

# Metal-Free $\sigma$ -Bond Metathesis in Ammonia Activation by a Diazadiphosphapentalene

Jingjing Cui,<sup>†</sup> Yongxin Li,<sup>‡</sup> Rakesh Ganguly,<sup>‡</sup> Anusiya Inthirarajah,<sup>§</sup> Hajime Hirao,<sup>\*,†</sup> and Rei Kinjo<sup>\*,†</sup>

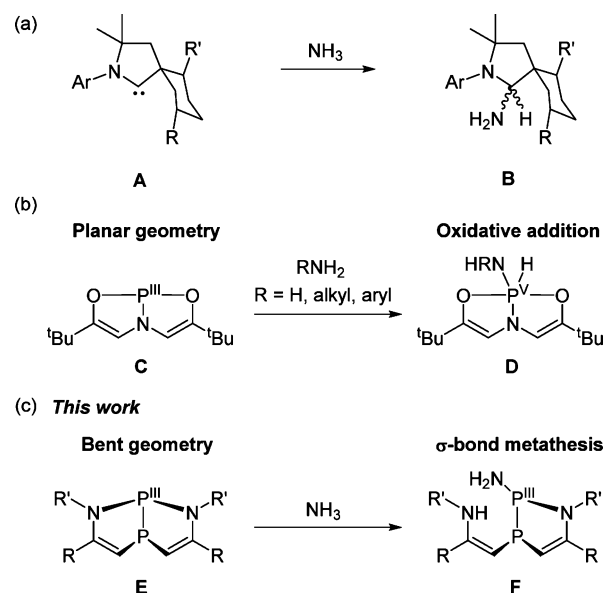
<sup>†</sup>Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, and <sup>‡</sup>NTU-CBC Crystallography Facility, Nanyang Technological University, Singapore 637371, Singapore

<sup>§</sup>School of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K.

**S** Supporting Information

**ABSTRACT:** A diazadiphosphapentalene derivative **5** featuring a bent geometry with two phosphorus atoms at the bridgehead has been synthesized. Under mild conditions, compound **5** readily activated ammonia to afford 1-aza-2,3-diphospholene derivative **6** bearing an enamine group. The reaction is therefore viewed as a formal  $\sigma$ -bond metathesis between an N–H bond of ammonia and an endocyclic P–N bond of **5**. Details of the reaction mechanism for ammonia activation as well as subsequent isomerization were explored by density functional theory calculations.

The development of synthetic methodology using ammonia ( $\text{NH}_3$ ) as a source of nitrogen in preparing N-containing derivatives has attracted great attention in synthetic chemistry over the past two decades.<sup>1–3</sup> Even with transition metals that enable the functionalization of N–H bonds of various amines, however, the activation of  $\text{NH}_3$  still remains highly challenging due to the enthalpically strong N–H bond ( $104 \pm 2 \text{ kcal mol}^{-1}$ ) and the propensity of  $\text{NH}_3$  to form Lewis acid–base adducts with electrophilic metals.<sup>4,5</sup> In 2007, Bertrand and Schoeller et al. reported the first example of ammonia splitting under metal-free conditions with (alkyl)(amino)carbenes (AACs) **A**, where the oxidative addition of N–H bond of ammonia occurred at a carbene center to form **B** (Figure 1a).<sup>6</sup> Since then, similar reactions employing various main group compounds containing group 13 and 14 elements have been reported.<sup>7–15</sup> Significantly, all these pioneering works relied on the high reactivity of low-valent p-block elements in their low-oxidation states, and accordingly, most reaction processes involved oxidation of the p-block element center. Very recently, Radosevich and Ess et al. have elegantly demonstrated the N–H cleavage of ammonia and amines with a group 15 derivative **C** featuring a unique planar structure (Figure 1b).<sup>16,17</sup> The activation sequence therein resulted in oxidation of the P atom from +III (**C**) to +V (**D**); thus, the reaction is also regarded as oxidative addition similar to those achieved by other main-group compounds. To establish an effective, direct functionalization of ammonia, the development of various activation pathways and a deep mechanistic understanding of them would be beneficial. Inspired by the work of Radosevich and Ess et al., we decided to target a hitherto unknown diazadiphosphapentalene derivative **E** (Figure 1c).<sup>18</sup> We reasoned that the presence of two phosphorus atoms at the bridgehead in the ring system would prevent the molecular



