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Carbene-Stabilized Main Group Radicals and Radical Ions

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Abstract

Shortly after their discovery at the end of the 80s, stable singlet carbenes have been recognized as excellent ligands for transition metal based catalysts, and as organo-catalysts in their own right. At the end of the 2000s, it has been shown that they can coordinate main group elements in their zero oxidation state, and even activate small molecules. This review covers examples in the literature dealing with the most recent application of stable singlet carbenes, namely their use to stabilize radicals and radical ions that are otherwise unstable.

Introduction

Radicals play essential roles in numerous chemical¹ and biological processes.² Many transition metal complexes and a few non-metal compounds such as molecular oxygen are examples of stable radicals under ambient conditions. However, most paramagnetic main group species are unstable as the unpaired electron makes the molecule highly reactive. Since the pioneering work by Gomberg over 100 years ago, demonstrating that the triphenylmethyl radical could be generated in a flask,³ radical species have been exciting synthetic targets. Typical methods for stabilizing such reactive molecules involve delocalizing the unpaired electron and/or utilizing bulky groups to prevent dimerization.⁴

Singlet carbenes have a lone pair and a vacant orbital, they are perhaps most well known for their great utility as ligands in transition metal catalysis.⁵ In their infancy,⁶ these species were viewed as strong σ -donors with negligible π -accepting character.⁷ Recent reports indicate that the substitution on the carbene centre is highly influential on the donor ability as well as electron accepting properties, giving ligands with diverse properties.⁸ The empty p-orbital can indeed engage in π -backbonding interactions and delocalize electron density. The recent realization that the π -accepting nature of carbenes can be exploited has led to new opportunities in transition metal catalysis⁹ and the activation of small molecules with the free carbenes themselves.^{10,11}

In recent years the electrophilicity of carbenes has also been utilized for stabilizing radicals and radical ions. With respect to the term stabilizing, we refer to either generating or observing species that can otherwise not be detected spectroscopically, and in some cases even isolating such compounds. This review focuses on the observation and isolation of main group radicals that are supported by carbene ligands. Although many interesting paramagnetic carbene-metal complexes have been observed or isolated,^{12,13} this area is beyond the scope of this review.

Carbene-stabilized boron centred radicals

Anionic boron radicals with the formula $\text{BR}_3^{\cdot-}$ have been studied for a long time,¹⁴ but other types of boron radicals are rare.¹⁵ The preparation of $\text{BR}_3^{\cdot-}$ is simply the population of the vacant p-orbital of an electron deficient borane with a single electron. A neutral analog requires a Lewis base (L) coordinate to the boron centre giving a L-BR_2^{\cdot} adduct. Carbenes are ideal ligands and can readily coordinate to boronium cations or BH_3 which are precursors for generating such species.

Recently, significant research has been performed on the parent species, BH_2^{\cdot} , as NHC-stabilized complexes **1** (NHC: N-heterocyclic carbene) (Figure 1).¹⁶ The UV irradiation of a mixture of NHC- BH_3 **1H** and di-*tert*-butylperoxide generates the corresponding radical, which can be characterized by EPR spectroscopy.^{16c} The EPR and corroborating theoretical results indicate that the spin density of the resulting radical is delocalized throughout the carbene ligand and boron centre. There is planarity through the NHC-B unit in contrast to the previously studied amine adducts $\text{R}_3\text{N-BH}_2^{\cdot}$, which feature a pyramidalized boron centre.¹⁷ The nitrogen ligated species are σ -type radicals whereas with NHCs they are of π -type. This is a direct result of the carbene being a better π -acceptor than amines.

The synthesis of NHC- BH_2^{\cdot} radicals is facile as the boron-hydrogen bond dissociation energy in the precursor is small (80-88 kcal/mol).^{16b} Although the rate of hydrogen atom donation of the NHC- BH_3 complexes is slower than Bu_3GeH , $(\text{TMS})_3\text{SiH}$ and Bu_3SnH , it is faster than Et_3SiH , making them useful in certain transformations. These complexes have been used with success as co-initiators of acrylate photopolymerizations as well as radical reductions of halides and xanthates.¹⁶

Hydrogen atoms can also be easily abstracted from NHC- BH_2Ar complexes to give the corresponding radicals (*e.g.* **2**).^{16g} The EPR spectra showed delocalization of the spin density throughout the NHC, boron centre and aryl groups. The H,Ar substituted derivatives dimerize two orders of magnitude slower than the corresponding H,H analogues (half life of the former ~10 s). This is rationalized by the extended π -system of the aryl group and by an increase in sterics at boron. Interestingly, a diboranyl radical **3** generated by hydrogen atom abstraction from the NHC- BH_2Ph precursor has been observed by EPR.^{16g} The proposed mechanism to form **3** involved H \cdot abstraction from the starting material to give a radical of type **2**, subsequent dimerization to the diborane, then a hydrogen atom is abstracted from the diborane to afford the diboranyl radical **3**. The SOMO of **3** is primarily localized on the NHC-BPh moiety, much like **2**.

Alkyl substituted boron radicals (BHR^{\cdot}) are more challenging to prepare as hydrogen atom abstraction from the NHC- BH_2R precursors usually occurs at the β -carbon on the alkyl chain with subsequent elimination of alkene and NHC- BH_2^{\cdot} generation.^{16g} Among the exceptions is the cyclopropyl radical **4** that can be observed by EPR and is resistant towards ring opening and alkene elimination.

The aforementioned hydrogen substituted boron radicals have only been observed by spectroscopic methods. Their meta-stable nature may be attributed to the lack of bulk at boron. Indeed, Gabbai *et al.* were able to isolate the two carbene- BR_2^{\cdot} derivatives **5**¹⁸ and **6**¹⁹ (Figure 2). In the first example (**5**), two bulky mesityl groups and a π -accepting acridinyl carbene are on boron as stabilizing groups.¹⁸ The EPR spectrum showed that the spin density is delocalized throughout the acridine framework with minimal density on boron; remarkably, negligible electronic contribution of the mesityl groups was observed. Radical **5** could even be structurally characterized, and the solid-state structure indicates that the B-C bond length lies between a single and double bond (1.56 Å vs. 1.59 Å and 1.48 Å, respectively). Interestingly, a second electron could be added to generate the

corresponding borataalkene with a drastically contracted B-C bond (1.46 Å) consistent with the population of a π -orbital.²⁰ The NHC stabilized derivative **6** could also be isolated but not structurally characterized.¹⁹ The EPR spectrum indicated that the spin density is delocalized throughout the mesityl groups, boron centre and the entire NHC framework. The larger hyperfine coupling with boron (7.90 G for **6** vs. 2.55 G for **5**) and the involvement of the mesityl groups clearly demonstrate the weaker π -accepting properties of the NHC compared to the acridinyl carbene.

