Nickel and palladium complexes of pyridine-phosphine ligands: synthesis, characterization, and ethene oligomerization
Flapper, J.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Summary

Megatons of α-olefins are produced annually. They find application in the fabrication of polymers, lubricants, surfactants, and various other products. The most common process for their production is the oligomerization of ethene. It has long been known that transition metals can catalyze this reaction and extensive research has been devoted to this. Still, the relation between the structure and the performance of a catalyst is poorly understood. Our goal was to obtain series of related ligands and their nickel and palladium complexes, and study the influence of systematic changes of the ligands on the catalytic properties of the complexes.

As ligands we chose pyridine-phosphine ligands of the general type depicted above on the left. These allow for modification at the pyridine donor site [R], at the phosphine donor site [Ar], or at the backbone connecting the two donor parts of the molecule [U].

For all ligands, nickel and palladium complexes were prepared, which are schematically depicted in the figure above. Nickel dichloride complexes were prepared and used as catalyst precursors. Activation was done in situ using MAO as cocatalyst. Methylpalladium chloride complexes were prepared and converted to the pre-activated, cationic methylpalladium complexes which were used in catalysis without cocatalyst.

The first series of ligands that was tested differed in the backbone connecting the two donor parts of the molecule, as drawn above. The ligands were obtained via reported or new methods. Formation of the metal complexes was straightforward and the expected complexes were obtained. The nickel complexes formed very active catalysts for ethene oligomerization, displaying high selectivities for butenes, although selectivity for 1-butene was low to moderate. A correlation between the natural bite angle of the ligand and the catalytic behavior of the complex was observed for the first three, strongly related, ligands.
The other two complexes deviated from this trend. The palladium complexes were almost inactive, forming only small amounts of mainly butenes. This work is described in chapter 2.

The ligands of the next series tested had different bulky groups at the pyridine part of the molecules, see the picture above. A synthetic route was developed for these new ligands, allowing facile introduction of the different substituents. The nickel complexes of the ligands could be readily obtained and they did not show any unusual coordination behavior. The methylpalladium chloride complexes, on the other hand, behaved differently from what was expected. When the ferrocenyl substituted ligand was reacted with the palladium precursor, an undefined mixture of complexes was obtained. The other ligands gave rise to insoluble, bimetallic complexes in which the ligands bridge two palladium centers, as depicted below.

Depending on the size of the aryl substituents and the conditions employed during the synthesis, the two metal centers may have the methyl and chloride anions both in a *cis* or both in a *trans* configuration or have one in a *cis* and one in a *trans* configuration. This coordination mode was never observed before for a homonuclear complex with identical ligands. Chapter 3 describes this part of the research.

Chapter 4 continues the research on these ligands and their complexes. From the bimetallic complexes (in case of the aryl substituents) or the mixture of complexes (in case of the ferrocenyl substituent), the cationic methylvchloride complexes were obtained through chloride abstraction. Contrary to their precursors, these complexes all appeared as monometallic complexes. Just like the palladium complexes of the first series of ligands, these complexes gave only a very low activity when they were employed in ethene oligomerization. The nickel complexes did show a high productivity, with the exception of the complex from the ferrocenyl-substituted ligand, which was inactive. The productivity of the other complexes was lower than that of the related complex of the first series, but the
selectivity for 1-butene was much higher and dependant on the bulk of the aryl substituent. This illustrates the influence of these substituents on catalysis.

\[
\begin{align*}
\text{PAr}_2 \\
\text{N} \\
\end{align*}
\]

The last series which was studied (and is described in chapter 5) had different aryl substituents at the phosphorus atom, see the figure above. The ligands were synthesized conveniently in two steps. They formed the expected metal complexes with nickel and palladium. The neutral and cationic palladium complexes of the toyl and anisyl substituted ligands showed hindered flipping of the metallocycle, possibly as a result of a repulsive Pd···H interaction. In catalysis, the steric bulk of the toyl and anisyl groups induced a lower productivity but high 1-butene selectivity, compared to the complex of the related ligand from the first series. The nickel complex of the anisyl substituted ligand deviated from this trend, giving a high productivity but moderate 1-butene selectivity. Again, the palladium complexes showed a very low ethene oligomerization activity.

In conclusion, we have developed synthetic routes to new classes of pyridine-phosphine ligands, allowing modification of different groups in these ligands. Nickel and palladium complexes were prepared and characterized, showing the influence of different ligands on the coordination behavior in the complexes. The palladium complexes proved to be hardly active in ethene oligomerization. The nickel complex formed active catalysts after MAO activation. Butenes were always the major product, and depending on the nature of the ligand activities and selectivities could be varied. Relations between the outcome of catalysis and the structure of the catalysts were observed, although accurate structure-performance predictions will still require further research.