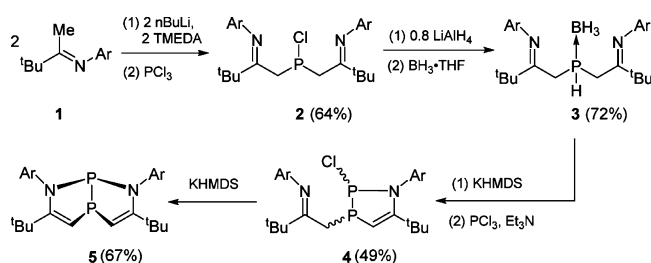
**Figure 1.** Splitting of a N–H bond by (a) (alkyl)(amino)carbenes **A** (Ar = 2,6-diisopropylphenyl) and (b) a planar  $\sigma^3$ -phosphorus species **C** via oxidative addition. (c)  $\text{NH}_3$  activation via metal-free  $\sigma$ -bond metathesis.

geometry from being planar as found in **C** and **D**, due to the high energetic barrier to achieve the optimum planar configuration at phosphorus. Consequently, a bent geometry will provide another low-energy means for ammonia activation other than oxidative addition. Herein we report the synthesis, single-crystal X-ray diffraction analysis, computational studies of a diazadiphosphapentalene derivative, and its reactivity involving a unique pathway for ammonia activation.

A cyclic phosphorus monochloride **4** was synthesized via three steps from the reported imine **1** (Scheme 1). Thus, deprotonation of imine **1** with *n*-butyllithium followed by the salt elimination reaction with a half equivalent of phosphorus trichloride ( $\text{PCl}_3$ ) afforded **2** in 64% yield. After the reduction of the P–Cl bond in **2** by lithium aluminum hydride, which gave the corresponding P–H compound, addition of  $\text{BH}_3$  produced **3** in 72% yield. Treatment of **3** with potassium bis(trimethylsilyl)amide (KHMDs) followed by the reaction with an equivalent of phosphorus trichloride in the presence of triethylamine afforded

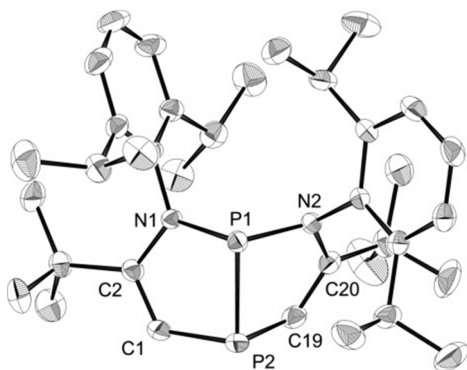
Received: October 4, 2014

Published: November 12, 2014

Scheme 1. Synthesis of **5** (Ar = 2,6-Diisopropylphenyl)

a cyclic phosphorus chloride derivative **4** (49%). Compounds **2**–**4** were fully characterized by nuclear magnetic resonance (NMR) spectroscopy and X-ray single crystallography.<sup>19</sup> Next, we attempted deprotonation of **4**. Treatment of a toluene solution of **4** with an equivalent of KHMDS led to a light reddish solution. After inorganic salts were filtered off, all volatiles were evaporated under vacuum, which afforded the desired bicyclic compound **5** as a slightly yellowish white solid in 67% yield. Note that **5** is the first example of an isolable diazadiphosphapentolene derivative.<sup>18</sup> In the <sup>31</sup>P NMR spectrum of **5**, two characteristic signals appeared at –30.8 ppm (CPC) and 173.2 ppm (NPN). The significant difference of these chemical shifts with respect to those [65.7 ppm (SPS) and 85.1 ppm (CPC)] in a fused benzo-1,2,3-thiadiphosphole derivative **G**<sup>18c,d</sup> probably reflects the larger difference in electronegativity between carbon and nitrogen atoms than that between carbon and sulfur atoms. Consequently, the P–P bond in **5** is likely more polarized than that in **G**, which leads to a smaller <sup>1</sup>J<sub>P–P</sub> coupling constant (195.4 Hz) of **5** than that (212.2 Hz) of **G**. Compound **5** exhibits a larger <sup>2</sup>J<sub>P–H</sub> coupling constant (40.6 Hz) than that (<sup>2</sup>J<sub>P–H</sub> = 12.0 Hz) of trivinylphosphine.<sup>20</sup> Compound **5** is thermally stable both in the solid state and in solution at ambient temperature, but it decomposes upon exposure to air.

