A Cationic, Macrocyclic, Six-Coordinate Phosphorus(V) Compound Containing a Mixed Valence P^{III}-P^{V}-P^{III} Linear Chain[**]

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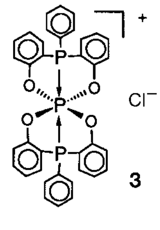
Many types of phosphorus–phosphorus bonds are known,[1] but it is rare to find such bonds in neutral hexacoordinate (σ^6) pentavalent (λ^5) phosphorus compounds in which the electrovalence and the apparent maximum of sixfold coordination are simultaneously satisfied.[2, 3] Furthermore, cationic species containing a hexacoordinate, pentavalent phosphorus atom are even more rare. Most such species have been derived from porphyrins,[4–7] and no examples known to date contain P–P bonds.[2, 3] Only one non-porphyrin σ^6 complex has been structurally characterized.[8] An early report of $[PCl_4(bpy)]^+$ (bpy = 2,2′-bipyridine) complexes did not contain structural details.[9]

Typically, hexacoordinate phosphorus(V) centers are formed on strong donor–acceptor interaction between the acidic phosphorus center and a base. The acidity of the phosphorus(V) center is determined by the nature of the substituents; thus a collection of highly electronegative substituents on phosphorus(V) is generally required. Many such compounds are formed as chelates through interaction of the P^V center with a basic site on one of the covalently bound ligands.[2] Recent studies of phosphorus(V) compounds with dianionic *o,o′*-thiodiphenolato ligands have shown a range of binding interactions between the central sulfur atom and the phosphorus(V) center.[2, 10–12] At one end of the range an example has no bond (i.e., very long P···S contacts), and the bound dianionic ligand forms large open, (typically eight-membered) macrocyclic rings through a series of nascent P–S bonds, in which the separations are of the order of van der Waals distances. The other limit is a clearly bonded sulfur atom in a compound that displays a pair of bis-chelated pentaatomic rings subtended from the phosphorus.[2, 10–12] The interaction strengthens with increasingly electronegative substituents on phosphorus, as illustrated by the short P–S bond (2.3307(8) Å) in trichloro(*o,o′*-thio-*κS*-diphenolato-*κ*^{2}*O*)phosphorus(V) $[Cl_3P\{S(o\text{-}C_6H_4O)_2\}]$.[13]

In principle, the strong Lewis base character of phosphanes should yield strong P^{III}–P^{V} adducts similar to the above S^{II}–P^{V} system. A series of neutral P^{III}–P^{V} donor–acceptor adducts were studied by Schultz et al. but none were structurally characterized. Two neutral compounds containing a single P^{III}–P^{V} bond to a hexacoordinate P^V center have been reported; 1-diethylamino-5-chloro-5-(tetrachlorocatecholato-O,O′)-2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1σ^4,5σ^6-diphosphabicyclo[3.3.0]octane-3,7-dione (**1**) by Bettermann et al.[14] and trifluoro(perfluoropinacolato)(trimethylphosphane)phosphorus (**2**) by Gibson et al.[15] Compound **1** [16] contained a short P^{III}–P^{V} bond (2.165 Å) between P^{III} and the hexacoordinate P^V center (also bonded to 2 O, 2 N, and one Cl atom), and in **2**[17] a P^{III} ligand (Me_3P) is bound to the hexacoordinate P^V center (which also subtends 2 O and 3 F atoms) with a short P^{III}–P^{V} bond distance of 2.234(5) Å, only 0.03 Å longer than the sum of the covalent radii (2.20 Å).

