Diphosphorus

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P≡P, a Laboratory Reagent?

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The P_4 versus N_2 conundrum is a question beloved of undergraduate examiners. A routine answer explains the interesting structural differences between these fundamentally important molecules in terms of the high strength of the homonuclear second period multiple bonds allied to the weakness of corresponding single bonds, a situation which is reversed in dealing with heavier homologues (Table 1).

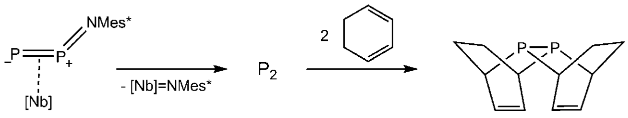
Table 1: Typical single and triple bond strengths for homonuclear group 15 element bonds.[1]

Nitrogen	[kJ mol^{-1}]	Phosphorus	[kJ mol^{-1}]
E(N≡N)	946	E(P≡P)	490
E(N−N)	159	E(P−P)	200
Ratio	5.95	Ratio	2.45

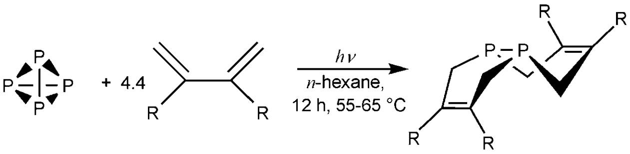
However, it has long been known that under appropriate conditions, phosphorus can exist as a dinuclear species. Hence it has been shown that an equilibrium exists between P_2 and P_4, but only under extreme conditions such as at temperatures greater than 800 °C and low pressures; at atmospheric pressure, dissociation of P_4 into $2P_2$ reaches ca. 50 % at 1800 °C. Thus, the application of such chemistry is mainly of interest to astronomers, plasma chemists and matrix isolation experimentalists. In communicating this fascinating chemistry to an undergraduate audience, one is often met with a polite chuckle and a realization that the dream of using P_2 as a reagent is beyond most accessible experimental methods. Or is it? Two recent studies from the group of Cummins shed an interesting light on this idea and offer the possibility of routine access to P_2 as a laboratory reagent.

In the first study, published in 2006,[2] a P_2NR moiety was assembled at a niobium center bearing sterically encumbered amido groups. Warming this species in cyclohexadiene led to formation of a stable Nb^V–imido species and concommitant formation of P_2 which was captured by its reaction as a dienophile in a double Diels–Alder reaction with the cyclohexadiene, leading to an interesting cage diphosphine as the ultimate product. Importantly, the whole procedure is carried out at temperatures no greater than 65 °C, suggesting that P_2 is accessible without recourse to extreme conditions. Despite this important observation, the synthetic protocol contains steps which represent a significant hurdle to the majority of synthetic chemists. Hence the widespread applicability of this method as an accessible route to P_2 is limited.

In trying to uncover alternative routes to these products, Tofan and Cummins[3] have reincarnated and updated some important work by von Rathenau[4] that has long lain dormant. Von Rathenau reported that the room temperature photolysis of P_4 using a mercury lamp yields red phosphorus, but importantly he suggested that this transformation occurs via the intermediacy of P_2. Amazingly, since it was published in 1937, this work has been cited by a mere three papers prior to the Cummins work. In trying to obtain the same product as shown in Scheme 1 using cyclohexadiene as eneophile, the product was found to be photoreactive and only trace amounts of the desired product were obtained. However, by using 1,3-dimethylbutadiene, the expected cycloadduct was obtained in moderate yields; a similar product is obtained using butadiene itself although again yields are very low (Scheme 2).



Scheme 1. [Nb] = Nb{N(Np)Ar}$_3$, Np = neopentyl, Ar = 3,5-$C_6H_3Me_2$, Mes* = 2,4,6-$C_6H_2(tBu)_3$.



Scheme 2. R = H, Me.

It remains to be seen whether this schematically simple approach to P_2 will be of general utility given that the conditions for the experiment are relatively specialist, employing a photochemical reactor with sixteen lamps emitting at 253.7 nm and with manipulations being carried out entirely within the inert atmosphere of a glovebox. Furthermore, the reaction conditions required for the formation of P_2 may preclude some otherwise desirable reaction partners. In this

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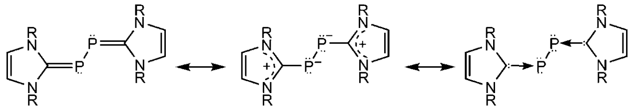
regard, it would be fascinating to know the lifetime of the photochemically generated P_2 and if it could be trapped for subsequent reactions. Nevertheless, despite these caveats, this study does emphasise that P_2 is both accessible in the laboratory under relatively mild conditions and that its lifetime is such that it may be employed as a reagent.

In addition to the beautiful work described above leading to free P_2, it is pertinent to note other recent examples where P_2 units have been prepared and stabilized. The earliest and most common method of stabilization has been coordination to transition metals. It is not the intention of this Highlight to document the range of reactions where P_2 has been observed coordinating to a transition element, but to note that several of the earliest reported reactions use a combination of transition metal substrate, white phosphorus and photochemistry—it would be fascinating in light of the work described above to know if this work should be reinterpreted with free P_2 being a key intermediate in these reactions. Additionally, a rather different method of stabilizing the P_2 moiety has recently emerged which involves its trapping using singlet carbenes. Robinson and co-workers reported[5] that potassium graphite reduction of a NHC–PCl_3 adduct yields [(NHC)PP-(NHC)]. Several canonical forms may be drawn for the product (Scheme 3), and analysis of the experimental data together with computational investigations favored a bis-phosphinidene formulation, with two P centers singly bonded to one another, each possessing two lone pairs of electrons and being ligated by a NHC group (Scheme 3, right).



Scheme 3. R = 2,6-diisopropylphenyl.

A similar product was observed by Bertrand et al. from the direct reaction of a cyclic alkylaminocarbene (CAAC) with P_4.[6] The bis-phosphinidene formulation of these products implies an electron rich P_2 unit which should be readily oxidized, and indeed this has recently been shown to be true.[7] Furthermore, the rather different ^{31}P NMR chemical shifts [$\delta = -52.4$ ppm for $P_2(NHC)_2$; $+59.4$ ppm for $P_2(CAAC)_2$] suggest that the P_2 fragment of the NHC-ligated species is rather more electron rich compared to the CAAC-ligated compound. Careful electrochemical studies identified the correct oxidant, and whereas the relatively electron-poor compound may only be singly oxidized to give the radical cation, the more electron rich species may be both singly and doubly oxidized, the latter yielding a carbene-stabilized P_2-dication. Given that this Highlight commenced with a comparison of the chemistry of phosphorus and nitrogen, it is pleasing to conclude that similar chemistry of singlet-carbene stabilized PN and its radical cation has recently been reported.[8]

In summary, these developments have shown that the chemistry of diphosphorus is not just the preserve of those with access to high-energy techniques. The true scope of the technique in terms of functional group tolerance and the possibility of stabilising the reactive moiety for use in subsequent reactions will doubtless be explored in the near future.

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