

A Crystalline Uranium Fischer-Type Carbyne

Corresponding Author: Professor Stephen Liddle

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Comments for the Author)

The refinements for 3-IAM and 3-HAR contain a restraint on the C-N distance, and it is not stated how this value was arrived at. This could have the knock on effect of alter the U-C C-N bound distance the authors rely on. So I would need to see the values with this removed before I would be happy that the crystallography supports the conclusions.

The Crystallography for 6, 7, 8 and 9 has been done well. The authors have use `_refine_special_details` explaining what they did in the refinement, and these are clear and make sense. The numbering scheme across these structure is consistent making it easier to compare bonds. Would be nice if the hydrogen name in 9 made more sense. CHECKCIF ALERT `_vrf`'s filled out and again explanations are reasonable.

3-IAM and 3-HAR.

Lack the explanation of what was done in the refinement and why, one AERTA not explained or fixed. The numbering scheme is straight out of SHELXT and no effort has be made to make it consistent with the other structure. As it stands is it difficult to compare bonds without have a numbered molecule and the table open together. This needs fixing.

Also in CHECKCIF: Why is the Calculated mu and reported different? Report F000 same as calculate F000' and not F000 why?

At the end of the CIFs both indicate the crystal was twinned, and if I read the operator correctly it would appear the twin law is a 2-fold rotation about the b-axis, this make not sense as this is a symmetry operator of the spacegroup. The use of `_refine_special_details` could have explained this and the other issue.

However, to me the biggest issue is that they both contain DFIX 1.2 N009 C00O. With the manuscript based around the U-C C-N bond lengths this restrain potential effects the values of these. The refinement needs to be repeated with the DFIX removed to make sure we are getting meaningful values. If that fails then a restraint could be use if the value can be justified from another source.

Reviewer #2

(Comments for the Author)

This manuscript describes the synthesis and characterization of a uranium complex assigned as a Fischer-type carbyne, representing an ambitious target in f-element chemistry. The synthetic and experimental characterization is notable.

However, the central claim—that the complex contains a uranium Fischer-type carbyne featuring a $\text{U}\equiv\text{C}$ triple bond—is not supported by the evidence presented and is significantly overstated. In its current form, the manuscript does not meet the standard required for publication in a high-impact journal.

The primary issue lies in the interpretation of the U–C bonding. The assignment of a formal triple bond is not justified by either structural or computational metrics. The reported U–C bond length of 2.379(15) Å, while shorter than typical U–C single bonds, is notably longer than established U=C double bonds (~2.28–2.31 Å). This places the interaction in an intermediate regime, inconsistent with a well-defined triple bond. This discrepancy is further reinforced by the computed bond order (~1.2–1.3), which falls far short of that expected for triple bonding. The U–C bond order is even smaller than the U–N (1.61). Rather than indicating a classical $\text{U}\equiv\text{C}$ interaction, the data support a polarized, delocalized multiple bond with limited π character. The manuscript does not adequately reconcile this inconsistency between structural parameters and the proposed bonding model.

The analogy to Fischer-type carbynes is also only partially applicable and is overstretched in its current presentation. The reported system features a bridging (μ -CNN) ligand and exhibits clear multi-center delocalization across the U–C–N–N–U framework. These features deviate substantially from the canonical donor–acceptor description of terminal Fischer carbynes in transition metal chemistry. While the system may exhibit some Fischer-like characteristics, it does not constitute a direct analogue, and the current description risks conflating distinct bonding regimes.

The computational analysis, while thorough in scope, does not provide sufficient rigor to support the strong bonding claims being made. The reliance on DFT, NLMO, QTAIM, and electron density visualization techniques is appropriate but inherently qualitative, particularly for f-element systems where near-degeneracy and correlation effects are significant. No meaningful benchmarking against known triple-bond systems or alternative bonding models is provided. As such, the computational results are consistent with a carbyne-like interaction but do not substantiate the assignment of a true triple bond.

Furthermore, the reactivity data do not meaningfully support the proposed bonding description. The reactions are largely sluggish or inconclusive, and the expected reactivity patterns that would help distinguish Fischer-type behavior are not clearly demonstrated. This limits the functional validation of the bonding assignment and weakens the overall argument.

Taken together, the manuscript presents a good synthetic result but overinterprets the nature of the bonding. The data support the presence of an unusual uranium–carbon multiple bond with donor–acceptor character, but not a definitive Fischer-type carbyne triple bond. The central claim, as currently framed, is therefore misleading.

Reviewer #3

(Comments for the Author)

The manuscript by Liddle, Hansmann, Bodensteiner and their respective co-workers and co workers presents the synthesis and reactivity of a uranium Fischer type carbyne complex. In broad terms the work is both interesting and timely, and the authors have produced a very clearly written paper in which the experimental methodology is of a uniformly high standard. The isolation of complex 3, in particular, constitutes a noteworthy addition to the f element literature, and the authors have invested considerable effort in probing its bonding beyond the mere acquisition of a crystal structure. Nevertheless, the reactivity of 3 is rather underwhelming. Apart from the reduction that furnishes complex 9 and the formation of the Lewis base adducts 7 and 8, the only other transformations observed are low yielding and give rise to unexpected side products. While I commend the thoroughness of the synthetic work, the modest scope of the reaction chemistry detracts from the overall impact of the study. A further concern relates to the claim that complex 3 is a “Fischer type carbyne”. This assignment rests heavily on the computational analyses; the experimental bond distances (U–C, C–N, N–N and N–U) do not unambiguously support such a description.

In Fig. 1c the authors invoke several resonance structures, yet natural resonance theory (NRT) – a tool that would be particularly appropriate for assessing the degree of covalency and bond order in this system – has not been employed. A more detailed discussion of the U–C force constant would also be desirable: does it really correspond to a bona fide $\text{U}\equiv\text{C}$ triple bond? The manuscript repeatedly discusses polar multiple bonds and relies on the results of the quantum chemical HAR analysis to justify the Fischer type carbyne label. However, the HAR treatment ultimately indicates interactions consistent with a Fischer carbyne but falls short of establishing a true $\text{U}\equiv\text{C}$ triple bond. In my view this stretches the analogy somewhat.

It would be valuable to know how the bonding picture would be altered if the TMS substituents were replaced (computationally) by a methyl group; such a model could illuminate the role of steric congestion in the U–C–N–N–U motif. Steric effects may also underpin the sluggish and poorly controlled reactivity of 3, a point that the authors attribute mainly to the formal Fischer carbyne character – an interpretation that perhaps warrants tempering.

In summary, the study is well executed and will interest a broad readership encompassing inorganic, organometallic and f element chemists. The experimental work is exemplary, yet the limited reactivity of complex 3 and the somewhat tenuous structural assignment make me hesitant to recommend this paper for Nature Chemistry in its present form. Journals such as JACS, Angewandte Chemie or Chemical Science might provide a more suitable venue, unless the authors can convincingly address the points raised below. Should the other reviewers be more enthusiastic, I would be prepared to reconsider my stance, provided that the concerns are fully resolved.

SI:

Figs. S34 and S35: an additional resonance at –7 ppm is observed. Please comment on its possible origin.