Our group has isolated a totally different type of paramagnetic carbene-stabilized boron derivative. The CAAC₂BH borylene **7** [CAAC: cyclic (alkyl)(amino)carbene]²¹ is a compound with a lone pair on boron, thus being isoelectronic with an amine.²² The reaction of borylene **7** with GaCl₃ results in the generation of the radical cation **7**⁺, the same type of oxidation that is observed for an amine (Figure 3). EPR data and theoretical calculations indicate that the SOMO is primarily located on the boron (50 %) and the nitrogen atom of both carbenes (33 % total). The carbon-boron bond lengths elongate upon oxidation (1.58 Å vs. 1.52 Å), and the C-N bonds within the CAAC slightly contract (1.36 Å vs. 1.38 Å). This trend is consistent with decreased electron density at boron and as a consequence decreased π -back donation from the boron to the carbene centres.

It is noteworthy that the use of carbenes has also allowed for the generation of various boron species, which were hitherto believed to be non-existent as exemplified by derivatives **A**²³ and **B**²⁴ (Figure 4). These compounds could serve as precursors for new carbene stabilized diboron radicals by one electron reduction or oxidation reactions.

Carbene-stabilized silicon centred radicals

Silyl radicals of type R₃Si· have been widely studied and used in chemical synthesis, as exemplified by the popular (Me₃Si)₃Si· discovered by Chatgililoglu *et al.*²⁵ Not surprisingly, the half-lives of these radicals increase with the steric bulk and (tBu₂MeSi)₃Si· was found to even be isolable in a crystal form (**C**, Figure 5).²⁶ Also of note, radical anions **D**²⁷ and **E**²⁸ were isolated and structurally characterized; they were prepared by reduction of a disilene.

Aside from species **C-E**, stable silicon radicals are rare. It is only in the last two years that carbene-stabilized silicon radicals have been isolated. NHCs can coordinate to the silylene **8**, which is based on the β -diketiminato ligand (Figure 6).²⁹ The reaction of muonium (atom made up of an antimuon and an electron, which is chemically similar to hydrogen) with the free silylene **8** resulted in the addition of muonium to two sites; the butadiene moiety in the ligand framework (**9a**) and the silicon centre (**9b**).³⁰ In the analogous reaction of muonium with the NHC-complexed silylene **10**, butadiene addition was also observed (**11a**), however the other product showed the unpaired electron on the carbene centre rather than on silicon (**11b**). This was deduced from the larger μ SR hyperfine coupling constants with the nitrogen atoms of the NHC ring compared to those of the silylene and the decreased coupling to silicon in **11b** vs. **9b**.

NHCs can also coordinate to bis(silyl)silylene as shown by compound **12** reported by Sekiguchi *et al.* (Figure 7).³¹ Oxidation with a trityl salt produces the corresponding radical cation **12**⁺. The EPR spectrum shows strong hyperfine coupling to a single silicon atom and weak coupling to the two NHC nitrogen atoms. The solid state structure of **12**⁺ shows a planar geometry at silicon indicating a π -type radical. A change in hybridization occurs upon removal of an electron from the pyramidal silylene adduct **12**. Calculations indicate that the majority of the positive charge (+0.62) resides on the silyl moiety indicating that the dative model drawn is the most accurate. Note that the radical cation **12**⁺ results formally from the replacement of an anionic substituent of **C** by a neutral NHC ligand.

The most surprising results in the field offered NHC-stabilized silicon radicals have been reported by Roesky, Stalke *et al.* The colourless NHC stabilized silicon dihalides **13a,b**³² are of course diamagnetic with a lone pair on the silicon centre (Figure 8). Addition of a 3-fold excess of CAAC **14** to **13a** results in the formation of the (CAAC)₂SiCl₂ adduct **15a**.³³ Remarkably, this product is a deep blue biradical with an unpaired electron residing on each carbene centre. Two polymorphs of **15a** were isolated, a singlet and a triplet biradical as the unpaired electrons can have the same or opposite spin. The singlet state is calculated to be between 2.2-7.5 kcal/mol higher in energy than the triplet state. The solid-state structures of the two polymorphs were essentially the same. The carbene-silicon bond distances are much shorter in **15a** than in the NHC complex **13a** (1.85 Å vs. 1.99 Å), indicating that a covalent representation is more accurate than the dative model. The N-C bond within the CAAC framework is longer than typical CAAC complexes. This is due to the p-orbital on the carbene carbon being occupied with a single electron, preventing delocalization of the nitrogen lone pair to form an N-C double bond. Remarkably, the singlet polymorph is air stable for up to a week.

The dibromide derivative **15b** could also be prepared from **13b** but is much less stable than the chloride analogue **15a**;³⁴ it decomposes rapidly in solution. With this knowledge of stability (SiCl₂ > SiBr₂), more electronegative substituents on silicon should assist in the stabilization of these types of biradicals. However, attempts to generate the SiF₂ derivative were unsuccessful,³⁴ although it appears to be a viable synthetic target.

Very interestingly, the silicon dichloride diradical **15a** could be reduced with KC₈ to generate the bis(carbene)Si compound **16** (Figure 9).³⁵ This species can be viewed as a carbene-stabilized single atom allotrope³⁶ of silicon. Theoretical calculations on **16**, indicate that the HOMO is a π -type orbital along the C-Si-C moiety, while the HOMO-1 is the lone pair on the silicon centre. Based on this, the authors describe the bonding between the carbene and silicon as σ -donation from the carbene to the silicon and π -backdonation of one lone pair of electrons on silicon with the two carbon atoms (**16''**). The bonding model with the electrons localized on the carbon atoms, as a biradical **16'**, can also be drawn. No EPR signal was observed, however it is believed that the dark blue color is consistent with a small HOMO-LUMO gap which could introduce biradical character. Crystals of **16** are stable for a day under ambient conditions.

