

# Stable singlet carbenes as mimics for transition metal centers

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This perspective summarizes recent results, which demonstrate that stable carbenes can activate small molecules ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{NH}_3$  and  $\text{P}_4$ ) and stabilize highly reactive intermediates (main group elements in the zero oxidation state and paramagnetic species). These two tasks were previously exclusive for transition metal complexes.

## Introduction

At the end of the 19th century, Sabatier observed the formation of ethane in the addition of  $\text{H}_2$  to ethylene over thin slivers of reduced nickel. Since this pivotal discovery the activation of  $\text{H}_2$  and other small molecules has attracted considerable interest. Until recently, most of the chemical and biological systems that have been successful in activating small molecules, and in more general terms unreactive bonds, involve a transition metal. Even the so-called iron-sulfur cluster-free hydrogenase (Hmd) uses an iron center in combination with an adjacent methenyl- $\text{H}_4\text{MPT}^+$ , which serves as a hydride acceptor.<sup>1</sup>

In 2006, our group discovered that acyclic<sup>2</sup> and cyclic(alkyl)-(amino)carbenes<sup>3</sup> react with carbon monoxide to afford the corresponding ketenes.<sup>4</sup> Examination of the literature showed that organic molecules were not known to react with  $\text{CO}$ , except a few transient carbenes<sup>5</sup> and silylenes,<sup>6</sup> whereas transition metal

centers classically do. This led to the question of whether singlet carbenes could mimic the chemical behavior of transition metals. This new paradigm appeared very reasonable since singlet carbenes possess both a lone pair of electrons and an accessible vacant orbital, and therefore resemble, at least to some extent, transition metal centers.

This perspective summarizes the results obtained during the last four years, which demonstrate that stable carbenes can do some of the tasks transition metal complexes are known for. The activation of small molecules such as  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{NH}_3$  and  $\text{P}_4$  will first be discussed. Then, as transition metals are also well known for stabilizing highly reactive species within their coordination sphere, examples showing that stable singlet carbenes can be equally stabilizing entities will be presented. This second aspect can appear paradoxical since it consists of using carbenes that were considered for a long time as prototypical reactive intermediates,<sup>7</sup> for isolating otherwise unstable molecules.

Although this review focuses on carbenes, the reactivity of their heavier analogues (silylenes, germynes and stannynes)

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David Martin

David Martin was born in 1976 at Clermont-Ferrand, France. After graduating from the Ecole Normale Supérieure (Lyon, France) in 2000, he joined Pr. G. Bertrand and Dr A. Baceiredo at the Université Paul Sabatier (Toulouse, France). He completed his PhD in 2004 and moved to Switzerland as a post-doctoral assistant in the group of Pr. A. Alexakis (University of Geneva). In 2006 he became CNRS research associate and joined Pr. G. Buono at the University of Marseille (France). He is currently a member of the UCR/CNRS Joint Research Laboratory at the University of California, Riverside.



Michele Soleilhavoup

Michele Soleilhavoup studied chemistry at the University Paul Sabatier in Toulouse and received her PhD in 1993 under the supervision of Guy Bertrand. From 1993 to 1995, she worked for BASF AG at Ludwigshafen. In 1995, she moved to the University Paris VI as a «Chargée de Recherche CNRS», and from 2000 to 2001, she worked in the Remi Chauvin's group at the Laboratoire de Chimie de Coordination in Toulouse, before joining the UCR/CNRS Joint Research Laboratory at the University of California, Riverside. Her current research interests are focused on carbene chemistry and their application as tunable ligands for transition metal catalysts.

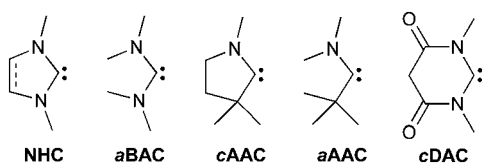


Fig. 1 Stable carbenes frequently used in this perspective.

will be briefly presented. In order to facilitate the reading, the five families of stable carbenes, which will often be involved, have been abbreviated as shown in Fig. 1.

## 1 Activation of small molecules

### 1.1 Activation of carbon monoxide

In 1994 it was claimed that imidazol-2-ylidene  $\text{NHC}_1$  reacts with CO to give the corresponding stable ketene.<sup>8</sup> However, a year later Arduengo *et al.*<sup>9</sup> were not able to duplicate these experimental results. They found computationally that there is no stable structure associated with the combination of the parent imidazol-2-ylidene and CO, other than “a non-bonded weakly interacting (van der Waals) complex”; the ketene not even being found as a transition state.

According to calculations,<sup>10</sup> the singlet–triplet gap and the HOMO for the parent acyclic and cyclic (alkyl)(amino)carbenes  $\text{aAAC}_0$  and  $\text{cAAC}_0$  are much smaller and higher in energy, respectively, than for the acyclic and cyclic bis(amino)carbenes  $\text{aBAC}_0$  and  $\text{NHC}_0$  (Fig. 2). Consequently, (alkyl)(amino)carbenes are more nucleophilic but also more electrophilic than their bis(amino) counterparts, and are therefore better suited for metal-like behavior. Calculations predicted that the reaction of CO with the acyclic bis(amino)carbene  $\text{aBAC}_0$  was endergonic ( $\Delta G = +4.6 \text{ kJ mol}^{-1}$ ), whereas with the acyclic (alkyl)(amino)carbene  $\text{aAAC}_0$  it was exergonic ( $\Delta G = -111.6 \text{ kJ mol}^{-1}$ ). Indeed, although  $\text{aBAC}_1$  is inert towards CO,  $\text{cAAC}_1$  and  $\text{aAAC}_1$  react instantaneously and quantitatively at room temperature, affording the corresponding ketenes **1** and **2**. Note that ketene **1** is by far less thermally stable than **2**, in agreement with the larger singlet–triplet gap and therefore weaker electrophilicity of

$\text{cAACs}$  compared to  $\text{aAACs}$ . Very interestingly, Bielawski *et al.*<sup>11</sup> have recently prepared cyclic di(amido)carbenes, such as  $\text{cDAC}_1$ , which are more electrophilic than classical NHCs and shown that they reversibly react with CO.

In 2009, Power *et al.*<sup>12</sup> reported the first example of a room temperature reaction of CO with a heavier group 14 carbene analogue.<sup>13</sup> Using a diaryl germylene, they observed formation of compound **3**, most likely resulting from the rearrangement of the first formed germaketene (Scheme 1).

