[Pd(NHC)(PR_3)] Complexes: Versatile Tools for Tandem Dehydrogenation/ Hydrogenation Processes

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Abstract: Homogeneous Pd(0) complexes are powerful tools for numerous catalytic reactions. Recent work has demonstrated the unique properties displayed by [Pd(NHC)(PR_3)] catalysts in the activation of ammonia borane (AB) and formic acid, with the subsequent formation of hydrogen. An understanding of the mechanism allowed for the design of a new dehydrogenation/hydrogenation tandem process using "*hydrogen storage materials*". The hydrogenations of alkenes and alkynes were successfully performed at low catalyst loadings of Pd(0) species and mild conditions. Such tandem process represents a safe and innovative alternative to classic hydrogenation protocols.

Key words: Tandem reaction – Hydrogenation – Dehydrogenation – Pd(0) – Hydrogen storage material

Over the last decade, *N*-heterocyclic carbene (NHC) based palladium systems have been the subject of intensive investigation.[1] What particularly attracted our attention is the possibility of synergistic effect between NHC ligands and phosphorus donors. In this context, we have developed and investigated different systems that showed excellent performance in the Suzuki–Miyaura reaction,[2] in the cross-coupling of Grignard reagents at low catalyst loadings,[3] in the Mizoroki–Heck reaction[4] and in the hydrodehalogenation of polychlorinated biphenyls substrates.[5] Among the extensively studied Pd(II) systems, the Cazin group has also been involved in the development of the NHC-based Pd(0) chemistry.[6] These studies led us to explore the unusual catalytic activities displayed by these complexes in hydrogenation and hydrogen production reactions.

1 Hydrogenation by mixed NHC/PR_3 Pd(0) complexes

Palladium-catalyzed hydrogenation of unsaturated substrates by homogeneous and heterogeneous Pd(II) complexes has been the subject of intensive investigations.[7] In spite of this fact, only a handful of studies focusing on well-defined Pd(0) homogenous systems have been reported.[8]

Puzzled by the ability of some Pd(0) species stabilized by η^2-alkenes to promote the partial hydrogenation of alkynes,[8b-c] we began to investigate the catalytic activity of NHC-based Pd(0) complexes in hydrogenation reactions (Figure 1).[9]

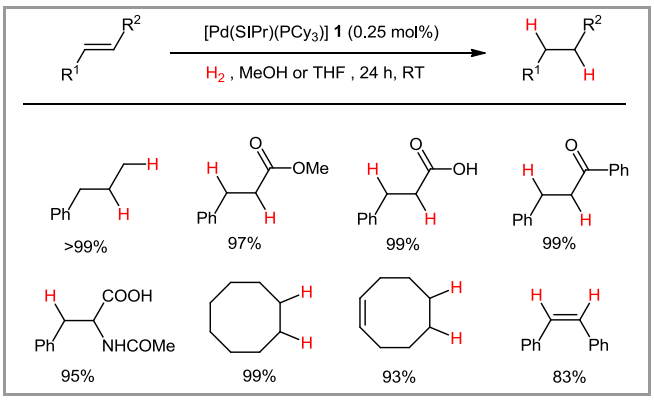


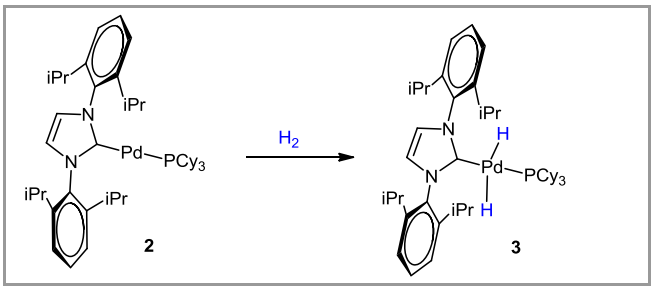
Figure 1 Hydrogenation of olefins catalyzed by mixed NHC/PR_3 Pd(0) species.[9]

Mixed NHC/PR_3 Pd(0) complexes were found to promote the hydrogenation of a wide range of alkenes under mild conditions (RT, 1 atm) and at low catalyst loadings (0.25 mol%). The selective reduction of alkynes into the *cis*-isomers was also achieved with ethynylfluorenol and diphenylacetylene. Interestingly, a *trans* Pd(II) dihydride-species was observed during NMR mechanistic studies, suggesting a direct activation of dihydrogen via oxidative addition to Pd(0) species. These results encouraged us to investigate the properties of mixed NHC/PR_3 Pd(0) complexes in the activation of various small molecules.