Fig. S32: the integration range does not encompass the full width of the resonances; please adjust the limits to ensure accurate integration.

complex 9 (tsgcy8): the X ray data are of limited quality. Were further diffraction experiments attempted to obtain a better data set? If not, explain the constraints. data?

Checkcif for tqgcy7: shows an undressed A alert. Please address this issue and, if necessary, provide the corrected model. The nomenclature of the checkcif files does not agree with the nomenclature used for the cifs, e.g. t8gcy7 vs. tsgcy8. This was rather confusing to me.

Reviewer #4

(Comments for the Author)

The authors report the product of the reaction between a classic, low-coordinate U(III) complex and the recently reported C-atom transfer reagent, Ph₃PCN₂. At the time of the report of the novel C-atom transfer reagent, this potential reaction and a range of related systems was intensely discussed in the actinide synthetic chemistry community. I am happy to see it reported in detail. In this regard, it is a timely report and should be pushed to print rapidly as it is an accessible and widely recognized reaction to study and many groups may be pursuing it. Unfortunately, the reaction does not directly form a terminal carbide – potentially a target that might yet be realized by other ligand systems. The observed product – a bridging diazomethanediide which results from the net 2 electron reduction of Ph₃PCN₂ with the elimination of Ph₃P – is the expected product for this reaction (the carbide was a low probability possibility). This paper derives its potential, high-level import though not from the reporting this expected product that is entirely congruent with established chemistry of [U(III)N³], rather the bold claim of its underlying bonding structure which inspires the title and the description of the product as a Fischer carbyne (rather than a diazomethanediide). Such an argument reminded me of similar descriptions for bridging carbon dianions in the uranium literature (wherein the most interesting extreme of a continuum of potential bonding interactions was presented, for example the report of a bimetallic uranium dicarbide – instead of a bridging acetylide, DT, 2010, 6632). It took me several readings of the authors' manuscript to warm to its final analysis. The authors may wish to consider whether the current presentation brings the community on board with their analysis effectively at the beginning of the manuscript (maybe more directly presenting the carbyne limiting structure as one of several contributing resonance structures).

The authors present significant crystallographic and spectroscopic studies to substantiate multiple bonding character of the U–C bond. The synthetic chemistry, magnetometry, UV-vis-NIR and IR spectroscopy, and crystallography are well-executed and well-presented. Having spent more time thinking about their analysis, I may yet be convinced that Nature Chemistry is an appropriate forum. However, the authors need to demonstrate that the interaction in this system substantially diverges from that observed in prior transition metal and actinide systems, or maybe in a continuum and establish a more broadly applicable bonding model for the bridging diazomethanediide ligand. With this goal in mind, I ask the authors to consider the following:

1) While the authors in ref 37 do not pursue deep analysis of the U-C bonding in their bridging diazomethanediide, whether this system presents similar bonding to this new diazomethanediide complex is central to the claim that this report is the first example of a uranium Fischer carbyne rather than another limited example of a bridging diazomethanediide with some multiple bonding character in the U-C bond that was not realized in the initial report. It would be helpful if the authors could delineate the spectroscopic and crystallographic differences between their compound 3 and the complexes 2 and 5 in the report from Walter and co-workers (maybe in detail in the SI beyond the brief crystallographic comparison in text). Revisiting Zi/Walter's complexes with the same level of theory as applied the manuscripts complex 3 would also be appropriate to substantiate this as a unique bonding rather than unrecognized feature of this area of chemistry that has not received much attention. To what extent do the Zi/Walter complexes have (or not) pi back-bonding from U to C by the same metrics applied herein?

2) Comparative IR analysis with compound 5 in Schneider's report (ref. 36) suggests that a similar, "marginal" pi-backbonding to the allenic fragment is taking place in the Pt system (the phrasing of Schneider and co-workers) – it is suggestive that the identification of Pt-carbyne resonance structure in this manuscript could have been presented as well. The observed IR stretch is higher than the U complex but lower than that of the Ph₃PCN₂ reagent. In light of literature comparisons in queries 1 and 2 might the results in the authors manuscript be representative of a continuum of pi backbonding to the diazomethanediide? The authors' assertion that "where no metal-carbon multiple bonding has been demonstrated in the small range of isolable CNN-complexes" is critical step in establishing the more wide-ranging import of this paper. The extant literature is not structured in its original form in a manner to readily support their claim, and therefore authors' should provide further analysis of the extant literature and potentially rework this claim. Is this bonding scenario unique to this complex, or all bridging diazomethanediide complexes potentially considered latent Fischer carbynes depending on the magnitude of metal to C pi-backbonding (and C to metal pi bonding)?

3) A thorium or cerium control complex is a necessary reference point that is missing from the authors' argument. The critical component of carbyne assignment in complex 3 is weak pi-backbonding from U to C. This bonding interaction should be absent in Th(IV) and Ce(IV). The comparable Th product cannot be prepared via redox route used by the authors, but could be accessible via a salt-metathesis route with Li[CN₂TMS] and 2 equivalents of [ThCIN³] (eliminating LiCl and TMSCl). The Ce analog might be prepared by the direct comparable redox reaction. Bonding in the bridging diazomethanediide in these complexes should demonstrably diverge due to the absence of this pi-backbonding interaction. Ideally, one or both of these complexes would be prepared for comparison. However, if these complexes cannot be prepared – they should be computationally considered and the differences in their bonding considered. Both should be diamagnetic and the ¹³C NMR (along with IR) should be used as a computational benchmark for the analysis.

The use of HAR refinement is central to the analysis of the bonding features. It is well done and significantly improves the argument of this manuscript.

Version 1:

Reviewer comments:

Reviewer #1

(Comments for the Author)

All my points have been answered to my satisfaction. The crystallography supports the authors' conclusions.

Reviewer #3

(Comments for the Author)

The authors responded well to all comments made by the referees and in my opinion most issues with the previous version of the manuscript are now resolved. Hence acceptance is now recommended.

Reviewer #4

(Comments for the Author)

I am very pleased with revisions and comments from the authors.

The manuscript is acceptable in its current form. I am looking forward to seeing it in print.

