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A Brief Survey of our Contribution to Stable Carbene Chemistry

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Abstract

This personal account summarizes our work, beginning with the discovery of the first stable carbene in 1988 up until the recent isolation of mesoionic carbenes. It explains why we have moved our focus from acyclic to cyclic carbenes, and shows that these stable species are not limited to the role of ligand for transition metals, but that they are also powerful agents for the activation of small molecules, and for the stabilization of highly reactive diamagnetic and paramagnetic species.

Keywords

Stable carbenes; ligands; mesoionic compounds; coordination chemistry; catalysis; metal-free bond activation; stable radicals

This account summarizes the work from our laboratory and is not intended to cover the entire field of stable carbene chemistry. It is obvious that many important discoveries have been made by numerous different research groups all over the world, and that the popularity of stable carbenes is a result of joint efforts.

Before discussing our contribution, it seems highly desirable to present a brief history of the chemistry of carbenes, and to recognize some of the great pioneers of this field. As early as 1835, attempts to prepare the parent carbene (CH_2) by dehydration of methanol had been reported by Dumas.ⁱ It is interesting to note that at that time the tetravalency of carbon was not established and therefore the existence of stable carbenes was considered to be quite reasonable. At the end of the XIXth and very beginning of the XXth century, Curtiusⁱⁱ and Staudingerⁱⁱⁱ demonstrated that carbenes, generated from diazo compounds or ketenes, were highly reactive species. It quickly became clear that their six valence-electron shell, which defied the octet rule, was responsible for their fugacity. However, carbenes, as transient species,^{iv} became popular in the 1940–1950s, when Doering^v discovered the cyclopropanation reaction. Also, at the end of the fifties, Breslow^{vi} and Wanzlick^{vii} realized that the stability of carbenes could be dramatically enhanced by the presence of amino substituents, but were not able to isolate a “monomeric” carbene. A few years later, carbenes were spectroscopically characterized in matrices at a few K and in the gas phase, and the reactivity of transient nucleophilic and electrophilic carbenes studied in detail by Moss.^{viii} Because nowadays, carbenes are very popular ligands for transition metals, it is important to mention also the synthesis of the first carbene transition metal complexes by Chugaev in 1925,^{ix} and much later by Fischer and Maasböl;^x also noteworthy are the pioneering works by Öfele^{xi} and Lappert.^{xii}

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We became interested in carbene chemistry in 1985,^{xiii} as an obvious development of our work dealing with phosphorus azides.^{xiv} In 1988, three years before the seminal discovery of a stable N-heterocyclic carbene (NHC) **2a** by Arduengo,^{xv} we reported the synthesis of the (phosphino)(silyl)carbene **1a**.^{xvi} This compound was prepared using the most classical route to transient carbenes, namely the decomposition of diazo compounds. It features all the typical reactivity associated with “classical” carbenes.^{xvii} Carbene **1a** was isolated by flash distillation under vacuum (10^{-2} torr) at 75–80 °C as a red oily material in 80% yield, and is stable for weeks at room temperature (Scheme 1).

However, despite many efforts,^{xviii} it is only in 2000 that we finally succeeded in designing a crystalline (phosphino)(silyl)carbene.^{xix} An X-ray diffraction study combined with an Electron Localization Function (ELF) analysis of carbene **1b** allowed us to conclude that (phosphino)(silyl)carbenes are best described by a phosphorus vinyl ylide structure with a lone pair at carbon (Scheme 2). Importantly, the electronic structure of carbenes **1** is not fundamentally different from that of NHCs **2**, in which both nitrogen lone pairs interact with the vacant carbene orbital giving rise to a four- π -electron three-center system. Later, an X-ray diffraction study of the (phosphino)(amino)carbene **3** even demonstrated that an R_2N substituent interacts much more strongly with the carbene vacant orbital than an R_2P group. Indeed, the amino group of **3** is planar and the NC bond short, whereas the phosphino group remains pyramidalized and the PC bond long.^{xx}

At that time, some chemists argued that the nature of stable carbenes, such as **1–3**, was strongly influenced by the interaction of the two heteroatom substituents with the carbene center, and therefore they were somewhat different from their transient cousins. Thus, we started a program aiming at the synthesis of stable carbenes with only one heteroatom substituent. We were quickly able to prepare a series of them,^{xxi} as exemplified by carbenes **4**^{xxii} and **5**,^{xxiii} which were fully characterized, including by X-ray diffraction studies (Scheme 3).