Herein we report a cationic bis-chelate complex of P^V, which provides an encapsulated hexacoordinate pentavalent phosphorus environment from which are subtended two short P^{III}–P^{V} bonds. The cation **3** also provides an example of an unusual mixed valence, linear triphosphorus chain. Triphosphorus (and polyphosphorus) chains are known for lower coordination environments in the P^V system[18, 19] and in several complex ions in which λ^4 phosphorus(V) substituents are bound to a formal P^{III} center. These examples are typically based on a low valent phosphorus subtended by σ^4,λ^5 centers, and generally the chains are nonlinear due to the presence of electron pairs on the central phosphorus center. They do not contain hexacoordinate (σ^6) phosphorus.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The complex containing the cation is an off-white, air-stable, crystalline solid. It was prepared by reaction of phenylbis(*o*-(trimethylsiloxy)phenyl)phosphane[13, 20, 21] with PCl_5 in toluene. The compound was insensitive to moisture and oxygen; even in Me_2SO, "wet" MeOH or $CHCl_3$ solution, the $^{31}P\{^1H\}$ NMR of the complex was unchanged after standing for a week. In contrast, the neutral trichloro(*o,o′*-thio-*κS*-diphenolato-*κ*^{2}*O*)phosphorus(V) complex was readily hydrolyzed.[13]

Full chemical, spectroscopic and structural analysis supports the proposed formulation. The shift of the IR bands relative to the free ligands (the hydrochloride salt of bis(*o*-hydroxyphenol)phenylphosphane)[22] or phenylbis(*o*-(trimethylsiloxy)phenyl)phenylphosphane) confirmed dianionic ligand binding. Mass spectrometric data confirmed the formation of the cationic complex. In methanol, the cation gave a typical AB_2 $^{31}P\{^1H\}$ NMR spectrum, with a $^1J_{PP}$ coupling between the P^V center and the two P^{III} donors of 512 Hz, smaller than the $^1J_{PP}$ coupling constants shown by **2** (710 Hz)[15] and Me_3PPF_5 (720 Hz).[23] A *trans* arrangement of the two P^{III} centers was deduced for the cation from the ^1H NMR spectrum, because the seven types of ^1H NMR signals (assigned by means of selective broad-band ^{31}P decoupling experiments) that were observed for the aromatic ring hydrogen atoms ($\delta = 5.0-8.5$) indicated that the cation possesses symmetry that makes the four bound phenoxy rings equivalent.

The solid-state X-ray structure[24] showed the cationic unit (central portion illustrated in Figure 1) containing a P^V center in a highly symmetric, nearly perfect octahedral environment with two facially bonded, dianionic bis(*o*-phenoxy)phenylphosphane ligands. The four phenolate oxygen atoms define the equatorial plane of the octahedron, and the P–O bond lengths are the same (1.726 Å) within experimental error, and somewhat longer than those previously observed for the phenolate oxygen bond to a P^V center in a similar environ-

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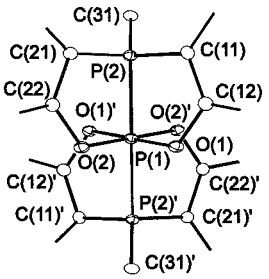

Figure 1. ORTEP drawing (20% probability thermal ellipsoids) showing the central framework and the atom labeling of the cation of **3**. Selected interatomic distances [Å] and angles [°]: P(1)–P(2) 2.2023(10), P(1)–O(1) 1.727(2), P(1)–O(2) 1.726(3), P(2)–C(11) 1.769(4), P(2)–C(21) 1.770(4), P(2)–C(31) 1.781(4), O(1)–C(12) 1.364(4), O(2)–C(22) 1.358(5); P(2)-P(1)-O(1) 89.39(9), P(2)-P(1)-O(1′) 90.61(9), P(2)-P(1)-O(2) 89.64(9), P(2)-P(1)-O(2′) 90.36(9), O(1)-P(1)-O(2) 89.86(13), O(1)-P(1)-O(2′) 90.14(13), P(1)-P(2)-C(11) 95.50(13), P(1)-P(2)-C(21) 95.98(13), P(1)-P(2)-C(31) 120.49(13).

ment.[13] The C_i symmetry of the cation confirmed the *trans*-(P^{III}, P^{III}) structure (i.e., the ligands are *fac* oriented) deduced from solution NMR data. This structural arrangement is unlike the behavior of this ligand toward transition metals: in these cases six-coordinated complexes of this ligand gave *cis*-related (*mer*) structures.[22, 25–29] The right angle binding within the chelate contrasts with the more acute bond angles (76–84°) that have been typically observed for similar PO or PS chelate rings bound to the transition metals.[22, 25, 27–29]