2 Activation of small molecules and hydrogen production

2.1 Activation of dihydrogen

Despite the ability of Pd(0) complexes to promote the hydrogenation of unsaturated substrates,[8b-c] the complete characterization (and isolation) of the intermediate dihydride was never successfully achieved. Our previous observation[9] convinced us to take up the challenge using mixed NHC/PR_3 complexes. Gratifyingly, the reaction of [Pd(IPr)(PCy_3)] (**2**) with H_2 (1 atm.) yielded quantitatively the *trans*-dihydride Pd(II) species **3** (Scheme 1).[10]



Scheme 1 Activation of dihydrogen by complex **2** and formation of the dihydride Pd(II) species **3**.

Complex **3** was fully characterized by NMR spectroscopy, and its solid-state structure was unambiguously confirmed by single-crystal X-ray diffraction (Figure 2).[10]

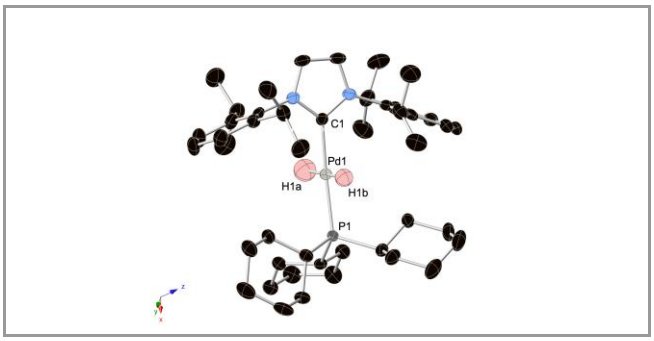
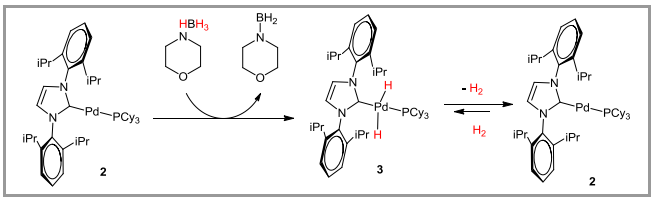


Figure 2 Molecular structure of $[Pd(H)_2(IPr)(PCy_3)]$ **3**. H atoms, with the exception of H1a and H1b, are omitted for clarity.[10]

The oxidative addition of dihydrogen is reversible and led upon heating to the reformation of the parent complex **2** with the release of H_2. Several failed attempts to reproduce those result with homoleptic Pd(0) complexes emphasize the unique properties displayed by these Pd complexes bearing mixed ligands.[10]

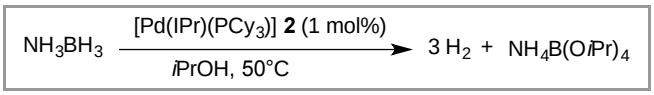
2.2 Production of hydrogen from ammonia borane

Encouraged by these results with hydrogen, we next assessed the catalytic performance of mixed NHC/PR_3 Pd(0) complexes in the activation of ammonia borane (**AB**). Such "hydrogen storage materials" are easily transportable sources of hydrogen that have attracted considerable attention due to safety reasons.[11] A preliminary reaction between $[Pd(IPr)(PCy_3)]$ **2** and morpholine borane resulted in hydrogen release with formation of morpholinoborane (Scheme 2). NMR experiments unambiguously identified the dihydride complex **3** as an intermediate in the hydrogen formation process.[12]



Scheme 2 Activation of morpholine borane and hydrogen formation pathway.

The catalytic dehydrogenation of **AB** promoted by complex **2** was then successfully performed under mild conditions at low catalyst loading (Scheme 3).

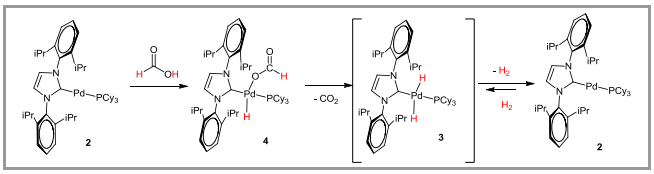


Scheme 3 Hydrogen production from ammonia borane catalyzed by complex **2**.

Although the use of isopropanol was found to be crucial in the optimum catalytic conditions, the reaction can also be carried out in non-alcohol solvents such as THF and toluene.[12]

2.3 Production of hydrogen from formic acid

The activation of formic acid by mixed NHC/PR_3 Pd(0) complexes was then examined. Reaction of **2** with formic acid in THF led (at room temperature) to the rapid formation of hydrogen and CO_2 (Scheme 4).[13]



Scheme 4 Hydrogen formation pathway, starting from formic acid.

