ChemPubSoc Europe
DOI: 10.1002/chem.201402031
CHEMISTRY
A European Journal
Full Paper

Bond Activation

Reversible, Photoinduced Activation of P_4 by Low-Coordinate Main Group Compounds

Jonathan W. Dube,[a] Cameron M. E. Graham,[a] Charles L. B. Macdonald,[b]
Zachary D. Brown,[c] Philip P. Power,[c] and Paul J. Ragogna*[a]

Abstract: Two unique systems based on low-coordinate main group elements that activate P_4 are shown to quantitatively release the phosphorus cage upon short exposure to UV light. This reactivity marks the first reversible reactivity of P_4, and the germanium system can be cycled 5 times without appreciable loss in activity. Theoretical calculations reveal that the LUMO is antibonding with respect to the main group element–phosphorus bonds and bonding with respect to reforming the P_4 tetrahedron, providing a rationale for this unprecedented activity, and suggesting that the process is tunable based on the substituents.

The investigation of p-block elements in unusual bonding environments has been a prominent area of research over the past two decades. Justification for the continued study of these compounds is born from their potential for unprecedented reactivity, which previously was thought to be reserved only for transition metals.[1] Dominating this area of main group chemistry are the “frustrated Lewis pairs” (FLPs),[2] stable singlet carbenes,[3] and low-coordinate or multiply bonded main group compounds,[4] all of which have been shown to activate a variety of small molecule substrates, most notably H_2 and NH_3. Furthermore, reversible activation of small molecule substrates by p-block elements is extremely rare, limited to H_2, CO_2, and ethylene by special FLP systems or uniquely bonded heavy main group elements.[5] Furthering the discovery of main group systems capable of activating and releasing substrates is paramount for the continued development of chemical modification of organic molecules without the aid of transition metals.

White phosphorus, P_4, is a commodity reagent used for the production of the majority of phosphorus-containing compounds. The controlled activation of this reagent provides access to atomically precise phosphorus fragments for the building of more complex molecules or for use as a single-source precursor for subsequent chemistry. Early and late transition metals have a long history of reactivity with white phosphorus; an array of products have been isolated, and transfer of phosphorus fragments to other substrates has also been achieved.[6] Two exceptional examples of this are by anionic niobium compounds reported by Cummins (**A**, **B**), which can transfer phosphorus to main group and transition metal electrophiles, giving unique structures.[7] Metal-free activation of P_4 has only recently been accomplished, most commonly with low-coordinate, amphiphilic, main group centers.[8] Insertion into one, or multiple, P–P bonds of the P_4 tetrahedron has been observed for dicoordinate mimics of singlet carbenes. The neutral group 13 or 14 compounds controllably break one or two P—P bonds depending on the main group element (**C**, **D** in Figure 1),[9] while cationic phosphenium ions can activate one, two, or three P—P bonds with the product ratio depending on the reaction stoichiometry (**E**, **F**).[10] N-heterocyclic carbenes (NHCs) have shown diverse reactivity involving the degradation or aggregation of P_4-producing base-stabilized P_1, P_2,[11a] P_4,[11b] P_8,[11c,d] or P_{12} fragments,[11e] with the product depending on the electronic nature of the carbene (**G**, **H**, **I**). The utility of these compounds has been limited to very special cases where the phosphorus atoms can be functionalized by conjugated dienes in situ,[11] transition metal Lewis acids,[9f] or selenation with elemental selenium.[12] A crucial development in this field is the controlled release or transfer of the activated phosphorus fragment to a new substrate, while pushing forward to the catalytic functionalization of P_4 to a single product is considered the ultimate goal. While Weigand et al. have recently demonstrated that a compound similar to **E** can be stoichiometrically fragmented into two phosphorus containing products by the addition of an NHC, the phosphenium ion required for the initial activation remains in one of the prod-

---

[a] *J. W. Dube, C. M. E. Graham, Prof. P. J. Ragogna*
Department of Chemistry and Center for Advanced Materials
and Biomaterials Research (CAMBR)
The University of Western Ontario
1151 Richmond St., N6A 5B7 London, Ontario (Canada)
Fax: (+1) 519-661-3022
E-mail: pragogna@uwo.ca

[b] *Prof. C. L. B. Macdonald*
Department of Chemistry and Biochemistry
The University of Windsor
601 Sunset Ave., N9B 3P4 Windsor, Ontario (Canada)

[c] *Dr. Z. D. Brown, Prof. P. P. Power*
Department of Chemistry
The University of California
1 Shields Ave., 95616 Davis, California (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201402031.

