

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Isolation of a Lewis Base Stabilized Parent Phosphenium ( $\text{PH}_2^+$ ) and Related Species

Liu Liu,<sup>a,b</sup> David A. Ruiz,<sup>a</sup> Fatme Dahcheh,<sup>a</sup> and Guy Bertrand<sup>\*a</sup>Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The parent phosphenium ion ( $\text{PH}_2^+$ ), and even any phosphenium salts bearing a hydrogen ( $\text{HRP}^+$ ), have never been observed. The addition of trifluoromethanesulfonic acid and carbon electrophiles to an NHC-PH adduct, featuring a very bulky NHC, allows for the preparation and isolation of such compounds. Computational investigations show that most of the positive charge is localized at phosphorus, demonstrating the phosphenium nature of this compound. Further, the PH moiety is able to utilize one or both of its lone pairs to bind to one or two metals.

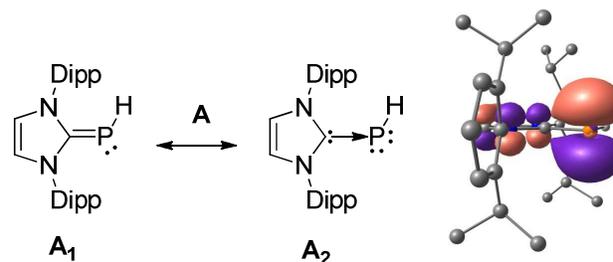
The synthesis of phosphinidenes (RP) within the coordination sphere of metals is an established and continuously growing field.<sup>1</sup> Various base-stabilized phosphinidenes, coordinated or not to metal centres or Lewis acids, have also been reported.<sup>2,3</sup> In contrast, there are only a few examples of complexes featuring the parent phosphinidene (HP) fragment bridging two metals,<sup>4</sup> and only one metal-stabilized terminal PH complex.<sup>5</sup> Lastly, NHC-PH adducts **A** (Fig. 1) have been described by a few synthetic protocols.<sup>6</sup>

Similarly, phosphenium ions ( $\text{R}_2\text{P}^+$ ),<sup>7</sup> both free and base stabilized, have been widely studied due to their fascinating coordination chemistry,<sup>8</sup> their use as building blocks for larger phosphorus clusters,<sup>9</sup> and their ability to react with organic substrates.<sup>10</sup> These compounds, which are isoelectronic with singlet carbenes, are very electrophilic.<sup>11</sup> As free species, at least one  $\pi$ -electron donating substituent (typically  $-\text{NR}_2$ ) is necessary to allow for their isolation. Most commonly, phosphines,<sup>12</sup> *N*-heterocyclic carbenes (NHCs),<sup>13,14</sup> and transition metals<sup>15</sup> are utilized to stabilize phosphenium ions. In contrast to the assortment of phosphenium derivatives ( $\text{R}_2\text{P}^+$ ), the parent system ( $\text{H}_2\text{P}^+$ ), and even  $\text{RHP}^+$  have never been observed even in the coordination sphere of transition

metals or with Lewis base stabilization. The lighter analogues ( $\text{CH}_2$  and  $\text{NH}_2^+$ ) stabilized by an NHC have been explored in some detail. The carbon analogue was described as a mixed carbene “dimer”<sup>16</sup> and reactivity studies show that it acts as a nucleophilic olefin.<sup>17</sup> The  $\text{NH}_2^+$  derivative was obtained by adding excess acid to the corresponding NHC- $\text{N}_2\text{O}$  adduct.<sup>18</sup>

Herein, we describe the isolation of the first base-stabilized  $\text{RHP}^+$  and  $\text{H}_2\text{P}^+$  fragments. These compounds are prepared from a base-stabilized parent phosphinidene **1**, in which the Lewis base is a very bulky NHC. Additionally, we show that depending on the metal precursor, the PH moiety of the NHC-PH adduct **1** is able to utilize one or both of its lone pairs to bind one or two metals; similarly, **1** reacts with two equivalents of  $\text{BH}_3$  to give the corresponding bis(borane) adduct.