### 1.2 Activation of dihydrogen

As mentioned in the introduction, for a long time, the splitting of  $\text{H}_2$  was almost exclusively the domain of metals. The only exceptions were compounds only stable in matrices at a few K such as subvalent group 13 species,<sup>14</sup> triplet carbenes<sup>15</sup> and nitrenes,<sup>16</sup> and the highly electrophilic singlet difluorovinylidene.<sup>17</sup> In the last few years considerable progress has been achieved in the metal-free activation of  $\text{H}_2$ . Power *et al.*<sup>18</sup> showed that room temperature stable digermynes and distannynes ( $\text{ArE}\equiv\text{EAr}$ ,  $\text{E} = \text{Ge}, \text{Sn}$ ) were able to split  $\text{H}_2$  under mild conditions. Li and Zu<sup>19</sup> reported that fullerenes, fullerene anions, and their combination can activate hydrogen under UV irradiation at room temperature; even more striking, these species are able to catalyze the reduction of nitrobenzene into aniline. Stephan *et al.*<sup>20</sup> have reported the reversible activation of hydrogen using intramolecular phosphine–borane pairs. The latter system, the so-called frustrated Lewis pairs (FLPs), has received considerable attention. Several intramolecular and intermolecular combinations of Lewis acids/bases have been proven to efficiently split  $\text{H}_2$ , reversibly or irreversibly, and even catalyze the hydrogenation of reactive unsaturated compounds.<sup>21</sup>

Although NHCs have been used as the Lewis base component of the FLPs,<sup>22</sup> acyclic and cyclic bis(amino)carbenes, on their own, are inert towards  $\text{H}_2$ .<sup>23</sup> In marked contrast, cyclic and acyclic (alkyl)(amino)carbenes  $\text{cAAC}_1$  and  $\text{aAAC}_1$  can operate as single-site molecules for the activation of  $\text{H}_2$  under mild conditions (Fig. 2).<sup>10</sup> The calculated energy changes ( $\Delta E$ ) show that although the reactions of all carbenes with  $\text{H}_2$  are exothermic, the reactions are significantly more favored in the case of mono(amino)carbenes ( $\text{cAAC}_0$  and  $\text{aAAC}_0$ ) than bis(amino)carbenes ( $\text{aBAC}_0$  and  $\text{NHC}_0$ ).<sup>24</sup> More importantly, the activation energy is at least  $45 \text{ kJ mol}^{-1}$  lower in the case of mono(amino)carbenes, which readily rationalizes the experimental results. Note that although di(amido)carbenes  $\text{cDAC}$ , react with CO and  $\text{NH}_3$  (vide infra), they are inert towards hydrogen even under forcing conditions ( $65 \text{ atm H}_2$ ,  $200^\circ\text{C}$ ).<sup>25</sup>

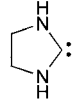



Importantly, the mode of activation of  $\text{H}_2$  by mono(amino)carbenes and transition metals is totally different. For the latter,  $\text{H}_2$ -splitting results from the primary interaction of a vacant orbital at the metal and the  $\sigma$ -bonding orbital of  $\text{H}_2$ .<sup>26</sup> In the case of carbenes, the cleavage comes from the primary interaction of the carbene's lone pair with an  $\text{H}_2$  antibonding orbital. In the transition state, the H–H bond is considerably elongated ( $1.071 \text{ \AA}$  versus  $0.77 \text{ \AA}$  for  $\text{H}_2$  gas) and polarized with the positively charged H ( $+0.178$ ) already bonded to the carbon ( $1.206 \text{ \AA}$ ) (Fig. 3). In other words, in contrast to the electrophilic activation/proton transfer pathway favored by transition metal centers, carbenes act by initial nucleophilic activation followed by hydride transfer.



Guy Bertrand

Guy Bertrand was an undergraduate in Montpellier, and obtained his PhD from the University of Toulouse. From 1988 to 1998 he was a “Director of Research” at the Laboratoire de Chimie de Coordination du CNRS, and from 1998 to 2005 the Director of the Laboratoire d'Hétérochimie Fondamentale et Appliquée at the University Paul Sabatier (Toulouse). Since 2001 he has been Distinguished Professor and Director of the UCR/CNRS Joint Research Chemistry Laboratory

at the University of California at Riverside. His research spans a wide range of topics at the border between organic and inorganic chemistry. He is a member of the French Academy of Sciences.

Carbene	$\Delta E(S-T)$ (kJ/mol)	$E_{HOMO}$ (eV)	$\Delta E(H_2)$ (kJ/mol)	$\Delta E(H_2)^{\ddagger}$ (kJ/mol)	$\Delta E(NH_3)$ (kJ/mol)	$\Delta E(NH_3)^{\ddagger}$ (kJ/mol)
 <b>NHC<sub>0</sub></b>	285.1	-5.2	-106.3	150.0	-70.8	141.3
 <b>aBAC<sub>0</sub></b>	214.0	-5.1	-121.0	147.8	-73.3	137.5
 <b>cAAC<sub>0</sub></b>	193.5	-5.0	-189.4	99.1	-139.3	94.5
 <b>aAAC<sub>0</sub></b>	139.2	-5.0	-211.8	93.0	-161.9	87.4

