

Communication

## Triazenyl Radicals Stabilized by N-Heterocyclic Carbenes

Jisu Back, Junbeom Park, Youngsuk Kim, Haneol Kang,  
Yonghwi Kim, Moon Jeong Park, Kimoon Kim, and Eunsung Lee

*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b08753 • Publication Date (Web): 17 Oct 2017

Downloaded from <http://pubs.acs.org> on October 17, 2017

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

# Triazenyl Radicals Stabilized by *N*-Heterocyclic Carbenes

Jisu Back,<sup>†,‡</sup> Junbeom Park,<sup>†,‡</sup> Youngsuk Kim,<sup>†,‡</sup> Haneol Kang,<sup>‡</sup> Yonghwi Kim,<sup>†</sup> Moon Jeong Park,<sup>‡</sup> Kimoon Kim<sup>†,‡,#</sup> and Eunsung Lee<sup>\*,†,‡,#</sup>

<sup>†</sup> Center for Self-assembly and Complexity, Institute for Basic Science (IBS), Pohang, 790–784, Republic of Korea

<sup>‡</sup> Department of Chemistry, Pohang University of Science and Technology, Pohang, 790–784, Republic of Korea

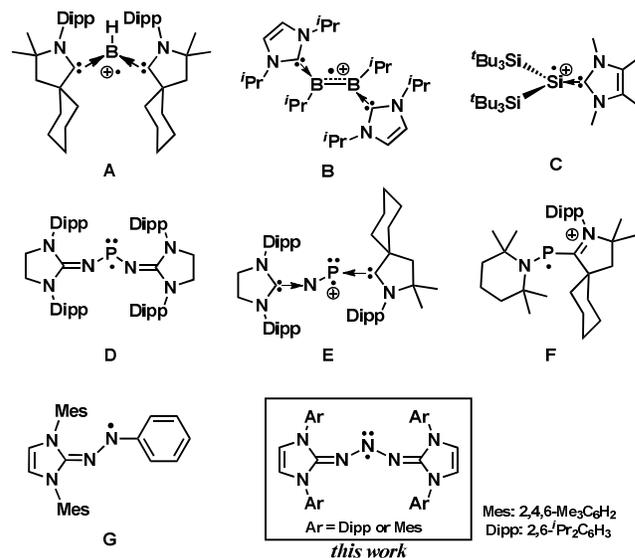
<sup>#</sup> Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang, 790–784, Republic of Korea

Supporting Information Placeholder

**ABSTRACT:** Notwithstanding the notable progress in the synthesis of *N*-heterocyclic carbene-stabilized radicals, aminyl radicals, supported by NHCs or otherwise, have been scarcely studied due to synthetic challenges. Triazenyl radical is a particular form of aminyl radical that contains three adjacent nitrogen atoms, and offers intriguing possibilities for unique reactivity and physical properties stemming from expected delocalization of the spin density over the NNN moiety and its conjugated substituents. Here, we report the synthesis and full characterization of the first NHC-stabilized triazenyl radicals, obtained by one-electron reduction of the corresponding triazenyl cations with potassium metal. These radicals reversibly oxidize back to the cations upon treatment with transition metal sources or electrophiles, and abstract H atom from xanthene to form a new N-H bond at the center nitrogen atom. Potential application of the redox couple between triazenyl cation and triazenyl radical was demonstrated as cathode active materials in lithium ion batteries.

species may exhibit distinctly unique reactivity and physical properties, and contribute to our understanding of chemical bonding in general. Previously, free triazenyl radicals have only been detected by EPR spectroscopy – such as 3,3-disubstituted triazenyl radicals obtained by reaction of organic azides and triorganosilyl radicals by Roberts *et al.*,<sup>8</sup> or identified formally as ligands in transition metal complexes – such as in the ruthenium system by Kaim *et al.*<sup>9</sup> We found one-electron reduction of 1,3-bis(NHC)triazenyl cations ([NHC]<sub>2</sub>N<sub>3</sub><sup>+</sup>) with potassium metal to offer an expedient synthetic route to the corresponding radicals [NHC]<sub>2</sub>N<sub>3</sub><sup>•</sup>, and report herein the synthesis and full characterization of the first examples of triazenyl radicals stabilized by two NHCs.