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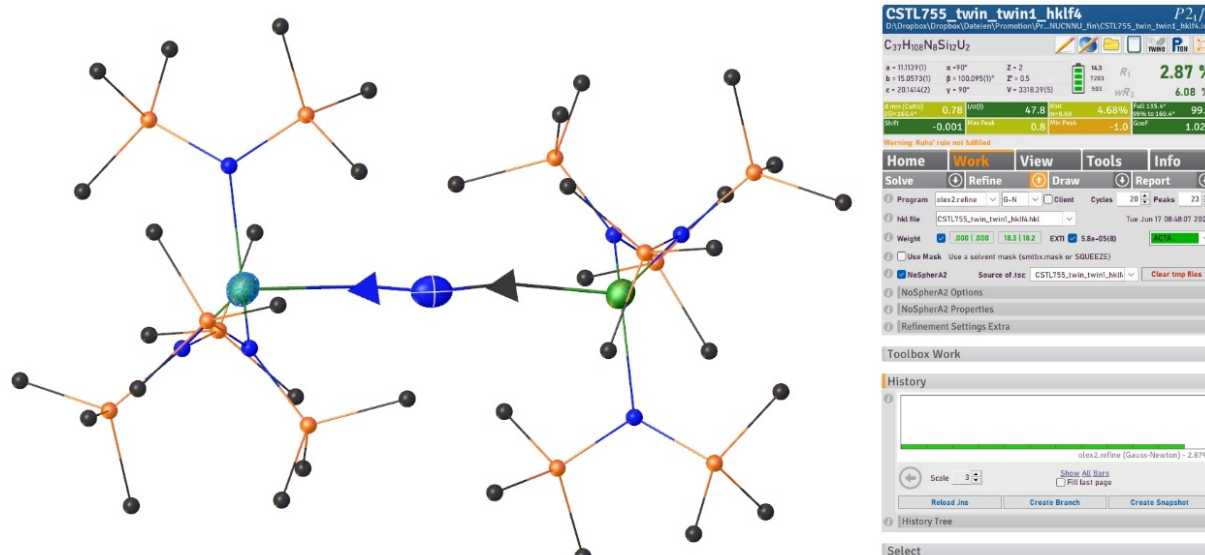
We thank the reviewers for their comments. A number of points have been raised which we are grateful for, and we are delighted to say we have been able to address them all. The manuscript is definitely stronger as a result so we sincerely thank the reviewers for their input.

Reviewer comments:

Reviewer #1 (Comments for the Author):

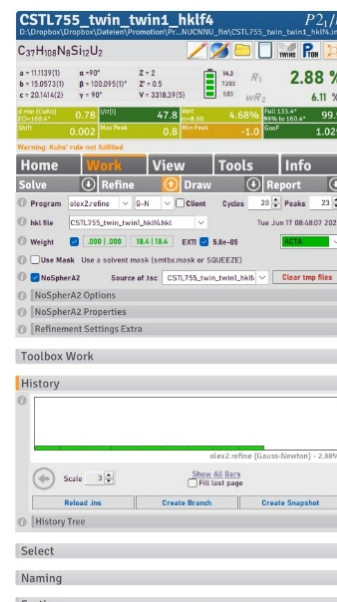
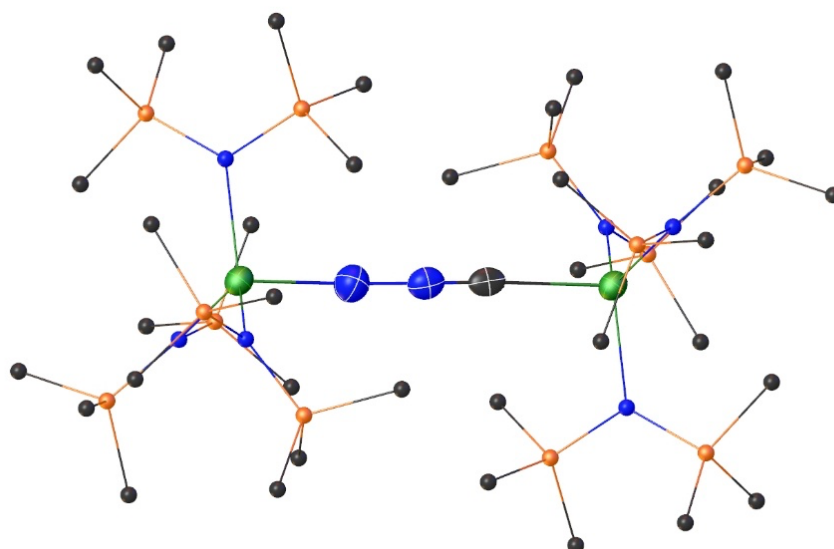
The refinements for 3-IAM and 3-HAR contain a restraint on the C-N distance, and it is not stated how this value was arrived at. This could have the knock on effect of alter the U-C C-N bound distance the authors rely on. So I would need to see the values with this removed before I would be happy that the crystallography supports the conclusions.

RESPONSE: We thank the reviewer for their thorough checking of our HAR crystallographic model of UCNNU. The structure of **3** exhibits a centre of inversion almost directly on N1. Without any constraints, the CNN unit converges to non-physical, non-positive-definite atoms (see figure below; the N-atom drifts onto the inversion centre when it is clearly located off to either side), with essentially the same R-factors.



3HAR after removing restraints on the UCNNU unit. Pyramids show negative atomic displacement parameters. Hydrogen atoms omitted for clarity.

The applied restraints are a combination of a crystallographic and a DFT-guided approach. First, we applied prominent restraints to the model in order to reach a physically sensible model, and then weakened the restraints to the point where refinement finds an optimum. We checked that these restraints are in agreement with the DFT-optimised structure. In the case of **3**, this optimum shows essentially the same quality indicators and needed a very soft, standard DFIX restraint on C1 and N1 to a distance of 1.2 Å as well as a rigid unit restraint on the whole UCNNU unit for ADP behaviour in a flat refinement landscape. Despite the distance restraint, the crystallographic model had the freedom and converged on a C1-N1 distance of 1.115(15)Å, further cementing that this restraint is for *guidance*, not *enforcement*, exactly how restraints should be applied. Fortunately, **9** crystallises with an ordered CNN unit, and that structure helps us to have confidence in **3**, and indeed the reviewer (below) mentions they consider **9** to be done well supporting **3** more. Specifically, in **9** there is increased U→C back-bonding which should lengthen and shorten the C-N and N-N distances from **3** to **9**, and that is exactly what we observe.



3HAR in the submitted crystal structure with applied restraints. Hydrogen atoms omitted for clarity.

The Crystallography for 6, 7, 8 and 9 has been done well. The authors have use `_refine_special_details` explaining what they did in the refinement, and these are clear and make sense. The numbering scheme across these structure is consistent making it easier to compare bonds. Would be nice if the hydrogen name in 9 made more sense. CHECKCIF ALERT `_vrf`'s filled out and again explanations are reasonable.

RESPONSE: We thank the reviewer for spotting the strange H labels in 9. We are not sure what happened there, but these have now been fixed.

3-IAM and 3-HAR.

Lack the explanation of what was done in the refinement and why, one AERTA not explained or fixed. The numbering scheme is straight out of SHELXT and no effort has be made to make it consistent with the other structure. As it stands is it difficult to compare bonds without have a numbered molecule and the table open together. This needs fixing.

RESPONSE: We thank the reviewer for spotting this. When the cif of 3HAR was finally renamed for the upload to the name used in our manuscript, the second cif data block containing the fcf information was not renamed, raising an A-ALERT for missing the fcf part. We changed the datablock name accordingly and report that, as before, the structure does not raise A- and B-level alerts. We adapted the naming scheme in the cif to the ones in the other structures.

Also in CHECKCIF: Why is the Calculated mu and reported different? Report F000 same as calculate F000' and not F000 why?

RESPONSE: This is due to the different definitions of F000 and F000'. While F000 is the fully elastic form factor, F000' takes into account inelastic and resonant effects, mostly anomalous dispersion corrections, which indicate the real scattering power.

