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Hydrogenation of Carbonyl Derivatives with Well-Defined Rhenium Pre-Catalyst

Duo Wei, [a] Thierry Roisnel, [a] Christophe Darcel, [a] Eric Clot [b] and Jean-Baptiste Sortais [a]

Dedication (optional)

Abstract: The first efficient and general rhenium catalyzed hydrogenation of carbonyl derivatives has been developed. The key to success of the reaction is the use of a well-defined rhenium complex bearing a tridentate diphosphino-amino ligand as catalyst (0.5 mol%) at 70 °C in the presence of H₂ (30 bar). The mechanism of the reaction has been investigated by DFT (PBE0-D3) calculations.

Hydrogenation reactions have been of central importance in chemistry for more than a century.[1] Nevertheless, it remains an important field of investigation, notably with the current challenge of the transformation of highly oxygenated biomass-resources into less functionalized chemical building blocks.[2] Compared to the transition metals of groups 8, 9, and 10 (Fe, Co, Ni) which are classical in reduction area, group 11 transition metals have been scarcely applied in hydrogenation or related reduction reactions.[3] For example, with manganese, only one recent article describes the hydrogenation of carbonyl derivatives[4] and one the dehydrogenative coupling of alcohol with amines.[5] In the case of rhenium, after the seminal work of Ephritikhine on dehydrogenation of alkanes to alkenes,[6] rare examples of stoichiometric[7] and catalytic[8] hydrogenation of alkenes have been described with rhenium nitrosyl hydride complexes mainly by Berke, and a single example of the hydrogenation of acetophenone is reported.[9] Interestingly, Berke has also developed a bifunctional rhenium complex, bearing a non-innocent cyclopentadienol ligand, as hydrogen transfer catalysts for the reduction of ketones and imines.[8f, 9] Due to the importance of cooperative metal-ligand complexes in hydrogenation,[10] notably through the so-called NH-effect,[11] we became interested in the preparation of well-defined rhenium PN(H)P pincer complexes as catalysts for reduction reactions. We report herein the first efficient and broad scope hydrogenation of carbonyl derivatives with a well-defined rhenium complex based on a PN(H)P ligand.

Until now, rhenium PNP pincer type complexes have been sparsely discussed in the literature.[8f, 9] To start our study, we have selected commercially available Re(CO)₅Br as metal precursor and NH(CH₂)₃P(Pr)₂ as ligand. Upon stoichiometric reaction in toluene at 100 °C, the air-stable cationic tricarbonyl rhenium bromide complex 1 was conveniently prepared in a straightforward manner and high yield (92%, Figure 1). The resulting white complex was fully characterized by X-ray diffraction analysis. Surprisingly, in the solid state, as well as in solution, the ligand adopts a facial coordination at Re contrary to other octahedral complexes with Mn,[12] Fe,[13] Ru[14] or Os[15] that exhibit a meridional coordination mode of the ligand.

Our initial investigations, aiming at probing the hydrogenation catalytic activity of 1, were carried out on acetophenone a1 (Table 1). Full reduction of a1 to the corresponding 1-phenylethanol b1 was achieved in the presence of 5 mol% of complex 1, 10 mol% t-BuOK, 50 bar of H₂ at 110 °C for 16 h (entry 1). Interestingly, these conditions resulted in full conversion already after 2 hours (entry 2). Using only Re(CO)₅Br, without any ligand, resulted in no hydrogenation activity (entry 3). The same lack of reactivity was also observed in the absence of base (entry 4). The influence of reaction parameters such as temperature, catalyst loading and pressure was investigated. At 70 °C, full conversion of a1 was still observed after 16 hours (entry 5), but lowering the temperature to 30 °C completely shuts down catalytic activity (entry 6). Under 50 bar of H₂, at 70 °C, the catalyst loading could be decreased to 0.5 mol% without losing any activity, however, with only 0.1 mol% of 1, the conversion dropped to 63% (TON 630, entries 7-8). The pressure of hydrogen can be lowered to 30 bar in the presence of 0.5 mol% of catalyst (entry 9). Ketone hydrogenation still takes place with lower pressure, down to 1 bar, even with a balloon of H₂, although at the expense of the charge of catalyst and temperature (entries 10-12). The optimal
The scope of the reaction are 0.5 mol% of 1, 1.0 mol% of base, 30 bar of H₂, 70 °C for 16 hours (Figure 2).