Two axial P^{III}–P^{V} bonds (2.2023(10) Å) lie perpendicular to the "octahedral" equatorial plane. These P^{III}–P^{V} bonds are significantly shorter than the single P^{III}–P^{V} donor–acceptor bond in **2** (2.234(5) Å).[17] and slightly longer than the single P^{III}–P^{V} bond length in **1** (2.165 Å).[16] As the central P^{V} in our cation is surrounded by a collection of atoms with a total electronegativity smaller than that contributed by the atoms connected to P^{V} in **1**, it is perhaps not too surprising that the bond lengths are a little longer. If substituent electronegativity were the dominant factor controlling the bond length, the sum of the electronegativity of the ligands at the P^{V} in the case of **2** would indicate that an even shorter bond was appropriate; however, this P^{III}–P^{V} bond is the longest of the three examples. Regardless of these small variations, the short bond and the unreactive nature of the pentavalent center in the complex suggests that the P^{III}–P^{V} donor bonds are strong and that the P^{V} center is protected. We surmise therefore that the anchored *o*-phenoxy groups provide an unstrained bis-chelate environment about the P^{V} center which also contributes to the stabilization of the P^{III}–P^{V} bonds.

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[20] Bis(*o*-hydroxyphenylo)phenylphosphane[13, 20, 21] was prepared[21, 22] and silylated as previously described.[13] PCl_5 (1 mol) was treated with phenylbis(*o*-(trimethylsiloxy)phenyl)phosphane (2 mol)[13, 20, 21] under reflux conditions in toluene for 2 h. Solvent was then removed, and the solid dried in vacuo for 4 days, to yield an off-white powder (51.6% based on PCl_5) soluble in MeOH, EtOH, Me_2SO, $CHCl_3$, and CH_2Cl_2, but insoluble in Et_2O. Analysis calcd (found) for $[P\{P(o\text{-}C_6H_4O)_2Ph\}_2]Cl\cdot(CHCl_3)_{0.15}$ ($C_{36.15}H_{26.15}Cl_{1.45}O_4P_3$: C 64.91 (64.70), H 3.94 (3.81), Cl 7.69 (7.45). FAB-MS: m/z = 615 ($[P\{P(o\text{-}C_6H_4O)_2\}_2Ph]^+$), 323 ($[P\{P(o\text{-}C_6H_4O)_2Ph\}]^+$). $^1H\{^{31}P$, bb} NMR (CD_3OD): $\delta = 8.16$ (d, $^3J_{HH} = 8.4$, 4H, *p-H* on Ph); 7.98 (t, ^3JHH = 7.5, 2H, *p*-H on Ph); 7.93 (d, ^3JHH = 7.7, 4H, *m*-H on (o-$C_6H_4O)_2P$); 7.88 (t, ^3JHH = 7.7, 4H, *m*-H on Ph); 7.60 (td, ^3JHH = 7.9, ^4JHH = 1.5, 4H, *m′*-H on (o-$C_6H_4O)_2P$); 7.22 (t, ^3JHH = 7.4, 4H, *p*-H on Ph); 6.79 (d, ^3JHH = 8.4, 4H, *o′*-H on (o-$C_6H_4O)_2P$). $^{31}P\{^1H\}$ NMR (CD_3OD): AB_2 spin system with $J/\Delta\nu \approx 0.05$, $\delta = -34.83$ (P^{III}), -107.8 (P^{V}), J_{PP} = 512 Hz.

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[24] Recrystallization from $CHCl_3/Et_2O$ gave colorless crystals of *trans*-$\{P^{III},P^{III}\}$-$[P\{P(o\text{-}C_6H_4O)_2Ph\}_2]Cl\cdot 4CHCl_3$ ($C_{40}H_{30}Cl_{13}O_4P_3$); triclinic, space group $P\bar{1}$, $a = 9.7705(15)$, $b = 9.826(2)$, $c = 13.336(3)$ Å, $\alpha = 103.94(2)$, $\beta = 90.253(15)$, $\gamma = 101.020(14)°$, $Z = 1$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0578$ and 0.0988 ($wR_2 = 0.1406$ and 0.1625) for 4472 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ and all data, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101030. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (1223)336-033; e-mail: deposit§ccdc.cam.ac.uk).

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