The Olex2 F000 is equal to the number of electrons contributing to elastic scattering; the checkcif provides its F000' as F000 with a different source of anomalous dispersion correction. We applied

as described in our cif, Brennan and Cowan anomalous dispersion correction, which we found to be a superior description especially for heavy element structures. Some of us published a study on this exactly for uranium compounds: *Inorg. Chem.* **2024**, *63*, 15784–15790, (<https://doi.org/10.1021/acs.inorgchem.4c01772>).

At the end of the CIFs both indicate the crystal was twinned, and if I read the operator correctly it would appear the twin law is a 2-fold rotation about the b-axis, this make not sense as this is a symmetry operator of the spacegroup. The use of `_refine_special_details` could have explained this and the other issue.

RESPONSE: The crystal of **3** was twinned, with two domains of 61.8 to 35.2 % (2% were unindexed) and very little overlap (1.6%) of the respective indexed reflections. We carefully considered the twinning of this crystal using twinned processing in CrysAlisPro. Because of the low overlap, the corrected hklf4 reflection file provided the best indicators for intensity and Rint/Rmerge. Therefore, the hklf4 .hkl file was used for the crystallographic refinement. We added these details in the cif:

“During processing, non-merohedral twinning was detected. The major component was indexed with 61.8%, the second component with 36.8% and 2.9% unindexed reflections. The overlap was in 2% of indexed reflections.”

and

“Twinning was taking into account in CrysAlisPro, and the twinning corrected hklf4 file was used for refinement, as the intensity (17.0 vs 14.7 F²/sig(F²) in CAP) and internal agreement statistics (Rint for this hklf4: 4.7%, second component hklf4: 6.4%, mixed hklf5: 5.1%) indicated better data.”

However, to me the biggest issue is that they both contain DFIX 1.2 N009 C000. With the manuscript based around the U-C C-N bond lengths this restrain potential effects the values of these. The refinement needs to be repeated with the DFIX removed to make sure we are getting meaningful values. If that fails then a restraint could be use if the value can be justified from another source.

RESPONSE: We believe that our explanations ameliorate the reviewer’s queries and thank them for the opportunity to check and clarify these important points.

Reviewer #2 (Comments for the Author):

This manuscript describes the synthesis and characterization of a uranium complex assigned as a Fischer-type carbyne, representing an ambitious target in f-element chemistry. The synthetic and experimental characterization is notable. However, the central claim—that the complex contains a uranium Fischer-type carbyne featuring a U≡C triple bond—is not supported by the evidence presented and is significantly overstated. In its current form, the manuscript does not meet the standard required for publication in a high-impact journal.

RESPONSE: We thank the reviewer for their report and appreciate the opportunity to reply. We believe that our clarifications can convince the reviewer that all is in order, and indeed that we have secured a notable structural linkage with a conceptual advance which justifies publication in *Nature Chemistry*.

The primary issue lies in the interpretation of the U–C bonding. The assignment of a formal triple bond is not justified by either structural or computational metrics. The reported U–C bond length

of 2.379(15) Å, while shorter than typical U–C single bonds, is notably longer than established U=C double bonds (~2.28–2.31 Å). This places the interaction in an intermediate regime, inconsistent with a well-defined triple bond. This discrepancy is further reinforced by the computed bond order (~1.2–1.3), which falls far short of that expected for triple bonding. The U–C bond order is even smaller than the U–N (1.61). Rather than indicating a classical U≡C interaction, the data support a polarized, delocalized multiple bond with limited π character. The manuscript does not adequately reconcile this inconsistency between structural parameters and the proposed bonding model.

Re. bond lengths, the actinides are an area of the Periodic Table where bond lengths are not always linearly reflective of the bonding in the way they are for lighter elements. Indeed, this phenomenon extends to other heavy metals. For example, Power's plumblynes do not always follow anticipated trends due to the unusual bonding that they engage in. Even when such relationships hold for covalent and polar covalent bonds that is not what is reported here. In this submission we candidly describe $\sigma^2 \pi^1 \pi^1$ bonds which are not going to follow classical bond order/bond length relationships, especially when considering that the UC linkage in **3** is a mixture of polar covalent and donor-acceptor character so it is not appropriate to frame the UC bonding in **3** in the context of a formal triple [covalent] bond. Indeed, we think it is entirely consistent for a $\sigma^2 \pi^1 \pi^1$ covalent/dative/dative triple bond to be shorter than a σ^2 covalent single bond but longer than a $\sigma^2 \pi^2$ covalent double bond (i.e. $1 \times 2e \text{ covalent} > 2 \times 1e \text{ dative}$), which is what we find. As an aside, we would like to note that there is no such thing as "*a classical U≡C interaction*" in the sense that there is no uranium Schrock alkylidyne under normal experimental conditions, only the matrix example that we cited. We understand that phrase is used in the context of d-block examples, but we think it is important to be clear that there is not a universal standard for uranium to compare to.

Re. bond orders, because there are 4 electrons in the $\sigma^2 \pi^1 \pi^1$ bond then the maximum bond order would be expected to be 2 for this triple interaction, but it is polar covalent/dative/dative so then 1.2-1.3 is not unreasonable; indeed it is expected. In RSC Adv. **2019**, 9, 17072 the different contributions from σ and π components to a bond order are discussed, and that is what is going on here – to make up some numbers to illustrate the point, the bond order of 1.2 could be considered to be 0.8 from σ and 2×0.2 for the $2 \times \pi$ components; we note that σ -only **3Ce** and **3Th** also have computed bond orders that align with that. That would give a three-fold triple [bond] interaction but with a low bond order because it is 4 electron $\sigma^2 \pi^1 \pi^1$ instead of the 6 electron $\sigma^2 \pi^2 \pi^2$ of a formal covalent triple bond. We would also point out that both experiment (HAR) and computation (DFT) describe the same bonding picture and it cannot be ignored that the UC end looks very similar to the UN end. Conceptually, this is certainly not routine, and so novel, so the reviewer is not wrong to raise it so we have directly addressed these points in the revised manuscript.

The analogy to Fischer-type carbynes is also only partially applicable and is overstretched in its current presentation. The reported system features a bridging (μ -CNN) ligand and exhibits clear multi-center delocalization across the U–C–N–N–U framework. These features deviate substantially from the canonical donor–acceptor description of terminal Fischer carbynes in transition metal chemistry. While the system may exhibit some Fischer-like characteristics, it does not constitute a direct analogue, and the current description risks conflating distinct bonding regimes.

RESPONSE: We thank the reviewer for highlighting this and we agree that the system exhibits some Fischer-like character but is not a direct analogue. Indeed, that was the exact point we made in the final sentence of the abstract. On reflection, we think that in an [earnest] attempt to be clear we may have confused matters by over-using "type" since that is often attached to Schrock and Fischer labels, but including it here and calling **3** Fischer-type hasn't achieved the clarity we aimed for. We

have thus removed “type” from all references to classical Fischer and Schrock systems, hence increasing the contrast to when “type” is used – especially after the framing of the final sentence of the abstract – that so it should now be clear that we are referring to **3** as not being a direct analogue of a classical Fischer carbyne.