Single crystals of **5** were obtained from a saturated hexane solution at 14 °C, and X-ray diffraction analysis revealed the solid-state molecular structure (Figure 2).<sup>19</sup> In marked contrast

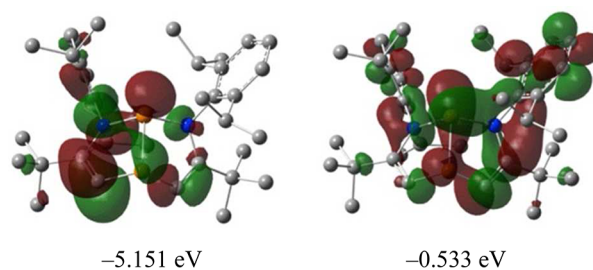


**Figure 2.** Solid-state structure of **5** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 30% probability.

to the flat structure of **C**,<sup>17</sup> **5** displays a pronouncedly bent geometry (the sum of angles: P1 = 295.99° and P2 = 284.30°), indicating sp<sup>3</sup>-hybridization of the P atoms. Thus, there are eight electrons around each phosphorus atom, which is different from the electronic situation of **C**.<sup>17</sup> Two P<sub>2</sub>NC<sub>2</sub> five-membered rings share a P–P bond, and all five atoms in each five-membered ring are nearly coplanar (the sum of internal pentagon angles = 536.08° and 533.45°). The P<sub>1</sub>–P<sub>2</sub> distance of 2.2099(9) Å, which

is in the range reported of typical P–P single bond,<sup>21</sup> is nearly identical to that (2.2145(8) Å) in **4** (see the Supporting Information). The P–C bonds [P2–C1 1.783(2) Å and P2–C19 1.807(2) Å] as well as the N–P bonds [N1–P1 1.776(2) Å and N2–P1 1.737(2) Å] fall in the ranges of those typical single bonds, respectively.<sup>22</sup> These structural parameters indicate that there is no conjugative delocalization of electrons on the five-membered rings.

To gain further insight into the electronic property, we performed a density functional theory (DFT) calculation on **5**.<sup>21</sup> The HOMO is a lone-pair orbital on the P atom between two N atoms, which exhibits conjugation with one of the C=C π-orbitals and lone-pair orbitals of the N atoms (Figure 3, left), whereas the LUMO is distributed significantly on the P atoms, with some contribution from the π orbitals of the aryl substituents on the N atoms (Figure 3, right).



**Figure 3.** Plots of the HOMO (left) and LUMO (right) of **5** calculated at the B3LYP/B1 level of theory (all H atoms are omitted for clarity);  $\Delta E_{(\text{HOMO-LUMO})} = 4.618$  eV.

