

「論文内容の要約」

イミノビピリジン配位子を有する鉄錯体を触媒とする  
オレフィンのヒドロシリル化反応に関する研究  
(Study on Hydrosilylation Reaction of Olefin Catalyzed by Iron Complex Bearing  
Iminobipyridine Ligand)

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Catalytic hydrosilylation of olefins is one of the most straightforward and atom-economic ways to synthesize organosilanes. Platinum catalysts are known to be very effective for olefin hydrosilylation. As natural resources of platinum are dwindling, it is important to develop an alternative catalyst. Iron is one of the best rare-metal surrogates because of its abundance and environmental compatibility. Several catalysts based on iron complexes for olefin hydrosilylation have been reported, but their performance in terms of catalytic activity and selectivity was inferior to that of platinum complexes. This paper reports the synthesis of iron complexes with iminobipyridine derivatives, (BPI)FeBr<sub>2</sub>, for hydrosilylation of olefins.

Several iron complexes bearing an iminobipyridine ligand, (<sup>R1</sup>BPI<sup>R2,R3</sup>)FeBr<sub>2</sub> (<sup>R1</sup>BPI<sup>R2,R3</sup> = 6-R<sup>1</sup>-6'-(CR<sup>3</sup>=NR<sup>2</sup>)-2,2'-bipyridine: R<sup>1</sup> = H, Me; R<sup>2</sup> = <sup>t</sup>Bu, Cy, Ad, Bn, Ph, Mes, Dipp; R<sup>3</sup> = H, Me, <sup>t</sup>Bu, CF<sub>3</sub>), were synthesized. These iron complexes exhibited high catalytic activities with the help of NaBHET<sub>3</sub> for the hydrosilylation of 1-octene with primary, secondary, and tertiary silanes. The reaction of 1-octene with PhSiH<sub>3</sub> produced three different species: monoalkylated silane (Ph(octyl)SiH<sub>2</sub>), dialkylated silane (Ph(octyl)<sub>2</sub>SiH), and trialkylated silane (Ph(octyl)<sub>3</sub>Si). The selective formation of Ph(octyl)SiH<sub>2</sub> and Ph(octyl)<sub>2</sub>SiH could be achieved by changing the reaction conditions. Single or double hydrosilylation reactions of secondary silanes (PhMeSiH<sub>2</sub> and Ph<sub>2</sub>SiH<sub>2</sub>) afforded the corresponding tertiary and quaternary silanes, respectively. The iron iminobipyridine complexes exhibited catalytic activity even in organic solvents such as hexane, toluene, diethyl ether, and THF; an appropriate solvent choice could reverse the selectivity between single/double hydrosilylation. In addition, a high catalyst turnover number of  $4.2 \times 10^4$  was achieved for the reaction between 1-octene and Ph<sub>2</sub>SiH<sub>2</sub>, and the catalyst remained active even at 100 °C without any loss of activity.