In general, electron-donating and electron-withdrawing substituents, e.g. o- and p-methyl (b2, b3), p- and o-methoxy (b4, b5), p-morpholinyl (b7), p-fluoro (b11), p- and o-chloro (b12, b13), p-bromide (b16, b20), p-trifluoromethyl (b8), p-amino (b10) and the more reactive p-iodo (b14) groups are well tolerated. Harsher conditions were needed for the hydrogenation of o-methoxy-acetophenone (a5). In addition, 2-acetonaphthone (a6) and diketones (a10) gave also good yields. Next, we explored the activity of the rhenium catalyst towards a collection of more sterically hindered ketones (a15-20, a23, a24). As an example, pivalophenone (a19) was successfully hydrogenated to the corresponding alcohol (b19) in 72% isolated yield. 1-Indanone (a21), α,β-tetralone (a22) could be converted to alcohols at 110 °C. Noteworthy, the α,β-unsaturated chalcone afforded selectively the saturated alcohol (b25) in good yield, and the reduction of benzylideneacetone (b26) led to 4-phenylbutan-2-ol as the major product, contaminated with unsaturated alcohol (ratio 90:10). Additionally, the heteroaromatic substrates (a27-34) based on thiophene, furane, pyridine, pyrole and thiazole were smoothly converted into alcohols.

Even the difficult di(p-dimethylaminophenyl)methane (a36) can be hydrogenated with this catalytic system. Then, we explored the...
scope of aliphatic ketones (a37–42). Under these conditions the rhenium-based catalyst tolerates cyclic, long-chain and remote C=C bond (b39, b40). Starting from the enantiopure (R)-carvone a40, (R)-cis-carveol is obtained as a single diastereoisomer b40. Besides, the internal tri-substituted conjugated C=C in a40 is not reduced. Notably, the cyclopropyl-substituted ketone furnished a quantitative yield of b41 indicating that the reaction does not proceed via stable radical intermediates. Hydrogenation of 4-(tert-butyl)cyclohexanone a42 gave a full conversion with a cis/trans ratio of 32/63.

Figure 3. Scope of the hydrogenation of aldehydes to give alcohols under the catalysis of [Re(NH(CH2CH3)2P(iPr)3]2(CO)3Br. General conditions: H2 (50 bar), tBuOK (10 mol%), 110 °C, toluene.

Aldehydes can also be reduced to the corresponding alcohols with this catalytic system (Figure 3). For example, 4-biphenylaldehyde b43 was hydrogenated to the corresponding primary alcohol smoothly in 2 h. Internal C=C triple bond and amide were tolerated (b44–b45).

Finally, despite this significant scope and functional group tolerance, a few limitations also need to be noted. No conversion was detected with substrates containing coordinating cyano group, acidic phenolic and boric acid on the aromatic ring as well as chelating β-ester and β-acetyl substituents. Next, γ-keto-esters, such as methyl 3-benzoylpropionate a46 were subjected to the reductive conditions in the presence of 1. To our delight, γ-phenyl γ-butyrolactone b46 was obtained in high conversion/yield, showing the tolerance toward ester/lactone functional groups. Interestingly, starting from the biomass derived ethyl levunilate a47, γ-valerolactone b47, which can be used as liquid fuel, additive, solvent or intermediate for organic synthesis,[18] was obtained in good yield (78%) using standard conditions, i.e. 5 mol% of 1, 50 bar of H2, at 110 °C for 2 h (Figure 4).[17]

Figure 4. Synthesis of γ-lactones from γ-keto-esters. Isolated yield in parentheses.

