

REVIEWER REPORT(S):

Referee: 1

Comments to the Author

This Review by Liu Leo Liu and co-workers covers the recent progress in the chemistry of stable/isolable carbene analogues. This focuses on the last 10 years in this field and adequately covers the key complexes that have contributed to main group chemistry's recent revival. For this reason, it is a timely review. Whilst this is a nice concise review, it could be made stronger through further discussion and comparison of the compounds within to highlight the observed trends or strategies required to isolate related Group 13-15 compounds. The following points need to be addressed:

The introduction states it will provide the brief history of the carbene chemistry. Here it would be better to put the Figure with the timeline together with important discoveries, possibly separate Figure for each group (Group 13, 14, and 15).

Whilst the synthetic protocol and reactivity part are covered, there is generally a lack of further discussion regarding properties and the discussion in some parts rather reads like a list of reactions rather than a flowing discussion with general trends or context. It would be nicer if authors could bring reactivity trend of compound type. For example, coordination number/mode, neutral/cation/anion, etc. Also, very limited discussion of bond lengths with the few examples mentioned, but these are important. Whilst it is hard to establish the general trends of the compounds in the text, a bit more general discussion of bond lengths (and/or bond angles) may aid the text to give the reader the opportunity to grasp what may be a long/short bond. Same point should be considered for some important NMR chemical shifts of compounds.

Group 14 carbene analogues (Figure 7) should have at least two more compounds class. Neutral three coordinate type (R₂EL, one donor) and neutral four coordinate type (R₂EL₂, two donors). These species have been well recognized in the community and widely used in many organic and inorganic reactions.

Same point for Group 15 species with other compound class. For example, two coordinate neutral species REL, two coordinate dicationic species [REL]²⁺, three coordinate cationic carbene [R₂EL]⁺ (one donor), three coordinate dicationic species RE₂+L₂, etc.

Singlet/triplet issue has been described for heavy Group 15 compounds in the last part, however, this point is very important and should be discussed for each section (Group 13, 14, and 15). Trend of single/triplet from lighter elements to heavier elements depends on group 13-15 will be very useful for the readers.

Although authors focused on the "isolable" main group carbene in this review, there are several isolable masked carbene analogues in the group 13, 14 and 15. I think these species are also important compound class in heavier carbene chemistry and peculiar to ignore. However, if authors think these compounds are beyond scope of this review, this point should be described.

In addition, donor-stabilised main group carbenes (i.e. NHC-stabilised) have also been well studied and their reactivity has been very well documented. Thus, these are also involved in the “isolable” main group carbenes.

Another concern is that authors did not touch any carbene analogues in Group 16. Some examples of dicationic Group 16 carbene analogues are also known.

Regarding the reactivity that covered in this review, coordination chemistry towards transition metals should also be highlighted. While some sentences described on this point, carbene analogues as ligands for transition metals play an integral role in this field. Also, nitride transition metal complexes are one of the hot topics in main group community.

In the conclusion part, authors should also consider describing the coordination number difference of these carbene analogues of Group 13-15. The electronic nature and reactivity are totally depending on this point (Lewis acidic, Lewis basic, or bifilic).

Referee: 2

Comments to the Author

The review by Liu et. al summarizes recent progress about Group 13, 14 and 15 analogues of carbenes. The authors refer to over three hundred of post-2010 literatures. However, some of the pre-2010 references are key to draw a comprehensive and balanced picture on the topic and thus should be included in the reference list.

It is stated, “the applications of carbene analogues are vast, encompassing realms like catalysis, not every aspect will be exhaustively covered here.” However, it remains unclear which aspects of chemistry of isolable main group carbene analogues were excluded in this review and why.

Moreover, it is not clear what the subsequent sections in the review are. In the subsequent section, only for Group 14 elements, generic synthesis methodologies are discussed. A similar discussion should be applied for Group 13 and 15 systems. Several topics were also not discussed in-depth and without much insights.

Overall, the submission contains many scientific, grammar and spelling mistakes as well as misuse of terminology. This work maybe suitable for publication but only after major alteration addressing the aforementioned issues and the following points:

Abstract: weak and should be rewritten, most of it is too vague

For example: some definition of carbenes should be included before further comparisons, and what exactly is meant by carbene analogues and which main group elements this applies to.

Intro: poorly structured, often too broad, not enough thoughtful discussion

First paragraph should be rewritten, again too vague. It is not wise to generalize about all main group carbene analogues. The reader would appreciate if the authors refer to specific examples.