The computational analysis, while thorough in scope, does not provide sufficient rigor to support the strong bonding claims being made. The reliance on DFT, NLMO, QTAIM, and electron density visualization techniques is appropriate but inherently qualitative, particularly for f-element systems where near-degeneracy and correlation effects are significant. No meaningful benchmarking against known triple-bond systems or alternative bonding models is provided. As such, the computational results are consistent with a carbyne-like interaction but do not substantiate the assignment of a true triple bond.

RESPONSE: We agree that it is wise to be cautious. Indeed, we were also rather sceptical of the DFT result at first, which is precisely why we conducted the quantum crystallographic HAR analysis to back up the computational bonding picture; in that regard it is important to not lose sight of the fact that the experimental (HAR) and computational (DFT) bonding descriptions are consistent with one another.

We considered benchmarking before submission but cannot see what would be gained from comparing the polar covalent/donor acceptor $\sigma^2 \pi^1 \pi^1$ UC bond reported here to a $\sigma^2 \pi^2 \pi^2$ UC “true triple bond” because they are completely different – we would be comparing apples and oranges. We would candidly predict that the latter would generate a UC bond order >2.5 but do not see what that would accomplish or prove given, as we addressed above, a $\sigma^2 \pi^1 \pi^1$ UC bond would be limited to a bond order of 2 and being polar a value between 1 and 2 would be expected, which is what we find. In the absence of specifics we are also not sure what alternative bonding models would be informative, we are not aware of any other $\sigma^2 \pi^1 \pi^1$ UC bonds to compare **3** to, except perhaps we have addressed this in the substantial number of extra calculations we have done in response to reviewer 4. However, we agree with the reviewer’s statement that the UC bond is “carbyne-like” and is not a “true triple bond” because it is a $\sigma^2 \pi^1 \pi^1$ UC bond of mixed polar covalent and donor acceptor character.

Lastly, we should not forget that when **3** is reduced to **9** the UC bond order increases which is exactly what would be expected for Fischer-type bonding. We agree that these are important issues, so have now directly addressed the in the introduction and the discussion where we have sought to be clearer that Fischer-type is not the same as a true Schrock alkylidyne covalent triple bond.

Furthermore, the reactivity data do not meaningfully support the proposed bonding description. The reactions are largely sluggish or inconclusive, and the expected reactivity patterns that would help distinguish Fischer-type behavior are not clearly demonstrated. This limits the functional validation of the bonding assignment and weakens the overall argument.

RESPONSE: As amply discussed in reference 9 (*Coord. Chem. Rev.* **2021**, 449, 214203), terminal Fischer carbynes are comprehensively established as not being very reactive, and the way to make them reactive is to have the carbyne centre bridging. To quote from that review “*The main chemical implication of the presence of the amino group is a sluggish reactivity, compared to classical alkylidyne compounds.*”. Therefore, we did the reactivity study not expecting much reactivity, and to be honest we were surprised to observe as much reactivity out of it as we did. The purpose of our reactivity study was to ascertain if our complex lacks reactivity and hence parallels classical

Fischer carbyne; that is exactly what we found. Given that we tested a hypothesis and confirmed it, it seems strange, perverse even, to then suggest that the lack of reactivity, which is confirmatory, is somehow a negative. We posit it is in fact the opposite. We have provided an additional statement in the reactivity section to further clarify this matter.

Taken together, the manuscript presents a good synthetic result but overinterprets the nature of the bonding. The data support the presence of an unusual uranium–carbon multiple bond with donor–acceptor character, but not a definitive Fischer-type carbyne triple bond. The central claim, as currently framed, is therefore misleading.

RESPONSE: We hope that our clarifications have demonstrated that our assignment is correct and indeed internally consistent. Indeed, the reviewer acknowledges that the complex contains a UC multiple bond. The issue is for us to better articulate the fundamental difference between donor acceptor $\sigma^2 \pi^1 \pi^1$ and covalent $\sigma^2 \pi^2 \pi^2$ UC triple bonds since that also reframes the bond orders. We hope the reviewer can agree that we have done that in the revision.

Reviewer #3 (Comments for the Author):

The manuscript by Liddle, Hansmann, Bodensteiner and their respective co-workers and co workers presents the synthesis and reactivity of a uranium Fischer type carbyne complex. In broad terms the work is both interesting and timely, and the authors have produced a very clearly written paper in which the experimental methodology is of a uniformly high standard. The isolation of complex 3, in particular, constitutes a noteworthy addition to the f element literature, and the authors have invested considerable effort in probing its bonding beyond the mere acquisition of a crystal structure. Nevertheless, the reactivity of 3 is rather underwhelming. Apart from the reduction that furnishes complex 9 and the formation of the Lewis base adducts 7 and 8, the only other transformations observed are low yielding and give rise to unexpected side products.

RESPONSE: We are delighted that the reviewer agrees that we have a noteworthy addition to the f element literature. We believe that we have also made a conceptual advance, but perhaps not conveyed it as clearly as we wished so appreciate the opportunity to provide clarifications and a revised manuscript.

As we mentioned earlier, amino-carbynes are well known for their lack of reactivity (reference 9, *Coord. Chem. Rev.* **2021**, 449, 214203) when terminal and the way to make them reactive is to have the carbyne centre bridging metals. We therefore sought to establish reactivity and were surprised to coax as much reactivity out of our system as we got, but the central and vital point is the general lack of reactivity is entirely consistent with Fischer character. We tested a hypothesis and confirmed it, so it is not logical to then suggest that the lack of reactivity, which is confirmatory, is a negative.

While I commend the thoroughness of the synthetic work, the modest scope of the reaction chemistry detracts from the overall impact of the study. A further concern relates to the claim that complex 3 is a “Fischer type carbyne”. This assignment rests heavily on the computational analyses; the experimental bond distances (U–C, C–N, N–N and N–U) do not unambiguously support such a description.

RESPONSE: We have addressed the reactivity earlier. We addressed concerns about computational analysis and bond lengths earlier in detail, but to summarise again here:

1. Bond lengths do not always fully correlate to bond orders for heavy elements.

2. The UC bond in **3** is a polar covalent/donor acceptor 4 electron $\sigma^2 \pi^1 \pi^1$ bond and hence very different to a covalent triple 6 electron $\sigma^2 \pi^2 \pi^2$ bond – they are not comparable.
3. It is actually completely consistent and expected for a $\sigma^2 \pi^1 \pi^1$ covalent/dative/dative triple bond to be shorter than a σ^2 covalent single bond but longer than a $\sigma^2 \pi^2$ covalent double bond
4. Noting that **3** has a 4 electron triple bonding interaction, its maximum bond order could be 2, but it is polar so then a bond order of 1-2 would be anticipated which is what we find and there is not any contradiction to that bond order and the bonding interaction being three-fold (RSC Adv. **2019**, 9, 17072).
5. The quantum crystallographic HAR analysis backs up the computational bonding picture; in that regard it is important to not lose sight of the fact that the experimental (HAR) and computational (DFT) bonding descriptions are consistent with one another.
6. We were candid that **3** is Fischer-type and hence not a classical Fischer carbyne. That is novel.
7. Reducing **3** to **9** produces a higher U-C bond order which is Fischer behaviour.