On the basis of previous works of other groups on related complexes with Fe and Ru,[19] as well as our DFT(PBE0-D3) calculations,[19] we propose the following mechanism (Figure 5). In a first step, the base activates the precatalyst 1 by exoergic deprotonation of the NH moieties to form 2 (ΔG = -46.6 kcal mol⁻¹), followed by the isomerisation to the more stable mer-[Re(P(N iPr)3]2(CO)3] complex 3 (ΔG = -3.9 kcal mol⁻¹). Dissociation of CO from 3 is slightly uphill (ΔG = 6.3 kcal mol⁻¹) and forms the 16-electron dicarbonyl complex 4 that is the active form of the catalyst. Endoergic coordination of H2 to form 5 (ΔG = 20.5 kcal mol⁻¹) is followed by facile heterolytic splitting of dihydrogen (ΔG°2 = 5.1 kcal mol⁻¹) to yield the amino-hydride intermediate 6, only slightly less stable than 4 (ΔG = 1.9 kcal mol⁻¹). Acetophenone forms an adduct with 6 essentially upon interaction of the carbonyl oxygen with the N-H proton (ΔG = 6.5 kcal mol⁻¹). The carbonyl reduction is a two-steps process with first hydride transfer from Re to C (ΔG°4 = 13.5 kcal mol⁻¹ and ΔG = 10.5 kcal mol⁻¹), followed by proton transfer from N-H to O, regenerating the active species 4.[20] Overall, the rate-determining step is the H2 heterolytic splitting with an activation barrier of ΔG°4 = 31.9 kcal mol⁻¹ from 3.

Figure 5. Proposed catalytic cycle for the rhenium hydrogenation of ketones to give alcohols based on PBE0-D3 calculations. DFT computed Gibbs free energies (kcal mol⁻¹) relative to 3 are shown.

In conclusion, we have developed an efficient and general hydrogenation of carbonyl derivatives using a well-defined rhenium PN(H)P complex 1. Of notable interest, the reduction proceeds well for a large range of substrates with low catalyst loading (0.5 mol%) under mild conditions (70 °C) and 30 bar of H2. This article is protected by copyright. All rights reserved.
Experimental Section

Complex 1. Bis[2-di-isopropylphosphino]ethyl]amine (0.492 mmol, 1.7 mL, 10 wt% in THF, 1.0 equiv.) was added to a solution of Re(OC)Br₂ (0.492 mmol, 200 mg 1.0 equiv.) in toluene (8 mL). The mixture was stirred at 100 °C for 18 h. Toluene was then evaporated. The crude residue was then recrystallized from dichloromethane and pentane to afford white needle crystals (297 mg, 92%). Complete details of the X-ray analyses reported herein have been deposited at the Cambridge Crystallographic Data Center (CCDC 1501902). Typical catalytic hydrogenation. In an argon filled glove box, an autoclave was charged with complex 1 (8.2 mg, 0.5 mol%), and toluene (2.5 mL), followed by ketone (2.5 mmol) and i- BuOK (2.8 mg, 1.0 mol%), in this order. The autoclave is then charged H₂ (30 bar). The mixture was stirred for 17 h at 70 °C in an oil bath.

Acknowledgements ((optional))

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Keywords: Rhodium • hydrogenation • ketones • mechanism • DFT-D3 calculations

[20] Although TS-8-4 is computed at higher electronic energy than 8, this energy difference is reversed when Gibbs free energies are considered.
[22] See S.I for details.

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An efficient and general rhenium catalyzed hydrogenation of carbonyl derivatives has been developed based on a well-defined rhenium complex bearing a tridentate diphosphino-amino ligand. The mechanism of the reaction has been investigated by DFT (PBE0-D3) calculations.