In marked contrast with NHCs **2**, our stable singlet carbenes have found very limited applications.^{xxiv} Indeed, (phosphino)(silyl)- and (phosphino)(phosphonio)-carbenes **1** and **6**^{xxv} do not bind any transition metals, and complexes of carbenes **3–5**^{xxvi} are much more fragile than their NHC counterparts. Schoeller *et al.* have computationally rationalized the poor coordination behavior of these acyclic carbenes.^{xxvii} They concluded that because of the wide carbene bond angle (Scheme 4), conformational changes to a bent carbene structure are required to allow metal complexation, a process that is energetically too costly. In line with this conclusion, acyclic bis(amino)carbenes **7**,^{xxviii} which are closely related to NHCs **2**, also give rise to rather fragile complexes.^{xxix}

This short analysis prompted us to abandon our studies on acyclic carbenes, and in 2005 we turned our attention to the design of novel types of cyclic carbenes.^{xxx} We first prepared six-membered NHCs **8**,^{xxxi} which are based on the borazine skeleton, a family of heterocycles often regarded as the archetypical example of inorganic aromatic compounds (Scheme 5). Then, we prepared and isolated four-membered NHCs **9**,^{xxxii} which feature a 4- π -electron system. Even if the concept of aromaticity/anti-aromaticity is highly debatable in inorganic chemistry, considering the ring strain (carbene bond angle of 94°) and the presence of the Lewis acid center, the stability of **9** (they can be stored for weeks at room temperature) is rather striking. Interestingly, the lone pairs of the nitrogen atoms, adjacent to the carbene center of **8** and **9** can interact both with the carbene and the boron vacant orbital. Varying the nature of the R substituent(s) at the boron center(s), and thus modifying their Lewis acidity, allows for the preparation of carbenes with quasi-identical steric demands, but different electronic properties.

Also closely related to NHCs are PHCs **10**^{xxxiii} (Scheme 5). Our approach was based on calculations by Schleyer *et al.*^{xxxiv} who concluded that the inherent π -donor capabilities of the heavier elements (such as phosphorus) are as large or larger than their second row counterparts (such as nitrogen), and that the apparent inferior donor ability is due to the difficulty in achieving the optimum planar configuration. Indeed, using bulky 2,4,6-tri-*tert*-butylphenyl substituents at P, which forces the phosphorus to be almost planar, PHC **10** was found to be perfectly stable at room temperature. Interestingly, the values of the carbonyl stretching frequencies for the corresponding (PHC)Rh(CO)₂Cl complex (2059 and 1985 cm⁻¹) are dramatically lower than those observed for the analogous complex featuring Enders' triazolin-5-ylidenes as ligand (2089 and 2009 cm⁻¹).^{xxxv} These results suggest that **10** is a very strong electron-donor ligand, but unfortunately the sensitivity of the phosphorus centers of **10** towards oxygen, even when coordinated to a metal, considerably reduces its potential use in catalysis.

