

The search for new hydrogenation catalyst motifs based on N-heterocyclic carbene ligands

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Dedicated to Professor Brian James.

Abstract

A series of new iridium complexes containing N-heterocyclic carbene ligands (NHCs) has been prepared and tested for hydrogenation of primary (1-octene), secondary (cyclohexene), tertiary (1-methylcyclohexene) and quaternary (2,3-dimethyl-2-butene) alkenes. Taking inspiration from Crabtree's catalyst, $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$, the labile pyridine ligand was exchanged with an NHC ligand, and was found to produce catalysts with similar activities and rates. Further refinement of the ligands produced the optimal version of the iridium phosphine/NHC combination: Using a smaller phosphine, tri-*n*-butylphosphine, a saturated NHC and the non-coordinating anion, tetrakis(3,5-bis(trifluoromethylphenyl))borate (BARF), a highly active catalyst that has substantially better longevity and stability, but similar activity, to the parent Crabtree's catalyst was prepared in three steps. The effect of the BARF counteranion was explored, and was shown to improve even Crabtree's catalyst, and is thus a general phenomenon for iridium catalysts in non-polar solvents. Mechanistic studies suggest that the catalyst resting state is a dimeric complex, presumably hydride-bridged, that dissociates into catalytically active species under catalytic conditions. Thus, the catalyst dead-end for Crabtree's catalyst, hydride-bridged dimers and trimers, may in fact be a reversible resting state for the iridium complexes described here.

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1. Introduction

Hydrogenation reactions of unsaturated organic compounds are among the most basic and important reactions in synthetic organic chemistry [1]. In a close-to-ideal dem-

onstration of atom economy [2–4], both hydrogen atoms in the H_2 molecule appear in the reduction product, as shown in Fig. 1 [2]. Homogeneous-phase transition metal hydrogenation catalysts may have greater difficulties with respect to product/catalyst separations at the end of the reaction as compared to their heterogeneous cousins, but the potential for tailoring catalyst activity and selectivity, including enantioselectivity, render homogeneous catalysis an extremely important branch of catalysis, one that has directly contributed to two Nobel Prizes.

The earliest homogeneous hydrogenation catalyst platform was a neutral rhodium-based complex called Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (Fig. 2) [5]. The complex is active at 1 atm of H_2 pressure, at room temperature, and

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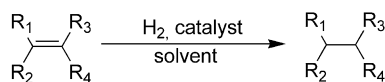
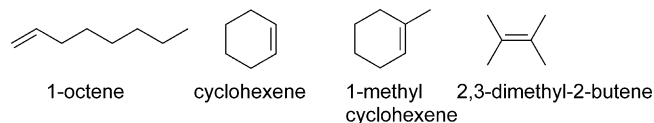
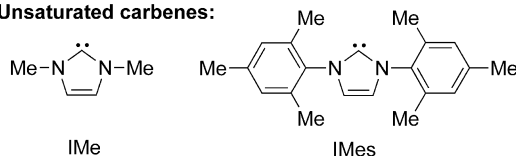
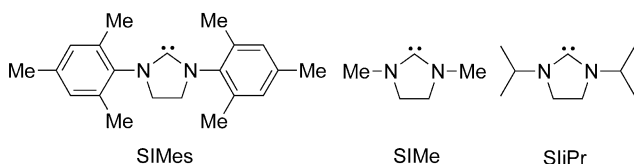
Hydrogenation scheme:**Substrates for hydrogenation:****Unsaturated carbenes:****Saturated carbenes:**

Fig. 1. Hydrogenation of olefins, substrates, and carbene ligands examined in this study.

can easily reduce monosubstituted and *cis*-disubstituted alkenes such as cyclohexene. The next generation of this catalyst, the Osborn–Schrock series, eliminated the chloride to render the complexes cationic and thus dissociation of a phosphine ligand was not a requirement for catalytic activity [6]. After a thorough examination of the high reactivity of the cationic rhodium(I) complexes, Osborn and co-workers looked to iridium but were soon discouraged due to its low reactivity. It was in 1977, however, that Crabtree and co-workers [7] reported that by changing the solvent of the system from coordinating to non-coordinating could a catalyst system be obtained that was more reactive toward the hydrogenation of olefins with different degrees of substitutions, even more hindered than *cis* disubstituted alkenes. The best catalyst precursor in the series is known as Crabtree's catalyst, $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$ (Fig. 2). This compound arguably leads, under hydrogenation conditions, to the most active and general homogeneous hydrogenation catalyst that can tackle even highly hindered tetrasubstituted olefins.

