The reductive elimination of a diphosphine from a thorium compounds is examined in this communication (*Organometallics* **2017**, *ASAP*). The reductive elimination occurs due to participation of a redox active ligand and does not affect the valence of the thorium.

1. Reductive elimination is a common reaction in organometallic chemistry. It is typically observed with late transition metals and is not common for early transition metals or f-block metals. Why?
2. Why is thorium, in particular, unwilling to participate in reductive elimination reactions?
3. The starting material for this study is compound 1 in Scheme 2. Classify this compound, determine the ligand bond number and the valence of the metal. iThis is a tricky system to count, you need to look very closely at the group connecting the two five-membered rings.
4. The bidentate ligand in this compound contains two N-heterocyclic carbene groups that bond to the thorium. Describe the orbital interactions between an NHC ligand and the thorium.
5. The reaction of compound 1 with 2 equivalents of KHPMes results in the formation of compound 2Mes. Classify compound 2Mes, determine the ligand bond number and the valence of the metal. i In a brief sentence or two, compare your answers for 2Mes to your answer to question 3, in particular focusing on the valence of thorium in both compounds and the classification of the I and PHMes ligands.
6. The description of the NMR data for compound 2Mes on the second page of the paper introduces the terms magnetically nonequivalent and virtual coupling. The 31P{1H} NMR spectrum of compound 2Mes displays a singlet (Supporting Information Figure S14). The 31P NMR spectrum of compound 2Mes appears to be a doublet of triplets (Supporting Information Figure S11). Shown below is a drawing of 2Mes without the NHC ligands and with the mesityl groups replaced with an R. In addition, the phosphorus and hydrogen atoms are numbered to make referring to them easier. This particular representation is chosen because these groups have NO impact on the observed patterns in the 31P{1H} and 31P NMR spectra. In addition, thorium does NOT have a naturally occurring NMR active isotope. Based on this information, answer the following questions.



1. Why is there a singlet in the 31P{1H} NMR spectrum of 2Mes?
2. What is the difference between a 31P{1H} and a 31P NMR experiment?
3. How would you account for a doublet of triplets in any spectrum in which there are only spin ½ nuclei? Your explanation should NOT specifically refer to 2Mes, but rather just provide a rationale for this pattern. Using a tree diagram might prove helpful
4. Consider the picture of compound 2Mes above. Would you expect the coupling of P1 to be the same to H1 as to H2? Why or why not?
5. Based on your answer to question d, are the P atoms equivalent when taking the 31P NMR spectrum?
6. How do you account for the doublet of triplets observed in the 31P NMR spectrum?
7. The reaction of 2Mes with bipy results in the formation of compounds 3 and 4 as shown in Scheme 3. The authors describe this as a ligand-based reductive elimination as opposed to a classical reductive elimination, both of which are shown in Scheme 1. From this scheme, describe the differences and similarities in these two types of reductive elimination reactions
8. If the formation of compound 3 is truly a ligand-based reductive elimination, how must the incoming ligand be classified? Your answer to question 5 might prove useful in answering this question. Is this how bipy is normally classified?
9. Pictured below are three different views of the LUMO for bipy. Based on these pictures, describe how increasing the electron density in this molecular orbital by reducing it will likely impact the structure.

View 1: Perpendicular to the plan of the rings.



View 2: Perpendicular to view 1 with N atoms in back.



View 3: Perpendicular to view 1 with N atoms in front.



Calculated LUMO of bipy using density functional theory (B3LYP/6-311G) and Gaussian 09.

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

1. The crystal structure of compound 3 has been reported in another paper (Garner, M. E.; Hohloch, S.; Maron, L.; Arnold, J., *Organometallics*, **2016**, *35*, 2915). In that structure the C-C distance for the carbon atoms linking the two six-membered rings was determined to be 1.362(5) Å. In free bipy the C-C distance between the carbon atoms linking the two six-membered rings is 1.490(3) Å (Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H., *J. Am. Chem. Soc.*, **1981**, *103*, 4945). Describe how the molecule/ligands depicted in blue in scheme 3 indicates that the reductive elimination is ligand-based. As part of your discussion, you should consider the number of electrons in π-type orbitals on the ligand and the bond distances that were given.
2. Describe what the authors were able to determine about the mechanism for this reductive elimination.