In 2008, Robinson *et al.*³⁷ reported the preparation of the bis(NHC)Si₂ complex **F** (Figure 10) which like **16** bears electron density at silicon.³⁸ It should be interesting if the analogous CAAC complex could be prepared to determine if the electron density is delocalized onto the carbene centres as a biradical. Furthermore, the redox chemistry of the carbene stabilized Si₂ allotropes could give rise to interesting radical anions and cations.

Carbene-stabilized pnictogen centred radicals

Phosphinyl radicals have been studied for a number of years.³⁹ Although they can be monomeric in solution, they typically dimerize in the solid state.⁴⁰ Consequently, a few examples of structurally characterized phosphorus radicals **G-K** have been reported (Figure 11), all of them being stabilized by very bulky substituents, and/or spin delocalization.⁴¹ In addition, two phosphorus centred radical cations **L** and **M** have recently been described.⁴²

The first attempt to use a carbene to stabilize a phosphorus radical was reported in 2007 by Apeloig *et al.*¹³ The phosphorus radical P(O)(O^{*i*}Pr)₂ was generated by the irradiation of {(*i*PrO)₂(O)P}₂Hg in the presence of free NHC (Figure 12).¹³ Although the resulting carbene-diisopropylphosphoryl radical complex **17'** cannot be isolated, its half life is prolonged to 7.1 seconds. The EPR spectrum and calculations show that considerable electron density resides on the carbon (39%) and the remaining N₂C₂ portion of the NHC

(37%), while only a small portion is on the phosphorus atom (7.5%). Hence, the resonance structure **17a'** is a better representation of the molecule rather than the donor-stabilized phosphorus radical **17b'**. Accordingly, the optimized geometry indicates that the carbon atom bonded to phosphorus is slightly pyramidalized ($\Sigma_{\text{angles}} = 352^\circ$). The corresponding reaction with the adamantyl benzimidazol-2-ylidene produces radical **18'** for which DFT calculations indicate that the carbon atom possesses an even larger portion of spin density (47%) than in **17'**.⁴³ As a result, the carbene centre of **18'** is more pyramidalized ($\Sigma_{\text{angles}} = 341^\circ$) than in **17'**, which hampers the delocalization of the spin density, and destabilizes complex **18'** ($\tau_{1/2} < 1\text{s}$).

In 2010, our group adopted a very different approach to generate a carbene-stabilized phosphorus radical.⁴⁴ We readily prepared phosphalkene **19** by the addition of a CAAC to an aminodichlorophosphine and subsequent reduction with magnesium. Due to the substitution pattern, **19** is electron-rich and an electron could be removed by reaction with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ to afford the stable radical cation **19⁺** (Figure 13). Surprisingly, the spin density is primarily localized on phosphorus (68%) rather than on the π -accepting CAAC ligand. A single crystal X-ray diffraction study showed that the N-C bond in the CAAC is significantly contracted in comparison to the phosphalkene precursor (1.32 Å vs. 1.38 Å) and is consistent with a double bond. The phosphoniumyl cation structure is the most accurate with the positive charge localized on the nitrogen of the carbene. The reaction of **19⁺** with ${}^t\text{Bu}_3\text{SnH}$ produced the phosphine (**19H⁺**) confirming the presence of the unpaired electron on phosphorus.

In order to isolate a stable neutral radical, we were inspired by the work of Cummins *et al.* who reported that vanadium–iminato ligands can stabilize phosphinyl radicals (**J**, Figure 11).^{41a} Since carbenes can behave similarly to transition metals (both have an occupied and vacant orbital),¹⁰ⁱ we just replaced the metal fragment of **J** by an NHC. Reduction of the corresponding phosphonium triflate **20** afforded the desired radical **20'** (Figure 14).⁴⁵ This paramagnetic species displayed a significant amount of electron density at the phosphorus centre (64%), greatly exceeding that of the bis(vanadium–iminato) analog **J** (31%). To directly compare the radical stabilization offered by NHCs versus vanadium centres, the mixed complex **21** was prepared similarly. In **21** only 1% of the spin density resides in the phosphorus 3p orbital, a miniscule amount compared to 67% at the vanadium centre. These results clearly demonstrate that the vanadium fragment is much more efficient than the NHC to delocalize spin density. However, the NHC group still provides sufficient stabilization to allow for the isolation and structural characterization of **20'**.

Dinitrogen is the most abundant molecule in the atmosphere but little is known about its heavier congeners, which do not exist under ambient conditions. However, carbene stabilized versions of the heavy group 15 elements^{36,46} have been isolated for P_2 ,^{10k,47} As_2 ⁴⁸ as well as the heterodiatom species PN.⁴⁹

The structure of the bis(carbene)- P_2 species can be drawn as a bis-phosphinidene coordinated by two carbenes (**22a,b**) or as diphosphalkene (**22a',b'**) or (Figure 15).⁴⁷ The latter representation shows the P_2 fragment to be electron rich, and therefore prone to oxidation. Cyclic voltammetry on the $(\text{NHC})_2\text{P}_2$ complex **22a** shows two reversible one-electron oxidations whereas the CAAC_2P_2 complex **22b** has only one.⁵⁰ CAACs are better π -accepting ligands than NHCs and consequently withdraw more electron density from the P_2 core. This is a very good demonstration of the different electronic properties of NHCs and CAACs.

Both diphosphorus species are easily oxidized by $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ to the radical cations **22a⁺** and **22b⁺**.⁵⁰ Crystallographically, the metrical parameters only showed slight

deviations between the two structures. However, the CAAC derivative **22b**⁺ gave an EPR signal as a triplet of quintets with large hyperfine coupling to the phosphorus centres and small coupling to the two nitrogen atoms of the CAAC ligands. This differed from its NHC counterpart **22a**⁺ which only displayed a triplet indicative of hyperfine coupling only to the two phosphorus atoms. The calculated spin density and the EPR data suggest that CAACs are more efficient than NHCs to delocalize the electron density; this is reflected by the smaller amount of spin density on the P₂ moiety in **22b**⁺ (54% vs. 77% in **22a**⁺). The NHC complex could be oxidized further to the dication **22a**⁺⁺ which was not possible with the CAAC derivative, attributed again to the π-accepting nature of the CAAC.

