

# A Highly Active Ylide-Functionalized Phosphine for Palladium-Catalyzed Aminations of Aryl Chlorides

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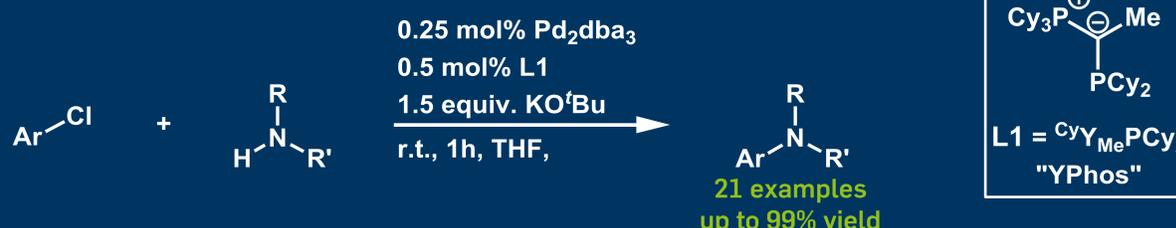
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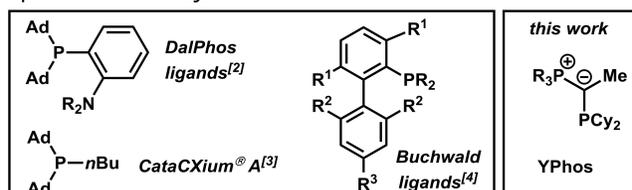


Ylide-functionalized phosphine ligands (YPhos) were rationally designed to fit the requirements of Buchwald-Hartwig aminations at room temperature. This novel ligand class combines high steric demand comparable to biaryl phosphines with a strong electron-donating ability similar to NHC ligands. Stabilization of the active Pd species occurs via weak C–H...Pd interaction. This agostic interaction is easily cleaved to open a free binding site. The utility of the catalyst was demonstrated by benchmark studies and the synthesis of various arylamines in high yields using low catalyst loadings within short reaction times at room temperature.



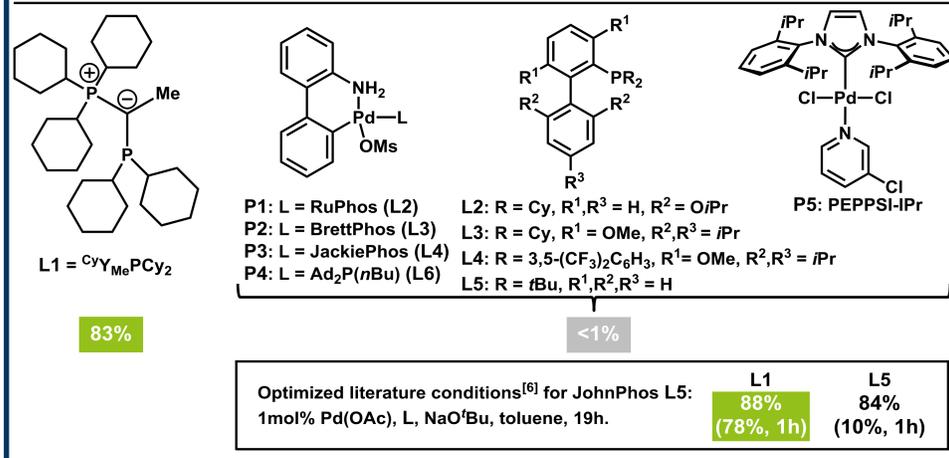
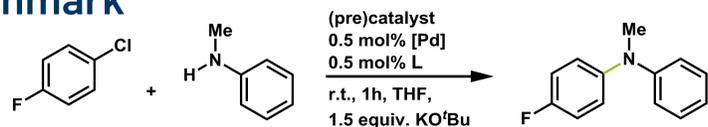
## Introduction

The development of catalysts with new activity levels is linked to the discovery of new ligand systems. Electron-rich phosphine ligands are often needed to stabilize active metal species, to facilitate bond activation processes, or to displace other ligands from the metal center. Typical commercially available and industrially relevant phosphines contain electron-donating cyclohexyl, *tert*-butyl or adamantyl groups. The development of yet more potent catalysts, which would operate under milder reaction conditions, is limited by the finite electron-donating capacity of these alkyl substituents. Therefore Gessner and co-workers developed a novel class of monodentate electron-rich phosphine ligands bearing an ylide substituent at the phosphorus atom. The electron-releasing properties of these "YPhos" ligands were found to exceed even those of commonly used *N*-heterocyclic carbenes (NHCs) depending on the substitution pattern of the ylide.<sup>[1]</sup>