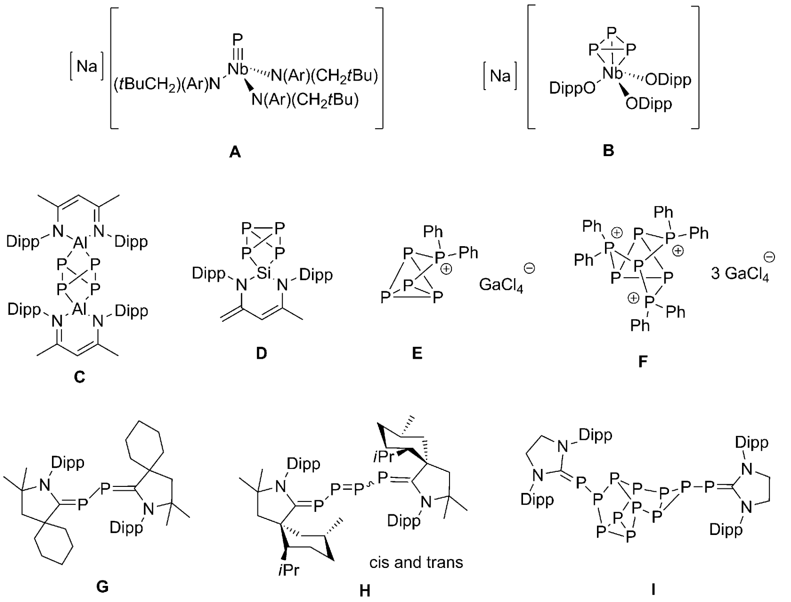
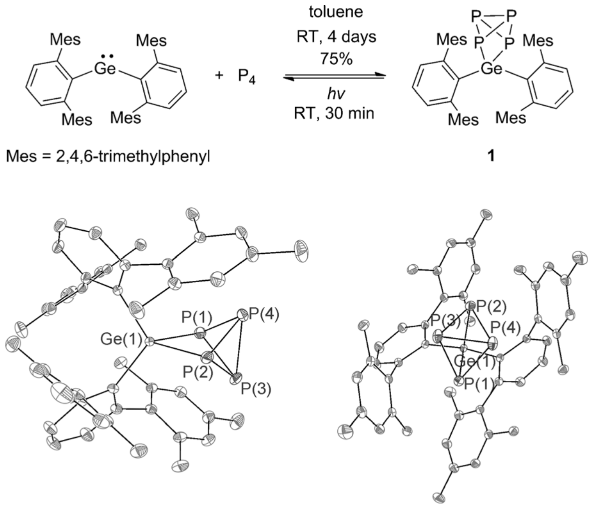


Figure 1. Two examples of transition metal compounds resulting from P_4 activation that can also transfer the phosphorus fragment to a new substrate (**A**, **B**; Ar = 3,5-dimethylphenyl), and selected examples of the products from reaction of low coordinate main group compounds and NHCs with P_4 (**C**–**I**). Dipp = 2,6-diisopropylphenyl.

ucts.[13] To date there are no examples of products from metal-free P_4 activation releasing the phosphorus fragment from the p-block element containing starting material. This considerable problem could persist due to the strength of the newly formed main group element–phosphorus bonds, resulting in a reluctance to release the phosphorus component after activation. In this context, we report the controlled activation of a single P–P bond in the white phosphorus tetrahedron by a diarylgermylene,[14] producing **1** (Scheme 1), which was isolated in good yields and comprehensively characterized. This novel product, in addition to a known phosphorus-based system, quantitatively release P_4 upon short exposure to UV light, representing an unprecedented mode of reactivity for metal-free white phosphorus activation.