Arsenic radicals are much less prevalent than phosphorus. In fact the radical cation **23**⁺ is the only structurally characterized arsenic paramagnetic species documented (Figure 16).⁵¹ Similarly to the P₂ complexes, this compound has been prepared by simple oxidation of the diarsenic precursor **23** with two equivalents of GaCl₃. In the EPR spectrum, only hyperfine coupling to the arsenic atoms was observed. The calculated SOMO indicated that considerable electron density is localized on the diarsenic core of **23**⁺ (82%), which is slightly greater than on the diphosphorus core of **22a**⁺ (77%). The As-As bond is contracted upon oxidation (2.32 Å vs. 2.44 Å), indicating partial double bond character. This species could be oxidized a second time like **22a** with GaCl₃ to form the As₂⁺⁺ dication **23**⁺⁺.

The carbene stabilized phosphorus mononitride **24** that features an NHC on nitrogen and a CAAC on phosphorus could also be prepared (Figure 17).⁴⁹ The cyclic voltammogram of **24** shows a reversible one electron oxidation. In line with the electrochemical results, the PN radical cation **24**⁺ could be generated and isolated by the reaction of **24** with [CPh₃] [B(C₆F₅)₄]. Calculations on a model compound showed that the spin density is primarily on phosphorus (40%) with less on the central nitrogen (19%) and strikingly almost the same amount on the nitrogen atom of the CAAC (18%). As with the P₂ radical cations **22a**⁺ and **22b**⁺, this is a clear demonstration that CAACs are better π-acceptors in comparison to NHCs.

The activation of P₄ with singlet carbenes has produced carbene stabilized P⁺, P₂, P₄, P₈ and P₁₂ units.^{10j-n} These derivatives should also serve as good candidates to generate new 60 radical cations by oxidation reactions.

Carbene stabilized organic radicals

So far, applications of stable carbenes for stabilizing organic radicals are very rare. However, already in 1997, Fukuzumi *et al.* prepared models of the thiamin coenzyme, which feature a thiazolylidene scaffold (Figure 18).⁵² The electrochemical oxidation of enolate **25**⁻ produces the neutral radical **25**[•] identified by EPR spectroscopy that is persistent for several hours. The EPR indicates that almost no spin density resides on the aryl group and calculations show that the latter could be in fact perpendicular to the radical fragment. The oxidation of **25**⁻ occurs at a low potential indicating that *in vivo* thiamine-dependent acetylations by pyruvate could involve one-electron transfers. This electron transfer process was confirmed by the reaction of **25**⁻ with [Co(phen)₃]²⁺ (phen = phenanthroline) resulting in the redox reaction producing [Co(phen)₃]⁺ and **25**[•].

Reed *et al.* later conducted studies on the radical intermediate of the thiamin coenzyme and pyruvate.⁵³ EPR data obtained on isotopically labelled variants indicate that a π-type radical is generated within the system and confirmed that the spin density is delocalized throughout the thiazolium ring (**25b**[•]). Interestingly, in the enzyme the authors postulated that a protonation can occur giving the corresponding radical cation **25H**⁺ but were not able to localize where the proton binds the thiamin.

We recently investigated the possibility of using carbenes to prepare stable radical cations, with a structure inspired by 25H^+ . We reasoned that the use of not only one but two carbenes would allow the isolation of such species. After observing that bulky carbenes react with CO to form amino-ketenes,^{11b,c} species typically unstable,⁵⁴ we reasoned that a less bulky carbene such as the anti-Bredt NHC 26 ⁵⁵ could allow for the attack of two carbenes to CO, giving the oxyallyl derivative 27 (Figure 19). Although the latter could not be isolated, it was characterized by NMR spectroscopy at -40°C . Protonation of 27 gave rise to the corresponding oxyallyl cation 27H^+ , which by simple oxidation with air afforded the oxyallyl radical cation $27^{+\cdot}$.

Interestingly, two isomers of $27^{+\cdot}$ were isolated (*d,l*- $27^{+\cdot}$ and *meso*- $27^{+\cdot}$). According to X-ray diffraction studies, the former has the two carbenes conjugated with the CO fragment but in the latter only one carbene assists in delocalizing the spin density. Surprisingly, the two derivatives bear similar spin density on the CO core (*d,l*- $27^{+\cdot}$: 51.6%; *meso*- $27^{+\cdot}$: 48%) indicating that one anti-Bredt NHC is probably sufficient in stabilizing such radical species. Note that, prior to this, oxyallyl radicals were only observed in inert matrices at low temperatures⁵⁶ or by mass spectrometry.⁵⁷ These results suggest that a variety of carbene-stabilized organic radicals should be isolable at ambient conditions.

Why carbenes are so effective to stabilize radical species and which carbenes are the best?

Protonated “classical” unsaturated NHCs, as exemplified by the imidazolium cation (28H^+), show an irreversible single electron reduction (-2.76 V vs. $\text{FeCp}_2/\text{FeCp}_2^+$).⁵⁸ The corresponding chemical reduction in a flask with potassium produces the free carbene 28 , believed to result from the decomposition of radical 28H^\cdot , indicating that this neutral radical is highly reactive (Figure 20).

Experimental results from μSR spectroscopy showed that carbene 28 reacts with muonium exclusively at the carbene centre to generate a radical 28Mu^\cdot similar to 28H^\cdot with muonium in place of hydrogen (Figure 21).⁵⁹ Calculations show that the reaction at this site is preferred by 14 kcal/mol over the double bond in the framework giving 29Mu^\cdot . Radical 28Mu^\cdot , which of course cannot be isolated, is calculated to be pyramidalized at the carbon atom by about 40° , and 74.9% of the spin density resides at this site.