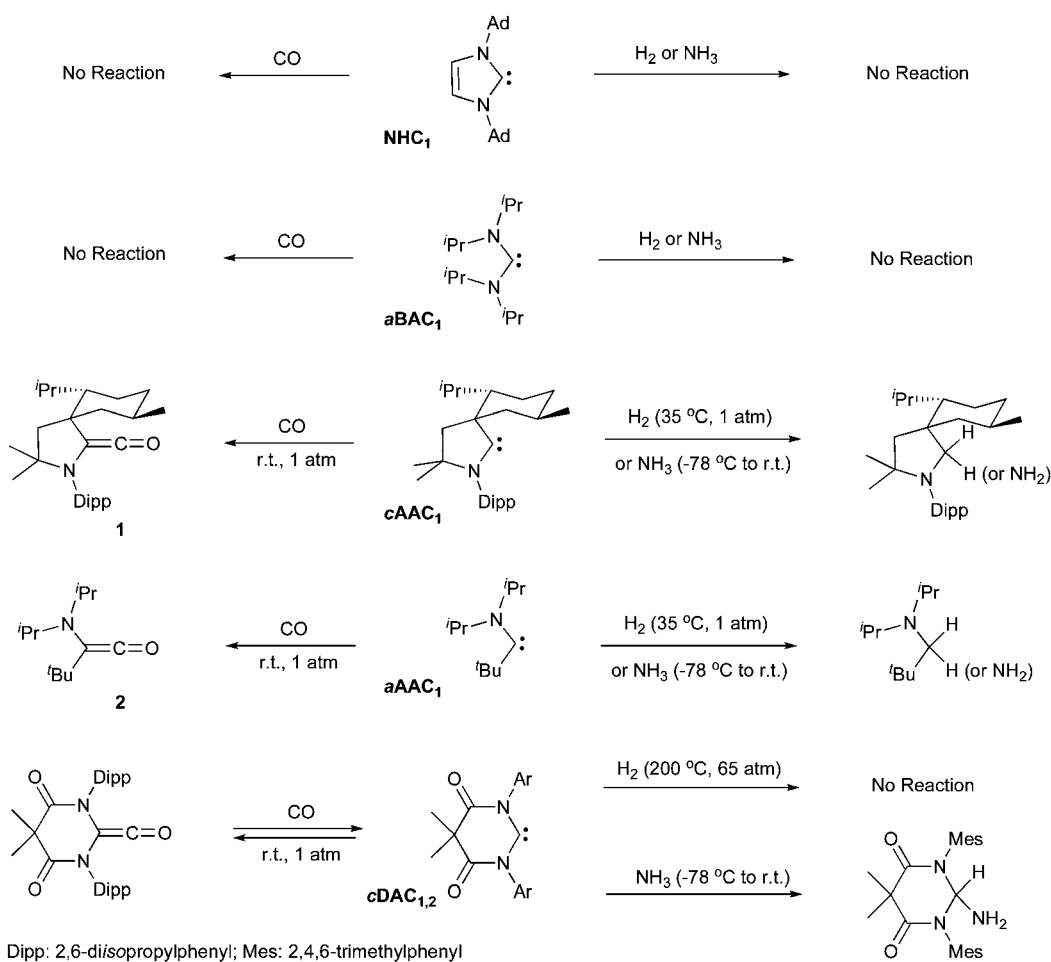
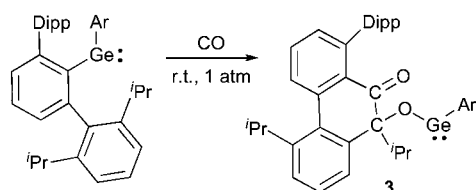


Fig. 2 Activation of CO, H<sub>2</sub> and NH<sub>3</sub> by stable carbenes.



Dipp: 2,6-diisopropylphenyl; Ar: 2,6-diDippphenyl

Scheme 1 Activation of CO by a germylene.

There are also recent reports covering the activation of hydrogen by germylenes and stannylenes (Scheme 2).<sup>27,28</sup> These reactions occurred under relatively mild conditions; however, depending on the nature of the aryl substituents, subsequent arene elimination sometimes occurs.

### 1.3 Activation of ammonia

In contrast with H<sub>2</sub>, NH<sub>3</sub> is reluctant to be split by transition metal centers.<sup>29</sup> Since H–H and N–H bond dissociation energies

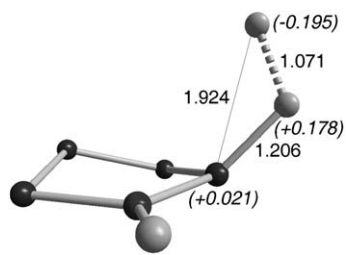
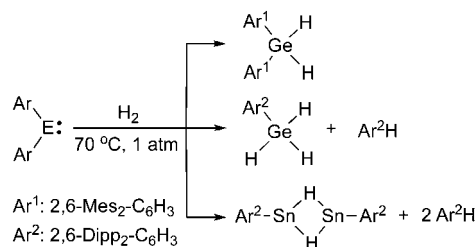


Fig. 3 Transition state for H<sub>2</sub> activation by cAACs.



Scheme 2 H<sub>2</sub> activation by heavier carbene analogues.

are comparable, the main obstacle is the electrophilicity of the metal, which instead favors the formation of the so-called Werner complexes L<sub>n</sub>M-NH<sub>3</sub>. As mentioned above, the activation of H<sub>2</sub> by mono(amino)carbenes relies on the primary interaction between the HOMO of the carbene (lone pair) and the LUMO of the reactant. This suggests that no Lewis acid–base adducts can be formed between a carbene and NH<sub>3</sub>. According to calculations, the reaction barriers for NH<sub>3</sub> splitting by carbenes are comparable to those for H<sub>2</sub> activation, although the former processes are less exothermic (Fig. 2).

Consistent with the computational results, NHCs are inert towards NH<sub>3</sub>,<sup>30</sup> but cAAC<sub>1</sub> and aAAC<sub>1</sub> rapidly react with liquid ammonia, even at −40 °C, cleanly affording the corresponding adducts.<sup>10</sup> Similarly, Bielawski *et al.*<sup>25</sup> have found that the rather electrophilic N,N'-di(amido)carbene cDAC<sub>2</sub> also activates NH<sub>3</sub> under mild conditions.

The mode of approach of NH<sub>3</sub> to cAACs was calculated to be very similar to that observed with H<sub>2</sub>. In the transition state, one of the N–H bonds elongates up to 1.50 Å, and becomes strongly polarized with the positively charged H (+0.316) bonded to the carbon (1.155 Å) (Fig. 4). Note that the nitrogen lone pair is pointing away from the carbene vacant orbital, supporting the nucleophilic character of the activation process.

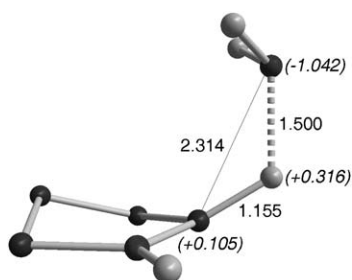
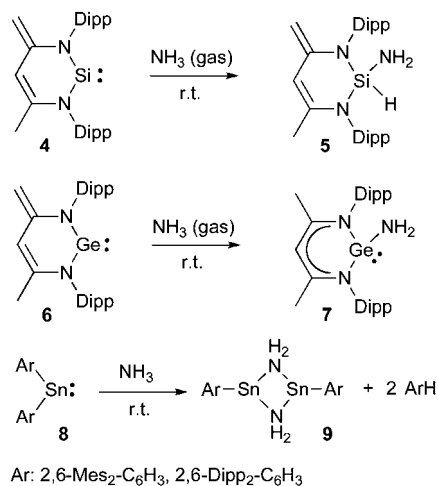


Fig. 4 Transition state for NH<sub>3</sub> activation by cAACs.