NHC-phosphinidene adducts **A** fall into the family of compounds featuring an inversely polarized CP bond, denoted by two extreme forms **A**<sub>1</sub> and **A**<sub>2</sub> (Fig. 1).<sup>19</sup> Interestingly, the HOMO of **A** shows the  $\pi$  back donation of a phosphorus lone pair into the carbene empty orbital. The coefficient at P (0.50) is much larger than that at C (0.05), indicating that the P lone pair will attack electrophiles. Furthermore, NHCs have been prominent in stabilizing a wide variety of main group compounds,<sup>20</sup> especially involving phosphorus.<sup>21</sup> These properties led us to believe that the addition of appropriate electrophiles should lead to the desired phosphenium compounds.



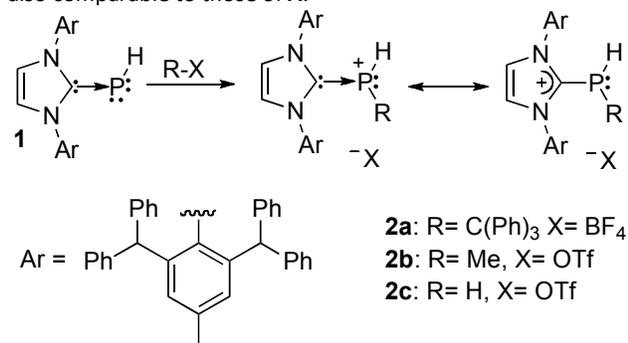
**Fig. 1** Two bonding modes and HOMO (isovalue = 0.05) of **A**. Dipp: 2,6-diisopropylphenyl.

<sup>a</sup> UCSD-CNRS Joint Research Chemistry Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0343 (USA). E-mail: guybertrand@ucsd.edu.

<sup>b</sup> Department of Chemistry, College of Chemistry and Chemical Engineering, Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen 361005, Fujian, China.

† Electronic Supplementary Information (ESI) available: Converged Cartesian coordinates and crystallographic data for **1-5**. CCDC 1404598-1404603. See DOI: 10.1039/x0xx00000x

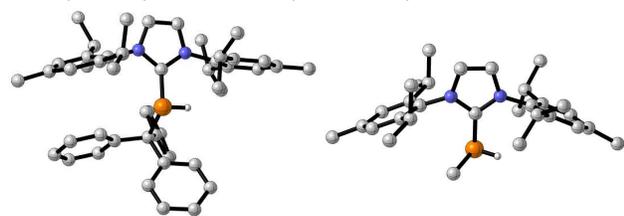
Since we presumed that NHC-PHR<sup>+</sup> and obviously NHC-PH<sub>2</sub><sup>+</sup> adducts would be extremely reactive, we chose a sterically encumbering NHC. Markó *et al.* described the synthesis of the bulky IPr<sup>22</sup> and since then several groups have taken advantage of the beneficial aspects that the added bulk provides.<sup>23</sup> Using a slightly modified route described by Grützmacher *et al.*<sup>6c</sup> for the preparation of **A**, compound **1** was prepared and isolated in 87% yield. The <sup>31</sup>P NMR signal appears as a doublet (*J*<sub>PH</sub> = 172 Hz) at -134.5 ppm, which is very similar to that observed for **A** (-136.7 ppm, *J*<sub>PH</sub> = 164 Hz). In the solid state structure, the geometric parameters of **1** are also comparable to those of **A**.