Next, we investigated the reaction of **5** with ammonia. At ambient temperature, gaseous ammonia was introduced into the degassed test tube containing a THF solution of **5** (Scheme 2). The reaction mixture was stirred overnight, which gave a colorless solution. The <sup>31</sup>P NMR spectrum of a crude product showed a clean generation of a new compound, and a new set of signals was observed at –40.1 and 108.9 ppm, which significantly shifted upfield with respect to that of **5** but downfield-shifted compared to the chemical shift ( $\delta = 58.9$  ppm) for the corresponding P atom in the related –[N–P–P–C=C]–azadiphospholene derivative **H**.<sup>23</sup> The <sup>1</sup>J<sub>P–P</sub> coupling constant (253.4 Hz) is greater than those of **5** (195.4 Hz) and **H** (229.5 Hz), and the <sup>2</sup>J<sub>P–H</sub> coupling constant (22.2 Hz) is in the range of typical values for the *geminal* P–C–H coupling constant (<sup>2</sup>J<sub>P–H</sub> = ~25 Hz).<sup>24</sup> In the <sup>1</sup>H NMR spectrum, two peaks at 5.30 and 4.63 ppm were detected for CH protons, and a peak for NH was observed at 4.95 ppm, which is in line with the formation of a 1-aza-2,3-diphospholene derivative **6**. Compound **6** was purified by washing with hexane, and the single crystals were obtained by recrystallization from a solvent mixture of THF and hexane. An X-ray diffraction study confirmed the presence of a NH<sub>2</sub> group on one P atom and an enamine group on the other P atom in the P<sub>2</sub>NC<sub>2</sub> five-membered ring, indicating that the formation of an exocyclic P–N bond and an N–H bond of enamine is concomitant with the cleavage of a N–H bond of ammonia.<sup>19</sup> Thus, the activation process can be viewed as a formal σ-bond metathesis between an N–H bond of ammonia and an endocyclic P–N bond of **5**.<sup>14a,25</sup> Not surprisingly, compound **6** gradually tautomerizes in a THF solution even at ambient temperature, and after 16 h a formation of an imine derivative **7** was observed (81%, crude yield) (Scheme 2). Moreover, we observed further slow isomerization via an inversion of the P lone

Scheme 2. Reaction of **5** with NH<sub>3</sub> Followed by Isomerizations to **8** via **6** and **7**, and Molecular Structures of **6**–**8** (Ar = 2,6-Diisopropylphenyl; Hydrogen Atoms except for Those on N Atoms Are Omitted for Clarity)