In Fig. 1c the authors invoke several resonance structures, yet natural resonance theory (NRT) – a tool that would be particularly appropriate for assessing the degree of covalency and bond order in this system – has not been employed. A more detailed discussion of the U–C force constant would also be desirable: does it really correspond to a bona fide $\text{U}\equiv\text{C}$ triple bond? The manuscript repeatedly discusses polar multiple bonds and relies on the results of the quantum chemical HAR analysis to justify the Fischer type carbyne label. However, the HAR treatment ultimately indicates interactions consistent with a Fischer carbyne but falls short of establishing a true $\text{U}\equiv\text{C}$ triple bond. In my view this stretches the analogy somewhat.

RESPONSE: We looked at NRT before submission. Sadly, the program will not run due to hardwired memory issues as shown below:

NATURAL RESONANCE THEORY ANALYSIS, alpha spin:

This calculation has attempted to allocate 153806663 words of scratch memory, but NBO is currently configured with only 131072000 words. If you have the NBO6 source distribution, you can reconfigure the NBO program by editing maxmem.fh in nbo6/src/nbo/include and rebuilding the executables.

Maximum scratch memory used by NBO was 128806663 words (982.72 MB)
Maximum scratch memory used by GENNBO was 899994 words (6.87 MB)

That occurred for the heavily truncated molecule $(\text{H}_2\text{N})_3\text{UCNNU}(\text{NH}_2)_3$. It is already questionable whether such a truncated model would return a meaningful answer with respect to the full molecule – a H atom is not a consequence-free surrogate for SiMe_3 – yet even at that greatly truncated level the calculation is not accessible to us. The only thing left would be to use a DZP basis set, but double ζ simply isn't sufficient and the result would be far too compromised to be of value. Recompiling would not assist due to hard limits on the central high performance computing cluster.

However, NRT has well-known shortcomings. As an example, when Bertrand reported his phosphinidene (Chem **2016**, 1, 147) NRT did not do a good job of modelling NHCs, which does not give confidence for computing a linkage involving an actinide.

There are at least 2 IR UC stretches for **3**, so it is not clear to us which of those would be sensible and meaningful to quote in terms of force constants – because there are two but also they are not isolated, they are part of UCNU chains where the UN bond will affect the UC bond and there is no way to decompose this in a consistent isolated way.

Also, again, since the UC bond in **3** is a 4 electron $\sigma^2 \pi^1 \pi^1$ bond it would be apples and oranges to compare it to a “bona fide $\text{U}\equiv\text{C}$ triple bond” – in advance we would predict the UC bond in **3** to be weaker because it is not a “bona fide $\text{U}\equiv\text{C}$ triple bond” it is a polar covalent/donor acceptor $\sigma^2 \pi^1 \pi^1$ UC triple bonding interaction.

As to the reviewer’s final sentence, we are pleased that the reviewer states that the HAR analysis is robust and indicates a Fischer carbyne, and hence a triple bonding interaction, but, again, we did not claim “a true $\text{U}\equiv\text{C}$ triple bond”, we have been clear that it is a 4 (not 6) electron $\sigma^2 \pi^1 \pi^1$ bond.

However, we do thank the reviewer for challenging us, since we clearly have not been effective in getting our point over clearly in the previous version of the manuscript; evidently there needs to be better clarity between Fischer and Schrock formulations, so we have revised the manuscript in this round to address that matter.

It would be valuable to know how the bonding picture would be altered if the TMS substituents were replaced (computationally) by a methyl group; such a model could illuminate the role of steric congestion in the U–C–N–N–U motif. Steric effects may also underpin the sluggish and poorly controlled reactivity of **3**, a point that the authors attribute mainly to the formal Fischer carbyne character – an interpretation that perhaps warrants tempering.

RESPONSE: This is a good suggestion so we have computed the Me_2N analogue of **3**. The UC distance contracts by $\sim 0.012 \text{ \AA}$, as expected, along with a modest (0.02) increase in UC bond order. We fully appreciate what the reviewer means about sterics, but the facile formation of **7** and **8** suggest that sterics while not irrelevant are likely not decisive. However, we take the reviewer’s point so have tempered our language in that regard.

In summary, the study is well executed and will interest a broad readership encompassing inorganic, organometallic and f element chemists. The experimental work is exemplary, yet the limited reactivity of complex **3** and the somewhat tenuous structural assignment make me hesitant to recommend this paper for Nature Chemistry in its present form. Journals such as JACS, Angewandte Chemie or Chemical Science might provide a more suitable venue, unless the authors can convincingly address the points raised below. Should the other reviewers be more enthusiastic, I would be prepared to reconsider my stance, provided that the concerns are fully resolved.

RESPONSE: We hope that following our clarifications the reviewer can agree with our interpretations and hence support publication in *Nature Chemistry*.

SI:

Figs. S34 and S35: an additional resonance at -7 ppm is observed. Please comment on its possible origin.

RESPONSE: We do not know what that resonance corresponds to, but it is clearly a minor impurity. It integrates to only $\sim 3\text{H}$ so we have added a note to the figure captions now.

Fig. S32: the integration range does not encompass the full width of the resonances; please adjust the limits to ensure accurate integration.

RESPONSE: This has been fixed.

complex 9 (tsgcy8): the X ray data are of limited quality. Were further diffraction experiments attempted to obtain a better data set? If not, explain the constraints. data?

RESPONSE: The crystal of **9** appeared to degrade during the data collection. Data were therefore truncated to remove the lowest quality data from the refinements while maintaining a high completeness (99.9% at IUCr limit of 0.84 Å). Multiple attempts were made to obtain better quality data with other crystals, but none were successful due to repeated oiling out during crystal growth or decomposition during data collections. This has been addressed in the cif file.

Checkcif for tqgcy7: shows an undressed A alert. Please address this issue and, if necessary, provide the corrected model.

RESPONSE: This was also raised by reviewer 1. The unresolved level A alerts were due to mislabeled cif/fcf data blocks. This has now been fixed.

The nomenclature of the checkcif files does not agree with the nomenclature used for the cifs, e.g. t8gcy7 vs. tsgcy8. This was rather confusing to me.

RESPONSE: The checkcifs and cifs are now consistent. To be honest, we are not sure where the codes the reviewer mentions (e.g. t8gcy7) originate from since we cannot find any of them in our files.