**Fig. 2** Synthesis of NHC-stabilized phosphonium ions **2a**, **2b**, and **2c**.

To test the possibility of preparing a stable NHC-phosphonium adduct, we chose the bulky triphenylcarbenium as the electrophile (Fig. 2). The reaction of **1** with the tetrafluoroborate salt [(Ph<sub>3</sub>C<sup>+</sup>)(BF<sub>4</sub><sup>-</sup>)] proceeded rapidly. Within 5 minutes, complete conversion was observed by <sup>31</sup>P NMR spectroscopy, which shows a doublet at -49.4 ppm (d, *J*<sub>PH</sub> = 278 Hz). Compound **2a** was isolated in 89% yield as a white solid. We then used a smaller electrophile, namely methyl trifluoromethanesulfonate (MeOTf). Here also, the reaction with **1** was very rapid and cleanly led to **2b**, which was isolated in 87% yield ( $\delta^{31}\text{P} = -86.3$  ppm, d, *J*<sub>PH</sub> = 240 Hz). Single crystal X-ray diffraction studies of **2a** and **2b** were performed. The X-ray diffraction study of **2a** revealed, as expected, a drastic lengthening of the C<sub>carb</sub>P bond (1.845(2) Å) compared to that of **1** (1.755(4) Å). Repeated crystallization attempts of **2b** yielded crystals of poor quality, nonetheless preliminary X-ray studies confirmed its formulation (Fig. 3).

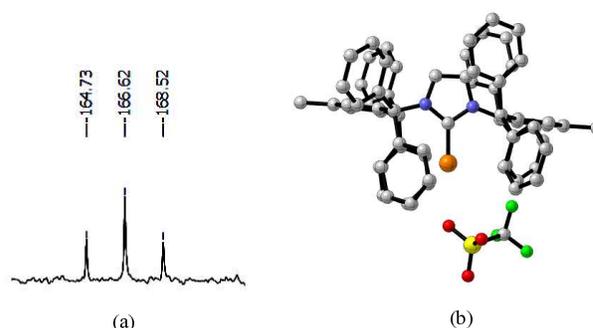
Although **2a** and **2b** are very sensitive to air and moisture, they are thermally stable and can be stored in the solid state for months under an inert atmosphere, which prompted us to attempt the synthesis of the parent compound **2c**.



**Fig. 3** Solid-state structures of **2a** (left) and **2b** (right). Hydrogen atoms except P-H, anions, and the phenyl groups on the 2,6-dibenzhydryl-4-methylphenyl are omitted for clarity.

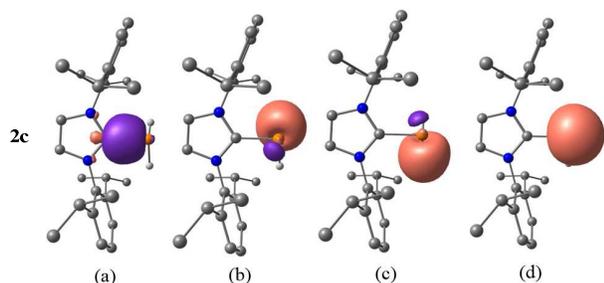
Selected bond lengths [Å] and angles [°]: **2a** C<sub>carb</sub>-P 1.845(2), C<sub>CPh<sub>3</sub></sub>-P 1.921(2); C<sub>carb</sub>-P-H 91(1), C<sub>carb</sub>-P-C<sub>CPh<sub>3</sub></sub> 117.20(9), C<sub>CPh<sub>3</sub></sub>-P-H 99(1).

Adding trifluoromethanesulfonic acid to a benzene solution of **1** led rapidly to the formation of **2c**, which was readily isolated as a white powder in 85% yield.<sup>24</sup> The <sup>31</sup>P NMR spectrum displays a triplet at -166.6 ppm (t, *J*<sub>PH</sub> = 223 Hz), which collapses into a singlet upon proton decoupling, demonstrating the presence of a PH<sub>2</sub> fragment (Fig. 4a). The ionic nature of **2c** was ascertained by single crystal X-ray diffraction analysis (Fig. 4b). It was not possible to locate the hydrogen atoms on phosphorus but the presence of the anion along with a terminal P atom in line with the NMR data confirmed the structure. As observed previously, the C<sub>carb</sub>-P bond extends to 1.840(4) Å, indicating a decrease in the bond order.