The 1:1 stoichiometric addition of the diarylgermylene, $GeAr_2$ (Ar = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$(CH_3)_3C_6H_2$) to P_4 at room temperature results in the gradual appearance of two doublet of doublets, consistent with an A_2X_2 spin system ($\delta_P = -275$, 135 ppm; $^1J_{P\text{-}P} = 155$ Hz in toluene), in the $^{31}P\{^1H\}$ NMR spectrum (Scheme 1).[15] The reaction does not go to completion in one week as evidenced by the characteristic purple color of $GeAr_2$ in the reaction mixture and the distinctive signal of P_4 in the $^{31}P\{^1H\}$ NMR spectrum ($\delta_P = -521$ ppm). After removing the reaction solvent the remaining starting materials are isolated by extraction into pentane leaving a white powder. The ^1H NMR spectrum of the colorless solids show two sets of signals for the terphenyl substituents, differing from that of the free $GeAr_2$. An X-ray diffraction study on a single crystal grown from a saturated benzene solution at room temperature confirms the identity of the product to be **1**, isolated consistently between 60–65 % as a purified powder. The combined pentane fractions give back the appropriate mass balance of the reactants, which can be reused for the repeated synthesis of **1**. The reaction can be accelerated by heating a 1:1 stoichiometric mixture of $GeAr_2$ and P_4 at 60 °C for 24 h, however the isolated yield is comparable to the room temperature reaction (cf. 65 %) as heating the germanium starting material for prolonged periods of time results in decomposition. The reaction rate also increases when four stoichiometric equivalents of P_4 are used, with a 75 % isolated yield obtained after 4 days at room temperature. It should be noted that **1** is the only phosphorus-containing product observed in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixture over the range of conditions employed. Compound **1** is very insoluble in aliphatic hydrocarbon solvents, however is reasonably soluble in aromatic solvents. This compound is also extremely stable in the solid state, melting at 240 °C, and shows no signs of decomposition when stored at room temperature under a nitrogen atmosphere.



Scheme 1. Top: The synthesis of **1** from P_4 and $GeAr_2$ in toluene as well as the reverse reaction upon exposure to UV light. Bottom: The solid-state structure of **1** with a side view on the left and the end on view on the right. Ellipsoids are drawn to 50 % probability and hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Ge(1)–P(1) 2.3433(7), Ge(1)–P(2) 2.3509(9), Ge(1)–C(1) 1.9975(12), Ge(1)–C(25) 1.9932(12), P(1)–P(3) 2.2091(7), P(1)–P(4) 2.2432(8), P(2)–P(3) 2.2470(7), P(2)–P(4) 2.2146(7), P(3)–P(4) 2.1746(9), C(1)–Ge(1)–C(25) 111.39(5), P(1)–Ge(1)–P(2) 82.29(2), P(3)–P(1)–P(4) 58.47(3), P(1)–P(3)–P(4) 61.55(2), P(1)–P(4)–P(2) 87.71(2).

Compound **1** represents the first activation of white phosphorus by a germanium-containing compound, which has been recognized as an obvious omission during the diverse reactivity studies of N-heterocyclic carbenes and N-heterocyclic silylenes with P_4.[8a] A germanium analogue of these systems has been noted to *not* react with P_4 in refluxing toluene.[9b] The rationale for the difference in reactivity is the lower reduction potential of germanium compared to silicon due to the inert pair effect. This behavior clearly differs greatly from that of the diarylgermylene, **1**, which mildly activates white phosphorus at room temperature, albeit over several days. It is likely that the lack of electronically stabilizing nitrogen atoms allows the germanium atom to be electrophilic enough to initiate the activation process. There is only one example of a low-coordinate tin center controllably reacting with white phosphorus,[16] however the reaction of $SnAr_2$ and P_4 results in decomposition of the stannylene and no phosphorus containing products are observed in the $^{31}P\{^1H\}$ NMR spectrum.

The solid-state structure of **1** is also shown in Scheme 1 and confirms the single insertion of $GeAr_2$ into one P–P bond.[17] The P_4 unit exists in a butterfly confirmation while the germanium atom is in a distorted tetrahedral geometry. This structure resembles that of other heavy p-block element carbenoids (i.e., **D**, **E**) in which a single P–P bond is broken and two main group element–phosphorus bonds are formed. The Ge–P bond lengths are nearly identical at 2.3433(7) and 2.3509(9) Å. The phosphorus atoms adjacent to the germanium atom possess P–P bond lengths of 2.2091(7), 2.2432(8), 2.2146(7), and 2.2470(7) Å. The P–P bond on the exterior of the tetrahedron is slightly shorter at 2.1746(9) Å. These are all consistent with P–P single-bond lengths in the literature, which typically range from 2.15 to 2.30 Å. The C–Ge–C bond angle has decreased slightly from the free $GeAr_2$ at 111.39(5)° (cf. 114.4(2)°) while the P–Ge–P bond angle is much smaller at 82.29(2)°.[14] The steric bulk of the terphenyl substituents likely prevents the activation of a second P–P bond as the flanking aryl rings extend around the P_4 fragment. This considerable steric pocket could also partially explain the slow reaction times.