While extremely fast at catalyzing the hydrogenation of a wide range of alkenes, Crabtree's catalyst's Achilles' heel has been the fact that it rapidly deactivates [8]. After one hour of reaction under hydrogenation conditions and in the presence of sterically hindered olefins, considered to be poor ligands, the catalyst irreversibly forms inactive hydride-bridged trimers [8]. These trimers are also formed during the hydrogenation of secondary and primary olefins after complete consumption of olefin. Total conversion of sterically unhindered alkenes to hydrogenated product at higher substrate/catalyst ratios can only be obtained

through multiple additions of the catalyst precursor. This increases the total amount of catalyst and manipulations required, but nevertheless, this catalyst remains popular since hydrogenation of highly substituted olefins is extremely challenging, and the allure of harnessing the reactivity for enantioselective hydrogenation is powerful.

In order to take advantage of the high reactivity of Crabtree's catalyst while introducing some stability to avoid degradation, a number of workers have recently begun to look to N-heterocyclic carbenes (NHCs) [9–12] as a possible solution to replace one or both of the donating ligands in Crabtree's catalyst (PCy_3 and/or pyridine) [13,14]. The NHCs behave like strong σ -donor ligands with little or no π -accepting capabilities and while not entirely free of side reactions [15], they are not susceptible to some of the same problems as phosphine ligands, such as oxidation and the Arbusov P–C bond cleavage. The steric environment of the NHCs can be modulated by changing the substituents on the nitrogen atoms, but have a 'fan' or 'fence'-type structure [16], as opposed to the classic cone angle analysis of phosphines [17]. All NHC ligands mentioned here, and utilized in this study are shown in Fig. 1.

Late transition metal–NHC complexes serve as pre-catalysts for numerous catalytic reactions such as Heck [18], Suzuki [19] and Sonogashira coupling [20], transfer hydrogenation [21], hydroformylation [22], hydrosilylation [23,24], and olefin methathesis [25,26], among others [12,27,28]. More specifically related to the catalyzed direct addition of H_2 to alkenes, in the year 2002, Nolan and co-workers reported the synthesis of a rhodium complex analogous to Wilkinson's catalyst containing one NHC ligand [29]. The complex, $[\text{Rh}(\text{PPh}_3)_2(\text{IMes})\text{Cl}]$, was tested for alkene hydroboration, hydrogenation and other reactions. The catalyst was shown to have activity comparable to Wilkinson's catalyst for the hydroboration of olefins, but lower activity for olefin hydrogenation. In 2001, the same group reported the substitution of the phosphine in Crabtree's catalyst by a NHC ligand producing $[\text{Ir}(\text{COD})(\text{SIMes})(\text{py})]\text{PF}_6$ [13]. The new catalyst was used in the hydrogenation of simple alkenes, and while it showed a lessened reactivity toward the hydrogenation of olefins than compared to the parent Crabtree's catalyst, it was thermally more stable. Soon after, Burgess [30–33] reported the substitution of the phosphine portion of a bidentate chiral phosphine–oxazoline ligand by an NHC group, and its subsequent binding to an Ir(I) centre. This new catalyst can efficiently hydrogenate primary, secondary and tertiary olefins with good to high enantioselectivities at 1 atm H_2 which is much improved compared to the 50 atm required for the phosphine–oxazoline ligand system [34]. Earlier work by our group has shown that the phosphine in Crabtree's catalyst may be maintained, and the pyridine instead substituted by an unsaturated carbene (Fig. 2) [35]. This catalyst motif is therefore $[\text{Ir}(\text{COD})(\text{NHC})(\text{phosphine})]\text{X}$. These complexes have reactivity similar to the parent Crabtree's catalyst for

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