

## Chemistry of Phosphaalkynes

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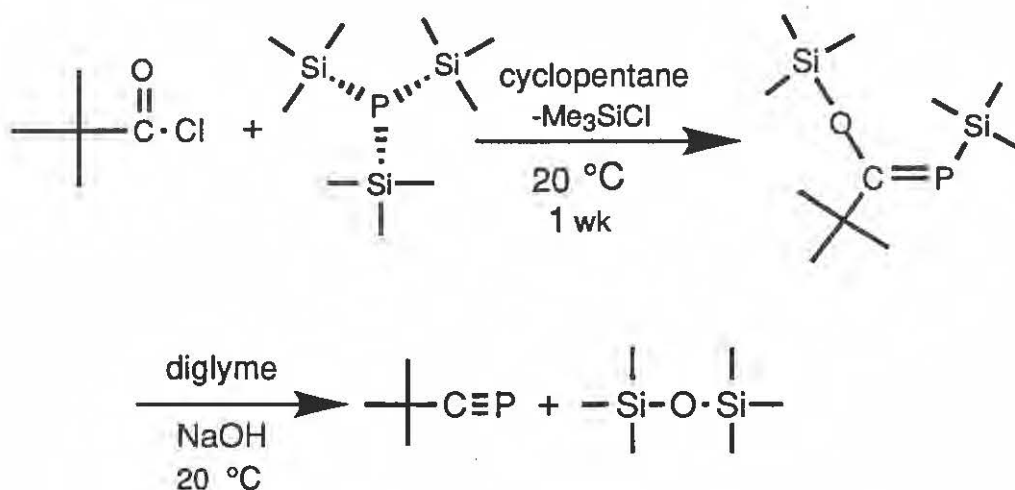
The heavier main-group elements are known for their reluctance to support multiple bonds; this observation has been formulated as the "double-bond rule". This behavior has been attributed to the relatively poor  $p\pi$ - $p\pi$  overlap for the heavier elements [1,2]. For example, it is thermodynamically favorable for a P atom to form three single bonds to other P atoms in white phosphorus, instead of one triple bond to form  $P_2$  gas. In addition to this thermodynamic consideration, there is also a kinetic factor which stabilizes multiple bonds between elements of the carbon row. Acetylene is an example of this; it will trimerize (explosively) only under pressures above 15 psig.

The concept of an isolobal analogy between a CH (or C-alkyl group) and phosphorus, combined with the discovery of compounds which violate the double-bond rule, prompted the search for compounds containing carbon-phosphorus triple bonds. The first confirmed instance of such a compound was the result of passing phosphine gas through an arc between graphite electrodes, resulting in phosphaacetylene, HCP [3]. This compound will polymerize, however, above  $-124^\circ\text{C}$ . MeCP was prepared, much later, by dehydrohalogenation of ethyldichlorophosphine at  $900^\circ\text{C}$ . It was also found to be stable only at low temperatures [4].

Microwave spectroscopy is a useful characterization technique for these unstable phosphaalkynes. Gas-phase infrared spectra of small molecules typically display rotational fine structure; microwave spectroscopy measures the absorptions caused by pure rotational energy-level changes. After correcting for factors such as centrifugal distortion, rotational constants can be derived, which correspond to the moments of inertia along different axes of a molecule. Detailed information on molecular geometry can be deduced from these data.

In addition to determining bond lengths and angles, microwave spectroscopy is also used for measuring dipole moments. This is done by taking advantage of the Stark effect, by which otherwise-degenerate rotational quantum states are split by the application of an electric field. The magnitude of this splitting is related to the dipole moment of the molecule. The direction of the dipole moment, however, cannot be measured using this technique. For HCP, the dipole moment was determined to be 0.392 D; the positive end of this dipole had originally been assumed to reside on P [5]. This, however, did not explain the downfield chemical shifts in the  $^{13}\text{C}$  NMR spectra of the phosphaalkynes [6]. Reversing the assignment of the dipole moments served not only to explain the NMR spectra, but also accounted for the observed trend in dipole moments following replacement of H- with various other substituents.

Systematic investigations into the reactions of phosphaalkynes, as opposed to their intrinsic properties, had been hampered by their thermal instability. The preparation of a phosphaalkyne species was accomplished by kinetically stabilizing the triple bond by using a tert-butyl substituent on the carbon, resulting in the compound  $\text{Bu}^t\text{CP}$ . This clear, distillable liquid (bp  $61^\circ\text{C}$ ) was synthesized by treating tris(trimethylsilyl)phosphine with  $\text{Bu}^t\text{COCl}$ , the driving force for this reaction being the formation of silicon-oxygen bonds in the  $\text{Me}_3\text{SiOSiMe}_3$  by-product [9,10].



Once this stable compound became available, research into transition-metal coordination chemistry and controlled oligomerizations began.

