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Neutral hexacoordinate pentavalent phosphorus fluorides and related compounds

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We have previously attached tightly bound monoanionic, bidentate ligating groups to phosphorus to develop an extensive series of neutral, pentavalent, hexacoordinate fluoro, chloro and trifluoromethyl phosphorus compounds. These compounds are of interest in defining the bonding and stereochemistry of a highly oxidized and highly coordinated 'hypervalent' atomic center. We have now extended these studies using dianionic, tridentate ligating groups derived from *N*-(2-hydroxyphenyl)salicylideneamine and 2,2′-dihydroxyazobenzene to form analogous compounds. These were synthesized from the bis-trimethylsilylated derivative of the ligands and the appropriate phosphorane, (Eq. (1)):

$$PX_4Y + (Me_3Si)_2L \longrightarrow X_2YPL + 2Me_3SiX\uparrow \qquad (1)$$

$(X = Cl$ or $F;\ Y = Cl$, F or $CF_3;$

$H_2L =$ protonated tridentate ligand)

The crystal structure of {*N*-(4-t-butylphen-2-oxy)salicylideneaminato}trichlorophosphorus(V) has been determined and shows that the ligand is coordinated to the phosphorus atom in the meridional conformation formed from a bicyclic five- and six-membered chelate ring using an ONO donor set. The hexacoordinate phosphorus compounds were characterized by their diagnostic ^{31}P NMR chemical shift values and their P–F spin–spin coupling constants where appropriate. During formation of (2,2′-azodiphenoxy)trifluorophosphorus(V) [^{31}P NMR δ: -144 (d,t) ppm; ^{19}F NMR δ: -51.2 (d,d; axial); -80.0 (d,t; radial) ppm; $^{1}J_{PF(ax)} = 841$, $^{1}J_{PF(rad)} = 769$, $^{2}J_{FF} = 47$ Hz], an intermediate was observed in solution [^{31}P NMR δ: -151 (quintet) ppm; $^{1}J_{PF} = 818$ Hz], consistent with a hexacoordinate $F_4P(LSiMe_3)$ species composed of a bidentate chelate with four fluxional fluorine substituents bound to a central phosphorus(V).

Both of the trifluoromethyl-substituted derivatives, i.e. {*N*-(phen-2-oxy)salicylideneaminato)}(trifluoromethyl)difluorophosphorus(V) (**1**) and (2,2′-azodiphenoxy)(trifluoromethyl)difluorophosphorus(V) (**2**) can form two possible geometrical isomers corresponding to *cis*- and *trans*-difluoro groups. Only one isomer was observed in compound **1** by NMR. This was assigned as the *cis* isomer on the basis of the two different environments observed for the fluorine groups [^{31}P NMR δ: -144 (d,d,quart) ppm; ^{19}F NMR δ: -50.8 (d,d,quart; axial); -69.3 (d,d,d; CF_3); -76.9 (d,d,quart; radial) ppm; $^{1}J_{PF(ax)} = 811$, $^{1}J_{PF(rad)} = 835$, $^{2}J_{PF} = 125$, $^{2}J_{FF} = 54$, $^{3}J_{FF(cis)} = 13$, $^{3}J_{FF(trans)} = 4$ Hz]. Both *cis* and *trans* isomers were observed in compound **2** [^{31}P NMR δ: *cis* isomer: -146 (d,d,quart) ppm; ^{19}F NMR δ: -57.7 (d,d,quart; axial); -69.3 (d,d,d: CF_3); -82.3 (d,d,quart: radial) ppm; $^{1}J_{PF(rad)} = 853$, $^{1}J_{PF(ax)} = 833$, $^{2}J_{PF} = 128$, $^{2}J_{FF} = 56$, $^{3}J_{FF(cis)} = 12$, $^{3}J_{FF(trans)} = 4$ Hz. ^{3}P NMR δ: *trans* isomer: -149 (t,quart) ppm; ^{19}F NMR δ: -62.1 (d,quart; axial); -68.9 (d,t: CF_3) ppm; $^{1}J_{PF} = 894$, $^{2}J_{PF} = 134$, $^{3}J_{FF} = 10$ Hz].

The electron-withdrawing NO_2 substituent in one of the aromatic rings is the compound {*N*-(4-nitrophen-2-oxy)salicylideneaminato}trifluorophosphorus(V) decreases the nucleophilicity of the coordinating nitrogen atom. In this case a pentacoordinate phosphorus(V) species [^{31}P NMR δ: -51 (quart) ppm; $^{1}J_{PF} = 895$ Hz] was observed and the ^{1}H NMR data suggested a possible tautomerism:

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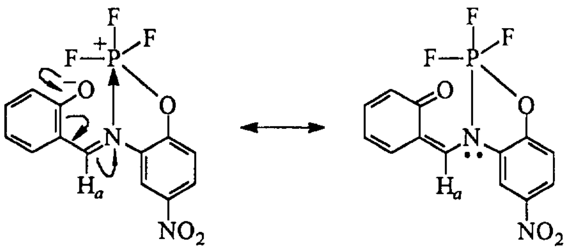

[H_a shifted to high field (7.1 ppm). Protons on quinoid ring broad. Protons on NO_2 subst. ring sharp.]

These new neutral hexacoordinate phosphorus(V) compounds provide further insight to the stereochemistry of 'hypervalent' phosphorus compounds. In addition, the tridentate nature of the ligands reduces the possibility of isomerization by twist mechanisms. The mechanistic character of these centers can be studied more readily due to the observation of intermediates.

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