E.g. Line 2, this sentence is too broad, which main group element carbene analogues are the authors referring to. For example, not all have singlet ground states. Seems strange to not mention NHCs,

as an example of singlet and nucleophilic carbenes, as a reference point first to then compare other similar species, e.g. starting with heavy Group 14 analogues.

Next two should also be restructured: it is meant to briefly describe some history but it feels too random:

“Historical inquiries into carbene analogues were largely centered on their stabilization and structural characterization”. This statement is vague too.

Suddenly jumps to tin and lead, it would make more sense to discuss carbenes briefly than compare to other main group elements with similar electronic structures.

Then jumps to the use of bulky aryl ligand, this should be mentioned separately a bit later as a paragraph about strategies to stabilize reactive main group compounds.

“Broadly, carbene analogues are isoelectronic/isolobal with carbenes and exhibit carbene-like ambiphilicity (Fig. 1)”

This could be explained much better, as mentioned already would make sense to discuss carbenes first before saying main group analogues are the same.

But again, it is didactically weak to be so broad. First of all, the types of carbenes are broad, and so are the heavy valent main group analogues.

However, the graphic Fig 1 is nice for showing the possibilities. The accompanying text should just explain this figure.

Group 13, 14 and 15 are all very different, and the lighter vs heavier elements are also very different to each other. This deserves some comment and discussion here. Touching on inert pair effect, relativities etc.

Also missing is a discussion of where carbenes are successful, for example in chemical catalysis and synthesis of reactive main group and TM species (also in catalysis), and why main group analogues could be useful and interesting and contribute to this field.

The authors mention amphiphilicity, but without really discussion. Also, this is not always the case, many main group carbene analogues are better described as nucleophilic (as for NHCs). Additionally, amphiphiles can often be predominantly Lewis basic or acidic, rather than equally both. So better to avoid being too broad in statements. Why is amphiphilicity interesting? This deserves explanation.

Section 2

Intro – revision is recommended

Change "a lone electron pair of electrons" to "a lone pair of electrons"

Page 4, “Lately, the spotlight seems to firmly favor aluminylene derivatives, leaving gallylenes, indylenes, and thallylenes in a sporadic narrative.” Why to say this? The authors should discuss boron first then mention the developments of Ga chemistry (many examples of borylenes and gallylenes) before discussing the breakthroughs in low valent Al chemistry.

Would be good to mention AlCp* and GaCp as the first isolated carbene-like species before mentioning how NHC-type of analogues such as (Nacnac)Al, (Nacnac)Ga and K(Ga[DAB]) have also been established for many years.

2.1

If the background of free borylenes is mentioned from the 80s and 90s, then it doesn't seem representative to neglect the GaR species (from P.P. Power et al.) that are monomers in equilibrium with loosely associated dimers. This is directly relevant to the use of terphenyl ligands later.

Structures, Bonding, and Reaction Chemistry of the Neutral Organogallium(I) Compounds (GaAr)_n (n = 1 or 2) (Ar = Terphenyl or Related Ligand): An Experimental Investigation of Ga–Ga Multiple Bonding | Journal of the American Chemical Society (acs.org)

Quasi-Isomeric Gallium Amides and Imides GaNR₂ and RGaNR (R = Organic Group): Reactions of the Digallene, Ar'GaGaAr' (Ar' = C₆H₃-2,6-(C₆H₃-2,6-Pri₂)₂) with Unsaturated Nitrogen Compounds | Journal of the American Chemical Society (acs.org) – first GaR monomer in solid state (2006)

Page 6, in “Further reactivity explorations reveal that the Al(I) center of compound 5 not only exhibits high ambiphilicity but also showcases unique coordination behavior (Scheme 2).” not only exhibits high amphiphilicity – this phrase doesn't make sense, please explain further; amphiphile is not a measurable quality but a description

Page 6, “tri-active amphiphilic ligand nature (an amphiphilic center with three reactive sites)” is not a good phrasing

2.2

Page 7, (Nacnac)Ga was also synthesised in 2000: Synthesis and characterization of the monomer Ga{(NDippCMe)₂CH} (Dipp = C₆H₃Pri₂-2,6): a low valent gallium(i) carbene analogue - Chemical Communications (RSC Publishing)

Complex 8 it is not mentioned as well as that the new Dipent derivative gives much higher yields, a significant recent development, and that this is a limitation in studying (Nacnac)Al chemistry (the literature yield is very low)

For completeness, some recent developments in (Nacnac)Al chemistry should be referenced, for example