Scheme 3 NH<sub>3</sub> activation by heavier carbene analogues.

Heavier carbene analogues have also been used for the activation of ammonia, and depending on the heteroatom very different reactions were observed (Scheme 3). Silylene **4**<sup>31</sup> reacts at room temperature with NH<sub>3</sub> gas to give adduct **5**, formally resulting from an oxidative addition at the silicon(II) center.<sup>32</sup> Conversely, the analogous germylene **6**<sup>33</sup> undergoes a 1,4-addition affording **7**.<sup>34</sup> The different behavior of **4** and **6** has not been rationalized. In the case of stannylenes **8**, the addition of NH<sub>3</sub> results in the formation of dimeric derivative **9** with concomitant elimination of an arene, as observed for the activation of H<sub>2</sub> by this species.<sup>27</sup>

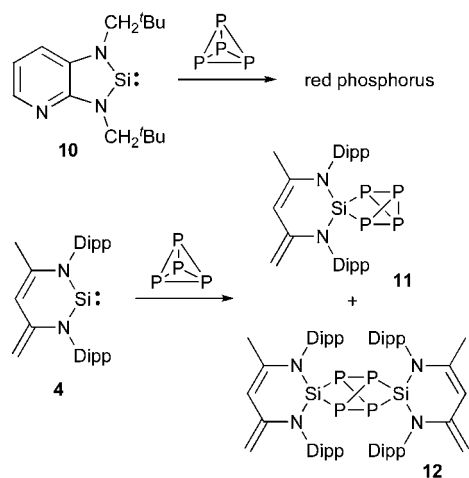
#### 1.4 Activation of white phosphorus (P<sub>4</sub>)

White phosphorus, the most reactive allotrope of the element, is another small molecule of industrial importance. It is the precursor to PCl<sub>3</sub> and PH<sub>3</sub>, and thus of most organophosphorus derivatives. To meet the increasingly stringent environmental regulations, new processes using P<sub>4</sub>, but avoiding chlorine, are highly desirable, which explains why its reactivity with organometallic compounds has been widely studied.<sup>35</sup> Consequently, P<sub>4</sub> is an excellent model to further explore the analogy between carbenes and transition metals.

At the end of the 1990s, West *et al.*<sup>36</sup> reported that stable silylene **10** catalyzed the conversion of white phosphorus to the red allotrope (Scheme 4). More recently, Driess *et al.*<sup>37</sup> reported the mono- and di-insertion of silylene **4** into P<sub>4</sub>, which leads to strained polycyclic silaphosphanes **11** and **12**.<sup>38</sup> Interestingly, the germylene analogue **6** is inert towards P<sub>4</sub> even in boiling toluene, possibly due to the lower reduction potential of Ge(II) versus Si(II). It should also be mentioned that mono insertion products similar to **11** have been observed in the reaction of white phosphorus with aluminium(I) derivatives<sup>39</sup> and phosphonium cations.<sup>40</sup>

In 2007, the clean formation of the bis(carbene) adduct **14a** was observed in the addition of two equivalents of the bulky cAAC<sub>1</sub> on P<sub>4</sub> (Scheme 5).<sup>41</sup> This was the first demonstration that stable singlet carbenes can activate white phosphorus. Compound **14a** has to be regarded as a 2,3,4,5-tetraphosphatriene, and a neutral P<sub>4</sub> chain as seen in **14a** is unprecedented.





Scheme 4  $P_4$  activation by silylenes.

This compound features highly reactive functional groups, a diphosphene and two phosphalkene fragments, thus allowing for the challenging and desirable direct formation of organophosphorus derivatives from  $P_4$ . For instance, **14a** reacts diastereoselectively with 2,3-dimethylbutadiene to afford the [4 + 2] cycloaddition product **15**.

Calculations, using the parent  $cAAC_0$ , predicted that the first step of the reaction is the nucleophilic attack of the carbene at one of the phosphorus atoms of  $P_4$ , affording triphosphirene **13**.<sup>41,42</sup> A second carbene then reacts at one of the unsaturated phosphorus centers of the triphosphirene moiety, giving a transient bis(carbene) adduct; the latter undergoes a facile ring opening to afford the observed 2,3,4,5-tetraphosphatriene **14**. Several complexes containing metal-stabilized mono-substituted triphosphirene fragments have been observed in the reaction of transition metal complexes with  $P_4$ .<sup>43</sup> The transient formation of **13** was demonstrated by reacting  $cAAC_1$  with  $P_4$  in the presence of a large excess of 2,3-dimethylbutadiene, which afforded the corresponding [4 + 2] cycloaddition product **19a**. Further proof of the initial formation of triphosphirenes was found when acyclic (alkyl)(amino)carbene  $aAAC_1$  was used, instead of  $cAAC_1$ . Indeed, the bicyclic compound **16** was obtained in 66% yield.<sup>44</sup>

Also similar to transition metals,<sup>45</sup>  $cAACs$  can promote the degradation of  $P_4$  into  $P_1$  and  $P_2$  fragments (Scheme 5).<sup>44</sup> Excess of the relatively small  $cAAC_2$ , instead of the bulky  $cAAC_1$  or more electrophilic  $aAAC_1$ , affords products **17a** and **18**, which were isolated in moderate yields. The formation of tris-carbene  $P_4$ -adduct **18** implies that two  $cAACs$  react on the primarily formed adduct of type **13**. The minor product **17a** is the desired bis-carbene- $P_2$  adduct, and the reaction leading to this compound represents the first example of fragmentation of  $P_4$  by a neutral organic species.

$P_2$ -adduct **17a** most probably results from the attack of the carbene to the  $\beta$ -phosphorus centers of a  $P_4$  bis-carbene adduct similar to **14a**; this fragmentation is made possible by the small size of  $cAAC_2$ . When the least sterically demanding stable carbene known was used, bis(diisopropylamino)cyclopropenyldiene **CP1**,<sup>46,47</sup> the cationic bis(carbene)- $P_1$  adduct **20** was obtained along with an anionic  $P_3$  fragment, which has not been fully identified.<sup>44</sup> Clearly, **20** results from the attack of the carbene at

a phosphorus center in a position  $\alpha$  to the carbene carbon(s) of adducts of type **13** or **14**. Notably, analogous  $(NHC)_2P^+$  systems have previously been reported by Schmidpeter<sup>48a</sup> and Macdonald,<sup>48b</sup> but using  $(R_3P)_2P^+$ ,  $(RNPCL)_2$ , or  $PCl_3$  as  $P_1$  sources.

