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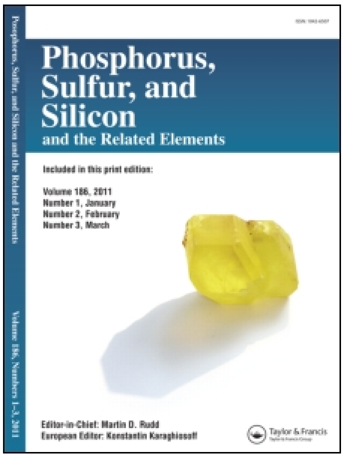

Phosphorus, Sulfur, and Silicon and the Related Elements

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HYPERVALENT PHOSPHORUS SPECIES AS AROMATIC AND METALLIC SPECIES

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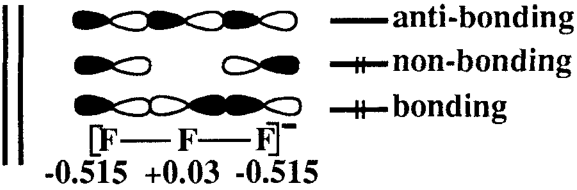
Abstract Hypervalent species are much better with equatorial groups which help the plus charge on the central atom. The apical atoms have negative charge and require groups to make the negative species stable. This is shown.

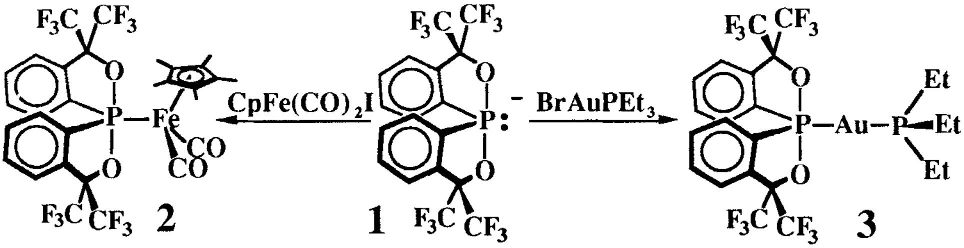
We have made some very stable 10-P-4 anionic species[1] with the two equatorial species being carbon and the two apical species were oxygens with two adjacent CF_3 groups.[2,3] These are the most stable 10-P-4 species to make the negative charge on the apical species and the positive charge on the central atom of the three-center four-electron (3c, 4e) hypervalent orbital. We did calculations of the anionic $(F_3)^-$ and found it to have a positive charge on the central fluorine of the anion.[4]

$$F:^- + F_2 = F_3^-$$



The plus charge on the central F (+0.03) makes this compound stable only at low temperature,[5] but if bigger central atoms have more stable positive charge we can use them at higher temperature. It is also helpful to have the apical atoms to stabilize the negative charge on these positions.

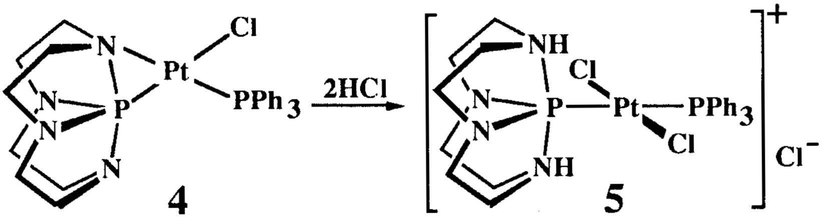
The 10-P-4 phosphoranide anion (**1**) is a very stable species with two equatorial phenyl groups and the two apical oxygens. This compound coordinates easily to a metal just on the phosphorus atom.[6]



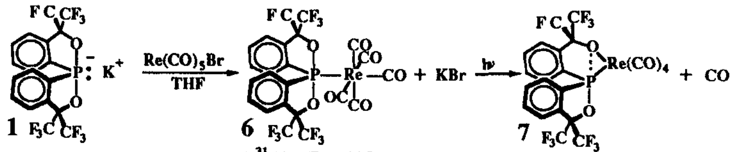
For several other species with four oxygens or four nitrogens, with the same groups of apical and equatorial atoms, these species are less stable and reactions of metals would often have the metals coordinate to both the phosphorus and one of the apical electron (3c,4e) orbital, but most metals coordinate both to the central and the apical atoms.[7,8]

