

A Retro Diels–Alder Route to Diphosphorus Chemistry: Molecular Precursor Synthesis, Kinetics of P₂ Transfer to 1,3-Dienes, and Detection of P₂ by Molecular Beam Mass Spectrometry

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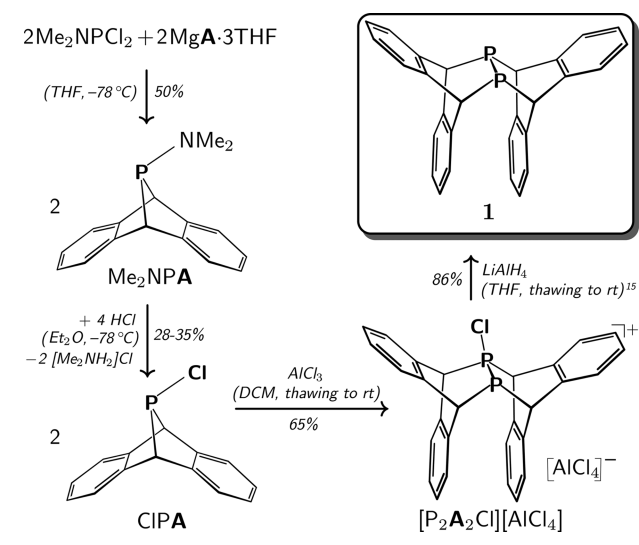
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S Supporting Information

ABSTRACT: The transannular diphosphorus bisanthracene adduct P₂A₂ (A = anthracene or C₁₄H₁₀) was synthesized from the 7-phosphadibenzonorbornadiene Me₂NPA through a synthetic sequence involving chlorophosphine CIPA (28–35%) and the tetracyclic salt [P₂A₂Cl][AlCl₄] (65%) as isolated intermediates. P₂A₂ was found to transfer P₂ efficiently to 1,3-cyclohexadiene (CHD), 1,3-butadiene (BD), and (C₂H₄)Pt(PPh₃)₂ to form P₂(CHD)₂ (>90%), P₂(BD)₂ (69%), and (P₂)[Pt(PPh₃)₂]₂ (47%), respectively, and was characterized by X-ray diffraction as the complex [CpMo(CO)₃(P₂A₂)] [BF₄]. Experimental and computational thermodynamic activation parameters for the thermolysis of P₂A₂ in a solution containing different amounts of CHD (0, 4.75, and 182 equiv) have been obtained and suggest that P₂A₂ thermally transfers P₂ to CHD through two competitive routes: (i) an associative pathway in which reactive intermediate [P₂A] adds the first molecule of CHD before departure of the second anthracene, and (ii) a dissociative pathway in which [P₂A] fragments to P₂ and A prior to addition of CHD. Additionally, a molecular beam mass spectrometry study on the thermolysis of solid P₂A₂ reveals the direct detection of molecular fragments of only P₂ and anthracene, thus establishing a link between solution-phase P₂-transfer chemistry and production of gas-phase P₂ by mild thermal activation of a molecular precursor.

An important theme in modern main-group chemistry is concerned with multiple bonds between the heavier members of the p-block elements.^{1,2} Noteworthy examples of unusual homo-diatomic triple bonds that could be stabilized using sterically demanding substituents or donor ligands include the diboryne reported by Braunschweig et al.³ and the disilyne reported by Sekiguchi et al.⁴ In this vein, we have been inspired to seek out access to the solution-phase chemistry of the triply bonded P₂ molecule by generating it as a reactive intermediate. Along these lines, we developed initially a niobium-complexed diphosphaazide ligand (P=P=NMe₂*, diphosphorus analogue of an organic azide) that was a molecular source of P₂, effecting transfer of the diphosphorus molecule to a variety of organic and inorganic acceptors upon mild thermal activation.^{5,6} Intrigued by the novel nature of several of the P₂-containing reaction products

Scheme 1. Synthesis of 1 (P₂A₂, A = C₁₄H₁₀ or Anthracene) Starting from Me₂NPCl₂ and MgA·3THF



so obtained, we sought to access P₂ by a photochemical route, reasoning that if indeed P₂ is a common reactive intermediate, then the same trapping products should result irrespective of the P₂ source. Our work on direct incorporation of P₂ units into organic molecules via UV irradiation of P₄/1,3-diene mixtures ensued,⁸ and theoretical studies suggest accordingly that a direct dissociation pathway exists for P₄ photo-cracking to 2P₂.⁹

