



New insight into role of *ortho*-metallation in rhodium triphenylphosphite complexes.
Hydrogen mobility in hydrogenation and isomerization of unsaturated substrates.

Autorzy

Anna M. Trzeciak

Józef J. Ziółkowski

Rok wydania

2000

Czasopismo

Journal of Organometallic
Chemistry

Numer woluminu

597

Strony

69-76

DOI

10.1016/S0022-
328X(99)00594-X

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The hydrogen transfer from two rhodium(I) hydrido complexes $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ to methyl acrylate and/or allylbenzene leads to the formation of *ortho*-metallated complexes $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3$ (**I**) and $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}(\text{CO})\{\text{P}(\text{OPh})_3\}_2$ (**II**), respectively. During these reactions unsaturated substrates, methyl acrylate or allylbenzene undergo stoichiometric hydrogenation. A similar reaction was also observed for $\text{HRh}\{\text{P}(\text{OR})_3\}_4$ complexes ($\text{R}=3\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$). The complex $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ catalyses the isomerization of hex-1-ene to hex-2-ene in the absence of H_2 ; however at 1 atm of H_2 the formation of hexane is observed. Hydrido complexes of the type $\text{HRh}\{\text{P}(\text{OR})_3\}_4$ in D_2 atmosphere undergo H/D exchange at the *ortho* position of coordinated triarylphosphite. Deuteration of the *ortho* protons in complexes with $\text{R}=\text{Ph}$, $3,5\text{-(CH}_3)_2\text{C}_6\text{H}_3$ and $4\text{-CH}_3\text{C}_6\text{H}_4$ is total, whereas only one *ortho* hydrogen is replaced in the case of $\text{R}=3\text{-CH}_3\text{C}_6\text{H}_4$. The formation of an *ortho*-metallated chelating ring causes a downfield shift in the ^1H -NMR signal of one proton from the phenyl ring to δ ca. 8 ppm.

Słowa kluczowe

Rhodium complexes, *ortho*-Metallation, Triarylphosphite,
Hydrogenation, Isomerization

Adres publiczny

[https://doi.org/10.1016/S0022-328X\(99\)00594-X](https://doi.org/10.1016/S0022-328X(99)00594-X)

Strona internetowa wydawcy

<http://www.elsevier.com>