The potential for this reaction to be reversible was first observed visually with an NMR sample that had been left under natural light for several days. The solution was originally colorless and gradually turned the characteristic purple/blue color of $GeAr_2$, while the presence of P_4 was also confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Irradiating **1** with UV light,[18] instead of ambient light, accelerates the reverse reaction considerably, while thermal conditions have no effect on the reaction. Irradiation of a saturated solution of **1** (30 mg mL^{-1} in toluene) for two hours results in a color change to an intense purple color. The rate is clearly dependent on concentration with normal samples suitable for ^1H NMR spectroscopy (10 mg mL^{-1}) requiring less than 30 min of irradiation (23.2 mW). The quantitative production of P_4 is easily identified by monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 2 A) while the clean reformation of $GeAr_2$ was confirmed by ^1H NMR spectroscopy (Figure S7 in the Supporting Information). The reaction reverts

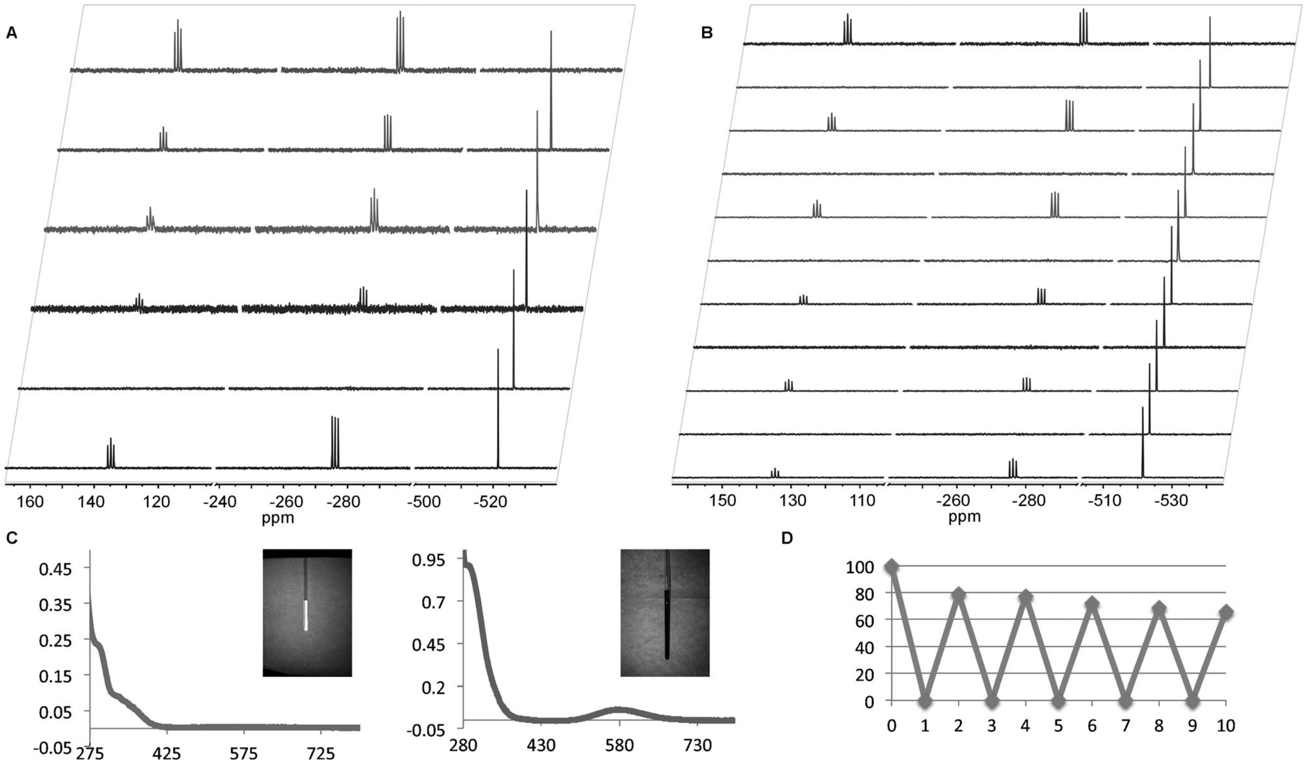


Figure 2. A) $^{31}P\{^1H\}$ NMR spectra of: purified **1** in toluene, **1** after 30 min radiation with UV light, 1 h UV light, 1.5 h UV light, 2 h UV light, and left standing for 5 days in the dark, from top to bottom, respectively. B) $^{31}P\{^1H\}$ NMR spectra of: purified **1** in toluene, **1** after 2 h radiation with UV light, left standing for 5 days in the dark, repeated 5 times, from top to bottom, respectively. C) UV/Vis spectra of a dilute solution of purified **1**, and **1** after exposure to UV light for 30 min from left to right, respectively. Insets show concentrated NMR samples. D) A plot of the percentage of **1** observed in the $^{31}P\{^1H\}$ NMR spectra for each cycle shown in (B). Note: UV light is generated from a low-pressure, high-intensity single-arc mercury lamp, 254 nm.