**Scheme 1. Recent Examples of NHC-Stabilized Main Group Radicals and the First Isolated Triazenyl Radicals.**

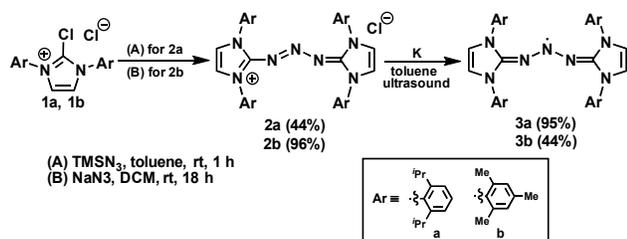


There has been an ongoing interest in the isolation of radical compounds of main group elements, as they expand our understanding of chemical bonding, serve as key intermediates in organic and biological reactions, and exhibit unique physical properties.<sup>1</sup> Recently, *N*-heterocyclic carbenes (NHCs) have begun to be actively used to support various main group radicals and radical ions that are otherwise unstable. NHCs enhance stability of such species by their own steric bulk and  $\pi$ -acceptor properties that delocalize the spin density from the radical onto the carbene moiety.<sup>1d,2</sup> Over the past decade, a variety of main group radicals, including boryl and silyl radicals, have been successfully prepared in NHC-supported forms (Scheme 1, **A-C**).<sup>3</sup> Among them, pnictogen-centered radicals attract particular attention for mediating chemical reactions of one-electron redox system,<sup>1,4</sup> and persistent efforts have yielded several NHC-stabilized phosphorous-centered radicals (Scheme 1, **D-F**).<sup>5</sup> However, nitrogen-centered radicals stabilized by NHCs have scarcely been investigated so far, while only a few unsupported aminyl radicals have been isolated to date.<sup>6</sup> In 2016, the Severin group obtained the first NHC-stabilized aminyl radicals by one-electron reduction of azoimidazolium dyes (Scheme 1, **G**).<sup>7</sup>

Of the aminyl radicals, triazenyl types are especially intriguing due to potential flexibility of their bonding. Featuring several comparably accessible resonance structures, these

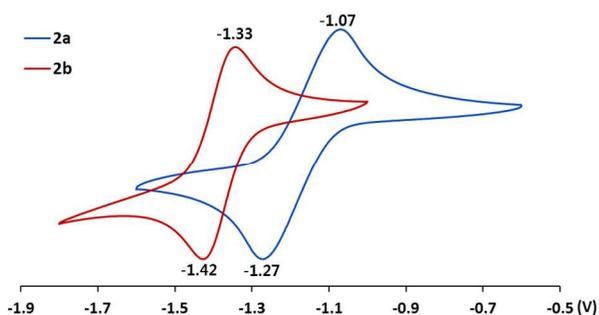
The 1,3-bis(NHC) triazenyl chlorides [*i*Pr<sub>2</sub>N<sub>3</sub>]Cl (**2a**) and [Mes<sub>2</sub>N<sub>3</sub>]Cl (**2b**) were prepared from *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride (*i*PrCl<sub>2</sub>, **1a**) with trimethylsilyl azide (TMSN<sub>3</sub>) and *N,N'*-1,3-bis(2,4,6-trimethylphenyl)-2-chloroimidazolium chloride (*i*MesCl<sub>2</sub>, **1b**) with sodium azide (NaN<sub>3</sub>), respectively (Scheme 2).