Another task that transition metal centers are capable of doing with  $P_4$  is to induce its aggregation, although complexes with more than six phosphorus atoms are usually obtained as byproducts in low yields.<sup>49</sup>  $NHC_2$ <sup>50</sup> reacts at 70 °C overnight with white phosphorus, giving the  $P_{12}$  cluster **21** in high yield (81%).<sup>51</sup> The architecture of the  $P_{12}$  core is very different from that found in the only known  $P_{12}$ -transition metal complex.<sup>52</sup> Trapping experiments with dimethylbutadiene demonstrated that mono- and bis(carbene) adducts of type **13** and **14b** were involved. The different outcome of reactions with NHCs *versus*  $cAACs$  can be rationalized by the different electronic properties of these two carbenes. As already mentioned,  $cAACs$  are more electrophilic ( $\pi$ -acceptor) and thus strengthen the PC bonds of **14**, while NHCs are less basic and therefore better leaving groups, favoring the formation of clusters such as **21**.

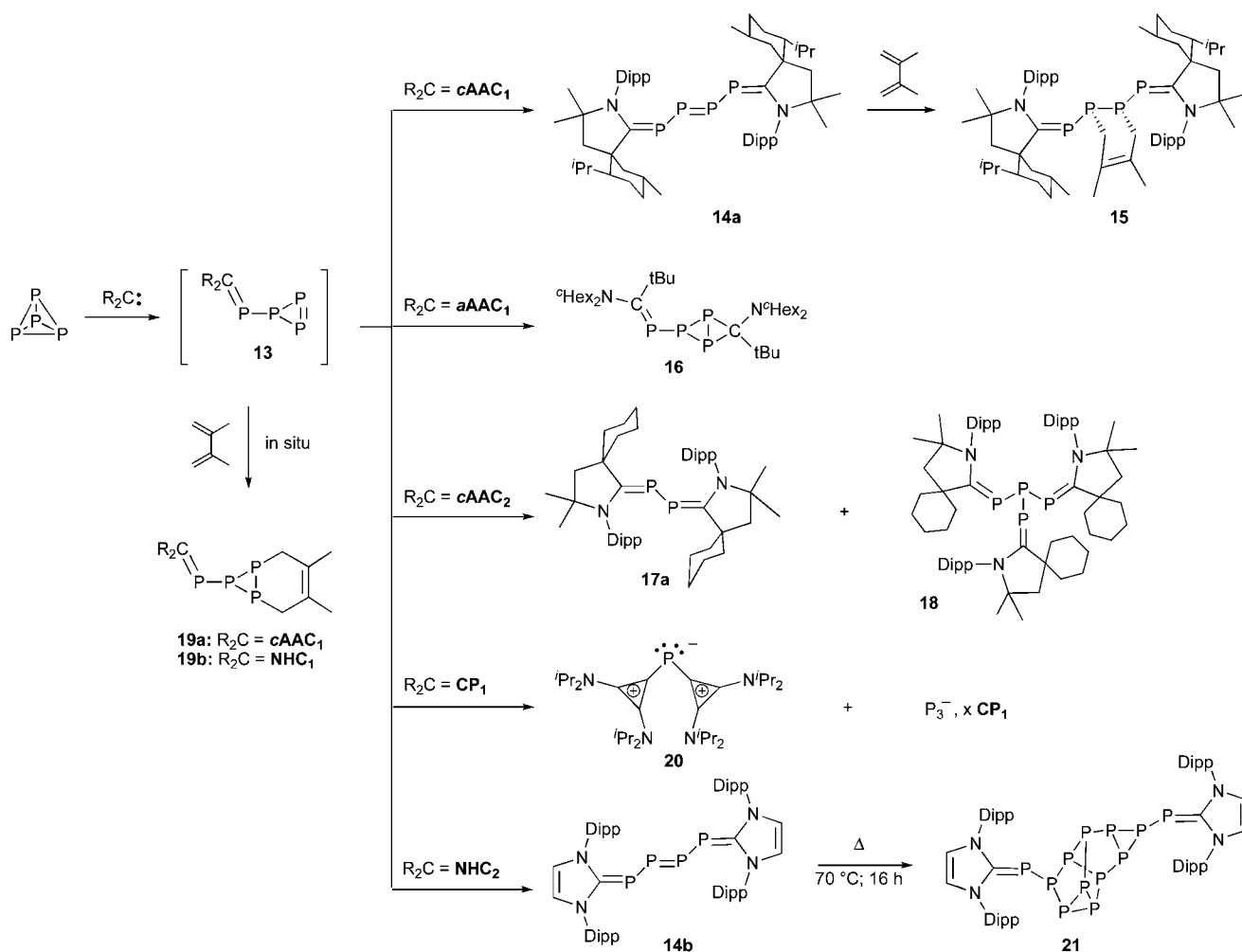
## 2 Stabilization of highly reactive species

There are numerous examples of the use of NHCs for stabilizing reactive Lewis acids as well as transition metal centers with unusual coordination and/or oxidation states. This section is limited to two recent applications of stable carbenes in main group element chemistry: the isolation of compounds featuring group 14 and 15 elements in the zero oxidation state, and the synthesis of phosphorus and boron centered radicals.

### 2.1 Stabilization of non-transition metal elements in the zero oxidation state

The zero oxidation state is classically found in metals, when stabilized by ligands that donate electron pairs into their empty orbitals. Such a state has been difficult to realize for main group elements except in their allotropes.