Carbon Chain Growth by Sequential Reactions of CO and CO₂ with [W(CO)₆] and an Aluminum(I) Reductant | Journal of the American Chemical Society (acs.org)

1st row transition metal aluminylene complexes: preparation, properties and bonding analysis - Dalton Transactions (RSC Publishing)

Reversible alkene binding and allylic C–H activation with an aluminium(i) complex - Chemical Science (RSC Publishing)

Complete deconstruction of SF₆ by an aluminium(i) compound - Chemical Communications (RSC Publishing)

Reactions of Fluoroalkenes with an Aluminium(I) Complex - Bakewell - 2018 - Angewandte Chemie - Wiley Online Library

2.3

Gallium analogue of 24 has been ignored, it is reported in the same paper - Synthesis, structure and

reaction chemistry of a nucleophilic aluminyl anion | Nature

Page 10, "...increasing the energy of the central p-orbital of Al(I)." –is incorrect, refer back to the review to describe correctly how the LUMO is lowered by the O-interaction as described in the review

Some comment about the nature of the metal counterion should be mentioned, and also the existence of the potassium-sequestered analogue of 24 that is more reactive

Page 12, Scheme 6, Reaction of 24 with LiI to get Al-Li complex is excluded, there is also another paper with Lithium and Sodium:

Dihydrogen Activation by Lithium- and Sodium-Aluminyls - Evans - 2021 - Angewandte Chemie International Edition - Wiley Online Library

There is also a paper with Rb, Cs counterions:

Rubidium and caesium aluminyls: synthesis, structures and reactivity in C–H bond activation of benzene - Chemical Communications (RSC Publishing)

Missing references to Al-Cu and Al-Ag complexes:

Coinage metal aluminyl complexes: probing regiochemistry and mechanism in the insertion and reduction of carbon dioxide - Chemical Science (RSC Publishing)

Scheme 6, would be better to include as many different metals/complexes as possible rather than 3 examples of a very similar methylated products and 3 quite similar Mg complexes, maybe the authors can show them in a more generalized way.

Bond activations

There are actually so many reports on bond activations. This reviewer thinks it would be better to say that these are a number of important examples but not necessarily all examples

Page 13, "Intriguingly, the configuration of the olefins (E/Z) did not alter the exclusive formation of product 33-P6." – throughout try to avoid unnecessary details in the main text

Missing reference Oxidative Addition of Hydridic, Protic, and Nonpolar E–H Bonds (E = Si, P, N, or O) to an Aluminyl Anion | Inorganic Chemistry (acs.org)

Page 12, "Coles reported the synthesis of aluminium analogues of carbonyl 25-P2 and peroxide 25-P3 – should be written as aluminium-selenium analogues of..."

-As there are also other examples of aluminium ketone-type species

Also not mentioned are recent papers about the reactivity towards azides and other unsaturated molecules, reactivity that is also prevalent for carbenes, e.g., examples of Al, Ga, In anions reacting with RN₃ to give M=N species (also M=O species for Al, In (Coles))

Carbon Monoxide Activation by a Molecular Aluminium Imide: C–O Bond Cleavage and C–C Bond Formation - Heilmann - 2020 - Angewandte Chemie International Edition - Wiley Online Library

Reduction of organic azides by indyl-anions. Isolation and reactivity studies of indium–nitrogen multiple bonds - Chemical Science (RSC Publishing)

Aluminium and Gallium Silylimides as Nitride Sources** - Heilmann - Chemistry – A European Journal - Wiley Online Library

Coordination and Homologation of CO at Al(I): Mechanism and Chain Growth, Branching, Isomerization, and Reduction | Journal of the American Chemical Society (acs.org)

Trapping and Reactivity of a Molecular Aluminium Oxide Ion - Hicks - 2019 - Angewandte Chemie International Edition - Wiley Online Library

Generation of a π -Bonded Isomer of $[P_4]^{4-}$ by Aluminyl Reduction of White Phosphorus and its Ammonolysis to PH_3 - Roy - 2021 - Angewandte Chemie International Edition - Wiley Online Library

Of course, there are many examples of interesting reactivity of Al(I) complexes known, but there shouldn't be big gaps. The authors should not discuss every example but at least include key references to the distinct subsets of reactions, or carefully define the domain of reactivity that is included in this review so that it is complete.

