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Perspective

Stable Carbenes, Nitrenes, Phosphinidenes, and Borylenes: Past and Future

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The different modes of stabilization for carbenes are briefly discussed in the context of the discovery of their first stable representatives. Largely because a diversity of stable carbenes are available today, their use has spanned across the chemical sciences, including medicinal and material applications. Much less is known about the isolobal group 15 cousins of carbenes, namely nitrenes and phosphinidenes, given that only one example of each has been isolated. The difficulties associated with their applications are discussed, and possible solutions are presented. As for group 13 element carbenoids, two types are considered: (1) mono(Lewis base)-stabilized borylenes that have been recently isolated and (2) borylenes, the only carbenoids discussed in this article that have eluded the synthetic skills of investigators. This Perspective describes potentially attainable targets, such as monocoordinated aminocarbanions, aminocarbynes, and aminocarbocations, which feature a carbon atom with six, five, and four valence electrons, respectively.

The Bigger Picture

Challenges and opportunities:

- Further development of carbenes to enable new and important chemical transformations and translation into medicinal and material chemistry applications.
- Stable nitrenes, phosphinidenes, (Lewis base)-stabilized borylenes, and their applications remain underdeveloped.
- Free borylenes have still eluded the synthetic skills of investigators, and species featuring a carbon atom with six, five, or four valence electrons should be exciting and attainable targets.

The octet rule, one of the fundamental principles of organic chemistry, dates back to Mendeleev at the end of the 19th century and Abbeg, Lewis, and Langmuir at the beginning of the 20th century.[1] Scientists love challenging rules, and one can argue that this motivated Gomberg to prepare the first stable radical, a species in which a carbon atom has only seven valence electrons. Similarly, Curtius and Staudinger attempted to synthesize carbenes, compounds in which a carbon atom features a six-valence-electron shell. In agreement with the octet rule, they found that carbenes were only transient intermediates but were involved in several important chemical transformations. Then, for many years, the quest for stable carbenes became an unreasonable target until the isolation of a distillable (phosphino)(silyl) carbene (**1**) in 1988[2] and a crystalline imidazol-2-ylidene (**2**) in 1991[3] (Figure 1). Interestingly, the mode of stabilization for singlet carbenes **1** and **2** is totally different. In agreement with Pauling's prediction,[4] our group believed that a π-donor and a π-acceptor substituent (a push-pull mesomeric substitution pattern) was necessary to decrease both the Lewis acidity and basicity of the carbene center of **1**. However, the isolation of Arduengo's carbene **2**, which features two π-donor substituents (a push-push mesomeric substitution pattern), showed that the instability of singlet carbenes was mainly due to their Lewis acid character, although one could argue that the amino groups have an inductive pull effect, decreasing the basicity of the lone pair.[5] During the next decade, after the discovery of **1** and **2**, it was believed that two electronic active substituents were required to allow for the isolation of carbenes. However, at the beginning of the 21st century, we showed that a single π-donor phosphino[6] or amino[7,8] substituent, as exemplified by **3**, was enough to extend the lifetime of carbenes to weeks, provided that the other substituent was sufficiently bulky.