Our recent report¹⁰ of easy access to the 7-phosphadibenzonorbornadiene skeleton now opens up a new possibility for thermal molecular precursor access to P₂ chemistry, one that is in line with traditional retro Diels–Alder routes for reactive intermediate generation.¹¹ Magnesium anthracene (MgA·3THF, A = C₁₄H₁₀ or anthracene) reaction with Cl₂PNMe₂ proceeds with formation of a 7-phosphadibenzonorbornadiene bearing a dimethylamino substituent at phosphorus (Scheme 1). Dimethylamino group replacement is effected by HCl treatment, providing the corresponding chloro-substituted 7-phosphadibenzonorbornadiene (CIPA, see Scheme 1 and Figure 1).¹²

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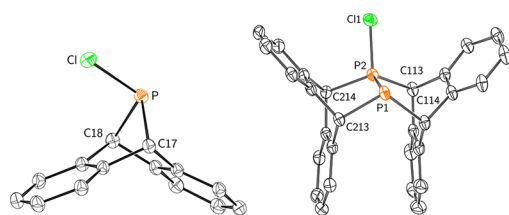


Figure 1. Solid-state molecular structures of ClPA and $[P_2A_2Cl][AlCl_4]$ (50% ellipsoids, 100 K) rendered using PLATON,⁷ with H-atoms, the $[AlCl_4]^-$ counterion, and the disordered solvent (see SI S.5) omitted for clarity.

The coupling together of two 7-phosphadibenzonorbornadiene groups occurred upon treatment of two ClPA with one $AlCl_3$,¹³ and subsequent rearrangement¹⁴ via an observable intermediate (see Supporting Information (SI) S.1.10 and S.1.11) resulted in a tetracyclic skeleton harboring a P_2 unit at the junction of two fused dibenzodiphosphabicycloocta[2.2.2]-diene bicycles. One P–Cl bond still remained in this phosphonium cation, $[P_2A_2Cl]^+$, isolated and structurally characterized as its tetrachloroaluminate salt (Scheme 1 and Figure 1). All that remained was to reductively dechlorinate cation $[P_2A_2Cl]^+$ by treatment with $LiAlH_4$,¹⁵ in order to afford the desired neutral P_2 precursor, P_2A_2 (**1**, title molecule boxed in Scheme 1),¹⁶ effectively a metastable sandwich of phosphorus (as P_2) between two anthracene molecules.

As expected under the assumption that compound **1** can serve as a thermal P_2 source, heating **1** in the presence of excess 1,3-cyclohexadiene (CHD) leads to high-yield formation of tetracyclic $P_2(CHD)_2$ (Scheme 2), a compound first encountered using niobium diphosphaazide as the thermal P_2 source.⁵ Heating compound **1** in the presence of excess unsubstituted 1,3-butadiene (BD) delivered the corresponding bicyclic derivative, $P_2(BD)_2$, in good yield for the first time (Scheme 2); it was previously isolated in trace quantities after being generated via the photochemical P_4 -cracking route and structurally characterized.⁸

Heating compound **1** in a benzene solution in the absence of an added trapping agent led to quantitative generation of anthracene, formation of an orange phosphorus precipitate and, interestingly, an appreciable amount of dissolved P_4 (see S.3.1). It should be noted also that compound **1**, which is colorless when pure, changes color to orange due to production of a form of polymeric red phosphorus upon exposure to light, with formation of anthracene.¹⁷

While we have not yet obtained the crystal structure of **1** by itself, we found that **1** forms a crystalline Mp^+ ($Mp = CpMo(CO)_3$) derivative in which the tetracyclic skeleton is intact (Scheme 2 and Figure 2). Interestingly, the thermolysis of a pyridine- d_5 solution of $[1-Mp][BF_4]$ revealed the formation of P_4 and the previously reported $CpMo(CO)_2P_3$ complex,¹⁸ along with anthracene. Treating **1** with the platinum ethylene complex $(C_2H_4)Pt(PPh_3)_2$, a competent acceptor of diphosphorus,⁶ led to the formation of the previously reported platinum diphosphorus complex $(P_2)[Pt(PPh_3)_2]_2$ ¹⁹ at room temperature, with release of anthracene and ethylene.