The four main allotropes of phosphorus are: white, red, violet and black. Except white phosphorus, all these compounds are polymeric and therefore it is easy to recognize that the  $P_{12}$  cluster **21** (Scheme 5) can be viewed as a carbene-stabilized phosphorus allotrope.<sup>51,53</sup> In 2008, Robinson *et al.*<sup>54</sup> discussed the structure of compound **17b** prepared by reduction of the  $(NHC)-PCl_3$  adduct **22** with potassium graphite (Scheme 6). Due to donation of the nitrogen's lone pair of electrons into the  $P=C$  double bonds, **17b** can be represented by the canonical forms **17b(I)** and **17b(II)**, or can even be viewed as a bis-phosphinidene unit coordinated by two carbenes, as shown by representation **17b(III)**. X-ray crystal data and DFT computations showed that the PC bonds of **17b** have a modest double bond character, while the PP bond is single. Moreover, each phosphorus has two lone pairs, supporting the carbene stabilized bis-phosphinidene structure **17b(III)**. Of course, the structure of this bis(carbene)- $P_2$  adduct is very different from the highly unstable diphosphorus allotrope ( $P_2$ ), which exhibits a phosphorus-phosphorus triple bond. Both compounds, however, have phosphorus centers with formal zero oxidation states. Note that a bis(carbene)-phosphonitride analogue  $(NHC-NP-cAAC)$  has recently been isolated.<sup>55</sup>

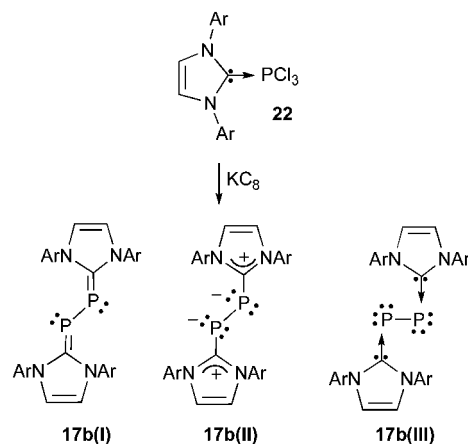


**Scheme 5** Activation, degradation and aggregation of  $P_4$  by stable carbenes.

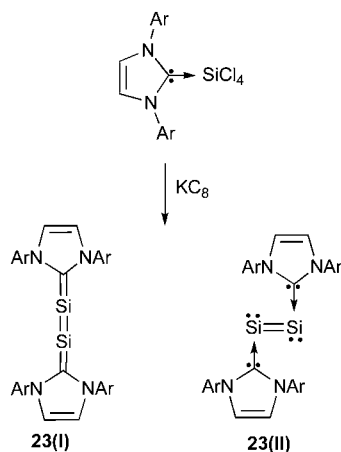
Robinson *et al.* used the same synthetic strategy for preparing other diatomic molecules of group 15 (arsenic),<sup>56</sup> and of group 14 elements (silicon),<sup>57</sup> in the formal oxidation state of zero (Scheme 7). Compound **23** represents a landmark in low coordinate silicon chemistry since each silicon center is involved in a multiple bond and, at the same time, features a lone pair of electrons, two attributes usually associated with extreme instability.<sup>58</sup> The zero oxidation state of silicon was clearly evidenced by a distinctly non-linear C–Si–Si–C backbone (C–Si–Si = 93.37°) and long C–Si bonds (1.927 Å). This geometry strikingly contrasts that expected for form **23(I)**, with silicon atoms formally in the +II oxidation state. The latter would exhibit a perfectly planar skeleton with a linear C–Si–Si–C arrangement and short carbon-silicon bonds. Thus, in compound **23**, the carbene ligand is only serving as a two-electron donor and is non-oxidizing (not withdrawing electron density from silicon), leaving a non-bonding electron pair on each silicon center as shown in **23(II)**. With such a bonding description,<sup>59</sup> compound **23** should be regarded as a diatomic silicon(0) unit coordinated by two L ligands; in other words it is a Lewis base-stabilized silicon allotrope. Note that a germanium analogue of **23** has also recently been isolated.<sup>60</sup>

What about carbon in the zero oxidation state? Several allotropes are known such as graphite, diamond, fullerenes, *etc.* and

atomic carbon has been identified in the interstellar space.<sup>61</sup> The latter is a short lived species with a triplet ground state, but most of the reactions reported so far involve a singlet excited state located 125 kJ mol<sup>−1</sup> higher in energy. A hallmark of atomic carbon chemistry is the large amount of energy that it brings, which makes it so reactive that it inserts into very inert bonds. A



**Scheme 6** Synthesis and different forms of  $P_2$ -biscarbene adduct **17b**.

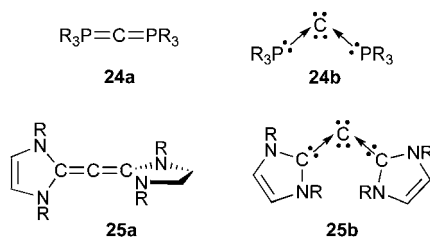


**Scheme 7** Synthesis and different forms of Si<sub>2</sub>-biscarbene adduct **23**.

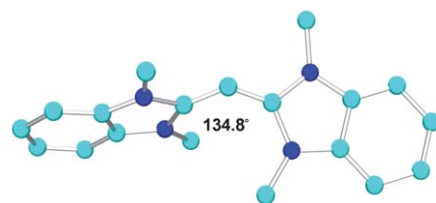
simplistic view of singlet atomic carbon is a carbon atom with two lone pairs and two vacant orbitals. Therefore one could hope that electron donation from two Lewis bases could stabilize such a species while maintaining neutrality of the compound. Frenking *et al.*<sup>62</sup> first tested this hypothesis computationally, using phosphines as Lewis bases. They showed that carbodiphosphoranes **24**, which have been known for decades,<sup>63</sup> feature a carbon atom with its four valence electrons in two orthogonal lone pairs that are not engaged in chemical bonding (**24b**) (Fig. 5). In other words, the commonly used allenic structure **24a** is not relevant because of the weakness of back-donation of the carbon lone-pairs into the antibonding P–C orbitals.

More surprisingly, Frenking *et al.*<sup>64,65</sup> also proposed NHCs as alternative ligands for carbon(0), and suggested to name the corresponding complexes “carbodicarbenes”. At first glance, the prediction that the central carbon of **25** prefers to keep its four electrons as two lone pairs as shown in **25b** seemed astonishing. Indeed, in contrast to the form **24a** of carbodiphosphoranes, in which phosphorus is hypervalent, **25a** is simply an allene with regular tetravalent carbon atoms.