Although the aforementioned results seem to indicate that carbenes are not prone to stabilize radical species, it is of foremost importance to realize that the experiments have been performed with unsaturated NHCs, which are probably among the weakest π -accepting carbenes. Indeed, an examination of the literature reveals that carbenes, which are only slightly more electrophilic than 28 , can accommodate an additional electron. Cyclic voltammetry on the free triazol-5-ylidene 30 indicates that the empty orbital can be populated with a single electron to generate the radical anion 30^- (Figure 22).⁶⁰ The electrochemically generated radical could even be observed by EPR. Moreover, calculations on annulated versions of NHCs, such as 31 , show that in the corresponding radical anion up to 30% of the spin density resides on the carbene carbon.⁶¹

Clearly, all the results presented in this mini-review suggest that π -accepting carbenes are more efficient for stabilizing radicals, because they better delocalize the spin density. This prompted us to develop a method to evaluate the π -accepting properties of carbenes.⁶² Note that the very popular TEP (Tolman Electronic Parameter)⁶³ measures the overall donor properties of carbenes, which is the σ -donation subtracted by the π -acceptance. Our method is based on the ^{31}P NMR chemical shift of readily synthesized phenylphosphinidene-carbene adducts 32 (Figure 23). These compounds can be represented by two extreme canonical structures. The resonance form 32a corresponds to a typical phosphalkene,

featuring a formal P=C double bond, and it is well-known that their ^{31}P NMR signals are at low field. In contrast, form **32b** corresponds to a carbene-phosphinidene adduct featuring a P-C dative bond with two lone pairs of electrons at phosphorus, and therefore give signals at high field. It is obvious that an increase of the π -accepting property of the carbene favors the contribution of resonance form **32a**, and thus more π -accepting carbenes will give a signal further downfield.

Conclusions

This report merely documents the infancy of this promising area of research. So far carbene stabilized paramagnetic main group species have only been reported for a few elements, namely boron, silicon, phosphorus, arsenic and carbon. As mentioned in the introduction, radicals play essential roles in numerous chemical processes, and almost nothing is known about the reactivity of carbene stabilized radicals. Importantly, the electronic properties of carbenes can be easily tuned, and therefore the reactivity of the corresponding radicals. The recent work by Roesky, Stalke *et al.*^{33,35} shows that carbenes can also stabilize biradicals. Consequently, it is reasonable to believe that they could also allow for the isolation of polyradicals, which can find numerous applications in materials science.

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Biographies

Caleb Martin was born in 1985 in New Brunswick, Canada. He completed his BSc at Mount Allison University in 2007. He then attended the University of Western Ontario for his PhD under the supervision of Paul Ragogna. Following graduation in 2011, he began working with Guy Bertrand as a Post Doctoral Researcher currently as a member of the UCSD/CNRS Joint Research Laboratory at the University of California, San Diego. In June 2013 he will begin his independent career as an Assistant Professor at Baylor University.

Michèle 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 and in 2012 the UCSD/CNRS. Laboratory at the University of California, San Diego. Her current research interests are focused on carbene chemistry and their application as tunable ligands for transition metal catalysts.

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). From 2001 to 2012 he has been Distinguished Professor and Director of the UCR/CNRS Joint Research Chemistry Laboratory at the University of California at Riverside, and now at the University of California, San Diego. 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.

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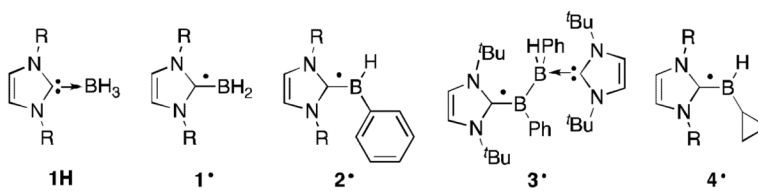


Fig 1. NHC-borane precursors **1H**, and radicals **1•-4•** observed by EPR spectroscopy.

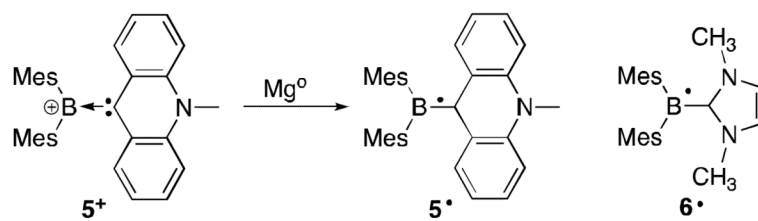


Fig 2.
Synthesis of 5^\bullet and radical 6^\bullet .

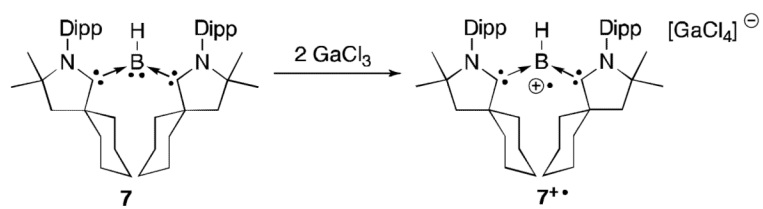


Fig 3.
Oxidation of borylene **7** to the radical cation **7^{+•}**.

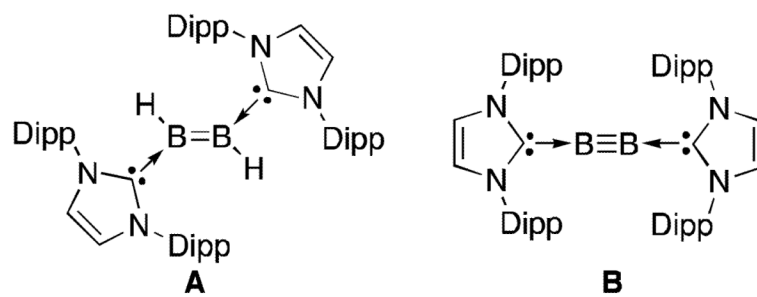


Fig 4. Recently reported unusual boron species stabilized by carbenes.

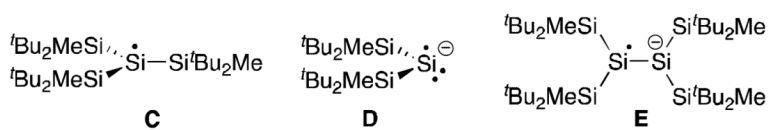


Fig 5.
Isolated neutral silyl radical **C** and radical anions **D** and **E**.

