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Technology Offer

# N-substituted pyridiniophosphines, processes for their preparation and their use

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**We offer novel phosphenium ligands and corresponding metal complexes (both air stable) that are claimed as substances by granted EP and US patents. The ligands can be prepared in multigram scale by simple direct condensation. The corresponding gold complexes are suitable as homogeneous catalysts in organic synthesis (such as cycloisomerization) that can be easily precipitated and recycled due to their salt properties.**

## Background

Stabilized phosphenium compounds can be used as ligands in catalytically active noble metal complexes. The commonly used approach for the phosphenium cations stabilization is the embedding of the phophorous atom into a heterocyclic scaffold or the reaction with bases of a different nature and the formation of the corresponding Lewis adducts. Unfortunately, due to their intrinsic positive charge, these compounds are weak σ-donor and strong π-acceptors and the coordination complexes derived from these compounds are extremely scarce.

## Technology

We offer novel phosphenium ligands stabilized with cyclopropenylylidene that can be easily prepared by direct condensation of the chlorocyclopropenium salt with secondary phosphines and subsequent anion exchange.

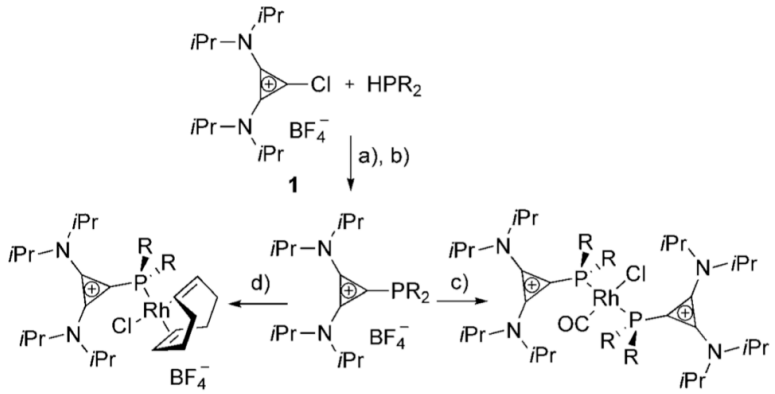


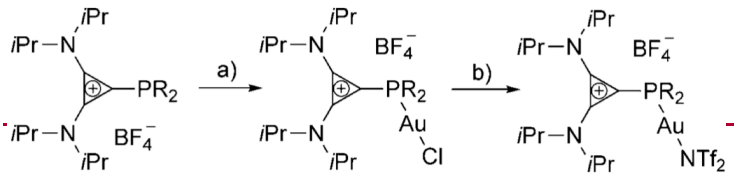

**Fig. 1:** Reagents and conditions (product yields in parentheses):

a) phosphine (2 equiv), THF, reflux, 24 h;
b) $NaBF_4$ (excess); ***2*** (90%); ***3*** (86%),

Cy = cyclohexyl, Ad = adamantyl, cod = 1,5-cyclooctadiene.

***4*** (79%); ***5*** (96%); ***6*** (76%); ***7*** (80%);
c) $[\{RhCl(CO)_2\}_2]$ (0.25 equiv), THF;
***8*** (93%); ***9*** (91%); ***10*** (quant.); ***11*** (quant.);
d) $[\{RhCl(cod)\}_2]$ (0.5 equiv), $CH_2Cl_2$;
***12*** (96%); ***13*** (88%);***14*** (98%);***15*** (97 %).

Using the salts (2,3 or 4) in solution with dichloromethane and $[(Me_2S)AuCl]$ leads to the formation of the corresponding gold complexes as air stable solids.

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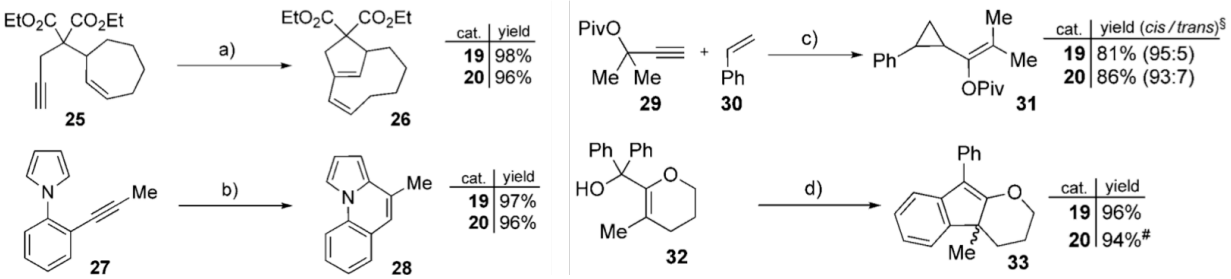
These gold complexes are suitable as catalysts in organic synthesis such as cyclo-isomerization.

**Fig. 3:** Versatility of catalysts ***19*** and ***20***. Reagents and conditions: a) cat. (1 mol%), $CH_2Cl_2$, RT, 40 min.; b) cat (2 mol%), $CH_2Cl_2$, RT, 5 h; c) cat. (1 mol%), $CH_3NO_2$, RT, 3 h. §: ratio determined by GC; d) cat. (1 mol%), $CH_2Cl_2$, RT, 30 min. #: reaction time 4 h; Piv = pivaloyl.




The recycling of gold catalyst 19 has been studied using the cycloisomerization of enyne 25 as a model reaction. Due to its cationic nature complex 19 is insoluble in diethyl ether, whereas diene 26 can be easily dissolved in this medium. Therefore, after full conversion, the reaction solvent was removed in vacuum, and diethyl ether was added. The catalyst precipitated, and it was separated from the product by simple filtration and reused for the next synthesis cycle. As shown in Fig 4, the test reaction could be performed up to four times with consistent excellent yields.

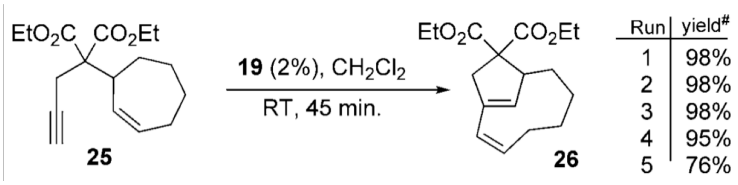



**Fig. 4:** Catalyst recycling in the cyclo-isomerization of enyne ***25***. Reaction conditions: enyne (0.13 mmol), ***19*** (2.0 mol%), CH2Cl2 (2 mL), 45 min, RT; #: runs *1–3* yield of isolated product, runs *4*, *5* yield determined by GC.

## Advantages

- Novel phosphenium ligands and corresponding metal complexes claimed as substances by granted EP and US patents
- Multigram ligand preparation by simple direct condensation
- Obtained ligands and metal complexes are air stable
- Easy isolation and recycling of metal complexes due to salt properties

## Literature

Petuškova, J., Bruns, H. and Alcarazo, M.: "Cyclopropenylylidene-Stabilized Diaryl and Dialkyl Phosphenium Cations: Applications in Homogeneous Gold Catalysis",
Angew. Chem. Int. Ed. (2011), 50, 3799–3802. doi:10.1002/anie.201100338



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## Patent Information

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