Referee 1 (R1)

Comments: In this contribution, Liu investigated the reactivities of gold-substituted phosphines regarding on the cleavage of the Au-P bond. The highly covalent character of the Au-P bond prevents inserting into unsaturated chemical bonds. The authors present three different protocols to cleave the Au-P bond. The results hint mechanistic insights into TM-catalyzed phosphination reactions. Overall, I am in favor of publication of this work in Zeitschrift für anorganische und allgemeine Chemie. However, I noticed a few minor points that may require further revision.

1. It should be noticed, [LAu]+ in some cases is erroneously denoted as [LAu].

2. For the reported Au-Se bond length of LAuSeCN (2.4142(8)Å), the related reference should be added.

3. In Figure 3, the explanation of CAAC and NHC should be added to the figure legend.

Referee 2 (R2)

Comments: The experimental observations in this manuscript are noteworthy and provide useful information about the chemistry of the Au-phosphido group. However, the discussion and comparison to the literature needs improvement before publication.

1. Introduction: terminal late TM-phosphido complexes are rare. This is not true, see this recent review for many examples. Adv. Organomet. Chem. 2022, 77, 243-330.

2. Page 1, right column, line 2. "Owing to the d-p lone pair repulsion" is presented as a fact, without citation, but this is controversial, as in Comments Inorg. Chem. 1999, 21, 115-129, and summarized in ref 1a.

3. Results/discussion compares reactivity of Cu-phosphido vs Au-phosphido complexes, but are these the same multiple-bond substrates?

4. They cite ref 15, Duan, for addition of Pd-PR2 to an unsaturated substrate, but this was not proposed to be an insertion, as claimed, but instead nucleophilic attack

5. The Figure 1 chemistry is interesting and perhaps novel; what is the driving force for these exchanges? A possibly relevant comparison would be Pt-PR2/HPR2 exchanges in Organometallics 1998, 17, 652-660.

6. Above figure 2 they cite ref 18 for catalytic phosphination, in which a PR3 ligand in a cationic complex is replaced by PR2H. From the context, it seems that they intended to cite J. Am. Chem. Soc. 2006, 128, 2788-2789 instead of the 2007 Glueck paper in ref 18b.

7. The last sentence is confusing and the wording "highly impossible" does not make sense.

8. For the PPh2Se2 complexes 7a-7b, I don't understand the reported 77Se and 31P NMR spectra. There are two inequivalent Se positions, one bound to gold and one not, so why is there only one chemical shift reported? Likewise for the 31P NMR spectrum, shouldn't there be two different P-Se couplings? Perhaps there is rapid exchange of the Se positions on the NMR time scale?

9. In the NMR spectra in the SI, it would be helpful to include the structures of the complexes with the spectra.

Referee 3 (R3)

Comments: In their present manuscript, Liu and coworkers examine the stability of the Au-P bond in their recently reported AuPhos ligands. The phosphines showed surprisingly high stability towards unsaturated or even protic compounds, but reacted with strong metal bases, i.e. polar organometallics such as KPTMS2 via bond cleavage and elimination of MPPh2. Moreover, P-Au cleavage is observed under oxidizing conditions with elemental selenium. Furthermore, as preliminary indicated by DFT studies the strong metal phosphide interaction is weakened upon protonation, which is experimentally confirmed through simple phosphine exchange in the protonated species.

Overall, the paper provides first insights into the stability of the Au-P bond in AuPhos ligands. Given the unique donor properties of these metallophosphines, these results will certainly attract interest in the community of phosphorus chemists. The experimental studies are conducted on a high level, so that I recommend publication of this work in Zeitschrift für anorganische und allgemeine Chemie after the following questions have been addressed by the authors.

1. I would recommend to perform the bonding analysis on a higher level of theory, i.e. with a triple instead of a double zeta basis set. What basis set was used for gold? Has an effective core potential been applied? This information should be given in the SI.

2. The DFT studies reveal differences in the Au-P bonding in the complexes 1-4. Are there also any changes in the carbene-Au bonding. The corresponding Au-C bond indices should be added to Table 1.

3. The authors state: „The positive charge of the phosphonium in 4 strengthens the [LAu]+ nature with the apparent contribution from the resonance structure 4'." 4 is either a phosphine coordinated LAu+, or a phosphonium salt. The authors presumably mean „protonation favors the LAu+ nature".

4. The authors show 2 Lewis structures for complex 4, but there is also a further possible structure with the positive charge residing on the NHC. Which part of the complex takes up the majority of the positive charge, when comparing the NBO charges of 2 and 4 in Table 1?

5. Page 2, column 2, line 19: results consist should probably read: results are consistent with

6. As illustrated in Figure 3b, two structural isomers of 7a were observed…" Are these isomers or rotamers?