back to an appreciable amount of product (79% by integration of the $^{31}P\{^1H\}$ NMR spectrum) after 5 days at room temperature in the dark. The yield obtained from the integrations in NMR spectrum is comparable to what is observed in the reaction of $GeAr_2$ and P_4 in a 1:1 stoichiometry for the same time period. The starting materials are regenerated with nearly no sign of decomposition upon further radiation with UV light for 45 min. Cycling the reaction again it is observed that compound **1** is produced in comparable amounts, 77% by integration, after 5 days in the dark. This process can be cycled 5 times (25 days in solution) without an appreciable reduction in the production of **1** (14% loss over the 5 cycles; Figure 2B, D). The percentage decrease can likely be attributed to the small decomposition of $GeAr_2$, which is inherently very sensitive in solution, over the 25 days of the experiment.

The UV/Vis spectrum of **1** shows an absorbance with a λ_{max} of 294 nm ($\varepsilon = 7933\ L\,mol^{-1}\,cm^{-1}$; Figure 2C left). After irradiating a sample of **1** with UV light for 20 min, a broad absorption consistent with the presence of $GeAr_2$ is observed with a λ_{max} of 579 nm (Figure 2C right) comparing well to the literature value (cf. 578 nm).[14] To understand the origin of the absorbance, time-dependent DFT calculations were performed on **1** and on a series of less-substituted model clusters derived from diarylgermylenes (Ph_2GeP_4 and $(2,6\text{-}Ph_2C_6H_3)_2GeP_4$). For all of the model complexes, the calculations reveal that the absorptions are primarily attributable to excitations from the highest-occupied MO's, which are bonding with respect to the P–Ge–P fragment in the molecule, to the lowest-unoccupied MO's, all of which are antibonding with respect to the Ge–P bonds in the P–Ge–P fragment and bonding in regard to formation of a P–P bond (orbitals and interactions are illustrated for Ph_2GeP_4 in Figure 3). The λ_{max} values for the series become increasingly redshifted as the substitution on the aryl group is increased, but all remain in the range of 300–350 nm. For comparative purposes, TD-DFT calculations were also performed on the diarylgermylene precursors and reproduce the experimental observations well: for example, the maximum absorbance for $(2,6\text{-}Mes_2C_6H_3)_2Ge$ is calculated to be at 567 nm even in the absence of a solvent correction.

In addition to the subtle substituent-dependent changes predicted for the UV/Vis spectra, thermochemical data obtained from models of all of the clusters, the precursor germylenes, and P_4 reveal that the insertion reaction becomes less favorable as the substituent on Ge is changed from Ph to a terphenyl group. For example, the insertion reaction of Ph_2Ge into P_4 to yield Ph_2GeP_4 has a ΔG of $-109\ kJ\,mol^{-1}$, whereas the analogous insertion reaction involving $(2,6\text{-}Ph_2C_6H_3)_2GeP_4$ has a ΔG of $-88\ kJ\,mol^{-1}$. Further DFT calculations provide insight into mechanistic details of the insertion process, which is summarized graphically in Figure 3. The process begins with the formation of a donor–acceptor complex between P_4 and the germylene involving a single very long P–Ge bond of 2.614 Å (no transition state was identified for that process). This is followed by the asymmetrical insertion of germanium atom into the most proximate P–P bond; examination of imaginary vibrational mode for this transition state confirms that the motion involves the breaking of the P–P bond and the formation of two Ge–P bonds (2.507 and 2.615 Å). The transition state leads directly to the final inserted compound, which has a nearly C_2 symmetric structure and much shorter Ge–P bonds (both are 2.334 Å). It should be noted that we also looked at the triplet surface and found it to be much higher in energy.