The complete transfer of P_2 from **1** to CHD has been the subject of a kinetic investigation and a computational study (Figures 3 and 4; eqs 1–6 below). The quantum chemical calculations suggest that retro Diels–Alder loss of anthracene (with formation of a $P=P$ double bond) is rate-determining. The first reactive intermediate thus formed, unobserved cyclic

Scheme 2. Transfer of P_2 from **1** (P_2A_2) to 1,3-Cyclohexadiene (CHD) and 1,3-Butadiene (BD) and to $(C_2H_4)Pt(PPh_3)_2$, Complexation of **1** with $[Mp][BF_4]$ ($Mp = CpMo(CO)_3$), and Thermolysis of **1** in Solution and in the Solid State

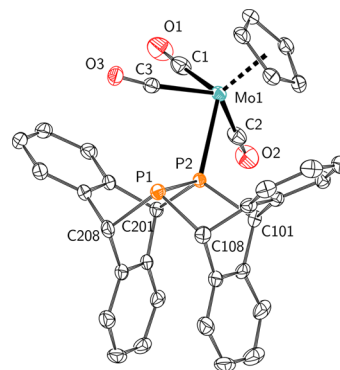
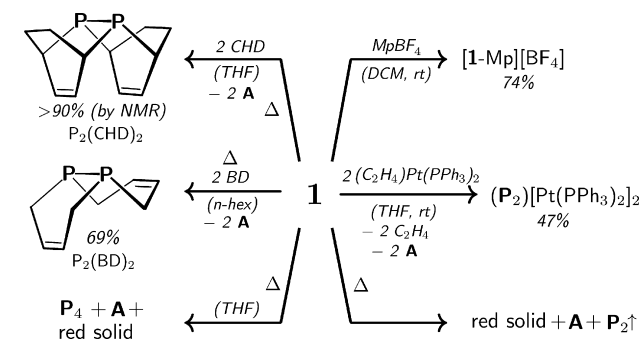
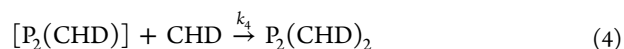
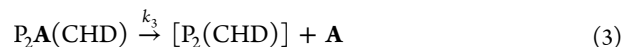
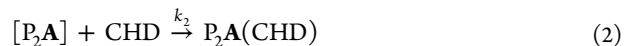


Figure 2. Solid-state molecular structure of $[1-Mp][BF_4]$ ($Mp = CpMo(CO)_3$) (50% ellipsoids, 100 K) and rendered using PLATON,⁷ with H-atoms and the $[BF_4]^-$ counterion omitted for clarity.

diphosphene $[P_2A]$, can either (eq 5) lose a second anthracene molecule by retro Diels–Alder to generate P_2 or (eq 2) undergo $[4+2]$ cycloaddition to CHD to generate the *observable* intermediate $P_2A(CHD)$. For computational consideration of further conceivable reactions of the reactive intermediate $[P_2A]$, such as dimerization or reaction with P_2 en route to P_4 , the reader is directed to SI Figure S.28.

Kinetic study of the P_2 -transfer reaction, monitored using phosphorus and proton NMR spectroscopy, has provided first-order rate constants for the decay of **1** as a function of temperature, listed in SI Table S.1. Importantly, the decay rate for **1** was found to be zero order in the concentration of CHD. To better understand the thermal transfer of P_2 to CHD, we undertook kinetic modeling of the process accounting simultaneously for decay of **1**, accumulation and decay of observable intermediate $P_2A(CHD)$, and formation of product $P_2(CHD)_2$. In the regime of high diene concentration, the simultaneous time evolution of all three observable species is accounted for nicely according to eqs 1–4:



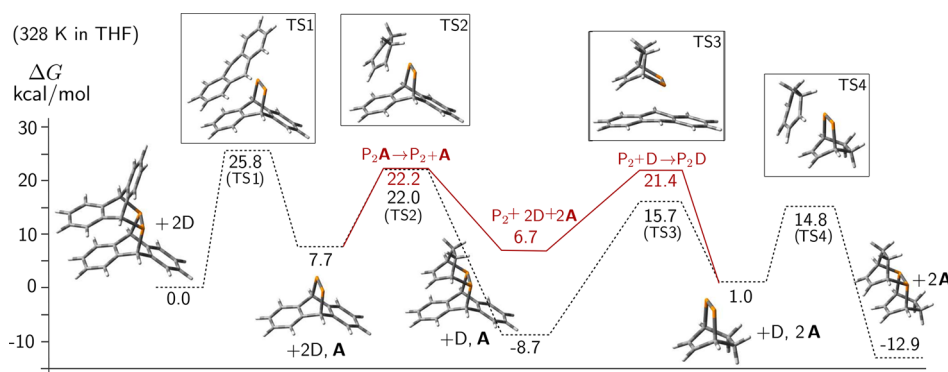


Figure 3. Combined DFT-calculated potential energy diagram (M06-2X, 6-311G(3df,2p), IEF-PCM in THF) for the thermolysis of P_2A_2 in the presence of 1,3-cyclohexadiene (D).

In modeling 1–4, loss of anthracene and addition of CHD were treated as irreversible, and unobserved diphosphene reactive intermediates $[P_2A]$ and $[P_2(CHD)]$ were treated with the steady-state approximation.²⁰ In the regime of low diene concentration, however, this simple linear model sequence was not satisfactory. Since low diene concentration would make reaction 2 less competitive with the alternative channel of second anthracene loss (reactions 5 and 6),



we added this channel to the model, resulting in a good fit of the simultaneous time evolution of all three observable species. The channel of reaction 5, “the P_2 pathway”, is suggested by the computational study to have a similar activation barrier in comparison with the competing pathway represented by reaction 2. The experimentally determined branching ratio (c , the microscopic rate of reaction 5 divided by that of reaction 2) is plotted in Figure 4 as a function of time and temperature in this regime of low diene concentration, where it applies. Note the increasing dominance of the unimolecular P_2 pathway (reaction 5) over bimolecular reaction 2 at elevated temperature, consistent with expectations based upon entropy considerations.

There is precedent for the thermal delivery of small-molecule reactive intermediates into the gas phase by retro Diels–Alder processes. Corey and Mock reported that, upon heating of a solid sample of the diimide (HN=NH) anthracene Diels–Alder adduct, it underwent decomposition “with evolution of a gas but without melting to give a solid residue of anthracene”.²¹ In a seminal report, the related Diels–Alder adduct of nitroxyl (HN=O) with 9,10-dimethylantracene was used to deliver HNO into the gas phase, where it was definitively characterized by microwave spectroscopy.²² Given this precedent, we were interested to discover whether mild thermal activation of solid samples of compound **1** would make possible the detection of diphosphorus in the gas phase.

Thermogravimetric analysis (TGA) of solid **1** evinced a mass change consistent with P_2 loss at 120 °C, a promising preliminary indication (Figure S.18). Heating solid samples of **1** in a sublimator resulted in pure anthracene on the cold probe and a red coating of phosphorus around the top of the apparatus near the vacuum exit port (Figure S.18). Attempts to detect P_2 in a combined TGA mass spectrometry (TGA-MS) study of **1** were inconclusive, likely due to the small-diameter, long pathlength

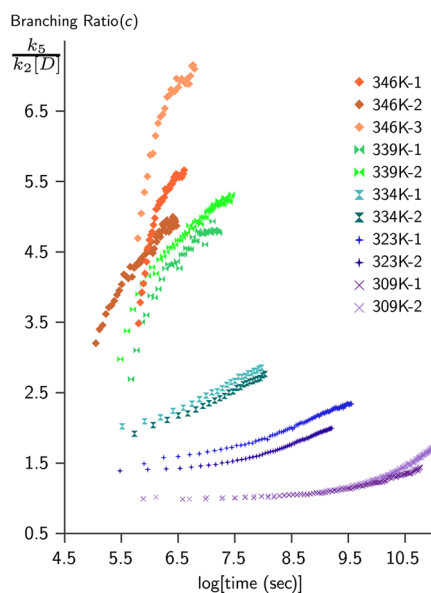


Figure 4. Plot displaying the branching ratio $c = k_5/(k_2[D])$ at temperatures ranging from 309 to 346 K, as a function of the logarithm of time (in seconds) for the thermolysis of P_2A_2 in THF in the presence of a small excess of 1,3-cyclohexadiene (D), with the initial molar concentration $[D]_0 = 89.16$ mM and ratio $[D]_0/[P_2A_2]_0 = 4.75$.

tubing connection between TGA and MS, in transit through which P_2 would need to survive many collisions.