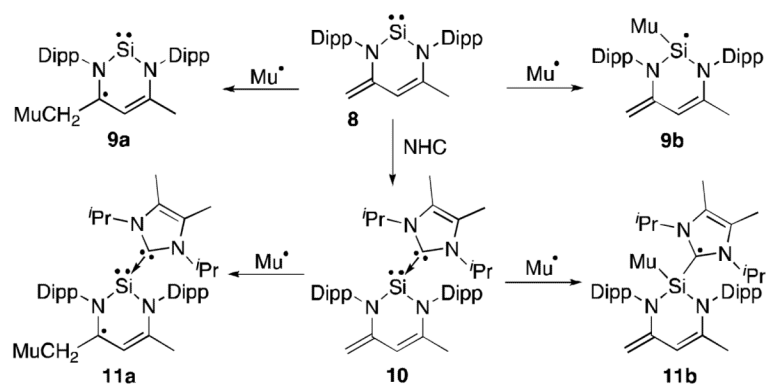


Fig 6.
Reaction of the silylene **8** and NHC-silylene adduct **10** with muonium.

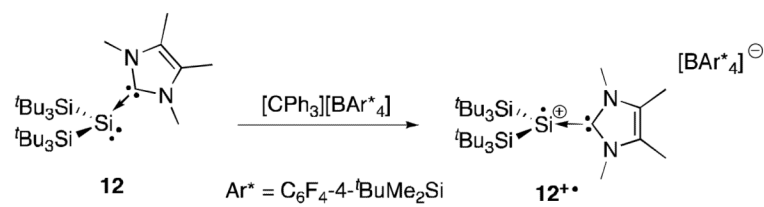


Fig 7.
Synthesis of silicon radical cation $\mathbf{12}^{+\bullet}$.

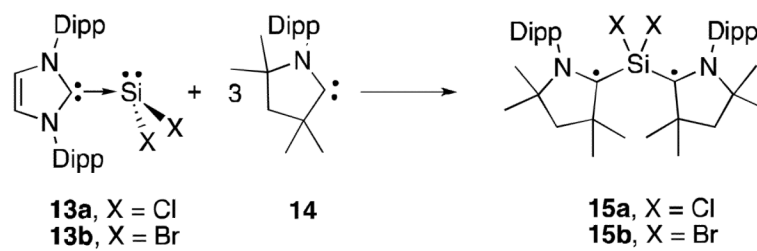


Fig 8.
Synthesis of silicon dihalide biradicals **15**.

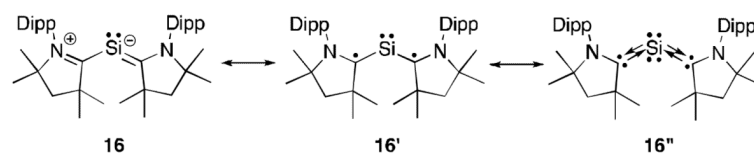


Fig 9.
Resonance structures of **16**.

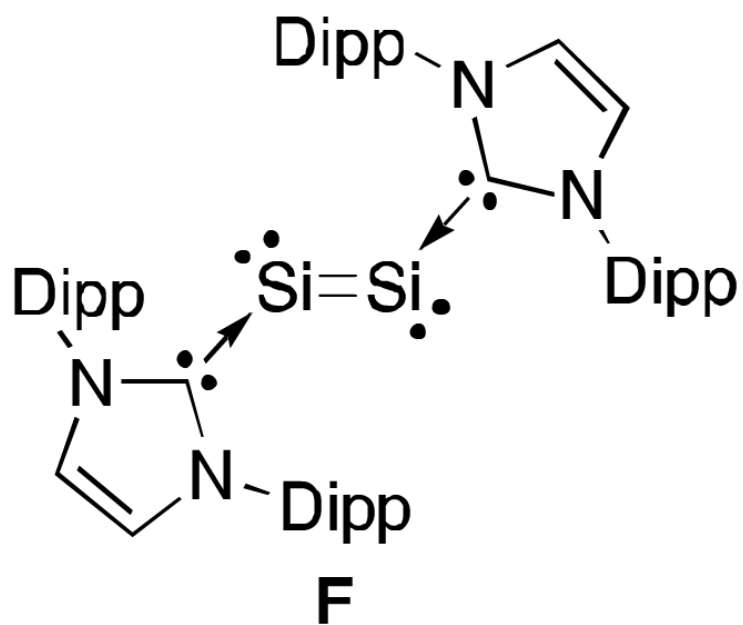


Fig 10.
Robinson's bis(NHC)Si₂ complex F.

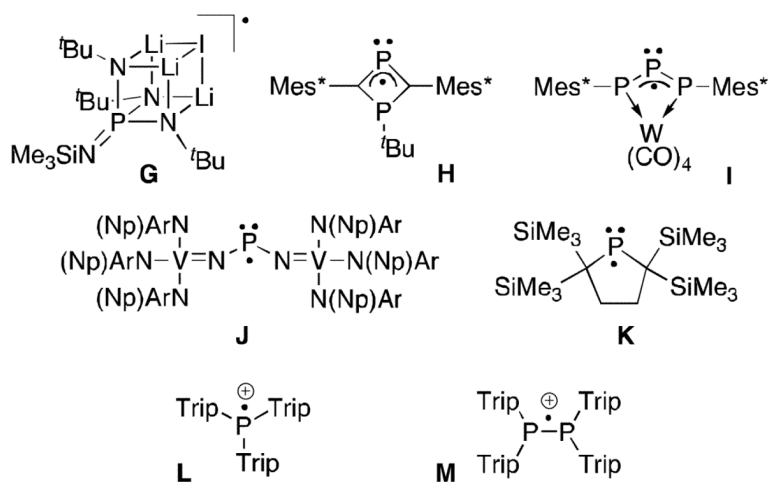


Fig 11.
Structurally characterized phosphorus radicals.