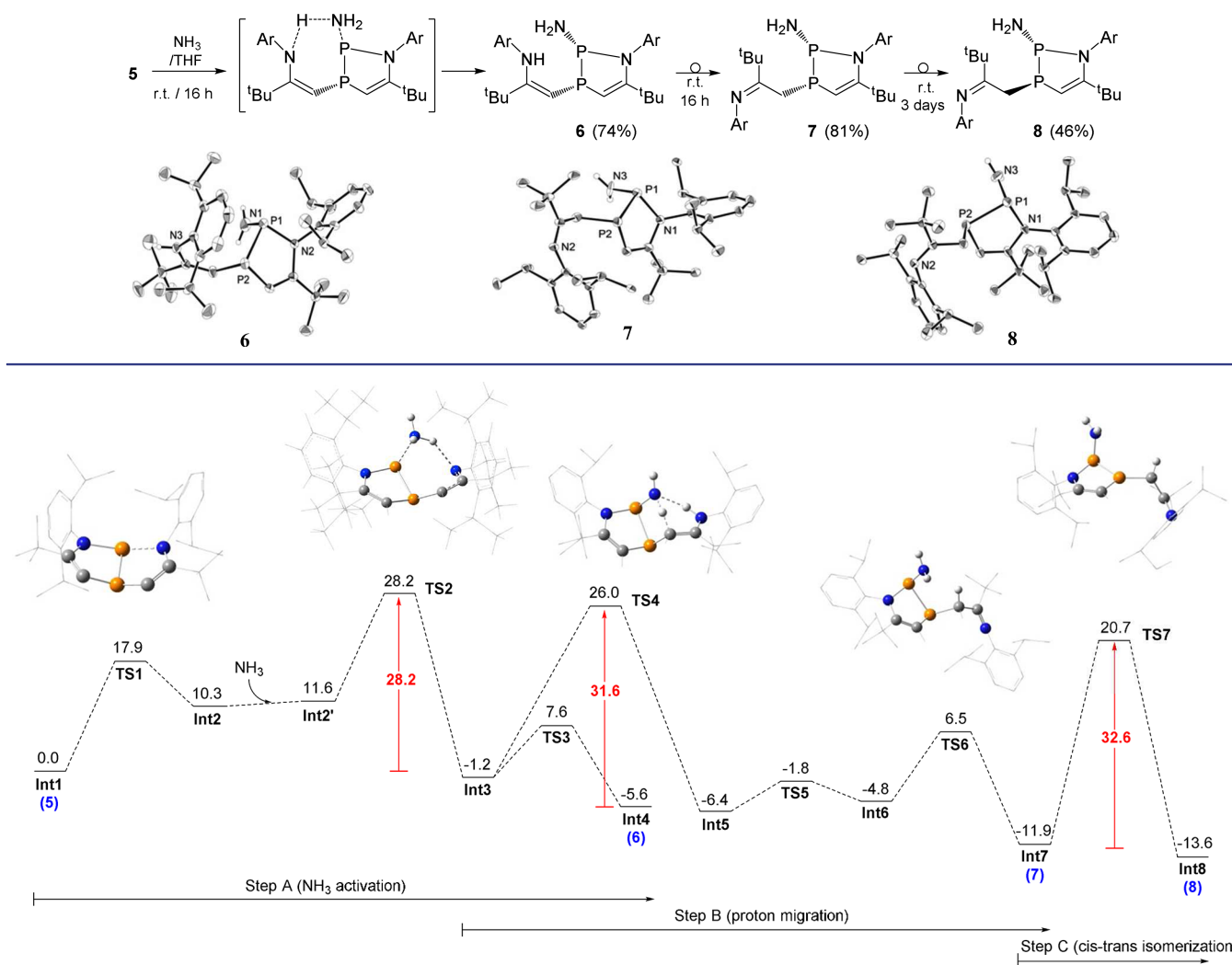


Figure 4. DFT-calculated free energy profile (kcal mol<sup>-1</sup>) for the proposed mechanism of NH<sub>3</sub> activation by **5**, and further isomerizations to **8** via compounds **6** and **7**. The blue-colored labels in parentheses indicate the nomenclature in Scheme 2

pair of **7**, and compound **8** was obtained (46% yield) after 3 days at room temperature (Scheme 2). Compounds **7** and **8** were fully characterized by NMR spectroscopy and X-ray crystallography.<sup>19</sup> To gain insight into the reaction mechanism, we carried out kinetic experiments for the ammonia activation. A THF solution of compound **5** and various concentrations of ammonia (0.08–0.40 M) in a sealed NMR tube was heated at 40 °C, and the reaction was monitored by <sup>31</sup>P NMR every 9 min. The pseudo first-order rate constants  $k_{\text{obs}}$  simulated from the kinetic conversion chart exhibited the best linear correlation with [NH<sub>3</sub>]<sup>1</sup> rather than [NH<sub>3</sub>]<sup>2</sup> and [NH<sub>3</sub>]<sup>3</sup>; thus, the rate law can be represented by  $k_{\text{obs}} = k'[\mathbf{5}]^1[\text{NH}_3]^1$  (see the Supporting Information). This result indicated that the process for the ammonia activation by **5** involved only one NH<sub>3</sub> molecule, which is in stark contrast to Radosevich and Ess's mechanism where three amines were involved in the process of an N–H oxidative addition at the planar  $\sigma^3$ -P atom.<sup>16</sup>

The pathway for the reaction from **5** and ammonia all the way to **8** was explored theoretically by DFT calculations using the B3LYP functional. Using the dispersion-corrected free-energy values, a reaction energy diagram was drawn (see Figure 4).