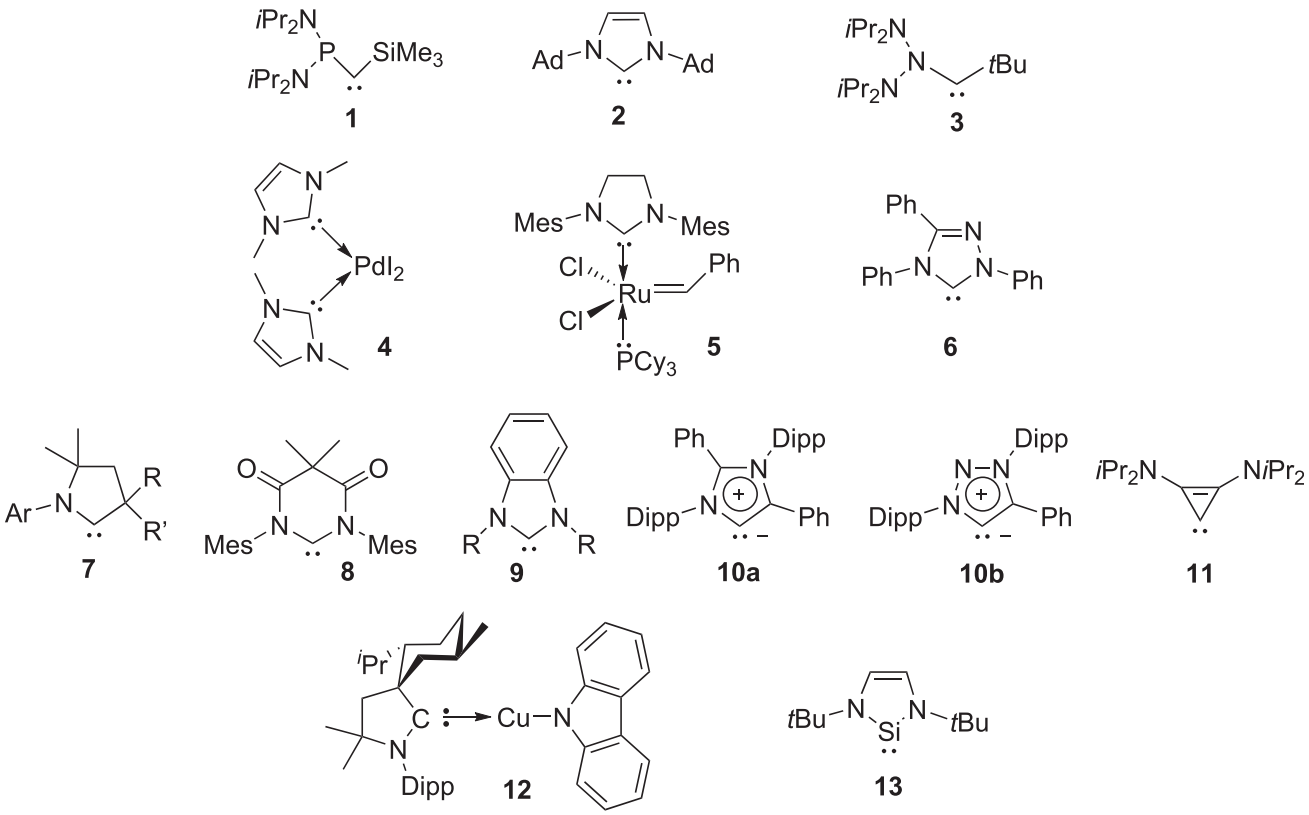

Figure 1. Stable Group 14 Carbenoids and Selected Complexes

Some of the first isolated carbenes (**1**–**3**), catalytically active complexes (**4** and **5**), an organocatalyst (**6**), some of the most popular carbenes (**7**–**11**), an efficient blue emitter for OLEDs (**12**), and the first stable silylene (**13**).

Very often in chemistry, when a novel type of compound is discovered, it is first considered a laboratory curiosity, and it sometimes takes decades for the first applications to appear. For example, phosphorus ylides were first synthesized in 1894 by Michaelis and Gimborn, but it was only in 1953 that Wittig and Geissler reported the so-called Wittig reaction, which was soon after used by BASF for the synthesis of vitamin A. This is not the case for carbenes given that already in 1995, Herrmann et al. reported that the palladium complex **4** bearing imidazol-2-ylidenes, similar to **2** as ancillary ligands, promoted the Mizoroki-Heck reaction.[9] After this discovery, transition-metal complexes bearing carbenes—such as **2** and their saturated version, i.e., imidazolin-2-ylidene,[10] the so-called N-heterocyclic carbenes (NHCs)—have been used for a variety of catalytic chemical transformations,[11] the most recognizable of which is the Grubbs second-generation olefin metathesis catalyst **5**.[12] In parallel, the 1,2,4-triazolin-5 ylidene **6**, reported by Enders,[13] has proven to be an excellent organocatalyst on its own, in line with the pioneering work by Breslow on the thiazolydene-catalyzed benzoin condensation.[14]