To decrease the carbene bond angle to a minimum, the obvious option is to include the carbene center into a three-membered ring. By appending π -electron donating amino groups to the triangular skeleton, we have prepared the cyclopropenylidene **11**^{xxxvi} that is stable at room temperature (Scheme 5). Note that before our work, the transient existence of **11** had been postulated based on chemical trapping experiments, but was described as a highly unstable molecule, defying isolation or even observation in the free state.^{xxxvii} So far, this is the only type of singlet carbene that does not require a heteroatom adjacent to the electron-deficient carbon to confer stability. Tamm *et al.*^{xxxviii} have prepared another stable cyclopropenylidene, bearing chiral amino substituents, and the first applications of **11** as ligand for transition metal based catalysts^{xxxix} have recently been reported.^{xl} For example, Montgomery *et al.*^{xli} have shown that the regioselectivity in aldehyde-alkyne reductive couplings could be reversed by using **11** instead of an NHC as ligand for nickel catalysts.

Although, our group has occasionally used stable cyclic carbenes **8–11** in organometallic chemistry, most of our studies have been done with cyclic (alkyl)(amino)carbenes (CAACs) **12** that we first isolated in 2005.^{xlii} The replacement of one σ -electron withdrawing and π -donating nitrogen center of NHC **2** by a σ -electron donating but not π -donating carbon makes CAAC **12** more nucleophilic but also more electrophilic than NHCs, as shown by comparing the energy of the HOMO and LUMO^{xliii,xliv} of both carbenes (Fig. 1). Moreover, due to the presence of a quaternary carbon in a position α to the carbene center, carbenes **12** feature steric environments that differentiate them dramatically from both NHCs **2** and also phosphines, and can have a chiral center in position α to the carbene.

CAACs **12** are readily synthesized in four steps from commercially available aldehydes. The key-step is the ring closure of the alkenyl aldiminium salt, which occurs regioselectively via formal “exo” addition of the nitrogen-hydrogen bond to the pendant carbon-carbon double bond (Scheme 6).^{xlv}

We quickly realized that rigid and bulky CAACs such as **12a,b** feature an electronically active wall of protection for metal centers, which allows for the preparation of low-coordinate metal complexes, hitherto not isolable with any other ligands. First, we prepared rhodium and palladium complexes **13** and **14** (Scheme 7).^{xlvi} The former is related to the active species of the Wilkinson's catalyst, and was the first example of T-shaped 14-electron Rh(I) complexes featuring a bridgeable halogen, whereas the latter was the first isolated cationic, formally 14 electron, Pd(II) species. The surprising stability of these complexes is mainly due to agostic interactions between the metal and the menthyl CH bonds. Later on, we were also able to isolate gold complex **15**,^{xlvii} a rare example of cationic [(L)Au(η^2 -toluene)] complex.^{xlviii}

Since low coordinate metals often play a key role in catalytic processes, these results encouraged us to investigate the catalytic properties of (CAAC)-transition metal complexes. We briefly studied the palladium-catalyzed α -arylation of carbonyl compounds, a process discovered concurrently in 1997 by Buchwald,^{xlix} Hartwig,^l and Miura,^{li} and we reported the first examples of α -arylation of ketones and aldehydes with aryl chlorides at room temperature (Scheme 8).^{xlvi}

Then, we turned our attention to gold chemistry, which was becoming very popular.^{lii} A very surprising and novel catalytic reaction was serendipitously discovered using the cationic gold(I) complex **15** (Scheme 9). Indeed, many transition metal complexes, including gold complexes, are known to catalyze the addition of terminal alkynes to enamines, affording propargyl amines.^{liii} In marked contrast, **15** efficiently mediates the catalytic coupling of enamines and terminal alkynes to yield allenes with loss of imines.^{xlvii}

Having in hand a gold complex, featuring a peculiar behavior, we turned our attention to the hydroamination reaction. Although a number of metal complexes^{liv,lv} are able to promote this reaction with aryl amines, and to a lesser extent with primary and secondary alkyl amines, no homogeneous hydroamination reaction involving ammonia and the parent hydrazine has been reported.^{lvi} More generally speaking, apart from a few exceptions, metals usually react with ammonia and hydrazine to afford supposedly inert Lewis acid-base complexes. Consequently, for a long time the homogeneous catalytic functionalization of NH_3 ^{lvii} and NH_2NH_2 ^{lviii} has remained elusive. We found that Werner complexes **16**^{lix} and **17**,^{lx} readily prepared by treatment of **15** by ammonia and hydrazine, respectively, were very efficient catalysts for the hydroamination of a variety of non-activated alkynes and allenes (Scheme 10). Since gold complexes display excellent functional group tolerance, as well as low air and moisture sensitivity, these reactions should be ideal initial steps for the synthesis of acyclic and heterocyclic bulk chemicals.