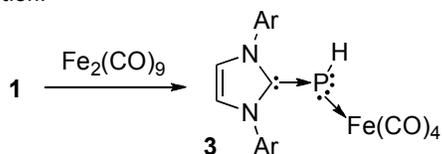
**Fig. 4** (a) <sup>31</sup>P NMR spectrum; (b) solid-state structure of **2c**. Hydrogen atoms are omitted for clarity.

For a better understanding of the bonding in **2c**, the natural bond orbital (NBO) analysis was performed at the M06-2X/6-311+G(2d,p)//M06-2X/6-31G(d) level. The NBOs corresponding to the C<sub>carb</sub>-PH<sub>2</sub> fragment are shown in Fig. 5. The phosphorus centre forms three bonds [C<sub>carb</sub>-P σ (a) and two P-H σ (b and c)], and a lone pair of electrons (d). No C<sub>carb</sub>-P π bonds could be located in the output file. To gain more insight into the stability of **2c**, the second-order perturbation theory of the NBO method was applied, which showed relatively high stabilization energy (11.1 kcal mol<sup>-1</sup>) by two-electron donor-acceptor interactions from the lone pair of P into the three centre antibonding orbitals (π\*(N-C-N)). The NBO charges of C<sub>carb</sub> and P in **2c** are 0.23 and 0.62e, respectively. Thus, a resonance structure showing delocalization of the positive charge over the NHC fragment only slightly contributes to the structure. The calculated Wiberg bond index (WBI) of C<sub>carb</sub>-P is 0.95, supporting the C<sub>carb</sub>-P dative bond nature. Therefore, the predominant resonance structure is the carbene stabilized phosphonium model.

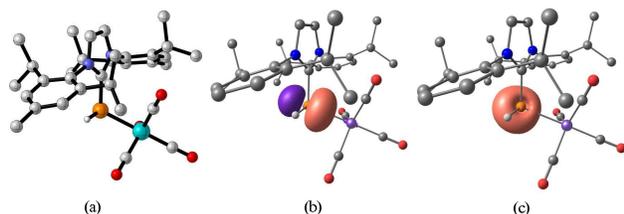


**Fig. 5** NBOs (isovalue = 0.05) of the  $C_{\text{carb}}\text{-PH}_2$  fragment of a simplified model of **2c** (2,6-diisopropylphenyl groups instead 2,6-dibenzhydryl-4-methylphenyl). (a)  $C_{\text{carb}}\text{-P}$   $\sigma$  (NBO 76); (b)  $\text{P-H}$   $\sigma$  (NBO 77); (c)  $\text{P-H}$   $\sigma$  (NBO 78); (d) lone-pair of electrons at P (NBO 114).

Knowing that the P centre of **1** readily reacts with electrophiles, we next wanted to investigate the coordination ability of **1** (Fig. 6). Reacting **1** with diiron nonacarbonyl [ $\text{Fe}_2(\text{CO})_9$ ] led to the formation of **3**, which gives a doublet at -96.4 ppm ( $J_{\text{PH}} = 208$  Hz) in the  $^{31}\text{P}$  NMR spectrum. The isolated product appeared to be stable in the absence of air, and single crystals were grown via vapour diffusion of hexanes into a chloroform solution. The X-ray diffraction study confirmed the coordination of the phosphorus to the metal (Fig. 7a). Upon coordination, the C-P bond elongates to 1.828(3) Å and the geometry around the phosphorus atom becomes trigonal pyramidal. The NBOs of **3** show that the P centre still possesses a second lone pair available for bonding (Fig. 7c). However, the addition of excess  $\text{Fe}_2(\text{CO})_9$  did not lead to further coordination.