According to our extensive DFT study, the reaction begins with the cleavage of one of the two P–N bonds of **5**, leading to **Int2** displaying a nearly planar geometry and a zwitter ionic character,<sup>26</sup> which can be contrasted to the planar but nonionic character of **C**. Subsequently, NH<sub>3</sub> is activated through transition state **TS2** to form **Int3**. After a minor rotation about a single bond via **TS3**, **Int4** is generated. A comparison between X-ray and DFT structures showed that compound **6** corresponds to **Int4**. To form **7**, the proton on the nitrogen atom should migrate to a carbon atom, which is possible via **TS4**, once **Int4** is converted back to **Int3**. This proton migration is mediated by the central P–NH<sub>2</sub> moiety. After several minor structural changes, **Int7** is generated, which corresponds to **7**. Finally, a cis–trans isomerization occurs through pyramidal inversion at the phosphorus between two carbon atoms, to yield the final product **8**. The cis–trans isomerization has a very high barrier (32.6 kcal mol<sup>-1</sup>), consistent with the fact that the conversion of **7** to **8** took 3 days (Scheme 2). The computationally estimated activation parameters for the initial step of ammonia activation were  $\Delta H^\ddagger = 19.5$  kcal mol<sup>-1</sup>,  $\Delta G^\ddagger_{(298)} = 28.2$  kcal mol<sup>-1</sup>, and  $\Delta S^\ddagger = -29.2$  e.u., while the experimental values were  $\Delta H^\ddagger = 13.8 \pm$

0.9 kcal mol<sup>-1</sup>,  $\Delta G_{(298)}^\ddagger = 22.8 \pm 1.8$  kcal mol<sup>-1</sup>, and  $\Delta S^\ddagger = -30.3 \pm 3.1$  e.u. (see the Supporting Information). Hence, reasonable agreement was obtained between theory and experiment.

In conclusion, we have demonstrated a metal-free ammonia activation under ambient conditions by utilizing a diazadiphosphapentalene derivative **5** that displays a butterfly geometry. As exocyclic P–N bonds of aza-phosphanes are reactive,<sup>27</sup> transfer of the NH<sub>2</sub> fragment from compounds **6–8** to other substrates would be plausible. Thus, this work paves the way for the development of metal-free ammonia activation-transfer reagents.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Synthesis, NMR spectra, and crystallographic data (CIF) of **2–8**; kinetic studies of **5** with NH<sub>3</sub>; and computational details including Cartesian coordinates for stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### ■ Corresponding Authors

\*[rkinjo@ntu.edu.sg](mailto:rkinjo@ntu.edu.sg)

\*[hirao@ntu.edu.sg](mailto:hirao@ntu.edu.sg)

### ■ Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to Nanyang Technological University and the Singapore Ministry of Education (MOE2013-T2-1-005) for financial support. H.H. thanks the High Performance Computing Centre of the university.

## ■ REFERENCES

- (1) Lawrence, S. A. *Amines: Synthesis, Properties and Applications*; Cambridge University Press: New York, 2004.
- (2) (a) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080. (b) Braun, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 5012.
- (3) (a) Klinkenberg, J. L.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 86. (b) Chow, C.; Taoufik, M.; Quadrelli, E. A. *Eur. J. Inorg. Chem.* **2011**, 1349. (c) van der Vlugt, J. I. *Chem. Soc. Rev.* **2010**, *39*, 2302. (d) Haggins, J. *Chem. Eng. News* **1993**, *71*, 23. (e) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1.
- (4) (a) Morgan, E.; MacLean, D. F.; McDonald, R.; Turculet, L. *J. Am. Chem. Soc.* **2009**, *131*, 14234. (b) Salomon, M. A.; Jungton, A.-K.; Braun, T. *Dalton Trans.* **2009**, 7669. (c) Hanna, T. E.; Lobkovsky, E.; Chirik, P. *J. Eur. J. Inorg. Chem.* **2007**, 2007, 2677. (d) Sykes, A. C.; White, P.; Brookhart, M. *Organometallics* **2006**, *25*, 1664. (e) Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13644.
- (5) Werner, A. Z. *Anorg. Chem.* **1893**, *3*, 267.
- (6) Frey, G. D.; Lavallo, V.; Donnadiu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.
- (7) Moerdyk, J. P.; Blake, G. A.; Chase, D. T.; Bielawski, C. W. *J. Am. Chem. Soc.* **2013**, *135*, 18798.
- (8) Hudnall, T. W.; Moerdyk, J. P.; Bielawski, C. W. *Chem. Commun.* **2010**, 46, 4288.
- (9) Siemeling, U.; Färber, C.; Bruhn, C.; Leibold, M.; Selent, D.; Baumann, W.; von Hopffgarten, M.; Goedecke, C.; Frenking, G. *Chem. Sci.* **2010**, *1*, 697.
- (10) (a) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433. (b) Appelt, C.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 4256.
- (11) Zhu, Z.; Wang, X.; Peng, Y.; Lei, H.; Fettinger, J. C.; Rivard, E.; Power, P. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2031.

