Synthesis and catalytic evaluation of phosphanylferrocene ligands with cationic guanidinium pendants and varied phosphane substituents.

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Rok wydania

2019

Czasopismo

European Journal of Inorganic Chemistry

Numer woluminu

2019

Strony

4846-4854

DOI

10.1002/ejic.201901057

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

This contribution expands the still narrow class of functional ferrocene phosphanes with polar cationic groups, focusing on the synthesis and catalytic use of a series of phosphanylferrocene ligands bearing positively charged guanidinium tags, $[R_2PfcCH_2NHC(NH_2)_2]Cl$ (**3a**–**d**), where fc = ferrocene-1,1′-diyl, R = isopropyl (**a**), cyclohexyl (**b**), phenyl (**c**), and 2-furyl (**d**). To probe the influence of phosphane substituents, these compounds were studied as supporting ligands in Pd-catalyzed Suzuki–Miyaura cross-coupling of acyl chlorides with arylboronic acids, in analogous coupling of aryl bromides with arylboronic acids, and in Rh-catalyzed hydroformylation of 1-hexene using *trans*-$[RhCl(CO)\{R_2PfcCH_2NHC(NH_2)_2$-κ*P*$\}_2]Cl_2$ complexes (**4a**–**d**) as pre-catalysts. The outcome of the cross-coupling reactions strongly depended on the starting materials, and no ligand generated a universally applicable catalyst when combined with $Pd(OAc)_2$. In the hydroformylation reactions, the catalyst based on **4d** led to lower conversions than all others, which performed rather similarly. Overall, the phenyl-substituted phosphane **3c** emerged as a good compromise, giving rise to reasonably efficient and stable catalysts in most cases (except for Suzuki–Miyaura biaryl cross-couplings, wherein electron-rich alkylphosphanes performed better than **3c**).

Słowa kluczowe

Phosphane ligands, Ferrocene ligands, Hydroformylation, Cross-coupling, Palladium, Rhodium

Adres publiczny

http://dx.doi.org/10.1002/ejic.201901057

Strona internetowa wydawcy

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