SYNLETT Spotlight 25

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Crabtree's Catalyst: $[Ir(cod)pyr(PCy_3)]PF_6$

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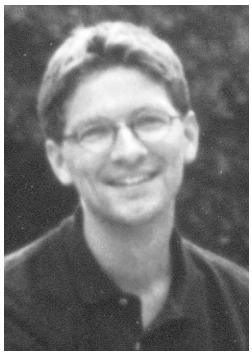
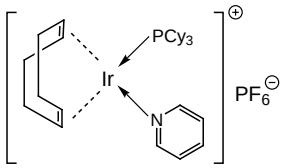


(1,5-Cyclooctadiene)(pyridine)(tricyclohexylphosphine)iridium(I) hexafluorophosphate **1** $[Ir(cod)pyr(PCy_3)]PF_6$, Crabtree's catalyst,[1] is a versatile catalyst for selective hydrogenation and hydroboration. It was first introduced by Crabtree, Felkin and Morris for the hydrogenation of hindered olefins, whether or not activating groups are present. It was later discovered that selective hydrogen addition to one face of a chiral molecule was possible in the presence of a coordinating hydroxyl group. Evans and Fu first reported the use of Crabtree's catalyst in the catalytic directed hydroboration.

Preparation: Crabtree's catalyst can be prepared from $[IrCl(cod)_2]$, pyridine, $NH_4[PF_6]$ and tricyclohexylphosphane[2] but it is also commercially available (Aldrich, Fluka). The complex is air-stable both in the solid state and in solution. It is soluble in CH_2Cl_2, $CHCl_3$ and acetone but is insoluble in water, alcohols, benzene, Et_2O and hexane. It can be recrystallized from CH_2Cl_2/Et_2O. The catalyst is stable in the presence of oxidizing functionalities, such as carbon-halogen bonds or O_2, and $-CO_2R$, -NHAc, $-OSiR_3$ or keto groups, but it is poisoned by $-CO_2H$, -CN, and $-NH_2$.



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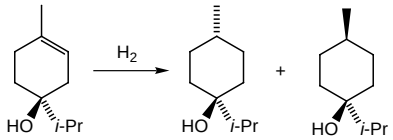
Abstracts

a) Hindered substituted double bond systems are difficult to hydrogenate. Catalyst **1** is a highly active catalyst for the hydrogenation of these olefins such that in CH_2Cl_2 even tetrasubstituted olefins are easily reduced at 0 °C. The table shows relative rates for the hydrogenation with **1** compared to those with Wilkinson's catalyst, $[RhHCl(PPh_3)_3]$.[3]

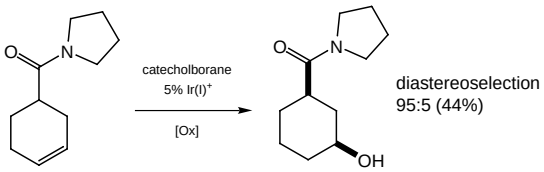
Catalyst	Solvent		
$[Ir(cod)pyr(PCy_3)]PF_6$	CH_2Cl_2	6400	4000
$[RhHCl(PPh_3)_3]$	C_6H_6	9000	0

b) Two sites are available for the coordination of **1** with a bidentate substrate. The addition of H_2 on one face of a cyclic molecule can thus be directed by the presence of a hydroxyl group on that face. This has been shown independently by Crabtree[4a] and Stork.[4b] Stereochemical control can also be achieved by catalyst coordination to amide carbonyl groups.[5]



Pd/C	20	80
1	99.9	0.1

c) Evans and Fu showed that amides effectively direct the $[Ir(cod)(PCy_3)pyr]PF_6$-catalyzed hydroboration of olefins with catecholborane.[6] The directing ability of the amide moiety is also evident in acyclic systems.



References and Notes

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