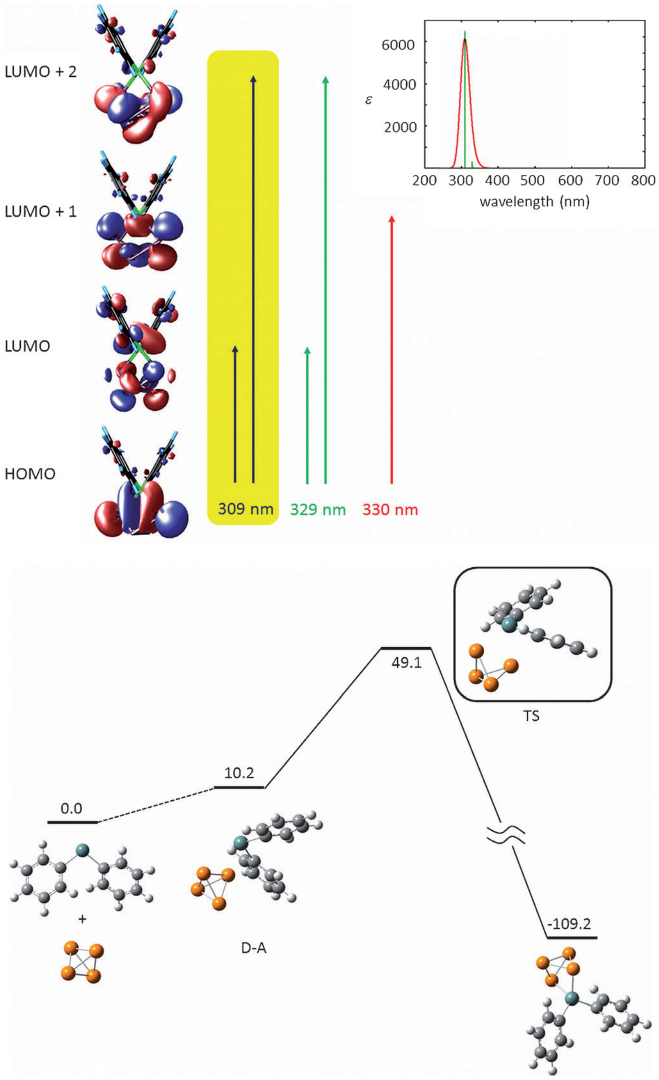
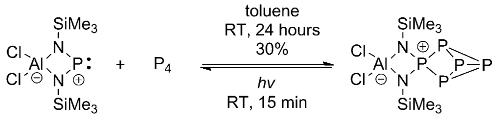


Figure 3. Top: Illustration of the important frontier orbitals for the model compound Ph_2GeP_4. The arrows indicate the important orbital interactions that give rise to the transitions calculated using TD-DFT; the calculated spectrum is illustrated in the inset and the transition with the largest oscillator strength is highlighted. Bottom: Reaction coordinate diagram of mechanism for the insertion of the model germylene Ph_2Ge into P_4 to produce Ph_2GeP_4. The stationary point listed D–A is the donor–acceptor intermediate and the transition state for the insertion process (TS) is boxed.

After observing and rationalizing the unique behavior of the diarylgermylene we were very curious to see if this reversible behavior persists in other systems known to activate P_4. A dicoordinate, zwitterionic, phosphenium ion was the logical choice as it is isolobal to the germylene, while also being net charge neutral. Compound **2** is easily prepared and cleanly inserts into one P–P bond of the P_4 tetrahedron, resulting in compound **3** which is structurally similar to **1** (Scheme 2).[10b]



2 3

Scheme 2. The reaction of the zwitterionic phosphenium ion (**2**) inserting into P_4 (**3**), and the previously unknown reverse reaction using UV light for only 15 min.

Much to our amazement, isolated **3** reverts back to the starting materials, as observed by $^{31}P\{^1H\}$ NMR spectroscopy, after irradiation with UV light for only 15 min (Figure S25, and S26 in the Supporting Information). This finding provides the very real possibility that many other main group systems that activate white phosphorus could do so reversibly. While this particular zwitterionic phosphenium ion system is not nearly as efficient as $GeAr_2$ at inserting into white phosphorus, and doing so repeatedly, calculations on model phosphenium systems involving Ph_2P^+ and $Cl_2Al(NSiMe_3)_2P$ and P_4 (see the Supporting Information) reveal that it is possible to tune the energetics of activation and release by altering the main group element carbenoid or the substituents on the ligand framework. Overall, the controllable insertion and release reactivity described herein is a completely unprecedented mode of chemistry for white phosphorus and it is ripe for further development and optimization.

In conclusion, we have demonstrated that a low coordinate germanium center can insert into one bond in the P_4 tetrahedron, representing the first such activation of white phosphorus by germanium. Remarkably, this process is completely reversible by irradiating a purified sample of **1** with UV light for a short amount of time. DFT calculations reveal that the UV/Vis absorption of **1** corresponds to depopulation of Ge–P bonding orbitals and population of orbitals with Ge–P antibonding character (and P–P bonding character) and explains the ability for the germanium atom to release the P_4 fragment. This reactivity also represents a rare instance of a main group element capable of *both* the oxidative addition and reductive elimination processes at a single site, mimicking the behavior of transition metal based catalytic systems.[19] These processes are very clean, with both reactions occurring at ambient temperature and pressure. It was also demonstrated that an isolobal, zwitterionic, dicoordinate phosphenium ion can also release P_4 upon exposure to UV light, providing the possibility for this transformation to be general over the range of main group elements that activate white phosphorus. Furthermore, the calculations also provide evidence for the system to be tunable based on the substituents of the p-block element. The functionalization of the phosphorus fragment followed by controlled release upon exposure to UV light could be a step towards the catalytic functionalization of P_4, and is currently a target in our laboratories. In a general sense, it is also possible that using UV photolysis to release functionalized fragments from activated main group compounds could become a fruitful new strategy for synthetic chemists.