As mentioned above, catalytic systems able to promote the intermolecular hydroamination of alkynes and allenes with secondary amines are also quite rare. We have found that in the presence of 5 mol% of cationic gold(I) complex **15**, diarylamines, arylalkylamines, benzocyclic amines, and even simple dialkylamines, such as diethyl amine, add to terminal and internal alkynes,^{lxi} as well as allenes,^{lxii} at temperatures between 60 to 150 °C, and reaction times between 7 to 24 h (Scheme 11). The availability of catalysts able to perform the hydroamination reaction of alkynes with secondary amines prompted us to investigate cascade reactions. For example, combining the hydroamination with the reaction showed in Scheme 9, allows from the one-pot preparation of allenes by coupling two alkynes, using a sacrificial secondary amine (THQ).^{lxi} This sequence appeared to be quite general, with some regioselectivity issues, and is of course limited to the use of terminal alkynes for the second step. Inspired by the recent works of Yi *et al.*,^{lxiii} and Che *et al.*,^{lxiv} who used a ruthenium based catalytic system, we also found a one-pot three-component synthesis of 1,2-dihydroquinoline derivatives, involving a tandem hydroamination-hydroarylation reaction.^{lxv} Both homo- and cross-coupling reactions are possible; the only serious limitation is the use of a terminal alkyne for the second step. Consequently the dihydroquinoline skeleton can be readily decorated with different substituents.

Cationic (CAAC)Gold(I) complex **15** also promotes the hydroammoniumation and methylation of alkynes (Scheme 12).^{lxvi} There are no precedents for the former reaction, while the latter can be classified as a carboamination reaction, a type of transformation, which is only known with relatively weak carbon-nitrogen bonds.^{lxvii} During this study, we also isolated complex **18**, which is a rare example^{lxviii} of gold(I) (η^1 -alkene) complex. It results from the addition of the tertiary amino group to the coordinated alkyne.

Note that most of the gold-catalyzed reactions summarized above occur under drastic conditions, which emphasizes the robustness of the catalysts.

In the last decade, a significant improvement for ruthenium olefin metathesis catalysts was achieved after exchanging a single PCy₃ ligand with an N-heterocyclic carbene (NHC).^{lxxix} The better results obtained with the second generation of Grubbs' catalysts are attributed to the increased σ -donor ability of NHCs over phosphines.^{lxxx} Since CAACs **12** are even more σ -donating than NHCs, we decided, in collaboration with R. H. Grubbs, to synthesize and test the activity of CAAC ruthenium complexes. We first prepared a series of Hoveyda-Grubbs catalysts, by exchanging the phosphine ligand with CAACs **12c–e** (Scheme 13). The air-stable complexes **19c–e** were found to be active in ring-closing metathesis, but only for the formation of di- and tri-substituted olefins.^{lxxxi} Note that a dramatic increase in activity was observed after slightly decreasing the steric bulk of the *N*-aryl group [Dipp (2,6-diisopropylphenyl) to Dep (2,6-diethylphenyl)]; this phenomenon was attributed to the catalyst initiation step. More striking are the results obtained with complexes **19c–e** for the ethenolysis of methyl oleate,^{lxxxi} a process that transforms internal olefins derived from seed oils to terminal olefin feedstocks.^{lxxxiii} We found that, at loading of 100 ppm, ruthenium complexes **19c–e** exhibited good selectivity (73–94%) for terminal olefins **a** and **b**, and achieved TONs ranging from 4,200 to 5,600. By lowering the catalyst loading of **19e** to 10 ppm, TONs of 35,000 were achieved, which is the highest TON reported so far for this reaction.^{lxxxiv}