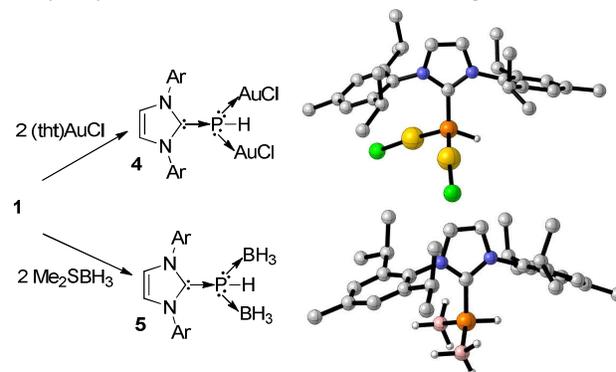
**Fig. 6** Synthesis of NHC-stabilized parent phosphinidene iron complex **3** (Ar = 2,6-dibenzhydryl-4-methylphenyl).



**Fig. 7** (a) Solid-state structure of **3**; hydrogen atoms except P-H and the phenyl groups on the 2,6-dibenzhydryl-4-methylphenyl are omitted for clarity. Selected NBOs (isovalue = 0.05) of simplified models of **3** (2,6-diisopropylphenyl groups instead 2,6-dibenzhydryl-4-methylphenyl); (b)  $\text{P-Fe}$   $\sigma$  (NBO 138); (c) a second lone pair of electrons on P (NBO 137). Selected bond lengths [Å] and angles [°]: C-P 1.828(3), Fe-P 2.334(1); C-P-H 96(2), C-P-Fe 113.9(1), Fe-P-H 107(2).

We reasoned that the impossibility of using the second lone pair of **1** with  $\text{Fe}_2(\text{CO})_9$  was due to the excessive steric bulk of the Fe complex in conjunction with the bulky NHC. Thus, we chose the singly ligated and linear (tht)AuCl in order to

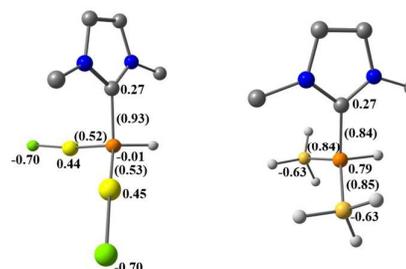
examine whether the second lone pair is accessible. Indeed, adding 2 equivalents of the gold complex to **1** led to the bis-metal complex **4** (Fig. 8). The  $^{31}\text{P}$  NMR spectrum is similar to the previous complex (-92.2 ppm, d,  $J_{\text{PH}} = 373$  Hz). Here also, the C-P bond elongates upon coordination to 1.827(7) Å and the phosphorus atom has a tetrahedral bonding environment.



**Fig. 8** Synthesis of NHC-stabilized parent phosphinidene bis-gold and bis- $\text{BH}_3$  complexes **4** and **5** (Ar = 2,6-dibenzhydryl-4-methylphenyl). Solid-state structures of **4** (top) and **5** (bottom). Hydrogen atoms (except P-H and B-H) and the phenyl groups on the 2,6-dibenzhydryl-4-methylphenyl are omitted for clarity.

Having demonstrated the availability of both lone pairs to interact with metals, the coordination to main group Lewis acids was explored. The reaction between **1** and  $\text{Me}_2\text{S-BH}_3$  led to the desired bis(borane) adduct **5**, which was fully characterized, including an X-ray diffraction study (Fig. 8).

To gain more insight into the bonding situations of **4** and **5**, an NBO analysis was carried out. Fig. 9 depicts the selected NBO charges and Wiberg bond indices. It is interesting to note that the P in **4** is almost neutral (-0.01 a.u.), whereas it is significantly positively charged in **5** (+0.79 a.u.), which might be attributed to the Lewis acidic character of  $\text{BH}_3$ . The P-Au bond indices of **4** (0.53 and 0.52) are much lower than P-B of **5** (0.85 and 0.84), which is indicative of a stronger bonding between P and  $\text{BH}_3$ . Indeed, **4** slowly decomposes overnight in solution, whereas **5** is stable in both solution and solid state over months.