Nowadays, aside from the carbenes mentioned above, a myriad of stable carbenes with distinct steric and electronic properties are available. Arguably, the most popular are the cyclic (alkyl)(amino)carbenes (CAACs) **7**,[15,16] *N*,*N*′-diamidocarbenes (DACs) **8**,[17,18] benzimidazolylidenes **9**,[19] mesoionic carbenes **10a**[20–22] and **10b**,[23,24] and the cyclopropenylidene **11**.[25] As a consequence of this diversity, the use of carbenes disseminated across chemical sciences at large, including medicinal[26] and material[27] applications. Furthermore, thanks in part to carbene's

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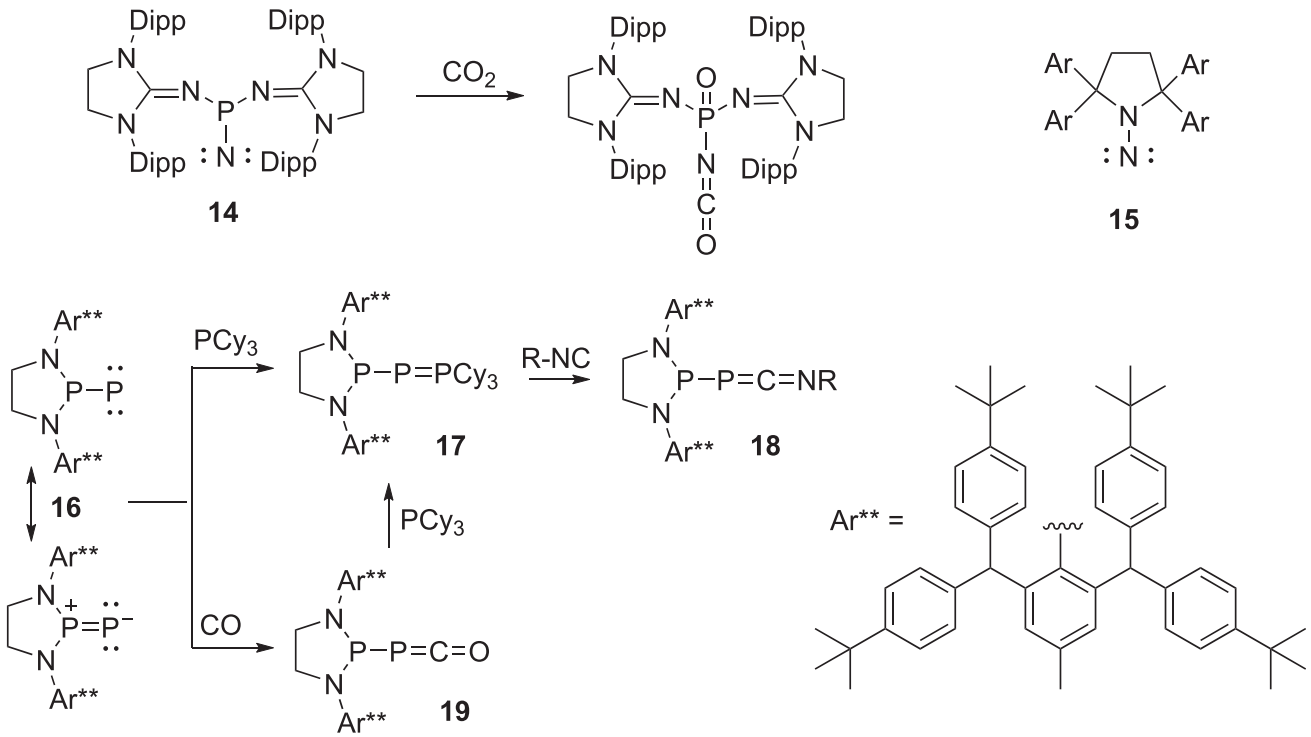

Figure 2. Group 15 Carbenoids

The isolated nitrene **14** and its reactivity with CO_2 exemplify the non-innocence of the phosphorus center. Aminonitrene **15** is an attractive target. The isolated phosphinidene **16** behaves as an electrophile, as shown by the formation of **17**, and to some extent as a transition metal given that it reacts with CO to give **19**, which undergoes ligand exchange, as shown by **17** and **18**.