## Scheme 2. The Synthesis of NHC-supported Triazenyl Radicals



Reaction between **1a** and 2 equiv. of  $\text{TMSN}_3$  in dry toluene at room temperature gave an orange mixture, which was purified to yield **2a** in 44% isolated yield. Reaction of **1b** with 2.9 equiv. of  $\text{NaN}_3$  in dry dichloromethane afforded **2b** in 96% yield. The stoichiometry of syntheses of **2a,b** in these reactions involves a two-electron reduction event, and we are currently scrutinizing their details.

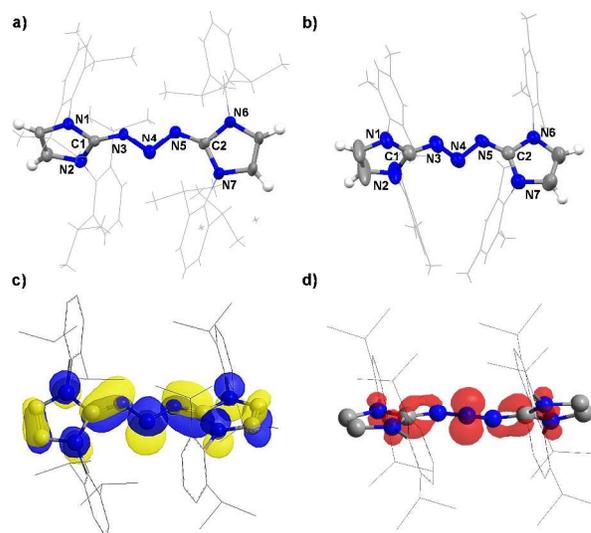
The X-ray crystallographic analysis of both triazenyl cations **2a** and **2b** showed a W-shaped  $\text{N}_3$  moiety with all bond lengths indicating a bond order of 1.5 (Figure S8). The experimental metrics were in good agreement with the DFT structures, optimized at B3PW91/6-31G(*d,p*) level (Table S7). The Stephan group reported a similar structure for the analogous triazenyl cation  $[(\text{SiMe}_3)_2\text{N}_3]^+$ , obtained from the reaction of an azidophosphonium cation and the free NHC, 1,3-dimesitylimidazolidin-2-ylidene ( $\text{SiMe}_3$ ).<sup>10</sup>



**Figure 1.** The cyclic voltammograms of **2a** and **2b** in THF with a sat.  $\text{Ag}/\text{AgCl}$  reference electrode; 0.1 M  $\text{NBu}_4\text{PF}_6$ ; scan rate 0.1 V/s;  $\text{N}_2$  atmosphere.

The cyclic voltammograms of both **2a** and **2b** in THF solution containing 0.1 M  $\text{NBu}_4\text{PF}_6$  as electrolyte showed reversible one-electron reductions at  $E_{1/2} = -1.17$  V (**2a**) and  $E_{1/2} = -1.38$  V (**2b**) versus sat.  $\text{Ag}/\text{AgCl}$  (Figure 1 and Supporting Information). The difference on the reduction potential of **2a** and **2b** illustrates how subtle changes in the structure of *N*-heterocyclic carbenes can affect their electrochemical properties. These electrochemical data encouraged us to attempt a chemical reduction of **2a** and **2b** and to isolate the corresponding triazenyl radicals. Gratifyingly, triazenyl radicals,  $\text{IPr}_2\text{N}_3^\bullet$  (**3a**) and  $\text{IMes}_2\text{N}_3^\bullet$  (**3b**), could indeed be formed *via* one-electron reduction of **2a** and **2b** with potassium metal in toluene (Scheme 2). Both **3a** and **3b** were isolated in 95% and 44% yields, and their structures were confirmed by single crystal X-ray diffraction. In the crystal structure of **3a**, the distances of C1–N3 (1.297(3) Å) and C2–N5 (1.291(3) Å) bonds fall between the typical single (1.46 Å) and double (1.21 Å) C=N bond lengths. The bond distances of N3–N4 (1.377(3) Å) and N4–N5 (1.366(3) Å) also indicate a bond order intermediate between single and double (Figure 2a). The crystal structure of **3b** showed a similar bond distance