2.3

The authors should mention how there are a couple of attempts in literature to synthesise (LB)2Al-R, but no cationic version as yet

An Elusive Hydridoaluminum(I) Complex for Facile C–H and C–O Bond Activation of Ethers and Access to Its Isolable Hydridogallium(I) Analogue: Syntheses, Structures, and Theoretical Studies | Journal of the American Chemical Society (acs.org)

Lewis-Base Stabilization of the Parent Al(I) Hydride under Ambient Conditions | Journal of the American Chemical Society (acs.org)

Of course, there are many (LB)2B-R borylene species too, but probably this is beyond the scope of the review but it should probably be at least mentioned.

However, there is an example of a (LB)3B+ cation, which are of relevance in this context
Synthesis, Structure and Reactivity of a Borylene Cation $[(NHSi)_2B(CO)]^+$ Stabilized by Three Neutral Ligands | Journal of the American Chemical Society (acs.org)

Examples of Group 13(I) cations stabilized by NHCs deserve to be mentioned too:

<https://onlinelibrary.wiley.com/doi/10.1002/anie.201209757>

Comparing to Section 3, where rubrics are divided up into quite specific categories, maybe this should be applied here too as some of the sections are very large

Section 3

Page 15, “In recent years, carbene analogues of group 14 with different coordination states have been reported”: different coordination states – rephrase to environments

Page 15, Structure IV (carbyne analogues)– please clarify how this is justified as being a carbene analogue, since it is not divalent nor does it have only one free lone pair of electrons and vacant p-orbital. It has a completely different oxidation state compared to I-III,. This should actually be outlined in the introduction.

3.1.2

Page 16, typo should say: (5) investigation of the excited state(s) of silylenes

Although the following silylenes were published before 2010, they should be cited as seminal NHSi compounds that have driven much further work in last 10 years, relevant background:

A New Type of N-Heterocyclic Silylene with Ambivalent Reactivity | Journal of the American Chemical Society (acs.org)

Synthesis and Characterization of [PhC(NtBu)₂]SiCl: A Stable Monomeric Chlorosilylene - So - 2006 - Angewandte Chemie International Edition - Wiley Online Library

Page 17, Fig 8 – Ar means aryl so it is incorrect here, should say R1 and R2

Page 18, Fig 10, the orbital diagram is not consistent with the structures of 44 and 45 (no direct Si-P bond)

3.1.3

Page 20, “In 1986, the first acyclic silylene Cp*₂Si was reported by Jutzi and coworker via the reduction of dichloro(bis-pentamethylcyclopentadienyl)silane with alkali metals.” The reducing reagents are alkali metal naphthalenides not alkali metals.

Page 20, “Jones achieved the isolation of acyclic aminoborosilylene 46”. This is a collaborative work by Aldridge and Jones groups; read: Jones, Aldridge et al. In addition, it is “aminoborylsilylene” not “aminoborosilylene”.

Page 20, “Power reported the study of a stable, acyclic, two-coordinated silylene by the reduction of bromosilane with Mg almost at the same time.” It is “two-coordinate” not “two-coordinated”. The reducing reagent is Jones’s Mg(I) dimer not Mg metal. In addition, add the substituents for bromosilane.

Page 20, “Jones introduced the aminosilyl silylene 47 by the same method”. Same issue. This is a collaborative work by Aldridge and Jones groups.

Page 20, “Aldridge prepared the acyclic bis-aminosilylene 48 via a salt elimination reaction of [SiCl₂-(IPr)] with alkali metal amides Li[TBON] in 2016.” Same issue. This is a collaborative work by Aldridge and Jones groups. In addition, it is “diaminosilylene” not “bis-aminosilylene”.

Page 21, the structure of 47-P1 is wrong.

Page 21, "Conversely, silylene 48 showcases a inert reactivity". Should be "an" instead of "a".

Page 22, "Notably, silylene 51 exhibits a unique behavior characterized by a reversible intramolecular C–C bond activation". Should be "an" instead of "a".

Page 22, "a reversible intramolecular C-C bond activation" It should be "C-C bond activation of arenes"

Page 22, the middle paragraph is very confused. Please rephrase it.

Page 23: "undergoes" instead of "unergoes"

Page 24, "Schulz showed that transient gallium-substituted silylene". It is "gallyl-substituted" not "gallium-substituted".

Page 24, for the structure of 56, the ligand is incorrect.

Page 24, "have been devised and utilized for metallylene stabilization". should be "metallylenes" instead of "metallylene".

There are several awkward uses of vocabulary such as "aligning as" (Page 24, para 2, line 4).

Page 24, "Their enhanced stability renders dihalides such as $\text{GeCl}_2 \cdot (\text{dioxane})$, SnCl_2 , and PbCl_2 both stable in solid form and commercially available." "dihalides", "both...and..."