pronounced ability to reversibly activate enthalpically strong bonds and small molecules,[28,29] there has been significant development toward their use as transition-metal surrogates. They can also stabilize low-coordinate main-group compounds[30–32] and organic and inorganic paramagnetic species[33] and can be used for the functionalization of nanoscale and bulk surfaces.[34] They even enabled the preparation of organic light-emitting diodes (OLEDs) based on earth-abundant metals,[35,36] which achieve performance comparable to that of the state-of-the-art luminescent complexes of iridium, platinum, and ruthenium. As an example, the two-coordinate copper(I) complex **12** achieved photoluminescence efficiencies > 99% and microsecond lifetimes, which lead to an efficient blue-emitting OLED.[37]

The discovery of stable carbenes was followed by the isolation of their heavier analogs, e.g., silylenes. Indeed, in 1994 Denk et al. reported the isolation of **13**,[38] the design of which was clearly derived from the corresponding NHC **2**. Although the applications of silylenes are still very limited, some encouraging results were obtained when they were used as ligands in transition-metal catalysis.[39]

Much less is known about the isolobal group 15 cousins of carbenes and silylenes, namely nitrenes and phosphinidenes (Figure 2). In 2012, our group isolated the first nitrene (**14**).[40] The bonding between phosphorus and nitrogen is analogous to that observed for metallonitrenes, which are postulated as key catalytic species in the industrial Haber-Bosch hydrogenation of N_2 into NH_3. However, since its discovery, no striking developments have occurred with **14**. This is mainly due to the presence of the phosphino substituent. Indeed, although nitrene **14** can activate small

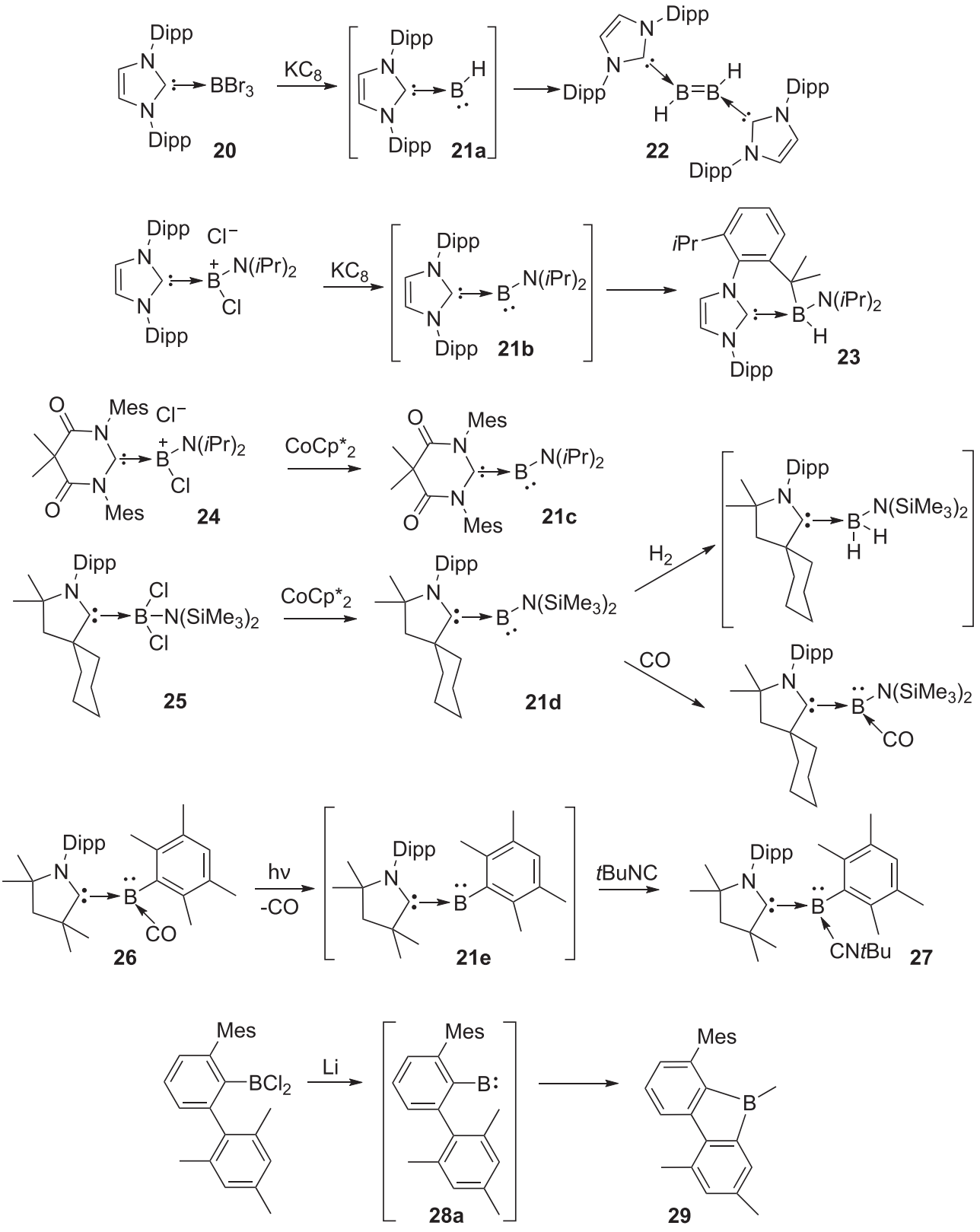
Dipp
BBr3
KC8
20
21a
22
Cl−
N(iPr)2
21b
23
Mes
24
CoCp*2
21c
N(SiMe3)2
25
21d
H2
CO
26
hv
-CO
tBuNC
CNtBu
27
BCl2
Li
28a
29