Reviewer #4 (Comments for the Author):

The authors report the product of the reaction between a classic, low-coordinate U(III) complex and the recently reported C-atom transfer reagent, Ph₃PCN₂. At the time of the report of the novel C-atom transfer reagent, this potential reaction and a range of related systems was intensely discussed in the actinide synthetic chemistry community. I am happy to see it reported in detail. In this regard, it is a timely report and should be pushed to print rapidly as it is an accessible and widely recognized reaction to study and many groups may be pursuing it. Unfortunately, the reaction does not directly form a terminal carbide – potentially a target that might yet be realized by other ligand systems. The observed product – a bridging diazomethanediide which results from the net 2 electron reduction of Ph₃PCN₂ with the elimination of Ph₃P – is the expected product for this reaction (the carbide was a low probability possibility). This paper derives its potential, high-level import though not from the reporting this expected product that is entirely congruent with established chemistry of [U(III)N³⁻], rather the bold claim of its underlying bonding structure which inspires the title and the description of the product as a Fischer carbyne (rather than a diazomethanediide). Such an argument reminded me of similar descriptions for bridging carbon dianions in the uranium literature (wherein the most interesting extreme of a continuum of potential bonding interactions was presented, for example the report of a bimetallic uranium dicarbide – instead of a bridging acetylide, DT, 2010, 6632). It took me several readings of the authors' manuscript to warm to its final analysis. The authors may wish to consider whether the current presentation brings the community on board with their analysis effectively at the beginning of the manuscript (maybe more directly presenting the carbyne limiting structure as one of several contributing resonance structures).

RESPONSE: We thank the reviewer for their thoughts. We agree with the continuum comment, it was what we attempted, but evidently failed, to completely convey initially. We have revised the manuscript and hope that this is all now clear[er] in terms of articulating the conceptual advance of this non-routine result.

The authors present significant crystallographic and spectroscopic studies to substantiate multiple bonding character of the U–C bond. The synthetic chemistry, magnetometry, UV-vis-NIR and IR spectroscopy, and crystallography are well-executed and well-presented. Having spent more time thinking about their analysis, I may yet be convinced that Nature Chemistry is an appropriate forum. However, the authors need to demonstrate that the interaction in this system substantially diverges from that observed in prior transition metal and actinide systems, or maybe in a continuum and establish a more broadly applicable bonding model for the bridging diazomethanediide ligand. With this goal in mind, I ask the authors to consider the following:

RESPONSE: In our original submission we attempted to convey that the title complex **3** is different (the final sentence of the abstract, analogous text in the conclusions) but in hindsight realise that suffixing everything as “type” confused matters, by removing “type” from all mentions bar that of **3** we hope to have created the contrast we initially aimed for.

1) While the authors in ref 37 do not pursue deep analysis of the U-C bonding in their bridging diazomethanediide, whether this system presents similar bonding to this new diazomethanediide complex is central to the claim that this report is the first example of a uranium Fischer carbyne rather than another limited example of a bridging diazomethanediide with some multiple bonding character in the U-C bond that was not realized in the initial report. It would be helpful if the authors could delineate the spectroscopic and crystallographic differences between their compound **3** and the complexes **2** and **5** in the report from Walter and co-workers (maybe in detail in the SI beyond the brief crystallographic comparison in text). Revisiting Zi/Walter’s complexes with the same level of theory as applied the manuscripts complex **3** would also be appropriate to substantiate this as a unique bonding rather than unrecognized feature of this area of chemistry that has not received much attention. To what extent do the Zi/Walter complexes have (or not) pi back-bonding from U to C by the same metrics applied herein?

RESPONSE: We thank the reviewer for the excellent suggestion. We have computed complex **2** in ref 37; unfortunately, complex **5** in that study was out of computational reach since it contains 12 unpaired electrons and is a hexamer. We find a very weak UC back-bond in complex **2**, but only one, which is straightforwardly recognised as being the consequence of the two Cp ligands soaking up the majority of the orbital capacity so the uranium does not have a filled orbital with the right spatial arrangement to engage in a second back-bond; given the same local geometries there is no reason to think complex **5** in ref 37 would be any different. It is also noticeable that the UC back-bond in complex **2** of ref 37 is much, much weaker than in **3**, which again will relate to the saturation from the two Cp ligands. We also note that the CNN stretching frequency of complex **2** in ref 37 is higher than the compounds in this report, and indeed clustered with other complexes with little or no back-bonding (Table SX). There are hence some key conclusions to take from this:

1. Our initial comment (“where no metal-carbon multiple bonding has been demonstrated in the small range of isolable CNN-complexes”) was, and remains, correct, because this had not been probed before, but we added “previously” to clarify the point.
2. Now that we have looked into this, we see that our complex **3** (and **9**) are unique, the first UC triple bonds with CNN and indeed in a routinely isolable complex free of trapping effects, because the closest any other complex gets is complex **2** of ref 37 and even then the double

bond interaction is exceedingly weak (UC bond order 0.84, $\rho = 0.6$, this is 0.8 for **3**). This takes nothing away from fullerene species, which are anyhow Schrock analogues.

3. Discovering the triple bond interaction in **3** and a weak double bond interaction in complex 2 of ref 37 demonstrates that the MC bond flexes as a function of ancillary ligands. This is as would be expected but also goes to the continuum point, so it is nicely internally consistent and instructive.

Thus, **3** is a genuine first and conceptual advance, but we would absolutely agree that it is better contextualised and clarified following this extra work and that is now reflected in the revisions we have made. Also, having arrived at this clarification the comments we originally made in the introduction about having the right ancillary ligands is strengthened.

2) Comparative IR analysis with compound 5 in Schneider's report (ref. 36) suggests that a similar, "marginal" pi-backbonding to the allenic fragment is taking place in the Pt system (the phrasing of Schneider and co-workers) – it is suggestive that the identification of Pt-carbyne resonance structure in this manuscript could have been presented as well. The observed IR stretch is higher than the U complex but lower than that of the Ph₃PCN₂ reagent. In light of literature comparisons in queries 1 and 2 might the results in the authors manuscript be representative of a continuum of pi backbonding to the diazomethanediide? The authors' assertion that "where no metal-carbon multiple bonding has been demonstrated in the small range of isolable CNN-complexes" is critical step in establishing the more wide-ranging import of this paper. The extant literature is not structured in its original form in a manner to readily support their claim, and therefore authors' should provide further analysis of the extant literature and potentially rework this claim. Is this bonding scenario unique to this complex, or all bridging diazomethanediide complexes potentially considered latent Fischer carbynes depending on the magnitude of metal to C pi-backbonding (and C to metal pi bonding)?

RESPONSE: We thank the reviewer for further very helpful suggestions. The original sentence from Schneider's paper (ref 36) was "*Furthermore, the computations reveal marginal π -MO contributions of the Pt ions with the heterocumulene ligands.*" There are indeed marginal π -MO contributions, but understanding their precise nature is vital to addressing the reviewer's question. Inspired by the reviewer's prior suggestion we computed compounds 5 and 6 from ref 36 (we call them **II** and **III** to follow on from **I**). It is clear that while the MO manifold exhibits an exceedingly weak, marginal PtC back-bond (the tail of one lobe of a d orbital, Figure S120h/S121e), this is cancelled out by the anti-bonding π -MO combinations that are populated (Figure S120a/b) as evidenced by low PtC bond orders (0.72/0.78) – this cancellation is analogous to the classic oxo-wall/nitrene phenomena. So, there is not any net PtC back-bonding in those complexes, which also comes across in the IR data where the CNN stretches are at the higher end (unless cationic, but a different charge state is not directly comparable); this is also corroborated by NMR calculations, see later. By contrast, in **3** there is UC back-bonding but no cancelling anti-bonding component.