Treatment of ethenebis(triphenylphosphine)platinum(0) with  $\text{Bu}^t\text{CP}$  resulted in replacement of the olefin by the phosphalkyne [11]. The product,  $\text{Pt}(\eta^2\text{-Bu}^t\text{CP})(\text{PPh}_3)_2$ , was the first phosphalkyne transition metal complex prepared by direct addition of a free phosphalkyne. It was found that the coupling constant between  $^{195}\text{Pt}$  and  $^{31}\text{P}$  was only 62 Hz for the phosphorus on the phosphalkyne, indicating the non-participation of the lone pair on the P in bonding to the Pt. The importance of  $\pi$  backbonding from the metal to the  $\pi$  antibonding MO on the phosphalkyne ligand is reflected in the lengthening of the C-P bond and in the absence of free rotation of the phosphalkyne (along the axis bisecting the phosphalkyne and passing through the Pt). The electron density in one of the  $\pi$ -bonding orbitals on the phosphalkyne serves as the  $\sigma$ -donor.

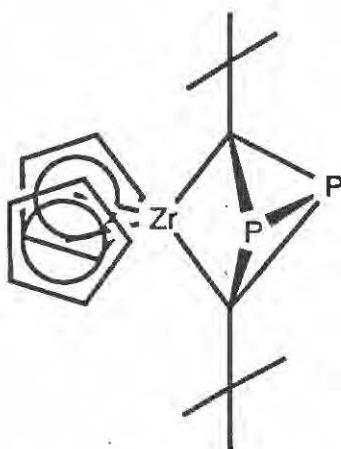
Both  $\pi$  bonds on the phosphalkyne can also act as a two-electron donors to a metal. Treating octacarbonyldicobalt(0) with  $\text{Bu}^t\text{CP}$  yields  $\text{Co}_2(\text{Bu}^t\text{CP})$ . The structure of this species--the intact phosphalkyne bridging two metal centers--was concluded from  $^{13}\text{C}$  NMR spectroscopic evidence and by analogy to known alkyne complexes [11,12]. The proposed structure indicates that the phosphalkyne acts as a four electron donor, with one  $\pi$  bond contributing electron density to each cobalt center.

In neither of these complexes--with the phosphalkyne acting as a two- or a four-electron donor--does the lone pair on the P interact with the metal. This has led to the idea that this lobe might donate, phosphine-like, to yet another metal. Such a bonding mode was determined by binding the above dicobalt complex to a pentacarbonyl-tungsten(0) moiety [12]. The phosphalkyne in this resulting complex donates a total of six electrons.

The complex  $\text{Pt}(\text{dppe})(\text{Bu}^t\text{CP})$  reacts with enneacarbonyldiiron(0) to give a cherry-red trimetallic complex, with the phosphalkyne phosphorus still bonded to the carbon and bridging all three metals and the carbon bridging two [13]. The presence of a platinum-phosphorus bond and the completion of the valence shells of the iron centers requires that the phosphalkyne donates six electrons. The  $^{31}\text{P}$  NMR spectrum, however, shows minimal (128 Hz) coupling between the platinum and the phosphalkyne phosphorus. To explain how six electrons can be donated without involving the phosphorus lone pair, a comparison was drawn between this and a few alkyne complexes which exhibit this bonding mode, such as enneacarbonyldiphenylethyneiron(0) [14]. The alkyne here assumed to become was olefin-like, leaving one  $\text{sp}^2$ -hybridized lobe to coordinate to one iron and the other to com-

bine with the remaining  $\pi$  bond to coordinate to the other two iron centers. This explanation, however, would involve a two-electron reduction of the alkyne, and oxidation products were not detected. Wade's rules provides a more satisfactory explanation of the observed structure: it only requires that the phosphaaalkyne donate four electrons.

Metal centers can also promote the oligomerization of  $\text{Bu}^t\text{CP}$ . A dimerization occurs along with ligation to cobalt in  $(\text{Cp})(\text{P}_2\text{C}_2\text{Bu}^t_2)\text{Co}$ , which is the first instance of a controlled oligomerization of a phosphaaalkyne [15]. The equivalence of the P-C bond lengths shows that the  $\pi$  density on the ligand is delocalized. A different type of dimerization occurs in  $\text{Zr}(\text{Cp})_2(\text{Bu}^t\text{CP})_2$  [16].



The bicyclic dimer can be removed from the metal by treating it with a mild chlorinating agent [17]. The dimers are then free to readily undergo a dimerization, which affords a high-yield synthesis of the tetraphosphacubane,  $(\text{Bu}^t\text{CP})_4$ . Characterization of the organic reactions undergone by this species has recently begun [18].

Research continues into the chemistries of both monomeric and oligomeric phosphaaalkynes; these investigations extend into main-group and transition-metal areas. Much has yet to be discovered about the ligating modes and the oligomerization pathways of these unique compounds.

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