Experimental Section

All experimental details, including general methods, methods for X-ray crystallography and the theoretical work, synthesis of **1**, and complete NMR spectra for characterization and reversibility studies are included in the Supporting Information.

Acknowledgements

The authors are grateful toNatural Science and Engineering Research Council (NSERC), the Ontario Government, the Canadian Foundation of Innovation (CFI), and the U.S. Department of Energy (FG02-07ER46475) for their generous funding. In addition, the University of Western Ontario, the University of Windsor, and the University of California at Davis are thanked for their funding contributions. Prof. C. D. Martin (Baylor University) is thanked for useful discussions.

Keywords: bond activation · germanium · main group chemistry · reversible reactivity · white phosphorus

[1] P. P. Power, *Nature* **2010**, *463*, 171 – 177.
[2] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50 – 81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46 – 76.
[3] D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389 – 399.
[4] a) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354 – 396; b) S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, *30*, 1748 – 1767; c) P. P. Power, *Acc. Chem. Res.* **2011**, *44*, 627 – 637; d) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877 – 3923; e) T. Sasamori, N. Tokitoh, *Bull. Chem. Soc. Jap.* **2013**, *86*, 1005 – 1021.
[5] a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124 – 1126; b) M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52 – 53; c) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770 – 6773; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643 – 6646; d) Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, P. P. Power, *Science* **2009**, *325*, 1668 – 1670; e) R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. De Cozar, F. P. Cossio, A. Baceiredo, *Angew. Chem.* **2011**, *123*, 10598 – 10600; *Angew. Chem. Int. Ed.* **2011**, *50*, 10414 – 10416; f) R. Rodriguez, Y. Contie, D. Gau, N. Saffon-Merceron, K. Miqueu, J.-M. Sotiropoulos, A. Baceiredo, T. Kato, *Angew. Chem.* **2013**, *125*, 8595 – 8598; *Angew. Chem. Int. Ed.* **2013**, *52*, 8437 – 8440.
[6] a) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178 – 4235; b) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164 – 4177; c) M. Peruzzini, L. Gonsalvi, A. Romerosa, *Chem. Soc. Rev.* **2005**, *34*, 1038 – 1047.
[7] a) B. M. Cossairt, C. C. Cummins, *Angew. Chem.* **2008**, *120*, 8995 – 8998; *Angew. Chem. Int. Ed.* **2008**, *47*, 8863 – 8866; b) B. M. Cossairt, C. C. Cummins, *Angew. Chem.* **2010**, *122*, 1639 – 1642; *Angew. Chem. Int. Ed.* **2010**, *49*, 1595 – 1598; c) J. S. Figueroa, C. C. Cummins, *Angew. Chem.* **2005**, *117*, 4668 – 4672; *Angew. Chem. Int. Ed.* **2005**, *44*, 4592 – 4596; d) B. M. Cossairt, M.-C. Diawara, C. C. Cummins, *Science* **2009**, *323*, 602; e) B. M. Cossairt, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 15501 – 15511; f) N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9524 – 9535; g) D. Tofan, B. M. Cossairt, C. C. Cummins, *Inorg. Chem.* **2011**, *50*, 12349 – 12358. For an excellent example of a uranium compound activating P_4 and transfer electrophiles: D. Patel, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2013**, *125*, 13576 – 13579; *Angew. Chem. Int. Ed.* **2013**, *52*, 13334 – 13337.
[8] a) S. Khan, S. S. Sen, H. W. Roesky, *Chem. Commun.* **2012**, *48*, 2169 – 2179; b) M. Scheer, G. Balazs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236 – 4256; c) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, *255*, 1342 – 1359.
[9] a) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. Hughes, *Angew. Chem.* **2004**, *116*, 3525 – 3527; *Angew. Chem. Int. Ed.* **2004**, *43*, 3443 – 3445; b) Y. Xiong, S. Yao, M. Brym, M. Driess, *Angew. Chem.* **2007**, *119*,

