

Referee 1 (R1)

Comments:

The manuscript by Liu and co-workers describes the synthesis and characterization of the first crystalline monometal-substituted free carbenes and their reactivity toward a C-H bond, styrene, and $\text{BH}_3\cdot\text{THF}$. Carbenes are a class of compounds that have received much interest from many different perspectives such as fleeting intermediates, stable ligands, catalytic intermediates, and materials building blocks. Despite the long history of carbene chemistry, metal-substituted carbenes are extremely rare and have been established only recently. The successful synthesis of the title compounds, thus, provides an important milestone in this subject area, particularly from the viewpoint of fundamental molecular science. The authors develop synthetic methodology that appears to be highly elegant and reliable. Additionally, the compounds reported are, probably, the first examples of terminal metal carbynes that display a metal-carbon single bond rather than a typical metal-carbon triple bond. Therefore, from the reasons of novelty, broad interest, and scientific ingenuity, I recommend publication of this paper in Chem, provided the following minor points have been addressed.

1. Compounds with $\text{P}=\text{C}$ double bonds generally exhibit ^{31}P chemical shifts that are far more downfield than those of $\text{P}-\text{C}$ singly bonded compounds. The reported ^{31}P chemical shifts for the carbenes **4** (-17.1 ppm) and **5** (-36.2 ppm) and their precursors **2** (124.5 ppm) and **3** (126.3 ppm) are opposite to this trend. Explanations should be given for this point.

2. Additionally, why is the $^1J_{\text{P-C}}$ coupling constants for **5** (47.4 Hz) significantly decreased compared to that for **3** (145.8 Hz), although the $\text{P}-\text{C}$ bond in **5** (1.529(3) Å) is significantly shortened compared to that in **3** (1.793(3) Å)?

3. The highly anisotropic thermal ellipsoid for the C(1) atom in the X-ray structure of **5** indicates a positional disorder for this carbon atom, reducing the accuracy of the reported $\text{P}(1)-\text{C}(1)-\text{Au}(1)$ bond angle (168.3(3) °). Is this bond angle consistent with the computed value for the optimized structure of **5**? Additionally, why does the central carbon (C(1)) in **5** exhibit such a large bond angle (fairly close to 180 °) despite having three valence electron pairs around itself.

4. A singlet carbene usually has a σ -type HOMO that represents a lone pair on the central carbon atom. However, the HOMO of **5** presented in Figure 3 (a) looks to my eyes like a $\text{P}(1)-\text{C}(1)$ π bonding orbital similar to HOMO-1. Can the HOMO of **5** be characterized as a σ -type carbon-centered lone pair orbital?

Referee 2 (R2)

Comments:

The authors report the first synthesis of two gold(I) substituted carbenes and their reactivity. The approach follows a series of papers, mainly from the Bertrand group, about isolable carbenes, where the singlet state is stabilized by one pi-donating substituents. This includes a primary carbene complex (ref. 38), and the AuL⁺ fragment in the current case is isolobal with the H⁺.

I think, this is a really nice contribution that provides access to a new class of isolable, subvalent carbon compounds, with high potential to spark new methodologies for chemical synthesis. I therefore support publication in CHEM, after the following points have been addressed:

1. As the main technical problem, there are no combustion analyses throughout the paper to confirm bulk purity. IR spectra of isolated carbene products should also be provided to support quantitative N₂ elimination. Similarly, the bulk purity of **7** and **8** need to be confirmed. The reaction with styrene takes 12h for full conversion, but within 3d the C-H insertion product **6** is also obtained. In fact, the ¹H and ¹³C spectra seem to show some additional signals. For **8**, the ¹H and ¹¹B spectra are not specific enough to assure the structural assignment.