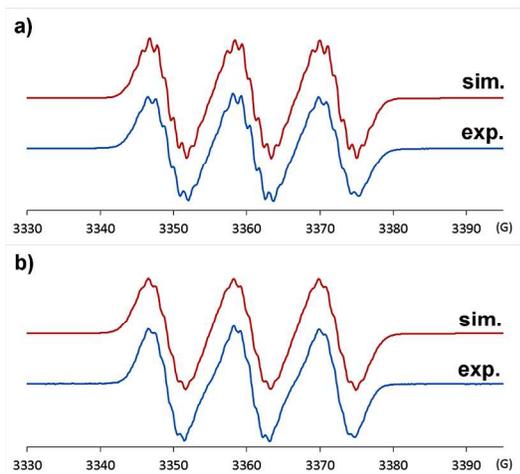
pattern (Figure 2b). These metrics were reproduced well by the DFT calculations at B3PW91/6-31G(*d,p*) level (Table S7), that also described the bonding with Wiberg bond orders as follows: C1–N3 (1.69), C2–N5 (1.69), N3–N4 (1.42), and N4–N5 (1.42). In addition, DFT calculations showed that the SOMOs of both **3a** and **3b** mainly consist of the *p*-orbitals of the triazenyl nitrogen atoms, the  $\pi$  systems of the NHC rings, and the  $\pi$  bonds between C1–N3 and C2–N5 (Figure 2c and S10). The computed spin densities reside largely on the central triazenyl nitrogen N4 (52% in **3a**, 55% in **3b**), with the remainder evenly spread over the other nitrogens and the carbene carbons (below 7%) (Figure 2d and S11). Thus, while **3a** and **3b** are classified best as aminyl radicals with two imidazol-2-iminato substituents, they do feature a strong delocalization of the unpaired electron over the entire conjugated  $\pi$ -system of the NHC–N–N–NHC moiety. Such  $\pi$ -delocalization may be the key means by which NHCs indeed stabilize triazenyl radicals. We note that analogous imidazolidin-2-iminato groups were also found to stabilize phosphinyl and aminyl radicals (Scheme 1, **D** and **G**, respectively).



**Figure 2.** (a) Crystal structure of compound **3a**. Selected experimental [calculated at the B3PW91/6-31G(*d,p*) level for the optimized structure] bond lengths [Å] and angles [°]. C1–N1 1.387(3) [1.401], C1–N2 1.389(3) [1.401], C1–N3 1.297(3) [1.300], N3–N4 1.377(3) [1.355], N4–N5 1.366(3) [1.376], N5–C2 1.291(3) [1.300], C2–N6 1.393(3) [1.401], C2–N7 1.394(3) [1.401]; N1–C1–N2 104.95(18) [104.2], N1–C1–N3 136.5(2) [118.8], N2–C1–N3 118.4(2) [136.9], C1–N3–N4 119.8(2) [122.8], N3–N4–N5 103.02(18) [104.5], N4–N5–C2 119.8(2) [122.8], N5–C2–N6 137.7(2) [118.9], N5–C2–N7 117.7(2) [136.9], N6–C2–N7 104.49(19) [104.2]. (b) Crystal structure of compound **3b**. See Figure S8 for the selected experimental/calculated bond lengths [Å] and angles [°] of **3b**. (c) SOMO of **3a** computed by B3PW91/6-31G(*d,p*) level (isovalue of 0.03). (d) Spin density for **3a** calculated at the B3PW91/6-31G(*d,p*) level (isovalue of 0.005).