4595–4597; *Angew. Chem. Int. Ed.* **2007**, *46*, 4511–4513; c) S. Khan, R. Michel, S. S. Sen, H. W. Roesky, D. Stalke, *Angew. Chem.* **2011**, *123*, 11990–11993; *Angew. Chem. Int. Ed.* **2011**, *50*, 11786–11789; d) S. S. Sen, S. Khan, H. W. Roesky, D. Kratzert, K. Meindl, J. Henn, D. Stalke, J.-P. Demers, A. Lange, *Angew. Chem.* **2011**, *123*, 2370–2373; *Angew. Chem. Int. Ed.* **2011**, *50*, 2322–2325; e) A. R. Fox, R. J. Wright, E. Rivard, P. P. Power, *Angew. Chem.* **2005**, *117*, 7907–7911; *Angew. Chem. Int. Ed.* **2005**, *44*, 7729–7733; f) G. Prabusankar, A. Doddi, C. Gemel, M. Winter, R. A. Fischer, *Inorg. Chem.* **2010**, *49*, 7976–7980.

[10] a) J. J. Weigand, M. Holthausen, R. Fröhlich, *Angew. Chem.* **2009**, *121*, 301–304; *Angew. Chem. Int. Ed.* **2009**, *48*, 295–298; b) M. H. Holthausen, C. Richter, A. Hepp, J. J. Weigand, *Chem. Commun.* **2010**, *46*, 6921–6923; c) M. H. Holthausen, J. J. Weigand, *J. Am. Chem. Soc.* **2009**, *131*, 14210–14211; d) M. H. Holthausen, K.-O. Feldmann, S. Schulz, A. Hepp, J. J. Weigand, *Inorg. Chem.* **2012**, *51*, 3374–3387.

[11] a) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530–5533; b) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7182–7185; *Angew. Chem. Int. Ed.* **2007**, *46*, 7052–7055; c) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold, G. Bertrand, *Chem. Commun.* **2013**, *49*, 4486–4488; d) C. L. Dorsey, B. M. Squires, T. W. Hudnall, *Angew. Chem.* **2013**, *125*, 4558–4561; *Angew. Chem. Int. Ed.* **2013**, *52*, 4462–4465; e) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181.

[12] M. H. Holthausen, A. Hepp, J. J. Weigand, *Chem. Eur. J.* **2013**, *19*, 9895–9907.

[13] M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking, J. J. Weigand, *Angew. Chem.* **2013**, *125*, 11284–11288; *Angew. Chem. Int. Ed.* **2013**, *52*, 11078–11082.

[14] R. S. Simons, L. Pu, M. M. Olmstead, P. P. Power, *Organometallics* **1997**, *16*, 1920–1925.

[15] For full details, including NMR spectra, see the Supporting Information.

[16] S. Khan, R. Michel, J. M. Dieterich, R. A. Mata, H. W. Roesky, J.-P. Demers, A. Lange, D. Stalke, *J. Am. Chem. Soc.* **2011**, *133*, 17889–17894.

[17] CCDC-991637 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

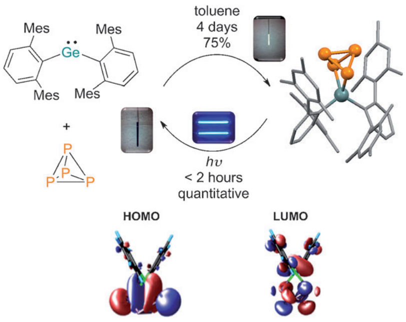
[18] UV light was generated by a low-pressure, high-intensity single-arc mercury lamp. The predominant wavelength produced is 254 nm. The power generated was measured to be 23.2 mW over the course of a 15 min irradiation cycle.

[19] a) N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330–11333; b) E. E. Coyle, C. J. O'Brien, *Nat. Chem.* **2012**, *4*, 779–780.

Received: March 4, 2014

FULL PAPER

Rooooxanne, put on the UV light: A low-coordinate germanium compound and a phosphenium ion are shown to quantitatively release a P_4 fragment upon exposure to UV light (see figure, Mes = 2,4,6-trimethylphenyl). Theoretical work reveals the LUMO to be antibonding with respect to the main group element–phosphorus bonds and bonding for reforming the P_4 tetrahedron, rationalizing this unique reactivity.



Bond Activation

*J. W. Dube, C. M. E. Graham, C. L. B. Macdonald, Z. D. Brown, P. P. Power, P. J. Ragogna**

■■ – ■■

Reversible, Photoinduced Activation of P_4 by Low-Coordinate Main Group Compounds