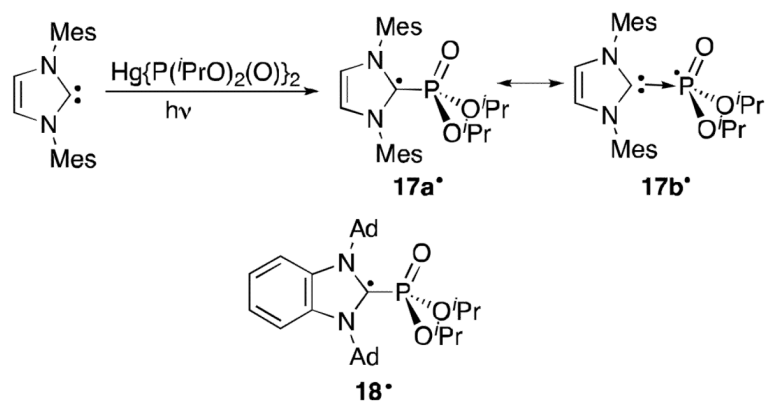


Fig 12. Synthesis and structural representation of persistent NHC-diisopropylphosphoryl radicals **17'** and **18'**.

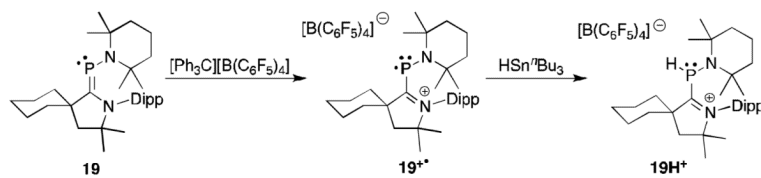


Fig 13. Synthesis and reactivity of the structurally characterized CAAC-phospheniumyl radical **19⁺**.

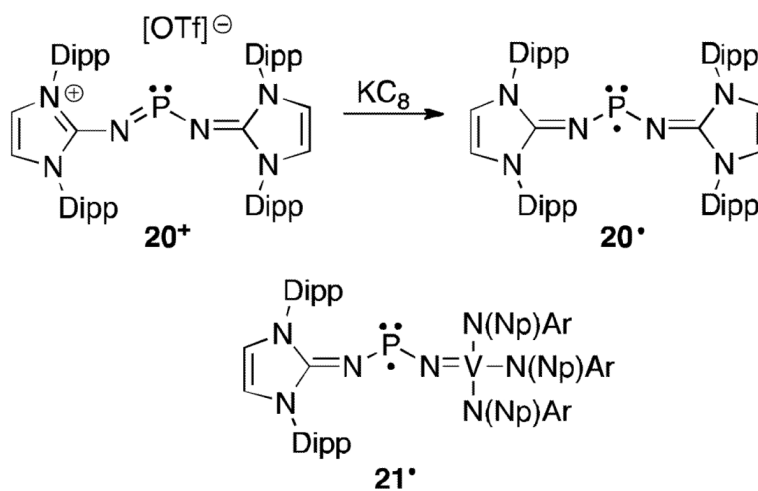


Fig 14.
Phosphinyl radicals featuring vanadium and NHC substituents.

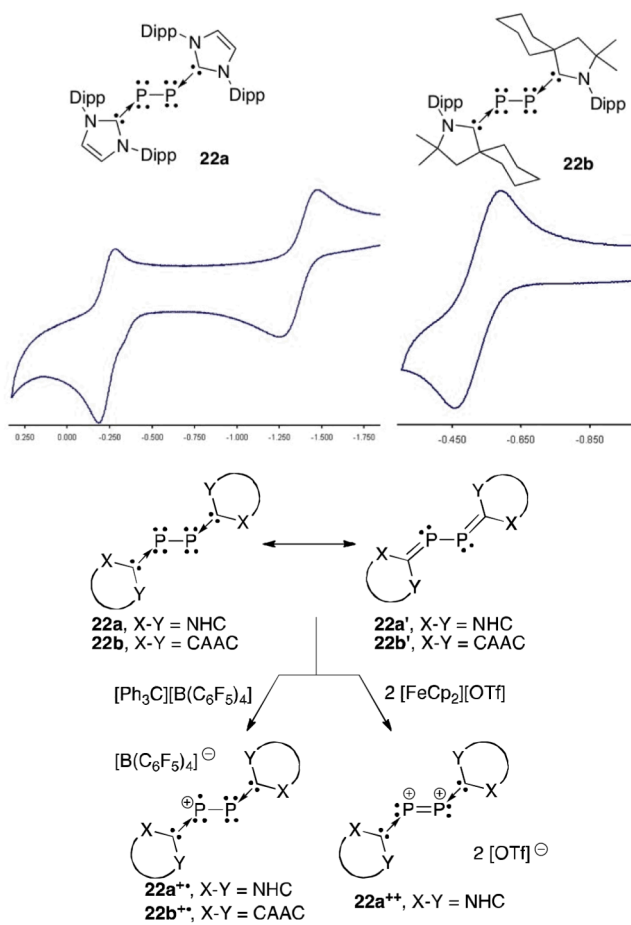


Fig 15.
Cyclic voltammograms of **22a,b** and their oxidation products.

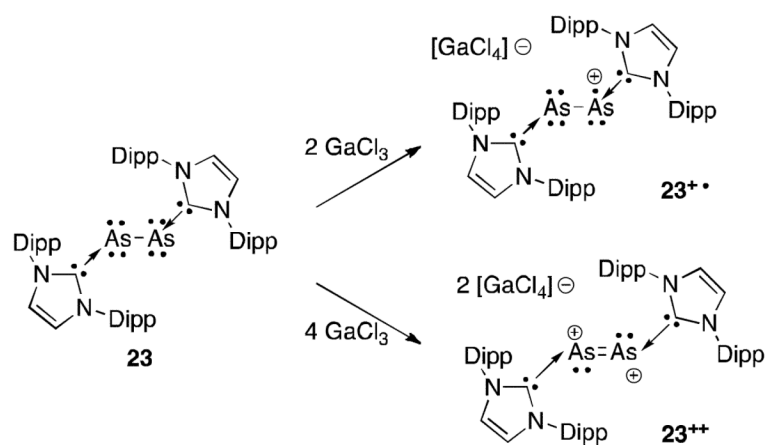


Fig 16.
Oxidation of the NHC stabilized As₂ molecule.