Radicals **3a** and **3b** were characterized by X-band electron paramagnetic resonance (EPR) spectroscopy (Figure 3). The room temperature EPR spectra of **3a** and **3b** in benzene both show a triplet signal ( $g = 2.0091$  for **3a** and  $g = 2.0090$  for **3b**), almost identical as expected from the similarity of their computed spin density patterns (Figure 2d). The observed EPR spectra were successfully simulated based on the calculated hyperfine coupling constants (Figure 3, Supporting Information). The three major peaks are due to the large hyperfine coupling of N4 ( $a(^{14}\text{N}) = 32.7$  MHz for both **3a** and **3b**), while the splitting of each peak is originated from other nitrogen atoms which have much smaller hyperfine coupling of below 4 MHz (see Supporting Information for the specific values of

the hyperfine coupling constants). The large coupling constant of  $a(^{14}\text{N4}) = 32.7$  MHz clearly indicates that the spin density mainly exists at the N4, and is in a good agreement with the computed spin density.

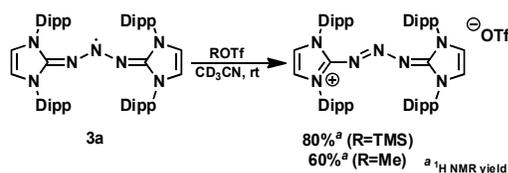


**Figure 3.** (a) EPR spectrum of **3a** in benzene at 298 K (blue) and simulated EPR spectrum (red). (b) EPR spectrum of **3b** in benzene at 298 K (blue) and simulated EPR spectrum (red).

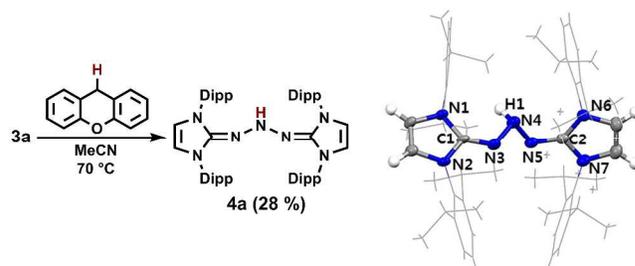
The UV-Vis absorption spectrum of **3a** in benzene at room temperature shows one characteristic absorption at 364 nm (Figure S12). In accordance with time-dependent DFT (TD-DFT) calculations at the B3PW91/6-31G(*d,p*) level of theory, this peak is attributed to SOMO( $\alpha$ ) to LUMO( $\alpha$ ) transitions.

We find that triazenyl radical **3a** can be chemically oxidized back to triazenyl cation **2a** by treating **3a** with transition metal sources or electrophiles. To see whether **3a** could be used as a redox-active auxiliary ligand, transition metal sources, CuCl, CuCl<sub>2</sub>, Pd(MeCN)<sub>4</sub>(OTf)<sub>2</sub>, and Ni(MeCN)<sub>6</sub>(OTf)<sub>2</sub>, were reacted with **3a** in acetonitrile at room temperature. Unfortunately, **3a** did not coordinate to the transition metal ions but oxidized to the triazenyl cation, which was confirmed by <sup>1</sup>H NMR and ESI-MS analysis. <sup>1</sup>H NMR yield of the triazenyl cation from each reaction ranges from 86% to 98% (Supporting Information). The metal cations (Pd<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>+</sup>) seem to be reduced, as black precipitates were observed after the reactions. Since the reduction potential of each triazenyl radical (**3a** or **3b**) can vary depending on the *N*-substituents (see Figure 1), the radicals can be further utilized as a tunable and soluble organic reducing reagent.<sup>11</sup>