(12) (a) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600. (b) Meltzer, A.; Inoue, S.; Präsang, C.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 3038.

(13) (a) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Organometallics* **2011**, *30*, 6490. (b) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, *48*, 798.

(14) (a) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettinger, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 16272. (b) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 12268.

(15) Alberto, M. E.; Russo, N.; Sicilia, E. *Chem.—Eur. J.* **2013**, *9*, 7835.

(16) (a) McCarthy, S. M.; Lin, Y.-C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136*, 4640. See also: (b) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134*, 11330. (c) Zeng, G.; Maeda, S.; Taketsugu, T.; Sakaki, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 4633.

(17) Arduengo, A. J.; Stewart, C. A. *Chem. Rev.* **1994**, *94*, 1215.

(18) Only a few diphosphapentalene derivatives have been reported: (a) Ionkin, A. S.; Marshall, W. J.; Fish, B. M. *Dalton Trans.* **2009**, 10574. (b) Silberzahn, J.; Pritzkow, H.; Latscha, H. P. *Angew. Chem., Int. Ed.* **1990**, *29*, 799. (c) Baccolini, G.; Mezzina, E.; Todesco, P. E.; Foresti, E. *J. Chem. Soc., Chem. Commun.* **1988**, 304. (d) Baccolini, G.; Mezzina, E.; Todesco, P. E. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3281.

(19) CCDC 1021264–1021270 (**2–8**) contain the supplementary crystallographic data for this communication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

(20) Chernysheva, N. A.; Mikhailenko, V. L.; Gusarova, N. K.; Fedorov, S. V.; Trofimov, B. A. *Russ. J. Gen. Chem.* **2011**, *81*, 470.

(21) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(22) (a) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770. (b) Trinquier, G.; Ashby, M. T. *Inorg. Chem.* **1994**, *33*, 1306. (c) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *Chem. Soc., Perkin Trans. 2* **1987**, S1. (d) Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568.

(23) Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E. *Chem. Commun.* **2003**, 39, 1142.

(24) Kühn, O. *Phosphorus-31 NMR Spectroscopy*; Springer-Verlag: Berlin, Germany, 2008.

(25) Selected recent examples of ammonia activation by metals without involving oxidative addition: (a) Gutsulyak, D. V.; Piers, W. E.; Borau-Garcia, J.; Parvez, M. *J. Am. Chem. Soc.* **2013**, *135*, 11776. (b) Uhe, A.; Hölscher, M.; Leitner, W. *Chem.—Eur. J.* **2013**, *19*, 1020. (c) Aguado-Ullate, S.; Carbó, J. J.; Moral, O. G.; Martín, A.; Mena, M.; Poblet, J.-M.; Santamaría, C. *Inorg. Chem.* **2011**, *50*, 6269. (d) Dunne, J. F.; Neal, S. R.; Engelkemier, J.; Ellern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2011**, *133*, 16782. (e) Kimura, T.; Koiso, N.; Ishiwata, K.; Kuwata, S.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 8880. (f) Mena, I.; Casado, M. A.; García-Orduña, P.; Polo, V.; Lahoz, F. J.; Fazal, A.; Oro, L. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 11735. (g) Ni, C.; Lei, H.; Power, P. P. *Organometallics* **2010**, *29*, 1988. (h) Ochi, N.; Nakao, Y.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2007**, *129*, 8615. (i) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mendiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 10318.

(26) (a) Gudat, D. *Acc. Chem. Res.* **2010**, *43*, 1307. (b) Nyulászi, L. *Chem. Rev.* **2001**, *101*, 1229. (c) Sanchez, M.; Mazières, M. R.; Lamandé, L.; Wolf, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Schere, O., Eds.; Thieme: Stuttgart, Germany, 1990; p 129. (d) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(27) Chong, C.-C.; Hirao, H.; Kinjo, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 3342.