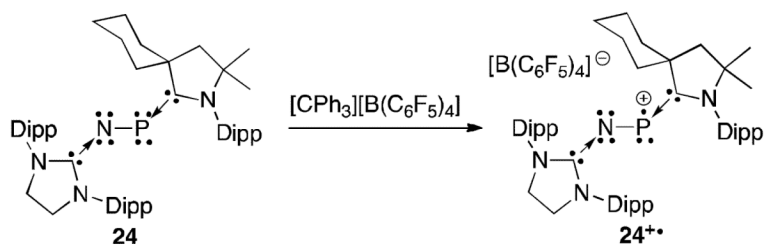


Fig 17.
Synthesis of radical cation **24⁺**.

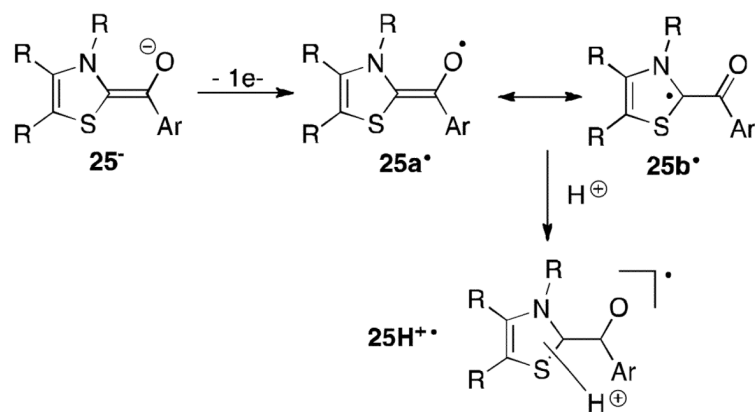


Fig 18.
Oxidation of the thiazolylidene based enolate **25⁻** to **25[•]**.

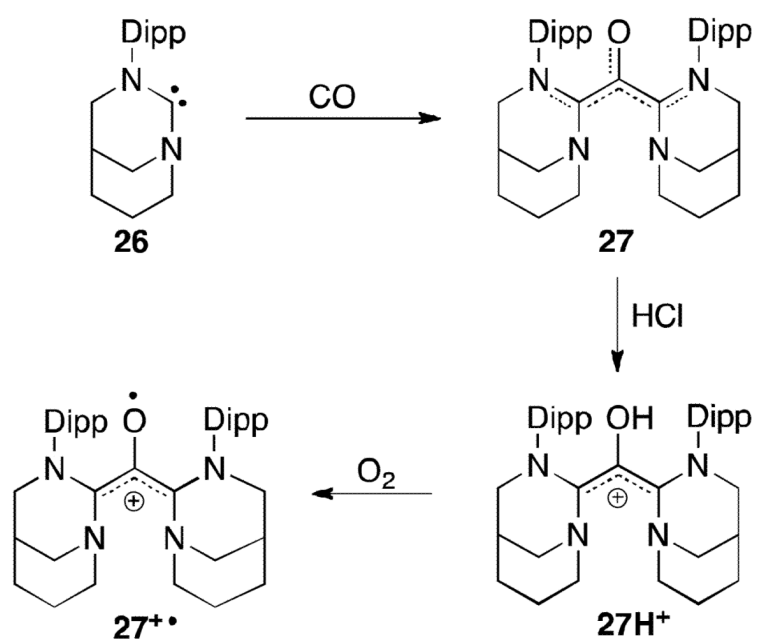


Fig 19.
Synthesis of oxyallyl radical cation **27H⁺**.

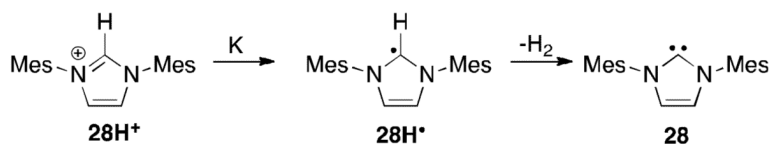


Fig 20.
The reduction of an imidazolium cation with potassium.

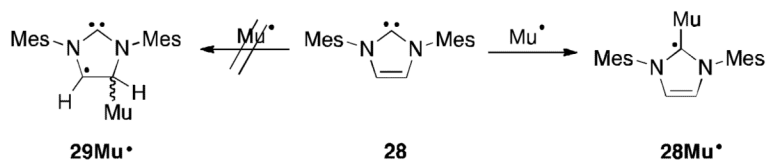


Fig 21.
Reaction of muonium with NHC **28**.

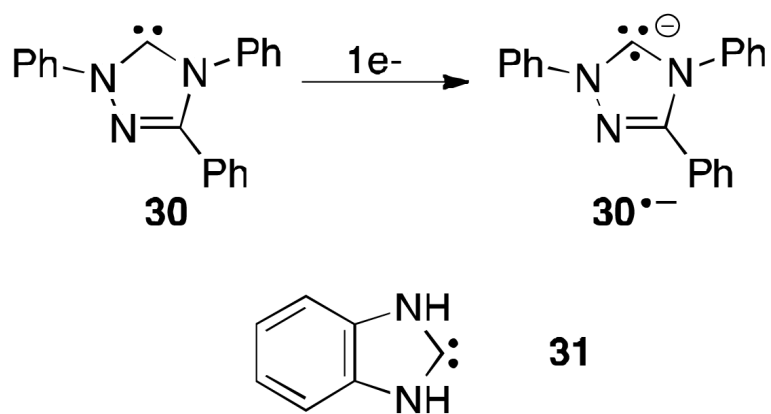


Fig 22.
Reduction of triazol-5-ylidene **30** and annulated-NHC **31**.

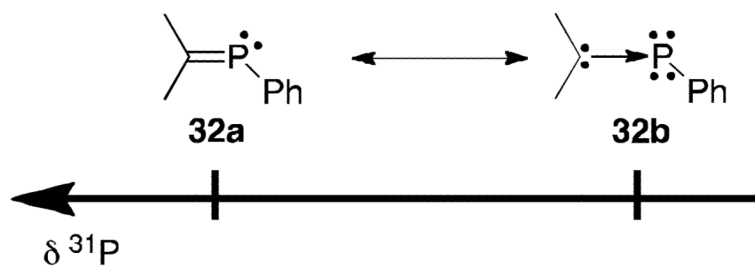


Fig 23.
Structures of **32** and their relative ^{31}P NMR chemical shifts.