Soon after the publication of this computational study, we reported the synthesis and isolation of the bis(benzimidazolin-2-ylidene)carbon(0) complex **26** (Fig. 6) that we classified as an acyclic bent-allene.<sup>66</sup> We simply reasoned that strong electron-donating groups at the carbon termini of the allene would induce a strong polarization, and therefore a weakening of the  $\pi$ -bonds. As a consequence, the CCC framework should be more flexible, and ultimately a bending of the otherwise rigid and linear CCC skeleton should occur. A single crystal X-ray diffraction study revealed that the four amino groups do cause a dramatic effect



**Fig. 5** Allenic structure **a** versus L<sub>2</sub>C(0) formulation **b**.



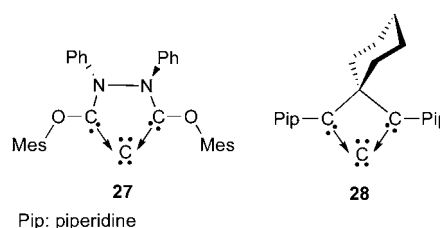
**Fig. 6** Solid state structure of acyclic bent-allene **26**.

on the geometry of **26**. Although the bond lengths are only slightly longer (C1–C2 = 1.343 Å) than the standard C=C bond length of an allene (1.31 Å), the two NCN planes are not perpendicular but twisted by 69°. Remarkably, the allene framework is severely bent with a CCC angle of 134.8°. Clearly the allene  $\pi$ -system has been severely perturbed, and the central carbon atom is no longer sp-hybridized as in typical allenes, but likely approaching a configuration with two lone pairs. As a consequence of its peculiar electronic structure, and in contrast with “regular allenes”, an  $\eta^1$ -coordination mode involving the central carbon was observed with metals.<sup>66,67</sup>

Interestingly, it has even been suggested that tetrakis(dimethylamino)allene, displays “hidden” lone pairs, despite a classical linear geometry.<sup>68</sup> Alcarazo, Fürstner *et al.* have shown that the reactivity of this compound is analogous to that of carbodiphosphorane **24** and carbodicarbene **26**. They stated that the bonding in the tetrakis(dimethylamino)allene is still best described by the capto-dative formalism, *i.e.*  $\sigma$ -donation from the L ligands to the central carbon, and  $\pi$ -back donation of the lone pairs of the carbon(0) to L, exactly as in metal complexes. They concluded that “carbon is capable of serving as the central atom of a complex – just as a metal can do”.<sup>68b</sup>

Although the bent geometry is not a common feature for carbodicarbenes, all of them are highly flexible. Calculations have shown that widening the bond angle of the carbodicarbene **25** from the equilibrium geometry (131.8°) up to the “classical” linear structure requires only 15.5 kJ mol<sup>−1</sup>.<sup>64</sup> As a consequence of its flexibility, the CCC framework of carbodicarbenes can be confined in rather small cyclic systems, as shown by the isolation of derivatives **27**<sup>69</sup> and **28**<sup>70</sup> (Fig. 7).

Carbodicarbenes, as well as other carbon(0) derivatives (L: → C ← :L'), are predicted to be extremely basic. Computational studies showed that **26** has not only a very high first proton affinity (1230 *versus* 1100 kJ mol<sup>−1</sup> for NHCs), but also a large second proton affinity (700 *versus* 300 kJ mol<sup>−1</sup> for NHCs).<sup>71</sup> Consequently, carbon(0) derivatives should be prone to double protonation, and should also be capable of bonding two transition metals at the same carbon site. This hypothesis is supported



**Fig. 7** Cyclic carbodicarbenes.

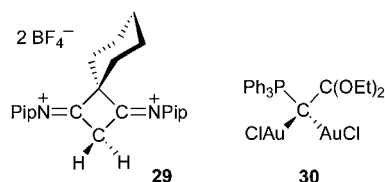


Fig. 8 Double protonation and metalation of carbon(0) derivatives.

by the existence of dimetallated carbodiphosphoranes,<sup>72</sup> and confirmed by recent results. Addition at room temperature of two equivalents of tetrafluoroboric acid to four-membered heterocycle **28** afforded dication **29**,<sup>70</sup> and Fürstner *et al.*,<sup>68b</sup> were able to prepare **30**, a dinuclear gold complex of a carbon(0) derivative, featuring a phosphine and a dialkoxycarbene as “ligands” (Fig. 8).

The concept of carbodicarbenes may be extended to heavier main group 14 elements (Fig. 9).<sup>73</sup> The central atom can be silicon(0), germanium(0) or tin(0), whereas the L ligands are silylenes, germaylenes or stannylenes.<sup>74</sup> Several combinations are known, although surprisingly neither compounds featuring a heavier main group 14 element(0) ligated by two carbenes, nor a carbon(0) stabilized by heavier carbene analogues, have been prepared. Interestingly, Kira *et al.* noted that most of these compounds are highly flexible, the X-ray analysis showing dynamic disorders of the central atom even at low temperature.

## 2.2 Stabilization of main-group element radicals

Recently, Malacria and Curran *et al.* used NHC-BH<sub>3</sub> adducts as hydrogen-atom donors in the Barton–McCombie deoxygenation reaction,<sup>75</sup> and as co-initiators for the radical photopolymerization of acrylate.<sup>76</sup> These results are particularly interesting since BH<sub>3</sub> itself, and even amine- and phosphine-boranes, are not suitable for these transformations. The higher reactivity of NHC-BH<sub>3</sub> complexes was rationalized by a considerable reduction of the B–H bond dissociation energy. For BH<sub>3</sub> and its amine and phosphine complexes, the calculated bond dissociation energies are in the 390–450 kJ mol<sup>−1</sup> range, whereas for NHC-BH<sub>3</sub> complexes the value dropped to 367 kJ mol<sup>−1</sup>.<sup>77</sup> This value is smaller than that of triethylsilane (397 kJ mol<sup>−1</sup>), and only slightly higher than those calculated for standard radical hydrogen transfer reagents such as (Me<sub>3</sub>Si)<sub>3</sub>SiH (351 kJ mol<sup>−1</sup>) and tributylstannane (328 kJ mol<sup>−1</sup>). This trend has been confirmed by implementing kinetic experiments to measure rate constants for radical hydrogen abstraction from NHC-boranes by alkyl radicals.<sup>78</sup> The lowering of the B–H bond dissociation energy points towards the enhanced stability of the NHC-BH<sub>2</sub> radical **32**, which is due to spin delocalization away from boron,<sup>79</sup> as shown by EPR studies.<sup>77,80</sup> Despite the presence of

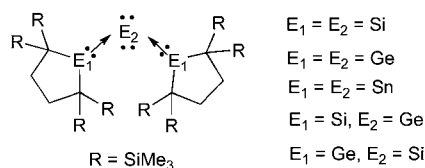


Fig. 9 Heavier group 14 element(0) derivatives.