Figure 3. Group 13 Carbenoids

The first attempts to prepare mono(Lewis base)-stabilized borylenes (**21a** and **21b**) and their isolated counterparts **21c** and **21d** (metallomimics), as shown by their reactivity with H_2 and CO. The elimination of CO under irradiation from **26** leads to a transient mono(Lewis base)-stabilized borylene (**21e**), which can be trapped by an isonitrile to give the bis(Lewis base)-stabilized borylene **27**. The transient formation of borylenes of type **28** has been postulated on the basis their chemical reactivity, as shown by **29**.

molecules,[41] the involvement of phosphorus in the reaction, as exemplified with CO_2, might preclude the use of this nitrene in catalytic processes. We believe, however, that a stable amino nitrene, such as that derived from Dervan's scaffold (**15**),[42] would be a more promising candidate. The only isolated phosphinidene (**16**) to date also features a bulky and strong π-donor phosphino substituent.[43] Of particular interest, despite its phosphorus-phosphorus (PP) multiple-bond character and the presence of a partial negative charge on the terminal phosphorus, **16** behaves as an electrophile, as expected for an atom featuring a formal valence sextet structure. Indeed, **16** reacts with Lewis bases, such as phosphines, and prefers the more basic PCy_3 over PPh_3.[44] Importantly, phosphinidene **16** resembles a transition metal to some extent given that it reacts with CO, giving **19**, and undergoes ligand exchange.[45] For example, **19** reacts with phosphines to afford the corresponding adduct **17**. Similarly, the latter reacts with isonitriles to give **18**. It is important to note that these ligand-exchange reactions can be performed starting from non-hindered phosphinidene-CO adducts, which are readily available from the reaction of the corresponding chlorophosphine with NaPCO.[46] Just as for nitrenes, amino-substituted phosphinidenes would be attractive targets because they might give the opportunity to isolate both the singlet and the triplet states of a given compound, which has never been done with carbenoid species.[47,48] Indeed, calculations by Nguyen et al.[49] predicted that the singlet-triplet gap for amino phosphinidenes would be below ±3 kcal/mol; in other words, the ground state would have two degenerate orbitals.[50]