Hence, our original statement in the introduction "*where no metal-carbon multiple bonding has been demonstrated in the small range of isolable CNN-complexes*" remains correct, though now we add "previously" to be clearer. Also, the above demonstrates that we have obtained a structurally novel and notable linkage and that it is analogous to transition metal analogues yet distinct, demonstrating once again how f-element systems are often different.

We should point out that we are reluctant to put too much stress on the IR data because in each case the MCNN part is not in isolation, the NNM part must also be considered, and there is no way to know the give-and-take from one complex to another, but we note that the IR data for the U

complexes (not including charged **9**) in this submission are clustered and, generally speaking, away from the compounds with little or no back-bonding (e.g. **II**, again not including **III** because it is charged), reported or hypothetically computed, that also constitute a cluster with respect to each other. Thus, there is a general high-level trend but we don't think it'd be a good idea to get into an overly detailed discussion given the number of interlinked variables.

However, as per our comment earlier we absolutely agree with the continuum comment and addressing the issues raised and we believe that our revised manuscript deals with these aspects more adequately now.

Lastly, yes, we believe CNN ligands have the potential to be Fischer carbynes depending on the metal, the metal oxidation state and electron richness, and of course the ancillary ligands. We hope this conceptual advance now comes across more effectively where we have revised discussion to accommodate the above points.

3) A thorium or cerium control complex is a necessary reference point that is missing from the authors' argument. The critical component of carbyne assignment in complex **3** is weak pi-backbonding from U to C. This bonding interaction should be absent in Th(IV) and Ce(IV). The comparable Th product cannot be prepared via redox route used by the authors, but could be accessible via a salt-metathesis route with Li[CN₂TMS] and 2 equivalents of [ThCIN''₃] (eliminating LiCl and TMSCl). The Ce analog might be prepared by the direct comparable redox reaction. Bonding in the bridging diazomethanediide in these complexes should demonstrably diverge due to the absence of this pi-backbonding interaction. Ideally, one or both of these complexes would be prepared for comparison. However, if these complexes cannot be prepared – they should be computationally considered and the differences in their bonding considered. Both should be diamagnetic and the ¹³C NMR (along with IR) should be used as a computational benchmark for the analysis.

RESPONSE: We thank the reviewer for the good suggestion. We attempted the reaction of [CeN''₃] with Ph₃PCN₂, but the outcome is different to that with uranium. The ¹H NMR spectrum reveals that the product is still Ce(III); evidently the Ce(III/IV) redox couple is not sufficiently reducing, unlike the strongly reducing U(III/IV) redox couple. We have determined that the product of that reaction is [(Ph₃PCN₂)Ce^{III}N''₃] (**1Ce2**); the characterisation data unequivocally show that **1Ce2** is an adduct, and that while there is weak Ce^{III}→N back-bond the Ce^{III} ions are clearly not reducing enough to activate **2**. Complex **1Ce2** is formed irrespective of whether **2** is treated with 1 or 2 equivalents of [CeN''₃].

Turning to Th, [ThN''₃] does not exist so the reductive route with Ph₃PCN₂ is not available. So, as the reviewer suggested we attempted the reaction of 2 × [ThN''₃Cl] with Li[N₂CNSiMe₃]. It does not work as proposed, likely due to complications from C-/N-silyl-group migration or that to cleave the C-Si bond leads to various decomposition. Certainly, we previously demonstrated that multiple bond cleavage and capture events can happen with Li[N₂CNSiMe₃] (*Angew. Chem. Int. Ed.*, **2011**, *50*, 10440), which may account [analogously] for the fact the ¹H NMR spectrum of the crude reaction mixture exhibits 8 silyl environments. These observations underscore the point we originally made in the introduction of the paper about how Ph₃PCN₂ could offer better synthetic utility since it evidently avoids C-Si cleavage and silyl-migration complications.

Even though the Ce and Th analogues are not experimentally accessible, as requested we computed geometry optimised structures and, as expected, find proportionally longer MC bond distances and much reduced MC bond orders because there is not any MC back-bonding. The MC back-bonding

combinations are present in each LUMO manifold but by definition are vacant and virtual. Everything is as would be expected, but it was certainly a good suggestion to check.

We also computed the ^{13}C NMR δ for the CNN unit of the hypothetical Ce and Th analogues of **3** that could not be made. There is some uncertainty over what the exact δ values would be in the absence of experimental verification, since the precise amount of necessary Hartree Fock mixing cannot be known *a priori*, but given that we have demonstrated accurate computations previously for ^{13}C landing within the HF05-HF55% region, we can draw confidence that the experimental ^{13}C δ values for the Ce and Th analogues (that lack back-bonding) of **3** would be ~ 130 ppm. We note that the corresponding experimental ^{13}C δ for Pt complex **5** in ref 36 is 35 ppm. Hence, we can see that for the very electron-rich Pt derivatives where back-bonding is not present the δ is very low, and then for the electron-deficient Ce and Th complexes that would be polar but not back-bonded we find δ values >100 .

It is not currently possible for us to compute the full spin-orbit δ for the CNN of **3** because of its $5f^4$ open shell nature that would introduce paramagnetic contact and pseudo-contact shift terms and also the uranium g values, which aren't known and can't be determined (uranium(IV) is a non-Kramers ion and the EPR selection rules are almost never met for uranium(IV) except for high symmetry materials), would also modulate the paramagnetic and spin-orbit shielding tensors that modulate the chemical shift. So it is not possible, but even if it parts could be done it wouldn't be comparable to the Ce and Th theoretical analogues. Compound **3** is a quintet open-shell species, if we forced the electronic structure to be a closed-shell singlet by moving two α -spin electrons into the β -spin manifold we would change the bonding and so the electronic structure would not be relevant. However, we can extrapolate based on leading literature studies and the hypothetical Ce and Th analogues. From that, even with conservative extrapolations, that don't even include the deshielding effects of the back-bonding that is experimentally demonstrated by the HAR analysis, we can see that the likely chemical shift of the carbyne in **3** will likely be approaching classical Fischer carbyne values. We sincerely thank the reviewer for their suggestions because they have helped us to construct what we believe is a more rigorous and compelling bonding picture that is now beyond reasonable objection. We have revised the manuscript to accommodate these points now.

The use of HAR refinement is central to the analysis of the bonding features. It is well done and significantly improves the argument of this manuscript.

RESPONSE: Thank you. We wholeheartedly agree.

---End---

Reviewer #1:

Comments for the Author:

All my points have been answer to my satisfaction. The crystallography support the authors conclusions.

RESPONSE: We thank the reviewer for their time and comments which helped to improve the submission.

Reviewer #3:

Comments for the Author:

The authors responded well to all comments made by the referees and in my opinion most issues with the previous version of the manuscript are now resolved. Hence acceptance is now recommended.

RESPONSE: We thank the reviewer for their time and comments which helped to improve the submission.

Reviewer #4:

Comments for the Author:

I am very pleased with revisions and comments from the authors.

The manuscript is acceptable in its current form. I am looking forward to seeing it in print.

RESPONSE: We thank the reviewer for their time and comments which helped to improve the submission.

---End---