Fig. 10 Planar versus pyramidalized boron radicals.

nitrogen centers in  $\beta$ -positions of the boron, larger  $a(^{14}\text{N})$  isotropic hyperfine coupling constants were observed for **32** than for R<sub>3</sub>N-boryl radicals **31**. In addition, radicals **32** display a much smaller  $a(^{11}\text{B})$ , showing that the boron center is in a planar environment and not pyramidalized as in **31** (Fig. 10). Stable boron-containing radicals are quite rare.<sup>81,82</sup> Therefore, although NHC-BH<sub>2</sub>, or even NHC-BAr<sub>2</sub> radicals,<sup>83</sup> have so far not been isolated, their superior stability compared to other Lewis base stabilized analogues is a clear indication of the stabilizing effect of NHCs on adjacent radical centers. This conclusion has been corroborated by recent results in phosphorus chemistry.

Until 2010, only resonance-stabilized phosphorus radicals, featuring a rather small spin density at phosphorus were structurally characterized by single crystal X-ray diffraction studies.<sup>84</sup> The few phosphinyl radicals, which are stable in solution at room temperature, such as **33**, dimerize in the solid state despite bulky substituents (Fig. 11).<sup>85</sup> In contrast, the phosphinyl radical cation **35**, readily available by oxidation of phosphalkene **34** (derived from a cAAC), is indefinitely stable both in solution and in the solid state.<sup>86</sup> The crystallographic study of **35** shows that both the PC (1.81 Å) and PN (1.68 Å) bond distances are comparable to those observed in the gas phase electron diffraction study of **33a** (PC: 1.85; PN: 1.62 Å),<sup>85</sup> and collectively are in agreement with those expected for a phosphinyl radical bearing a cationic substituent. Similarly, the isotropic hyperfine coupling constant with P [ $a(^{31}\text{P}) = 99$  G] is comparable to those observed for

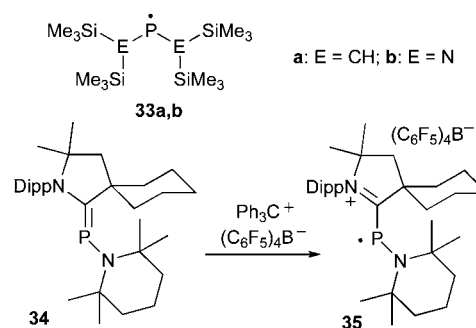


Fig. 11 Stable localized phosphinyl radicals.

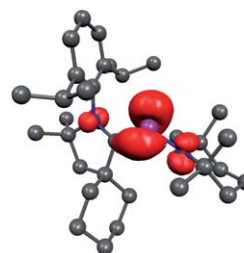


Fig. 12 Calculated spin density for **35**.



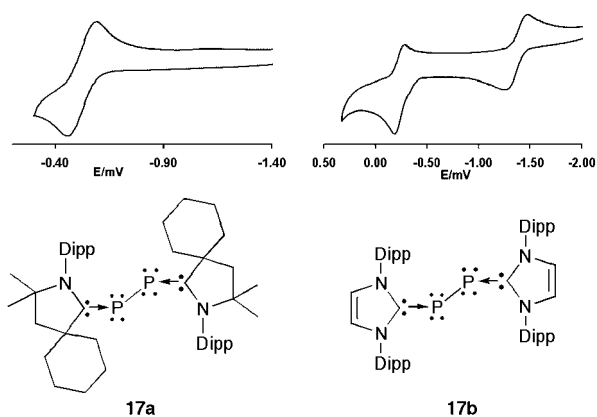


Fig. 13 Cyclic voltammograms of **17a** and **17b**.

phosphinyl radicals **33** [ $a(^{31}\text{P}) = 96.3 \text{ G}$  (**33a**) and  $91.8 \text{ G}$  (**33b**)], in which the odd electron resides predominantly in a  $3p(\text{P})$  valence orbital. Calculations and the EPR spectrum of **35** in a frozen fluorobenzene solution show that 67% of the spin density is localized at phosphorous, with only small contributions from the nitrogen atoms (Fig. 12). Therefore, the stability of phosphinyl radical **35** is partly due to steric factors, but more importantly to the presence of the cationic substituent. The latter prevents, by electrostatic repulsion, the dimerization observed for other phosphinyl radicals, such as **33**.

Radical cation **35** can also be regarded as a  $\text{R}_2\text{N}-\text{P}^{2+}$  unit stabilized by a carbene; in other words as a carbene–phosphoniumyl adduct. Along this line, it has been shown that singlet carbenes are also capable of stabilizing  $\text{P}_2^{2+}$  fragments (Fig. 13). One-electron oxidation of bis(carbene)- $\text{P}_2$  adducts **17a** and **17b** afforded the corresponding radical cations **17a** $^{+}$  and **17b** $^{+}$ , which have been fully characterized, including X-ray diffraction studies.<sup>87</sup> According to calculations and EPR spectroscopy, the spin density of **17a** $^{+}$  is distributed between the phosphorous atoms (0.27 e at each P) and the nitrogen atoms (0.14 e at each N) of the cAAC ligands. In contrast, the unpaired electron in **17b** $^{+}$  is nearly exclusively localized at phosphorous (0.33 e and 0.44 e) with less than 0.07 e for any other atoms.

In this review, there are numerous examples, showing that although the donor properties of cAACs and NHCs are comparable, the former are by far more electron accepting. The comparison of the cyclic voltammograms of **17a** and **17b** provides another striking illustration (Fig. 13). For the cAAC adduct **17a**, a reversible one-electron oxidation at  $E_{1/2} = -0.536 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$  is observed. In contrast, for the NHC adduct **17b**, two reversible one-electron oxidations can be seen. The first oxidation occurs at a much lower potential ( $E_{1/2} = -1.408 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ ) than **17a**, and the second at  $E_{1/2} = -0.178 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ ; consequently, even the  $\text{P}_2^{2+}$  bisNHC adduct **36b** can be prepared and isolated (Fig. 14).

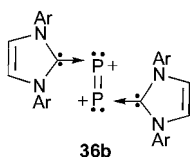


Fig. 14  $\text{P}_2^{2+}$ -bisNHC adduct.

## Conclusions

Beginning as laboratory curiosities at the end of the 20th century,<sup>88</sup> stable carbenes first found applications as ligands for transition metal based catalysts.<sup>89</sup> It was also quickly discovered that stable carbenes are excellent catalysts in their own right due to their Lewis basicity.<sup>90</sup> This perspective summarizes some novel applications of these fascinating species, and it is extremely likely that many others will soon be discovered. For example, there is already one publication demonstrating that stable carbenes can themselves induce organometallic transformations; in other words, a carbon-based catalyst can promote metal–metal bond formation.<sup>91</sup> Will carbon centers compete with or even surpass transition metals for applications the latter are known for?

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