In the course of mechanistic studies monitored by NMR spectroscopy, no trace of the dihydride species **3** was detected. The formation of a new hydridoformato palladium complex **4** was instead clearly observed. The new species was fully characterized by NMR spectroscopy, and the structure unambiguously established by single-crystal X-ray diffraction (Figure 4).

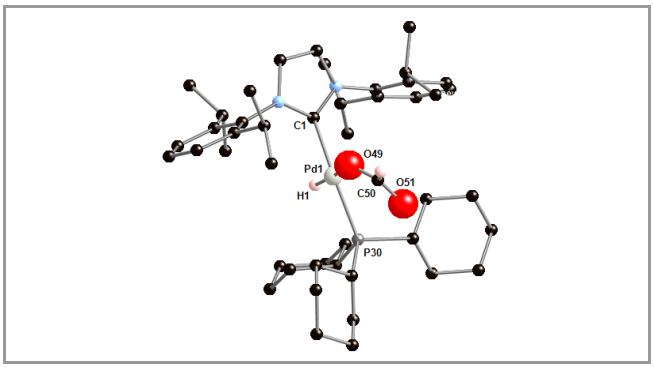
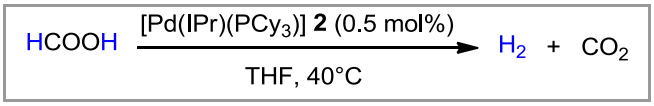


Figure 4 Molecular structure of [Pd{OC(O)H}(H)(IPr)(PCy$_3$)] **4**. H atoms, with the exception of H1, are omitted for clarity.[13]

Computational experiments suggested that the release of H_2 is achieved through the formation of the intermediate dihydride complex **3**. According to the calculations, the difference in the stabilities of the numerous catalytic species/intermediates formed explains why no dihydride complex was observed. Complex **2** was finally shown to promote the catalytic production of hydrogen from formic acid at 50°C in THF (Scheme 5).



Scheme 5 Hydrogen production from formic acid, catalyzed by **2**.

3 Tandem dehydrogenation/hydrogenation

The properties displayed by the mixed NHC/PR$_3$ Pd(0) complexes in both hydrogen production and hydrogenation of unsaturated substrates prompted us to consider the feasibility of a tandem dehydrogenation/hydrogenation process.

3.1 Ammonia borane as hydrogen source

The tandem process was first tested with ammonia borane as the hydrogen source. A large range of alkenes were thus successfully hydrogenated in isopropanol at low loading of [Pd(SIPr)(PCy$_3$)] (0.05-1 mol%) (Figure 5).[12] In the case of α,β-unsaturated carbonyl compounds, complete hydrogenation to the corresponding saturated alcohol was observed.

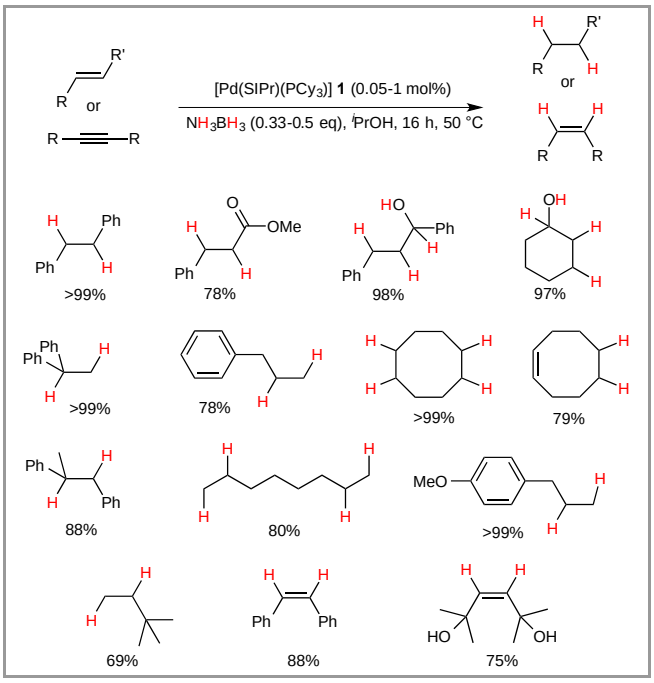


Figure 5 Substrate scope of hydrogenation using NH$_3$BH$_3$ as hydrogen source[12]

The system was found to selectively perform the semi-reduction of diphenylacetylene and dimethylhexynediol leading to the *cis*-alkenes.