Stable carbenes are not only powerful ligands for transition metals. Early after their discovery, Enders *et al.*,^{lxxv} possibly inspired by the work of Breslow^{vi} on the thiazolium catalyst for the benzoin condensation reaction, has demonstrated that singlet carbenes are also excellent organic catalysts in their own right.^{lxxvi} Yet a more recent development of stable singlet carbene chemistry is based on their resemblance with transition metal centers, due to the presence of both a lone pair of electrons and an accessible vacant orbital.^{lxxvii}

In line with this new paradigm we have shown that stable carbenes, especially (alkyl)(amino)carbenes **12**, are very rare examples of organic molecules that react with CO.^{xlili} They can also activate a variety of other small molecules, including H₂, NH₃,^{lxxviii} and P₄,^{lxxix} as well as enthalpically strong bonds such as Si-H, B-H, and P-H σ -bonds^{lxxx} (Scheme 14).^{lxxxi}

Stable singlet carbenes can also be used to stabilize reactive species, which seems odd, when one realizes that for a long time carbenes were considered as prototypical reactive intermediates. This is first exemplified by the isolation of “bent-allenes” **20a**^{lxxxii} (Scheme 15). According to theoretical studies by Frenking *et al.*,^{lxxxiii} these compounds have to be regarded as a carbon(0) coordinated by two NHC ligands (**20b**), and should be named “carbo(dicarbenes)”. In contrast to regular allenes, the two NCN planes are not perpendicular but twisted by 69°, and the allene framework is severely bent with a CCC angle of 134.8°. Clearly the allene π -system has been broken, and the central carbon atom is approaching a configuration with two lone pairs. As a consequence, and in marked contrast with “regular allenes”, an η^1 -coordination mode involving the central carbon is observed with metals. Alcarazo, Fürstner *et al.*^{lxxxiv} reported that the bonding situation in the tetrakis(dimethylamino)allene, which is linear, is still best described by the capto-dative formalism, in which “carbon is capable of serving as the central atom of a complex – just as a metal can do”. Although the bent geometry is not a common feature for carbodicarbenes, all of them are highly flexible. As a consequence, the CCC framework of carbodicarbenes can be confined in rather small cyclic systems, as shown by the preparation of persistent derivative **21**.^{lxxxv}

Interestingly, the concept of carbodicarbenes has been extended to other group 14 elements,^{lxxxvi,lxxxvii} and the use of singlet carbenes to stabilize main group elements in their zero oxidation state is not limited to monoatomic species. Robinson *et al.* reported the isolation of **22**, featuring a bis-phosphinidene^{lxxxviii} and bis(arsinidene)^{lxxxix} unit coordinated by two carbenes, as well as compound **23**^{xc,xcj} (Scheme 16). The latter represents a landmark in low coordinate main group element 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.^{xcii} Our group has shown that even much larger polyatomic molecules, featuring a main group element in the zero oxidation state can be prepared when capped by carbenes, as illustrated by the isolation in good yield of the P₁₂ cluster **24**.^{lxxixb} This polyphosphorus derivative can be regarded as a carbene-stabilized phosphorus allotrope,^{xciii} and it is quite likely that many other phosphorus clusters could be isolated thanks to the stabilizing effect of carbenes.

