Comments:

The article by Liu and coworkers continues the work of other authors on the development of highly basic phosphines, particularly gold terminal phosphides. The authors have synthesized, characterized and thoroughly analyzed many derivatives, with the aim of demonstrating the stereoelectronic tunability of these species and their potential use as ligands in transition metal chemistry and catalysis. The electron donating properties of these ligands, assessed by several methods, are indeed remarkable. The authors prepare and characterize complexes of Au, Ir, W, Rh and Mn, with different coordination environments, showcasing the direct applicability of these ligands, including its use in an Ir-catalyzed decarbonylation, where these ligands outperform a conventional bulky and electron-rich phosphine such as PCy$_3$. The preparation of di-AuPhos is remarkable, and while the isolation of free tri-AuPhos could not be achieved, the authors managed to trap it with Rh(acac)(CO)$_2$ and also identify complex 25. There is extensive crystallographic characterization, and the purity observed across the NMR data provided is excellent. The article is well written, the introduction achieves its goal of placing these results in context while also explaining the reasons of d-d repulsion and the results are well presented, analyzed and discussed. Overall, a well-executed, high-value scientific contribution for which I do believe the relevance and novelty of these results merit publication in Angewandte, should a few minor points be addressed:

1. In the preparation of compound 16 (pages 11-12 of the SI), the authors state the use of benzene-d8, which is likely an oversight. Furthermore, the resonance at 2.4 ppm in 1H NMR is assigned as step, which is likely a typo as well (likely for sept). The nature of the J coupling for the carbene carbon is not assigned (PC, it is also missing for 13C couplings in compounds 15, 17, 23, 27 and others).

2. Contrary to Rh 183W has 14.3 % natural abundance, and therefore the patterns observed in the NMR spectra are satellites. While the coupling constant value is very diagnostic and therefore important to report, the multiplicity of the signal should be indicated as that of the major component (for example, the 31P resonance is not a triplet (1:2:1 ratio) but a singlet with satellites due to the S=1/2 183W nuclei). This misassignment occurs for the 13C CO resonance at 199.6 as well; and it is possible that the satellites for the resonance at 202 ppm are not visible due to low S/N ratio. In turn, the ^{31}P resonance for compound 27 should be reported as a doublet, as the abundance of ^{103}Rh is 100 %.

3. For compound 25 it should be stated that 13C is 13C{1H}. In the same vein, most of the SI figures of 31P spectra should read 31P{1H} (like S53, for example).

Comments:

Electron-rich phosphine have been subject of intense research activities by many research groups in recent years and have led to remarkably discoveries ranging form superbasic systems to CO2 activation and highly active transition metal catalysts. Lui and coworkers continue on these efforts by presenting metallophosphines as next generation of extremely electron-rich phosphorus superbases. The AuPhos are prepared by salt metathesis and are shown to exhibit low TEP values and high basicities, which can be tuned by the ligand bound at the gold center and by the number of LAu moieties. Computational studies explain the increased donor strength by d-p pi repulsion. A series of metal complexes with the AuPhos ligands have been prepared to yield dimetallic phosphido complexes, amongst iridium complexes which also were employed in catalytic decarbonylation reactions.

Overall, the paper describes an interesting set of new phosphine ligands with unique properties. However, these systems are not without precedence, but just discussed from a different angle. Metallophosphines or better metal phosphides are known since many years. The novelty of this paper clearly lies in viewing them as ligands rather then complexes. This certainly is partly valid, since in contrast to many metal phosphides the metal-P bond is highly covalent for gold. However, the reactivity of **3** with [LAuPHPh2][BF4] and the instability of **1** and **4** already indicate the weakness of the Au-P bond, question the validity of this description and raise the question, where are the boundaries between ligand and metal. In my view, the authors describe a series of interesting bimetallic phosphide complexes and not a new class of phosphine ligands. However, if the authors could convincingly demonstrate that AuPhos are more stable than I assume (e.g. such as towards alcohols or amines) and that they exhibit unique reactivities or catalytic abilities that warrant the use of gold as substituent I would be happy to change my assessment. However, in the present form I think that the chemistry described is too specialized for Angew. Chem. and would be better placed in an inorganic chemistry journal.

Some further points for the authors to consider:

1. Figure 2 shows the change in HOMO energies when replacing H by AuL. How does the HOMO energy change with different L and does it correlate with the calculated Pauli repulsion energies for 1,2 3 and 4.

2. Figure 6 shows the NBOs of phosphine 3. As expected, several NBOs represent LPs at gold which one would expect for a linear d10 metal center. This Figure should be moved to the SI and the sentence on page 4 starting with "Inspection of the …" should be deleted. Does the NBO analysis also show any secondary interaction between Au and P?

Figure RX. Largest donor-acceptor interaction between Au and P by second order perturbation theory analysis.

3. Do 3 and 5 form stable complexes under the catalysis conditions. Has a mercury test been performed? Why are two equiv. of phosphine needed.

4. Why has no internal standard been used for determining the yield of the catalysis? What is the isolated yield? What is the yield of the catalysis with PPh3 after 24 hours.

5. The authors state that the selected reaction is best catalysed by electron-rich ligands. This is not reported in the paper cited.

6. The SI should be more clearly compiled, e.g. by smaller line spacing and passages between the description of the different compounds.

7. Has an ECP been used for Au? I couldn't find any explanation in the SI.

Referee 3 (R3)

Comments: In their manuscript, Liu and co-workers report a combined experimental-computational (DFT) study on the preparation, electronic properties and applicability in catalysis of different gold-substituted phosphines. To this end, the influence of the ligand attached to the transition metal on the electronic properties has been explored. In addition, the authors also succeeded to prepare the corresponding di- and tri-metallic analogues following a similar procedure to that reported by Corrigan (see reference #25). Although the work has been well-planned and competently carried out, my impression is that this work does not really provide new significant insights different from those already reported for strongly related systems by Corrigan (see above) and Bergman (reference #24). The real novelty of the work is the preliminary (and promising) application of these in phosphines in catalysis. Therefore, I think that this work, although interesting, does not meet the high novelty criterium required for a manuscript in a top chemistry journal such as AngewChem. Submission to ChemEurJ as a full-paper is recommended instead. Nevertheless, I would not oppose if the editor and other reviewers support publication in ACIE because, as commented above, the work has been competently carried out and may be of interest to the majority of the readers of the journal.

The following minor points should be addressed in a revision:

1. Given the d10-configuration of the transition metal, it would be helpful if the authors could compare the current EDA-NOCV data with those derived from the fragmentation using charged fragments, i.e. [LAu]+ and PPh2-. The orbital term will show which fragmentation better describes the bonding situation of the phosphines.

2. Reference #34 only refers to the NOCV method. References on the EDA method (Morukuma/Ziegler&Rauk and reviews by Frenking) should be cited as well.