### Scheme 3. Reactivity of Triazenyl Radicals with Electrophiles

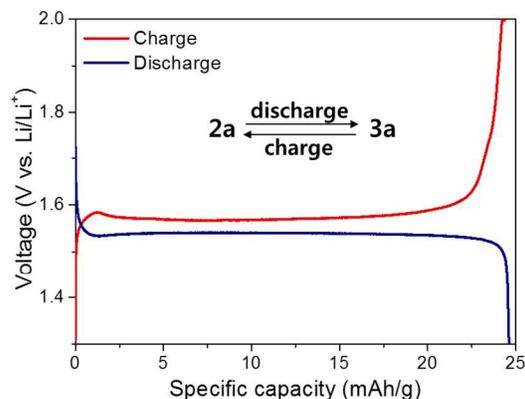


To assess the nucleophilicity of the triazenyl radical, **3a** was treated with trimethylsilyl trifluoromethanesulfonate (TMSOTf) as an electrophile. However, this reaction led to one-electron oxidation as well and gave **2a[OTf]** in 80% <sup>1</sup>H NMR yield, but no observable products of nucleophilic addition. The reaction with smaller electrophile methyl trifluoromethanesulfonate (MeOTf) also generated **2a[OTf]** in 60% <sup>1</sup>H NMR yield. The structure of **2a[OTf]** was confirmed by single crystal X-ray analysis (Scheme 3, Supporting Information).



**Figure 4.** Scheme of hydrogen atom abstraction of **3a** (left) and the X-ray structure of **4a** (right) (See Figure S8 for the selected experimental/calculated bond lengths [Å] and angles [°] of **4a**).

Hydrogen atom abstraction (HAA) by radicals is one of the significant reaction in chemical and biological processes.<sup>12</sup> To test HAA by triazenyl radicals, **3a** was reacted with xanthene, commonly used H atom donor reagent, in acetonitrile at 70 °C.<sup>13</sup> Indeed, **3a** successfully abstracted H atom from xanthene and formed *IPr*<sub>2</sub>N<sub>3</sub>H (**4a**) in 28% isolated yield as a crystalline material (Figure 4). The structure of **4a** was successfully characterized by NMR spectroscopy and single crystal X-ray analysis, which was in good agreement with the structure obtained from the DFT calculations at the B3PW91/6-31G(*d,p*) level (Table S7 and Figure S8). When other H atom donors such as 9,10-dihydroanthracene, triphenylmethane, and benzenethiol were used, only a trace amount of **4a** was detected in the <sup>1</sup>H NMR spectra of the reaction mixture.



**Figure 5.** Charge-discharge curves for Li/**2a** half cell at 0.1 C.

The replacement of LiCoO<sub>2</sub>, a commonly used cathode active material in lithium ion batteries, with organic cathode active materials is promising owing to environmental benefits and high energy density.<sup>14</sup> In this context, **2a** was also examined as a cathode active material in lithium ion batteries. A cyclic voltammogram of coin-type half-cell comprising lithium foil and **2a** cathode showed an oxidation potential of 1.65 V (vs Li<sup>+</sup>/Li) and a reduction potential of 1.51 V (vs Li<sup>+</sup>/Li) (Figure S13). In addition, the galvanostatic charge (**3a** → **2a**) and discharge (**2a** → **3a**) test was performed at a current density of 0.1 C in a voltage range of 1.3 – 2.0 V. The charge/discharge curves show an average voltage of 1.58 V for charging and 1.54 V for discharging and a discharge capacity of 25 mAh/g (Figure 5), corresponding to 76% of the theoretical value (33 mAh/g).

In conclusion, NHC-stabilized triazenyl radicals were prepared for the first time by direct reduction of corresponding triazenyl cations with potassium metal in toluene. The compounds were fully characterized using X-ray crystallography and EPR. The reaction of triazenyl radical **3a** with transition metal sources and electrophiles led to oxidation back to triazenyl cation **2a**, and with xanthene formed **4a** by H atom

1 abstraction reaction. Redox cycle between **2a** and **3a** was  
2 applied to a cathode reaction of lithium-ion batteries. These  
3 triazenyl radicals offer new examples of the p-block element  
4 radical compounds stabilized by NHCs, and their synthesis  
5 reported here opens exciting new avenues for structure and  
6 reactivity studies of these uncommon radical species.

## 7 ASSOCIATED CONTENT

### 8 Supporting Information

9 Detailed experimental procedures, spectroscopic data for all  
10 new compounds, crystallographic data for **2a**, **2b**, **3a**, **3b**,  
11 **2a[OTf]**, **4a** (CIF). This material is available free of charge via  
12 the Internet at <http://pubs.acs.org>.