Gradual heating of solid **1** on a temperature-controlled stage located within the source vacuum chamber of a pulsed-jet molecular beam instrument equipped with mass-spectrometric detection (MBMS)²³ led to the successful detection of gas-phase P_2 (62 m/z), P_1 (31 m/z),²⁴ and a fragment of anthracene (89 m/z), but not of P_3 , P_4 , or $[P_2A]$ fragments (Figure 5). By design, the molecular beam of the MBMS apparatus ensures a collision-free, post-thermolysis propagation of the molecular fragments to the mass spectrometer; the detection of P_2 from **1** thus implies that P_2 forms in a single, unimolecular event. Upon completion of the MBMS experiment, an orange residue was left inside of the sample holder. Its analysis using Raman spectroscopy revealed the formation of red phosphorus, while its combustion analysis indicated ~70% phosphorus content.^{17,25} To check if under identical experimental conditions of temperature (20–150 °C) and pressure ($\sim 8 \times 10^{-7}$ Torr) red phosphorus can generate P_2 , we proceeded to analyze a sample of commercially available red phosphorus using our MBMS apparatus.²⁶ However, no

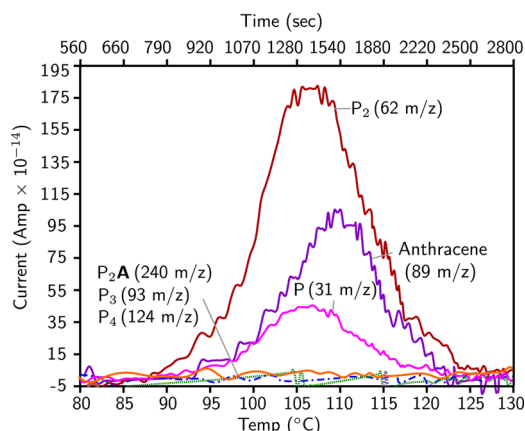


Figure 5. Plot displaying the measured current intensity of P_x fragments ($x = 1-4$), $[P_2A]$, and anthracene ($C_{14}H_{10}$) as a function of time and temperature, corrected for background signal intensity, and measured using a molecular beam mass spectrometry (MBMS) apparatus.

detectable amounts of P_x fragments were formed in the gas phase during the experiment. The unambiguous detection of P_2 from thermolysis of **1**, corroborated with the lack of P_2 detection upon heating red phosphorus under similar conditions, provides decisive evidence that **1** is indeed a thermal molecular precursor of P_2 .

The generation of reactive intermediates by retro Diels–Alder chemistry has previously afforded access to the solution-phase chemistry of interesting molecular species, including singlet O_2 ,²⁷ singlet S_2 ,^{28,29} HNO ,²² diazene,²¹ dimethyldisilyne,³⁰ and others;^{10,31} with the synthesis of **1**, we can now add P_2 to this list. The present work illustrates an exciting nexus of main-group element multiple-bond chemistry with that of reactive intermediates; we expect that this approach can be extended further to reactive intermediates involving novel combinations of main-group elements for study of reactivity patterns, evaluation of fundamental properties, and applications in synthesis.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic, kinetic, spectroscopic, computational, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(15) A precedent transformation,^{32,33} the reduction of chlorophosphonium salts with $LiAlH_4$ is known to produce phosphines, H_2 , and complex salts of formula $Li_xAlCl_yH_{4-y}$ ($x = 0-1$, $y = 0-4$).

(16) P_2A_2 displays a chemical shift of -42 ppm in its ^{31}P NMR spectrum, which shift compares well to those of other polycyclic diphosphanes.⁸ Isolated as a microcrystalline white solid sparingly soluble in benzene, but soluble in tetrahydrofuran, P_2A_2 is a light-sensitive material.

(17) It has been reported that red phosphorus forms upon the condensation of diphosphorus molecules.^{9,25} Also, detailed in SI S.4 is our computational investigation on P_4 formation by thermolysis of a solution of P_2A_2 in benzene, showing that it could proceed via the dimerization of $[P_2A]$.

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