–66 °C. The CH_2Cl_2 was removed from the mother liquor and

replaced with a minimum amount of hexane to allow dissolution at room temperature. The hexane solution was again cooled to −25 °C and, overnight, yielded a second crop of crystals: 434 mg, mp 63–66 °C. The hexane mother liquor was reduced to 2 mL volume and again cooled to −25 °C to yield a third crop of crystals, 1.04 g, mp 61–64 °C. The total yield was 1.85 g of DitBuADPO · HFPO (38%). DitBuADPO · HFPO could be further purified by recrystallization from hexane, and a sample afforded the following data. mp 63–66 °C. The NMR spectra (CD_2Cl_2): ^1H, δ 1.13 (d, $\Delta\delta$ = 1.2 Hz, CCH_3, 18H), 6.24 (average) (dm, J_{PH} = 35.4 Hz, NC*H*, 2H); ^{19}F δ 31.00 (ddqd, J_{FF} = 30.2 Hz, J_{FF} = 9.5 Hz, $^4J_{FF}$ = 7.8 Hz, $^3J_{PF}$ = 3.1 Hz, C(O)*F*), −52.99 (dm, $^1J_{PF}$ = 1021.3 Hz, P*F*), −70.67 ($dq_{(apparent)}$, $^3J_{FF}$ = 10.0 Hz, 3(J_{FF} ≈ 7.0 Hz), CF_3), −172.79 (dddq, $^2J_{PF}$ = 79.4 Hz, $^3J_{FF}$ = 29.0 Hz, $^3J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 12.2 Hz, *F*C(PF)(CF_3)(COF)); ^{13}C {^1H}, δ 27.2 (d, J_{PC} = 2.8 Hz, CCH_3), 32.7 (dd, J_{PC} = 1.6 Hz, J_{FC} = 5.2 Hz, $C(CH_3)_3$), 95.3 ($t_{(apparent)}$ddq, $^1J_{PC} \approx {}^1J_{FC} \approx$ 219.6 Hz, $^2J_{FC}$ = 33.5 Hz, $^2J_{FC}$ = 63.8 Hz, $^2J_{FC}$ = 47.05 Hz, FC(PF)(CF_3)(COF)), 104.1 (dm, $^2J_{PC}$ = 19.6 Hz, HCN), 121.0 (qdd, $^1J_{FC}$ = 285.5 Hz, J = 26.4 Hz, J = 4.0 Hz, CF_3), 150.4 ($t_{(apparent)}$, J = 4.8 Hz, *C*OP), 154.0 (ddq, $^1J_{FC}$ = 367.1 Hz, J = 26.4 Hz, J = 2.1 Hz, C(O)F); ^{31}P {^1H}, δ −32.55 (ddqd, $^1J_{FP}$ = 1021.1 Hz, $^2J_{FP}$ = 79.5 Hz, $^3J_{FP}$ = 6.5 Hz, $^3J_{FP}$ = 3.0 Hz); ^{15}N {^1H DEPT}, δ −266.8 (dd, $^1J_{PN}$ = 28.2 Hz, $^2J_{FN}$ = 17.7 Hz), {^{19}F DEPT}, δ −266.8 (dd, $^1J_{PN}$ = 28.44 Hz, $^2J_{HN}$ = 3.5 Hz); ^{14}N, δ −268.2 (brs). Elemental analysis: Calcd C, 44.23; H, 4.95; N, 3.44; F, 27.99; P, 7.60; Found C, 44.38; H, 4.98; N, 3.37; F, 27.91; P, 7.65.

DitBuADPO · F_2

A direct path microdistillation apparatus was charged with 2.1 g (5.16 mmol) of DitBuADPO · HFPO under nitrogen. The apparatus was evacuated and heated to 125 °C. A pink waxy substance began to sublime onto the cold finger. The apparatus was occasionally opened to vacuum to remove the volatiles. After 1 week, the apparatus was taken into a drybox and the waxy product was removed from the cold finger; yield 965 mg (67%). DitBuADPO · F_2 could be further purified by recrystallization from hexane, and a sample afforded the following data: mp 85–90 °C (dec). NMR spectra (CD_2Cl_2): ^1H, δ 1.14 (s, CCH_3, 18H), 6.15 (d, J_{PH} = 33.7 Hz, NC*H*, 2H); ^{19}F δ 53.17 (d, $^1J_{PF}$ = 876.4 Hz); ^{13}C {^1H}, δ 27.5 (d, J_{PC} = 2.8 Hz, CCH_3), 32.4 (dt, J_{PC} = 8.8 Hz, J_{FC} = 0.5 Hz, $C(CH_3)_3$), 103.1 (dt, $^2J_{PC}$ = 20.1 Hz, $^3J_{FC}$ = 1.5 Hz, HCN), 148.4 (d, J = 1.2 Hz, *C*OP); ^{31}P {^1H}, δ −33.96 (t, $^1J_{FP}$ = 876.7); ^{15}N {^1H DEPT}, δ −270.2 (dt, $^1J_{PN}$ = 30.0 Hz, $^2J_{FN}$ = 6.7 Hz); ^{14}N δ −271.4 (brs); ^{17}O, δ 150.8 (brs). Elemental analysis: Calcd C, 51.61; H, 7.22; N, 5.02; F, 13.61; Found C, 49.01; H, 6.62; N, 4.79; F, 13.61.

Crystal Data for DiCumylADPO at −70 °C with Mo K_α Radiation: a = 850.7 (4), b = 1603.4 (3), c = 1457.6 (6) pm, β = 101.46 (2)°, monoclinic, $P2_1/n$, Z = 4, μ(Mo) = 1.51 cm^{-1}, 2879 unique reflections with $I > 3\sigma(I)$. The structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix least squares on F. Phosphorus, oxygens, carbons, and nitrogen were refined with anisotropic thermal parameters. Hydrogens were placed in idealized positions (rC–H = 95 pm). The largest residual electron density in the final difference Fourier map was 0.30 $e/Å^3$ near phosphorus. The data/parameter ratio was 12.25. The final R factors were R = 0.044 and R_w = 0.052, the error of fit = 1.92, and max Δ/σ = 0.00. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

Crystal Data for DiBuADPO · F_2 at −35 °C with Mo K_α Radiation: a = 1194.3 (7), b = 1615.0 (4), c = 1591.2 (9) pm, orthorhombic, $Pna2_1$, Z = 8, μ(Mo) = 1.9 cm^{-1}, 1658 unique reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares on F. Phosphorus, oxygens, carbons, and nitrogen were refined with anisotropic thermal parameters. Hydrogens were placed in idealized positions (r_{C-H} = 97 pm). The largest residual electron density in the final difference Fourier map was 0.41 $e/Å^3$. The data/parameter ratio was 5.12. The final R factors were R = 0.083 and R_w = 0.089 and max Δ/σ = 0.02. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

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SUPPLEMENTARY MATERIAL AVAILABLE

A complete description of the X-ray crystallographic structure determinations on DiCumylADPO and DitBuADPO · F_2 has been deposited with the Cambridge Crystallographic Data Centre.

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