

Rh(acac)(CO)PR₃) and Rh(oxinate)(CO)(PR₃) complexes - substitution chemistry and structural aspects.

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Streszczenie

The substitution of CO in Rh(acac)(CO)₂ by the phosphorus ligands P(OPh)₃, P(NC₄H₄)₃, and PPh₂(NC₄H₄) has been studied kinetically by stopped-flow spectrophotometry as a function of temperature. With P(OPh)₃ and P(NC₄H₄)₃, both CO ligands are replaced in a stepwise fashion via the intermediate Rh(acac)(CO)(PR₃). However, the disubstituted complexes Rh(acac)(PR₃)₂ are thermodynamically unstable. Judged from the activation parameters, the individual steps are associative processes. In the case of PPh₂(NC₄H₄) only the monosubstituted complex is formed. The differences in the substitution rates as well as the stability of the various products are largely dominated by electronic (e.g. basicity) effects. X-ray structures of some of the mono-substituted complexes are given. In addition, also the reaction of Rh(oxinate)(CO)₂ with P(OPh)₃ has been studied kinetically showing that oxinate has a labilizing effect relative to acetylacetonate

Słowa kluczowe

Rhodium, Ligand substitution, Tertiary phosphines, Kinetics, Acetylacetonate

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