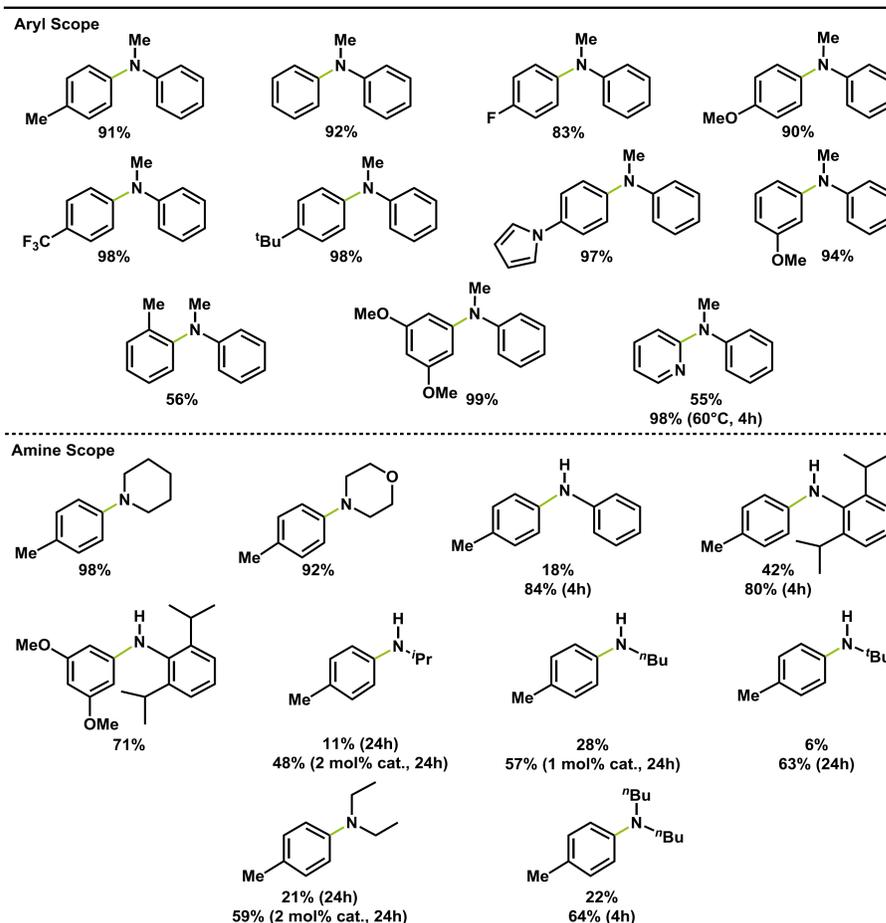
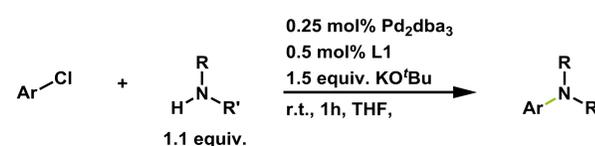


After first applications in gold-catalyzed hydroamination reactions<sup>[1]</sup>, we became interested in further exploiting the utility of YPhos ligands in other catalytic transformations and turned our attention towards Buchwald-Hartwig-type C–N coupling reactions. Due to ligand decomposition using Pd<sup>0</sup> it was necessary to change the R in the ligand from phenyl to cyclohexyl. The resulting arylamines are common motifs in natural products, agrochemicals and pharmaceuticals<sup>[5]</sup> and thus of substantial industrial importance.

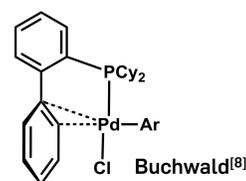
## Benchmark



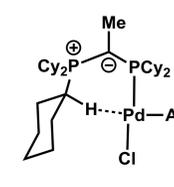
## Scope of the Amination<sup>[7]</sup>



## Stabilization of the low-coordinated Pd species



- Pd-arene interactions
- Rotation around P–C bond
- Fast conversion at r.t. seems critical



- Weak C–H...Pd interaction
- Requires less energy for de-coordination
- More facile C–N coupling

## References

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