## 13 AUTHOR INFORMATION

### 14 Corresponding Author

15 [eslee@postech.ac.kr](mailto:eslee@postech.ac.kr)

### 16 Notes

17 The authors declare no competing financial interests.

## 18 ACKNOWLEDGMENT

19 This work was supported by the Institute for Basic Science  
20 (IBS) [IBSR007-D1] and a National Research Foundation of  
21 Korea(NRF) grant funded by the Korean government [Minis-  
22 try of Science, ICT and Future Planning (MSIP)] (No. NRF-  
23 2016H1A2A1907415 – Global Ph.D.Fellowship Program). X-  
24 ray diffraction experiment with synchrotron radiation was  
25 performed at the Pohang Accelerator Laboratory (Beamline  
26 2D and 6D). We thank Dr. Dmitry V. Yandulov, Mr. Jun Ho Seo,  
27 Prof. Jun Sung Kim, and Prof. Chang Seop Hong for helpful  
28 discussions.

## 29 REFERENCES

- 30 1. (a) Mondal, K. C.; Roy, S.; Roesky, H. W. *Chem. Soc. Rev.* **2016**, *45*,  
31 1080-1111. (b) Soleilhavoup, M.; Bertrand, G. *Acc. Chem. Res.* **2015**,  
32 *48*, 256-266. (c) Wang, Y. Z.; Robinson, G. H. *Inorg. Chem.* **2014**, *53*,  
33 11815-11832. (d) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem.*  
34 *Sci.* **2013**, *4*, 3020-3030. (e) Abe, M. *Chem. Rev.* **2013**, *113*, 7011-7088.  
35 (f) Breher, F. *Coord. Chem. Rev.* **2007**, *251*, 1007-1043. (g) Power, P. P.  
36 *Chem. Rev.* **2003**, *103*, 789-809.  
37 2. (a) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature*  
38 **2014**, *510*, 485-496. (b) Huang, J. K.; Nolan, S. P. *J. Am. Chem. Soc.*  
39 **1999**, *121*, 9889-9890. (c) Arduengo, A. J.; Rasika Dias, H. V.;  
40 Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724-9725.  
41 3. (a) Tanaka, H.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2012**,  
42 *134*, 5540-5543. (b) Bissinger, P.; Braunschweig, H.; Damme, A.; Horl,  
43 C.; Krummenacher, I.; Kupfer, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 359-  
44 362. (c) Zeng, X. M.; Frey, G. D.; Kinjo, R.; Donnadiou, B.; Bertrand, G. J.