Page 25, "Beyond this classic reactivity, when coordinated with specific transition metals, NHMs can serve as catalysts". Usually, the NHM-transition metal complexes serve as catalysts not NHMs.

Page 25, Fig. 16, please rename compounds 60, 62, 65, 68.

Page 26, scheme. 16, no indication for R group in 70-P1, 70-P2 and 70-P3. In addition, compound 59 is different from that in Fig 16.

Page 26, "phosphane functional groups can lead to the synthesis of pincer-type germlyenes". The "phosphane" is very weird, author may have meant "phosphino".

Page 27, scheme 17, It should be $\text{W}(\text{CO})_6$ instead of $\text{W}(\text{CO})_5$. It is $\text{Ni}(\text{cod})_2$ not $\text{Ni}(\text{COD})_2$.

Page 27, "Replacing one of the π -electron donating and σ -electron withdrawing amino group with a σ -donating alkyl counterpart amplifies the electrophilicity at the germylene center". The electronegativity of C is higher than that of Ge, why the alkyl is a σ -donating group?

Page 30, “The presence of disparate substituents however modulates the properties of each side differently.” Should be “Modulate” instead of “Modulates”.

Page 30, “Over the past decade, a series of acyclic metallylenes has been unveiled”. should be “have” instead of “has”

3.2

Page 39, “Group 14 monocoordinate metallylene anions $[R-E]^-$ (E = Si, Ge, Sn, Pb) are isoelectronic to carbenes, which are hitherto uncharted species.” is incorrect! Group 14 monocoordinate metallylene anions are not isoelectronic to carbenes because they have two lone pairs of electrons while carbenes have only one lone pair. This statement should be rephrased.

In Fig.26, Li(THF) should be drawn as Li(thf).

Page 39, line 12: Change "was occurred" to "occurred."

Page 40, “Progressing into 2018, Roesky reported the synthesis of silanylidene and germanylidene anions (125a and 125b) by introducing KC8 into a mixture of TripEC13 (E = Si, Ge) and CAAC, followed by a reduction reaction.²³⁵”. This work was reported by Stalke, Koley, Roesky and their co-workers

Page 40, in “These resultant anions are crystallized as dimers, and theoretical calculations revealed the presence of multiple bonds between the carbene carbon and the Si/Ge atoms.”, “are crystallized” should be change to “crystallize”.

Page 41, “Nitrenes share similarities with carbenes in terms of both their electronic structure (being isoelectronic) and their patterns of reactivity.” Again, nitrenes have two lone pairs while carbenes have only one lone pair of electrons.

Page 41, “Dervan elucidated the synthesis and characterization of singlet aminonitrenes 126 and 127 (Fig. 29),²⁵²⁻²⁵⁴”. The work in ref 254 was reported by Dervan and Roberts, not from Dervan alone!

Page 39, In “Alkali-metal-substituted silylenes can be considered as silicon analogues of carbyne anion complex (silyne anion complex).” , read: complexes.

Page 39, In “Subsequently, upon reduction of above precursor with excess Li, an intramolecular cyclopropanation was occurred, which resulting in the formation of silanorcaradienyllithium 122.”, the word “which” should be removed.

Page 50, “The Bertrand group showed that CAACs with a six-membered backbone have more ambiphilic character than the five-membered ones.^c This trend should also apply to the NHPs and their analogues, although systematic research remains scanty.” The "c" between the two sentences should be removed, and a literature reference should be provided.

Page 50, “In the same year, Müller introduced the triazaphosphenium anion 154.306”. This work was documented by both Nyulaszi and Müller.

Page 51, “This strategy has been applied by the Mebs and Beckmann groups synthesize a bismuthenium and a stibeniumion ion with two bulky meta-terphenyl groups as ligands (Scheme 38).” should be corrected grammatically using “to synthesize”.

Page 51, “DFT calculations indicate the electrophilic attacking ability of the phospheniumion and arseniumion are stronger than that of the bismuthenium and stibeniumion analogues” should also be corrected grammatically.

Revise the figures to represent charges without using a circle for better clarity. For example, use "2+" or "3+" instead of "2⊕" or "3⊕." These changes will improve the clarity and accuracy of the document or manuscript.

Arrows, dashed lines, and solid lines are mixed in depicting dative bonds in the Lewis structures in the Schemes and Figures. The authors should unify these.

References 10 and 51 are the same: Review the references to avoid duplication, and ensure that they are correctly cited.