2. I might be confused about the nomenclature. The authors call the title compounds "Monometal-Substituted Free Carbenes", and at another point "masked monocoordinated carbanion". As a suggestion, I would call this ligand a "(singlet) phosphanylcarbyne anion". I think this best reflects the electronic structure analysis (negative charge on carbon, near linearity, C-centered HOMO). On that note, the transient phenylcarbyne anion has been prepared in situ (JACS, 1999, 121, 6310). Furthermore, Strausz et al. reported photolysis of mercury diazoacetates and the product distribution hints at the formation of divalent alkylidyne complexes as transient intermediates, which were also trapped by cyclopropanation (JACS, 1974, 96, 5723). I think this classic work should be cited to draw a connection to the relevance for chemical synthesis.

3. Maybe most strikingly, the Au-C-P unit is almost linear, but the bending potential might actually be quite flat. It would be nice to report s- and p-contributions to the NLMOs. **5** is quite a bit more linear than the silyl and hydro analogues. From that angle, I guess there is considerably more p-character to the C-lone-pair, which should also contribute to the higher HOMO energy (and nucleophilic character). At the same time, the authors draw the molecule in a distinctly bent way. I found that quite confusing as it does not seem to reflect the experimental structure.

4. I cannot follow the authors, why they call for ambiphilic carbene character from the electronic structure calculations. The lowest lying vacant MO at the carbene core (LUMO+10) is pretty high

in energy. From this picture, I would expect predominantly nucleophilic reactivity, which actually seems to be the case. The C-H insertion or the reaction with styrene does not necessarily indicate ambiphilic carbene character, but might proceed via the triplet surface, which is only 11 kcal/mol higher in energy. Or the olefin might even initially coordinate to the gold ion. This should be checked, by Hammett analysis or at least computationally. Radical pathways with olefins can also be probed by using internal E- and Z-alkenes and check for the stereoselectivity.

5. Regarding the reaction cascade with $\text{BH}_3(\text{THF})$ (Figure 6), the computations suggest that **IN2** should be observable with 1eq. The second addition is much less exergonic and the barrier is slightly higher. Did the authors check for this compound experimentally? It would demonstrate the "masked carbanion" reactivity even better.

6. I wonder if the carbyne complexes can be protonated at the carbon? There is a lot of interest in cationic gold carbene complexes as intermediates in enyne cyclization (Chem Soc. Rev. 2016, 45, 4533). Goddard and Toste proposed a bonding model (Nat. Chem. 2009, 1, 482) with varying degrees of Au-C pi-bonding. But to my knowledge the isolation of such species has not been reported.

7. In the summary: Maybe replace "low-spin" with "closed-shell"?

Referee 3 (R3)

Comments:

There are 9 structures in this paper. We examined

****1**** (CCDC 2119219)

****6**** (CCDC 2119220)

****4**** (CCDC 2119224)

****7**** (CCDC 2119221)

****3**** (CCDC 2119225)

****5**** (CCDC 2119222)

****8**** (CCDC 2119223)

****7'***** (CCDC 2162450)

****7''***** (CCDC 2162451)

Most of these structures suffer from being measured with copper radiation despite high absorption without careful absorption correction being applied. An face-indexed correction is strongly recommended for crystals with such high μ values, but this was apparently not carried out, a standard

size of 0.1x0.1x0.1 mm was specified for all crystals. Please perform a careful absorption correction so that these fine structures can be published according to the state of the art. For some structures, the data appeared to have been cut at a theta value where intensity was still clearly observed. Please change or explain. (Only the decrease of residual electron density is not a good reason).

Please note and explain at least under `_refine_special_details`, if and why strong restraints were used.

If you wish to use a solvent mask, you must also comment on the number and nature of the masked entities in the relevant fields of the CIF loops as well as provide a verbal note in `_refine_special_details`. Your assessment should be backed up by relevant independent data such as TGA or elemental analysis. Please note that your final reported sum formula and subsequent items like density etc. must contain all entities present in your crystal, including those that have been solvent-masked.

Structure 1 (CCDC 2119219): C30 H47 N4 P Si

These CheckCif A and B alerts are raised by this structure. This is for your information only - you may wish to address these issues before re-submitting your cif file to the CCDC.

112_ALERT_2_B ADDSYM Detects New (Pseudo) Symm. Elem B 93 %Fit

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item `_computing_data_collection` regarding the software used in this structure determination is missing. Please supply this value.