**Fig. 9** Selected NBO charges and WBIs (in parentheses) of simplified models of **4** (left) and **5** (right) (2,6-diisopropylphenyl groups instead 2,6-dibenzhydryl-4-methylphenyl). 2,6-diisopropylphenyl groups are omitted for clarity.

These results indicate that NHC-stabilized parent phosphonium salts can readily be isolated. However, it is important to note that when IPr (NHC with 2,6-diisopropylphenyl groups at nitrogen) is used, instead of the IPr\* (NHC with 2,6-dibenzhydryl-4-methylphenyl groups at nitrogen), the  $\text{PH}_2^+$  adduct can only be characterized by  $^{31}\text{P}$  NMR spectroscopy in solution ( $-165.3$  ppm,  $J_{\text{PH}} = 220$  Hz) as it rapidly decomposes in the absence of solvent. Computational studies revealed that a majority of the positive charge in **2c** resides on the phosphorus centre, and additionally a dative bond between the NHC and P is the best description of the bonding system. Accordingly, compound **2c** has a predominant phosphonium character. Interestingly, despite its large steric bulk, IPr\* is flexible enough to allow large electrophilic carbon species and metal complexes to react with the phosphorus centre of **1**. The use of IPr\* and even bulkier analogues to stabilize highly reactive fragments is under active investigations.

Thanks are due to the NSF (CHE-1359809) for financial support of this work, and the China Scholarship Council for a graduate fellowship (L.L.). D. A. R. acknowledges the U.S. Department of Education for a GAANN fellowship. Thanks are due to Dr. C. Moore for assistance with X-ray crystallography.