3.2 Formic acid as hydrogen source

The reduction of a large variety of substrates was then successfully performed using formic acid as the hydrogen source (Figure 6).[13] The system was found to be functional-group tolerant and no over reduction of the α,β-unsaturated carbonyl compounds was observed.

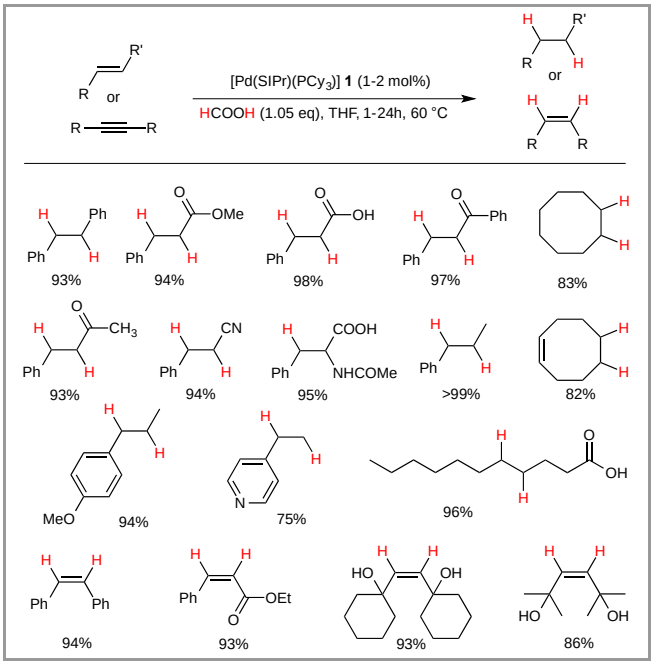


Figure 6 Substrate scope of hydrogenation using formic acid as hydrogen source[13]

The selective semi-reduction of alkynes was achieved, leading to the *cis*-alkene products.

4. Conclusion

Mixed NHC/PR_3 Pd(0) complexes have been shown to efficiently promote both hydrogen production starting from safe "hydrogen storage materials" and hydrogenation of unsaturated substrates at low catalyst loadings. These catalytic activities were successfully combined in tandem dehydrogenation/hydrogenation processes, leading to safe alternatives to existing hydrogenation processes/protocols where dihydrogen is used.

Acknowledgment

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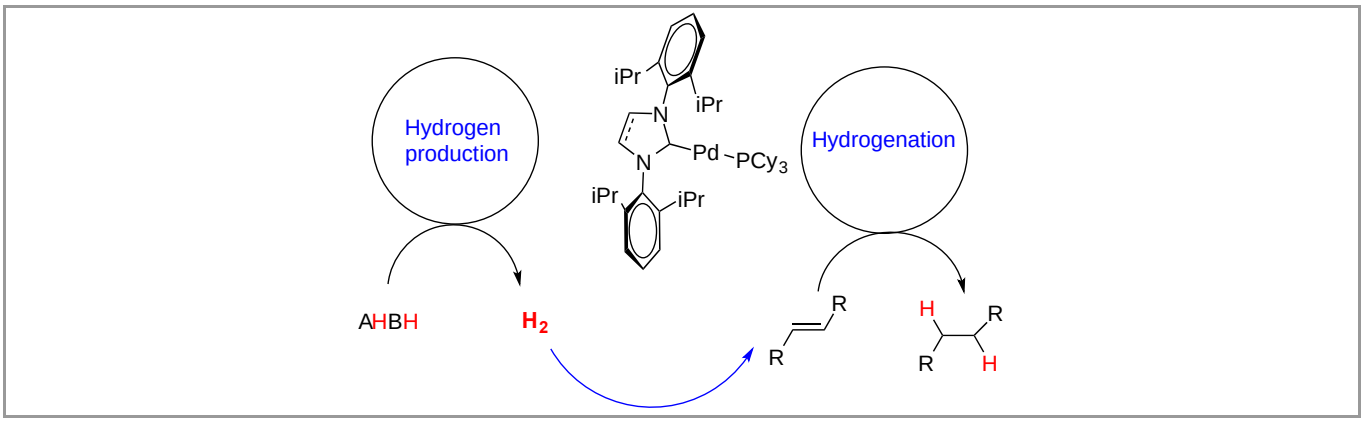

Tandem Dehydrogenation/ Hydrogenation processes