As for group 13 element carbenoids, two species have to be considered: mono(Lewis base)-stabilized borylenes (**21**) and borylenes (**28**) (Figure 3).[51] The former are isoelectronic with carbenes with a six-electron valence shell, whereas the latter have only a four-electron valence shell. The first attempt to isolate a compound of type **21** was reported in 2007 by Robinson and co-workers[52] through reduction of the (NHC)BBr_3 adduct **20**. They isolated the diborene **22**, which can be regarded as a dimer of the desired mono(Lewis base)-stabilized borylene **21a**. As already stated, carbenes and related species, featuring a sextet of electrons, need a π-donor substituent to be isolated. Although the (NHC)aminoborylene **21b** fulfilled this criterion, it was not isolable because an intramolecular CH insertion gave **23**.[31] Because of its electropositivity, boron was reluctant to be electron rich,[53] and thus more electrophilic carbenes than NHCs seemed more appropriate to stabilize a compound of type **21**. Indeed, reduction of the DAC adduct of the diisopropylaminodichloroborane **24** and of the CAAC adduct of the bis(trimethylsilyl)aminodichloroborane **25** afforded the desired mono(Lewis base)-stabilized borylenes **21c** and **21d**.[54,55] Unsurprisingly, both compounds feature an almost linear allenic structure (>C=B=NR_2), but their flexibility gives rise to a highly electrophilic boron center that has carbene-like behavior. Akin to electrophilic singlet carbenes, **21d** can activate small molecules, such as H_2, and coordinate an additional ligand, such as CO; in other words, compounds **21** are boron metallomimics.[56–58] Along this line, Braunschweig et al.[59] have shown that the CO ligand of **26** can be removed by photolysis to afford the transient mono(Lewis base)-stabilized borylenes **21e**, which can be trapped by Lewis bases to afford novel bis(Lewis base)-stabilized borylenes **27**.[60,61]

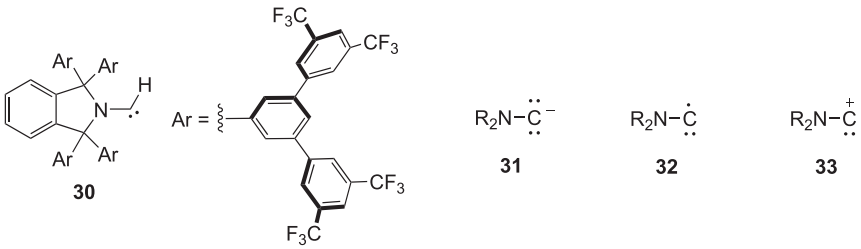

Figure 4. The Stable Mono-substituted Carbene 30 and Future Targets 31–33

In contrast to the other carbenoids, borylenes **28** have two vacant orbitals. These compounds are well known in the coordination sphere of transition metals, and Braunschweig et al. have shown that these complexes display a rich chemistry.[62,63] Until now, metal-free borylenes have been spectroscopically characterized only in the gas phase or in inert matrices at very low temperatures.[64] In addition, the transient formation of borylenes **28** has been postulated on the basis of their chemical reactivity,[65] as exemplified with the formation of **29**.[66]

In conclusion, it appears that borylenes **28** are the only carbenoids we discuss that have eluded the synthetic skills of investigators. However, contrary to carbenes, nitrenes, and phosphinidenes, which feature either a singlet or a triplet ground state, all computationally studied borylenes **28** have a singlet ground state;[67] therefore, we believe that with the right substituent, they should be isolable. Hope for a stable borylene **28** comes from the recent isolation of the mono-substituted carbene **30** (Figure 4), which demonstrates that a single bulky amino substituent could single handedly tame the intrinsic tendency of carbenes toward dimerization.[68] Along this line, we believe that monocoordinated aminocarbanions (**31**) could be isolated. They have six valence electrons, similar to carbenes, and two lone pairs and a vacant orbital, like phosphinidenes **16**. It might even be possible to undress carbon even more. What about aminocarbynes (**32**) and aminocarbocations (**33**),[69] compounds in which the carbon center formally features only five and four valence electrons, respectively? Not only are these molecules exciting synthetic challenges, but their unique properties should also unveil new applications. As an illustration, note that carbenes can simultaneously form two sigma bonds, whereas monocoordinated compounds could form three,[70] which opens a new mode of reactivity.

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AUTHOR CONTRIBUTIONS

M.S. and G.B. wrote the manuscript.

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