- Am. Chem. Soc.* **2009**, *131*, 8690-8696. (d) Jazzar, R.; Dewhurst, R. D.;  
Bourg, J. B.; Donnadiou, B.; Canac, Y.; Bertrand, G. *Angew. Chem. Int. Ed.*  
**2007**, *46*, 2899-2902. (e) Lavallo, V.; Canac, Y.; Prasang, C.;  
Donnadiou, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, *44*, 5705-  
5709. (f) Matsumoto, T.; Gabbai, F. P. *Organometallics* **2009**, *28*, 4252-  
4253. (g) Chiu, C. W.; Gabbai, F. P. *Angew. Chem. Int. Ed.* **2007**, *46*,  
1723-1725. (h) Mondal, K. C.; Roesky, H. W.; Stuckl, A. C.; Ehret, F.;  
Kaim, W.; Dittrich, B.; Maity, B.; Koley, D. *Angew. Chem. Int. Ed.* **2013**,  
52, 11804-11807. (i) Bertermann, R.; Braunschweig, H.; Dewhurst, R.  
D.; Horl, C.; Kramer, T.; Krummenacher, I. *Angew. Chem. Int. Ed.* **2014**,  
53, 5453-5457. (j) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.;  
Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.;  
Niepotter, B.; Stalke, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 1801-1805.  
4. (a) Armstrong, A.; Chivers, T.; Boere, R. T. *Acc. Chem. Res.* **2006**, *39*,  
66-80. (b) Marque, S.; Tordo, P. *New Aspects in Phosphorus Chemistry*  
**2005**, *250*, 43-76.  
5. (a) Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadiou, B.;  
Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 10262-10263. (b) Back, O.;  
Donnadiou, B.; von Hopffgarten, M.; Klein, S.; Tonner, R.; Frenking, G.;  
Bertrand, G. *Chem. Sci.* **2011**, *2*, 858-861. (c) Kinjo, R.; Donnadiou, B.;  
Bertrand, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 5930-5933. (d) Back, O.;  
Donnadiou, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.*  
**2010**, *2*, 369-373.  
6. (a) Miura, Y.; Tomimura, T.; Matsuba, N.; Tanaka, R.; Nakatsuji, M.;  
Teki, Y. *J. Org. Chem.* **2001**, *66*, 7456-7463. (b) Miura, Y.; Tomimura,  
T.; Teki, Y. *J. Org. Chem.* **2000**, *65*, 7889-7895. (c) Danen, W. C.;  
Neugebauer, F. A. *Angew. Chem. Int. Ed.* **1975**, *14*, 783-789. (d)  
Neugebauer, F. A. F., H. *Angew. Chem. Int. Ed.* **1971**, *10*, 732-733. (e)  
Neugebauer, F. A. F., H.; Bamberger, H.; Smith, S. O.; *Chem. Ber.* **1972**,  
105, 2694-2713.  
7. Eymann, L. Y. M.; Tskhovrebov, A. G.; Sienkiewicz, A.; Bila, J. L.;  
Zivkovic, I.; Ronnow, H. M.; Wodrich, M. D.; Vannay, L.; Corminboeuf,  
C.; Pattison, P.; Solari, E.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.*  
**2016**, *138*, 15126-15129.  
8. (a) Cooper, J. W.; Roberts, B. P.; Winter, J. N. *J. Chem. Soc. Chem.*  
*Commun.* **1977**, 320. (b) Roberts, B. P.; Winter, J. N. *J. Chem. Soc. Perkin*  
*Trans. 2* **1979**, 1354.  
9. Ehret, F.; Bubrin, M.; Zalis, S.; Kaim, W. *Angew. Chem. Int. Ed.* **2013**,  
52, 4673-4675.  
10. Winkelhaus, D.; Holthausen, M. H.; Dobrovetsky, R.;  
Stephan, D. W. *Chem. Sci.* **2015**, *6*, 6367-6372.  
11. (a) Hanson, S. S.; Richard, N. A.; Dyker, C. A. *Chem-Eur J*  
**2015**, *21*, 8052-8055. (b) Murphy, J. A.; Zhou, S. Z.; Thomson, D. W.;  
Schoenebeck, F.; Mahesh, M.; Park, S. R.; Tuttle, T.; Berlouis, L. E. A.  
*Angew. Chem. Int. Ed.* **2007**, *46*, 5178-5183. (c) Doni, E.; Murphy, J. A.  
*Chem. Commun.* **2014**, *50*, 6073-6087. (d) Murphy, J. A. *J. Org. Chem.*  
**2014**, *79*, 3731-3746.  
12. Mayer, J. M. *Acc. Chem. Res.* **2011**, *44*, 36-46.  
13. Buttner, T.; Geier, J.; Frison, G.; Harmer, J.; Calle, C.;  
Schweiger, A.; Schonberg, H.; Grutzmacher, H. *Science* **2005**, *307*, 235-  
238.  
14. (a) Nakahara, K.; Iwasa, S.; Satoh, M.; Morioka, Y.; Iriyama,  
J.; Suguro, M.; Hasegawa, E. *Chem. Phys. Lett.* **2002**, *359*, 351-354. (b)  
Tarascon, J. M.; Armand, M. *Nature* **2001**, *414*, 359-367. (c) Suguro,  
M.; Iwasa, S.; Kusachi, Y.; Morioka, Y.; Nakahara, K. *Macromol. Rapid*  
*Commun.* **2007**, *28*, 1929-1933.