We have added a very large number of metal species to **1** and each one coordinates only to the phosphorus, not to both the phosphorus and the apical oxygen. The ^{19}F NMR lets us have just two quartets when the metal is coordinated to the phosphorus. If one of the apical oxygens were coordinated to the metal, which are also coordinated to the phosphorus, then we would have four ^{19}F NMR quartets. We have used a large number of these metals and all of them was coordinated initially only to the phosphorus.[6] Both **2** and **3** were given X-ray structures and both were very close to the way they are drawn. The metals are equatorial and are coordinated only to the phosphorus of the 10-P-4 phosphorane. The way that **1** is a very stable hypervalent species has two trifluoromethyl groups adjacent to each of the apical oxygens. These two oxygens are negative and are stabilized by the CF_3 groups. The central phosphorus is positively charged like the central F of $(F_3)^-$ so it is much more stable if it has two equatorial carbons of the phenyl groups. The hypervalent species[1] make this phosphorus more easily positive charge than the F of $(F_3)^-$.

The coordination of four nitrogens to P, the Pt metal forms **4** with coordination to both P and N.[8c] But reaction of two HCl acids gives coordination only to the phosphorus (**5**). This is better because the two H^+ groups on the apical nitrogens make these apical species more stable. The Cl^- adds to the Pt of **5** and this also makes the Pt more equatorial in **5**.



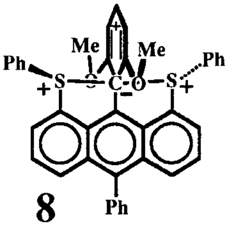
The reaction of $Re(CO)_5Br$ to **1** gives coordination for only the phosphorus of **6**. All of the reactions of **1** with metals act like **6** but this one when heated does remove one of the CO groups and provides the species of **7** that coordinates to both P and O to give four tetrahedral ^{19}F NMR groups.



Δ ^{31}P NMR = -14.5
^{19}F NMR: -72.90 (q, 6 F)
-73.26 (q, 6 F)

^{31}P NMR = +54.99
^{19}F NMR: -68.68 (q, 3 F), -73.45 (q, 3 F),
-73.64 (q, 3 F), -75.68 (q, 3 F)

We have very good evidence that the 10-C-5 species prepared by Forbus[9] was a 10-C-5 species. The compound (**8**) has very good evidence for having the hypervalent 10-C-5 carbon, since it does have ^{1}H NMR or ^{13}C NMR showing it to be like **8** rather than **9** even at low temperatures such as -100 °C. We think that the two electrons of the bonding orbital of the S-C-S species of **8** does coordinate to the five p-orbitals with four electrons and a plus charge in the top cyclic six carbons. With six electrons in the parallel p-orbitals this is an aromatic species for this part of the compound. We have found that all six of these ^{13}C compounds of this compound, even the hypervalent carbon, have ^{13}C NMR similar to an aromatic species.[9]



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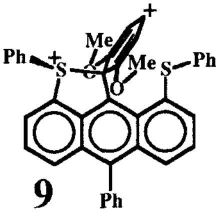

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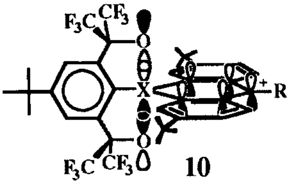
The X of **10** could be positive, neutral, or negative. The **X** is one of the main group elements. We expect the p-orbital of the **O-X-O**, with the electronegative apical oxygens, to make the p-orbital on the **X** a bit smaller. This could make it a better aromatic than **11**. The **Y** of **11** is either an element or a pair of electrons.

The two electrons in the bonding orbital, like that in (F-F-F)$^{-}$, could partly transfer into the plus orbital of the equatorial groups and would have six electrons in the six p-orbitals of the aromatic cycle. We are now trying the one with a phosphorus and expect that it will be a more stable aromatic than a compound like **11** where X is a phosphorus and **Y** is a pair of electrons or an element. We have some current work to make this new type of aromatic species with one hypervalent species element. We will try this with a large number of main-group elements for the **X** of **10**. We may be able to find new main-group element aromatic species that have not yet been made.



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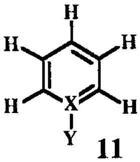

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It is very interesting that the three linear p-orbitals of the bonding and the non-bonding orbitals of the hypervalent species can interact with other equatorial ligands. We do find that the putting of an O^- on the phosphorus pair of electrons of **1** makes the apical P-O bonds longer by putting electrons from the p-orbitals of the O^- to the antibonding orbital of the 3c,4e species. It is interesting that **2** also makes the apical P-O bonds longer upon replacing the Fe to the pair of electrons of the phosphorus **1**. It makes the ^{13}C NMR of the $C_5(CH_3)_5$ group move down. This suggests that the d-orbitals on the Fe can move electrons into the non-bonding O-P-O hypervalent orbital. A large number of these new species for hypervalent species are being found.

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