Very recently, we have also shown that cyclic(alkyl)(amino)carbenes **12** can stabilize main group elements in other unusual oxidation states. Indeed, in marked contrast to the well-known tricoordinate boron(+3) derivatives, **25** features a boron in the +1 oxidation state (Scheme 17).^{xciv,xcv} This compound can be regarded as the parent borylene (H-B:) ^{xcvi} stabilized by two CAACs, and ab initio calculations show that the HOMO of the borane is essentially an electron pair in the p(π)-orbital of boron. Consequently, in contrast to classical boranes, which are the archetypical Lewis acids, derivative **25** is a Lewis base, and is isoelectronic with amines. Like the latter, compound **25** can be protonated to give **26** and is readily oxidized to give the radical cation **27**.

Note that radical cation **27** is a very rare example of isolated boron radical.^{xcvii,xcviii} Similarly, 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.^{xcix} We have shown that singlet carbenes are very efficient to stabilize these paramagnetic species. Indeed, phosphinyl radicals **28** and **29**,^c phosphinyl radical cation **30**,^{ci} diphosphorus radical cation **31**,^{cii} and phosphonitride radical cation **32**^{ciii} have been isolated, and structurally characterized (Scheme 18). Note that according to experimental and computational results, the paramagnetic species **28** is better described as a phosphorus-center radical, with little delocalization over the imidazolidin-2-iminato substituents. In contrast, **29** is best represented by the resonance structure **29'**, which corresponds to a vanadium(IV) complex containing an imidazolidin-2-iminatophosphinimide ligand.^{civ} Therefore, we have to conclude that carbenes are not as efficient as transition metal fragments to delocalize the spin density from the phosphorus nucleus; however it is quite likely that the stabilizing effect of carbenes is certainly strong enough to permit the isolation of other main group element centered radicals.

The results discussed so far in this account demonstrate the utility of “classical” stable carbenes, a journey that began more than 20 years ago. Now, it is time to look ahead and to briefly discuss a new generation of stable “carbene-like” species that we recently discovered, namely compounds of types **33**,^{cv} **34**,^{cvi} and **35**^{cvi} (Scheme 19). Due to their lineage, these compounds have also been referred to as abnormal ^{cviii} or remote^{cix} carbenes (*a*NHCs or *r*NHCs).^{cx} However, since no reasonable canonical resonance forms showing a carbene can be drawn without additional charges, we prefer to name them mesoionic carbenes, MICs, as first suggested by Araki *et al.*^{cx}

NHCs became ubiquitous ligands, mainly because of the robustness of their metal complexes, and their strong σ -donor properties, which result from the presence of the electropositive carbon center and the strength of the carbon-metal bond. MICs are also carbon-based ligands, and experimental and theoretical data suggest that MICs **33–35** are

even stronger electron-donating species than NHCs. Probably even more appealing, no obvious dimerization pathway can be foreseen for MICs, in contrast with the Wanzlick equilibrium pathway often observed for classical carbenes, which should lead to relaxed steric requirements for their isolation. Indeed, we have recently isolated a C-unsubstituted 1,2,3-triazol-5-ylidene **35a** (Scheme 20).^{cxii} However, that does not imply that all types of MIC are stable. Depending on the nature of heteroatoms in the ring skeleton, ring opening processes can occur as exemplified by tetrazol-5-ylidene **36**,^{cxii} and 1,3-dithiol-5-ylidene **37**^{cxiii} (Scheme 20). Interestingly, for the latter, a simple protonation or the addition of a transition metal fragment induces the ring closure. In other words, the ethynylcarbamodithioate **38** is a ligand equivalent of 1,3-dithiol-5-ylidene **37**. Since many different analogues of ethynylcarbamodithioate **38** [R-C≡C-X-C(Y)R'; where X and Y are heteroatoms featuring a lone pair of electrons] can readily be prepared, numerous MIC-complexes should become available, even when the MIC itself is not stable.