Structure 6 (CCDC 2119220): C54 H74 Au N4 P

The problem of this structure is not only the high residual electron density but the strange thermal motion of C36, which is strongly restrained. By the way, it refines nicely as nitrogen, chemically reasonably or not. Please explain this problem and the use of restraints e.g. in `_refine_special_details`. Additionally, the data seems to be cut at 125 deg in theta, even if there is still strong diffraction power. Why? Please change or explain.

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item `_computing_data_collection` regarding the software used in this structure determination is missing. Please supply this value.

Structure 4 (CCDC 2119224): C54 H74 Au N4 P

Please note and explain the use of the very strong restraints, e.g. under `_refine_special_details`

An EADP for carbon and gold is physically not reasonable and should be avoided. If that is not possible, it must be noted and explained.

The absorption coefficient is given as 5.867. Absorption correction must be carried out and reported correctly. Tmax is reported as 0.0237 and Tmin is given as 0.0008. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item `_computing_data_collection` regarding the software used in this structure determination is missing. Please supply this value.

Structure 7 (CCDC 2119221): C62 H82 Au N4 P

Why were the data cut? Please change or explain.

These CheckCif A and B alerts are raised by this structure:

342_ALERT_3_B Low Bond Precision on C-C Bonds 0.02192 Ang.

The absorption coefficient is given as 4.952. Absorption correction must be carried out and reported correctly. Tmax is reported as 0.0853 and Tmin is given as 0.0090. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item `_computing_data_collection` regarding the software used in this structure determination is missing. Please supply this value.

Structure 3 (CCDC 2119225): C₅₆ H₇₈ Au N₆ P

The absorption coefficient is given as 5.396. Absorption correction must be carried out and reported correctly. Tmax is reported as ? and Tmin is given as ?. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item `_computing_data_collection` regarding the software used in this structure determination is missing. Please supply this value.

Structure 5 (CCDC 2119222): C₅₆ H₇₈ Au N₄ P

These CheckCif A and B alerts are raised by this structure:

094_ALERT_2_B Ratio of Maximum / Minimum Residual Density 5.75 Report

The absorption coefficient is given as 5.778. Absorption correction must be carried out and reported correctly. Tmax is reported as ? and Tmin is given as ?. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The following cif items regarding the software used in this structure determination are missing:

`_computing_data_collection`

`_computing_publication_material`

Please supply values for these items.

Structure 8 (CCDC 2119223): C₅₄ H₈₀ Au B₂ N₄ P

Isn't it possible to model the disordered solvent? Please do or explain.

These CheckCif A and B alerts are raised by this structure:

094_ALERT_2_B Ratio of Maximum / Minimum Residual Density 6.66 Report

The absorption coefficient is given as 5.505. Absorption correction must be carried out and reported correctly. Tmax is reported as 0.1713 and Tmin is given as 0.0605. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item `_computing_data_collection` regarding the software used in this structure determination is missing. Please supply this value.

Structure 7' (CCDC 2162450): C₆₉ H₉₈ Au N₄ P

The absorption coefficient is given as 4.963. Absorption correction must be carried out and reported correctly. Tmax is reported as ? and Tmin is given as ?. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The following cif items regarding the software used in this structure determination are missing:

_computing_data_collection

_computing_publication_material

Please supply values for these items.

Structure 7" (CCDC 2162451): C68 H96 Au N4 P

Why were the data cut at 130 deg. in theta? Please change or explain.

The absorption coefficient is given as 4.943. Absorption correction must be carried out and reported correctly. Tmax is reported as 0.7540 and Tmin is given as 0.5859. The absorption correction type is reported as 'none'. Additional Info: The crystal size is given as 0.1 x 0.1 x 0.1 mm³.)

The crystal size is reported as 0.1 x 0.1 x 0.1 mm³. All crystal dimensions are the same. Please Check!

The cif item _computing_data_collection regarding the software used in this structure determination is missing. Please supply this value.