



## Research paper

## Reduction of imines catalysed by NHC substituted group 6 metal carbonyls

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## ABSTRACT

The catalytic activity of a series of metal carbonyls  $[M(CO)_6]$ , and the corresponding NHC substituted  $[M(CO)_5(NHC)]$ , ( $M = Cr, Mo, W$ ) complexes was examined in the reduction of *N*-benzylideneaniline and acetophenone using silyl hydrides and isopropanol/KOH as reductants. The use of various additives and ultraviolet irradiation to promote the reduction of imines using silyl hydrides as reductants was explored. From a comparison of the reactivity of  $[Mo(CO)_6]$ ,  $[Mo(CO)_5(NHC)]$ , and  $[Mo(CO)_4(bis\ NHC)]$  it was inferred that electron density on the metal centre plays a key role in the catalysis. Four of the best catalysts were then tested in the reduction of a variety of imines with different electronic and steric properties.

## 1. Introduction

Group 6 carbonyl complexes play an important role as catalysts or precatalysts in many organic transformations [1–8]. During the last two decades, a wide range of these carbonyl complexes with various ancillary ligands have been examined as precursors to  $M(VI)$  catalysts for the epoxidation of olefins [9–13], the *cis*-dihydroxylation of olefins [14], and the oxidation of amines [15], alcohols [16,17], and sulfides [18,19]. Surprisingly, there are not too many examples of the use of group 6 metal complexes in general and group 6 metal carbonyl complexes in particular for catalysing reduction reactions such as transfer hydrogenation [20–22], hydrogenation [23–26], and hydrosilylation [27,28]. This is in spite of the fact that group 6 metal-based complexes are attractive hydride transfer agents in view of their low cost and high coordination number enabling great flexibility in the design of the ligand sphere. Moreover, most of these complexes are readily available from the corresponding hexacarbonyl complexes [29].

Among the few reduction reactions catalysed by such metal carbonyls, fewer still utilize hydrosilanes as reducing agents. The conjugate reduction of various Michael acceptors, including  $\alpha,\beta$ -unsaturated ketones, carboxylic acids, carboxylic esters, amides, and nitriles with phenylsilane is catalysed rather sluggishly by  $M(CO)_6$  ( $M = Cr, Mo, W$ ) in refluxing tetrahydrofuran [30]. Hydrosilylation of 1,3-dienes catalysed by  $M(CO)_6$  is also known [31,32]. Tinnis and Adolfsson et al. reported  $Mo(CO)_6$  (5 mol%) catalysed chemoselective hydrosilylation of  $\alpha, \beta$ -unsaturated amides leading to allylamines (yield 51–95%) using 1,1,3,3-tetramethyldisiloxane (TMDS) (1.5 equivalents) for 24 h at 65 °C [33].  $[Mo(CO)_2(oxadiene)_2]$  (oxadiene = pulegone, pinocarvone and (E)-5-methyl-3-hexen-2-one), showed better catalytic activity in the

hydrosilylation of unsaturated ketones and aldehydes with phenylsilane. All aldehydes underwent 1, 2-addition exclusively whereas the ketones gave both 1,2-addition and 1,4-addition products [34]. Anionic  $\mu$ -hydride complexes of group 6 metals of the type  $[(CO)_5M(\mu-H)M(CO)_5][NEt_4]^+$  were reported to catalyse the hydrosilylation of aldehydes and ketones under rather harsh conditions using  $HSiEt_3$ , while silyl enol ethers were obtained using  $H_2SiPh_2$  [35]. A tungsten-based catalyst,  $[CpW(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$  (where  $Cp$  = cyclopentadienyl,  $IMes$  = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene, has been reported to catalyse the solvent-free hydrosilylation of ketones and an ester under mild conditions [36]. The catalytic activity of isocyanide complexes of group 6 metals in the hydrosilylation of olefins is also known [37]. Surprisingly group 6 carbonyl complexes have not been tested for the hydrosilylation of imines to give the corresponding amines.

Although the alkylation of ammonia using halo alkanes or alcohols is a simple way to prepare amines, the degree of alkylation is difficult to control with alkyl iodides and bromides [38]. The synthesis of amines by reduction of imines, amides, nitriles, and nitroarenes using stoichiometric amount of alkali hydrides, such as lithium aluminium hydride and boron hydrides is limited by the air and moisture sensitivity of these reductants, lack of tolerance to various functional groups and formation of metal salts as by-products [39]. The requirement of high temperatures and high pressures, and lack of chemoselectivity makes hydrogenation of imines using dihydrogen gas unsuitable for some substrates [40–43]. Reductive amination of carbonyl derivatives in the presence of primary amines, through sequential condensation/catalytic reduction often requires drastic reaction conditions [44–50]. Due to these reasons the hydrosilylation of imines is an attractive alternative

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