The study of the catalytic activity of MIC complexes is still in its infancy,^{cxiv,cxv,cxvi} but one has to keep in mind that although NHC-transition metal complexes have been known since the sixties,^{xi,xii} their first application in catalysis appeared only in 1995,^{cxvii} and clearly this has been facilitated by the availability of bottle-able NHCs. As an illustration of the peculiar properties of MIC complexes, we have recently shown that the mixed NHC/MIC ruthenium complex **39** behaves as a powerful latent catalyst in olefin metathesis (Scheme 21).^{cxii} In the presence of acid, the MIC ligand acts as a leaving group and allows the otherwise inactive metathesis complex **39** to enter the metathesis catalytic cycle. Under standard metathesis reactivity screening conditions, **39** is superior to the latest commercial catalysts and can complete ring closure metathesis reactions within a matter of minutes at RT.

Concluding remarks

Some twenty years ago, when both Arduengo and our group discovered the first stable carbenes, they were considered as laboratory curiosities, and none of us would have guessed that carbenes would become such powerful tools for chemists. It is only during the last decade that my group understood why Arduengo's carbenes are much better ligands than our acyclic carbenes, which prompted us to focus on cyclic derivatives. So far, our most useful carbenes are the cyclic (alkyl)(amino)carbenes. Compared to NHCs, CAACs are more nucleophilic and more electrophilic, which have advantages, as exemplified by the activation of small molecules and by the robustness and efficiency of cationic (CAAC)Au(I) catalysts. Looking at the future, we can just dream that the novel stable carbon-based species, such as MICs **33–35**, and tricoordinate boron compounds isoelectronic to amines, such as **25**, become as popular as Arduengo's carbenes.

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Figure 1.
Schematic representation of the steric environments for phosphines, NHCs **2** and CAACs **12**, and comparison of the energy level of the HOMO and LUMO for NHCs and CAACs.

1a (1988)bp: 75-80 °C/ 10⁻² torr **2a** (1991)

mp: 240-241 °C

Scheme 1.

The first isolated carbenes.

Scheme 2.

Resonance structures of crystallographically characterized **1b** and NHCs **2**, and the most significant resonance structure of **3**.

Scheme 3.

Examples of stable carbenes with only one heteroatom substituent.

Scheme 4.

Carbene bond angles of representative stable singlet carbenes

Scheme 5.
Our first stable cyclic carbenes

Scheme 6.
Synthesis of CAACs **12**.

Scheme 7.

Preparation of stable low-coordinate metal complexes using bulky CAACs **12a,b**.

Scheme 8.

Room temperature α -arylation of ketones and aldehydes using a (CAAC)Pd(All)Cl complex as catalyst.

Scheme 9.

Gold(I) complex **15** catalyzed the coupling of enamines and terminal alkynes to yield allenes.

Scheme 10.

Gold-catalyzed hydroamination of alkynes and allenes with ammonia and the parent hydrazine.

Scheme 11.

Hydroamination of alkynes and allenes with secondary amines, and cascade reactions promoted by cationic gold(I) complex **15**.

Scheme 12.

Gold-catalyzed hydroammoniumation and methylation of alkynes, and crystallographically characterized gold(I) (η^1 -alkene) complex **18**.

Scheme 13.
 CAAC-ruthenium complexes for olefin metathesis.

Scheme 14. Activation of small molecules and enthalpically strong bonds by metal-free CAAC **12**.

Scheme 15.

Bent-allenes or carbo(dicarbenes), compounds featuring a carbon(0).

Scheme 16.
Stable carbene-main group element(0) adducts.

Scheme 17.

A stable tricoordinate boron(I) derivative isoelectronic to amines.

Scheme 18.

Carbenes for stabilizing paramagnetic main group element species

Scheme 19.
Stable mesoionic carbenes.

Scheme 20.

Stable (**35a**) and unstable MICs (**36** and **37**); Ethynylcarbamodithioate **38** behaves as a ligand equivalent of MIC **37**.

Scheme 21.

Under acidic conditions, the MIC ligand of **39** acts as a leaving group, and allows the otherwise inactive metathesis complex **39** to enter the metathesis catalytic cycle.