## Notes and references

- H. Aktaş, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* 2010, **49**, 2102-2113.
- (a) V. A. K. Adiraju, M. Yousufuddin, H. V. Rasika Dias, *Dalton Trans.* 2015, **44**, 4449-4454; (b) T. G. Larocque, G. G. Lavoie, *New J. Chem.* 2014, **38**, 499-502; (c) A. J. Arduengo III, C. J. Carmalt, J. A. C. Clyburne, A. H. Cowley, R. Pyati, *Chem. Commun.* 1997, **33**, 981-982; (d) A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* 2014, **53**, 13568-13572.
- (a) B. A. Surgenor, M. Bühl, A. M. Z. Slawin, J. D. Woollins, P. Kilian, *Angew. Chem. Int. Ed.* 2012, **51**, 10150-10153; (b) S. Shah, J. D. Protasiewicz, *Coord. Chem. Rev.* 2000, **210**, 181-201.
- (a) K. F. Hirsekorn, A. S. Veige, P. T. Wolczanski, *J. Am. Chem. Soc.* 2006, **128**, 2192-2193; (b) M. R. Duttera, V. W. Day, T. J. Marks, *J. Am. Chem. Soc.* 1984, **106**, 2907-2912.
- B. M. Gardner, G. Balázs, M. Scheer, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2014, **53**, 4484-4488.
- (a) Y. Wang, Y. Xie, M. Y. Abraham, R. J. Gilliard, P. Wei, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *Organometallics* 2010, **29**, 4778-4780; (b) K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* 2013, **135**, 11795-11798; (c) A. M. Tondreau, Z. Benko, J. R. Harmer, H. Grützmacher, *Chem. Sci.* 2014, **5**, 1545-1554.
- (a) A. H. Cowley, R. A. Kemp, *Chem. Rev.* 1985, **85**, 367-382; (b) D. Gudat, *Acc. Chem. Res.* 2010, **43**, 1307-1316.
- D. Gudat, *Coord. Chem. Rev.* 1997, **163**, 71-106.
- (a) C. A. Dyker, N. Burford, *Chem. Asian J.* 2008, **3**, 28-36; (b) M. H. Holthausen, J. J. Weigand, *Chem. Soc. Rev.* 2014, **43**, 6639-6657.
- (a) J. J. Weigand, M. Holthausen, R. Fröhlich, *Angew. Chem. Int. Ed.* 2009, **48**, 295-298; (b) C. A. Caputo, J. T. Price, M. C. Jennings, R. McDonald, N. D. Jones, *Dalton Trans.* 2008, **37**, 3461-3469; (c) C. Hering, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* 2012, **51**, 6241-6245; (d) C. Hering, A. Schulz, A. Villinger, *Inorg. Chem.* 2013, **52**, 5214-5225; (e) C. Hering, M. Hertrich, A. Schulz, A. Villinger, *Inorg. Chem.* 2014, **53**, 3880-3892.
- J. M. Slattery, S. Hussein, *Dalton Trans.* 2012, **41**, 1808-1815.
- (a) N. Burford, P. J. Ragona, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* 2003, **125**, 14404-14410; (b) N. Burford, P. J. Ragona, *J. Chem. Soc. Dalton Trans.* 2002, 4307-4315.
- (a) I. Abdellah, C. Lepetit, Y. Canac, C. Duhayon, R. Chauvin, *Chem. Eur. J.* 2010, **16**, 13095-13108; (b) M. Azouri, J. Andrieu, M. Picquet, P. Richard, B. Hanquet, I. Tkatchenko, *Eur. J. Inorg. Chem.* 2007, **2007**, 4877-4883; (c) S. Gaillard, J.-L. Renaud, *Dalton Trans.* 2013, **42**, 7255-7270; (d) J. J. Weigand, K.-O. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* 2010, **132**, 16321-16323.
- (a) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* 2008, **47**, 3122-3172; (b) A. J. Arduengo, G. Bertrand, *Chem. Rev.* 2009, **109**, 3209-3210; (c) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* 2010, **49**, 6940-6952; (d) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* 2010, **49**, 8810-8849; (e) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* 2013, **42**, 6723-6753; (f) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* 2014, **510**, 485-496.
- L. Rosenberg, *Coord. Chem. Rev.* 2012, **256**, 606-626.
- (a) N. Kuhn, H. Bohnen, J. Kreutzberg, D. Blaser, R. Boese, *J. Chem. Soc., Chem. Commun.* 1993, 1136-1137; (b) A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* 1997, **119**, 12742-12749; (c) C. M. Weinstein, C. D. Martin, L. Liu, G. Bertrand, *Angew. Chem. Int. Ed.* 2014, **53**, 6550-6553.
- S. M. Ibrahim Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Commun.* 2011, **47**, 6987-6989.
- A. G. Tskhovrebov, B. Vuichoud, E. Solari, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* 2013, **135**, 9486-9492.
- (a) L. Weber, *Eur. J. Inorg. Chem.* 2000, **2000**, 2425-2441; (b) F. Mathey, *Angew. Chem. Int. Ed.* 2003, **42**, 1578-1604; (c) O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* 2013, **52**, 2939-2943; (d) R. R. Rodrigues, C. L. Dorsey, C. A. Arceneaux, T. W. Hudnall, *Chem. Commun.* 2014, **50**, 162-164.
- (a) Y. Wang, G. H. Robinson, *Inorg. Chem.* 2014, **53**, 11815-11832; (b) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* 2011, **2**, 389-399; (c) C. D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* 2013, **4**, 3020-3030.
- (a) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* 2007, **129**, 14180-14181; (b) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schäfer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* 2008, **130**, 14970-14971; (c) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* 2009, **48**, 5530-5533; (d) O. Back, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* 2010, **2**, 369-373; (e) Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* 2013, **135**, 19139-19142.
- G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Markó, *Dalton Trans.* 2010, **39**, 1444-1446.
- F. Izquierdo, S. Manzini, S. P. Nolan, *Chem. Commun.* 2014, **50**, 14926-14937.
- The value for the proton affinity of the simplified model of **1** is 250.0 Kcal/mol.