Reduction of carbonyl compounds via hydrosilylation catalyzed by well-defined PNP-Mn(I) hydride complexes

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Abstract
Reduction reactions of unsaturated compounds are fundamental transformations in synthetic chemistry. In this context, the reduction of polarized double bonds such as carbonyl or C=C motifs can be achieved by hydrogenation reactions. We describe here a highly chemoselective Mn(I)-based PNP pincer catalyst for the hydrosilylation of aldehydes and ketones employing polymethylhydrosiloxane (PMHS) as inexpensive hydrogen donor.

Graphical abstract

Keyword Manganese · Pincer complexes · Reduction · Silanes · Ketones

Introduction
The reduction of polarized double bonds such as carbonyl motifs is among the most important transformations in organic synthesis. To increase atom efficiency and avoid massive production of waste, catalytic reactions should be employed. Within this context, precious metals are frequently used. However, their production shows high environmental impact and their amount is limited. The usage of earth abundant metals would decrease the environmental impact and could be an interesting alternative to noble metals [1].

Within this context, manganese is an interesting candidate for investigations due to its low toxicity and high abundance [2]. Manganese-based complexes play a major role in sustainable oxidation [3–10] and hydrogenation [11–18] reactions by now. Although, the use of dihydrogen displays advantages such as low costs and easy removal from the reaction mixture, several drawbacks should be taken in account. Dihydrogen is explosive and expensive reactors have to be used. An attractive alternative to that is the use of hydrogen donors such as silanes [19, 20]. Since the first report on manganese-catalyzed hydrosilylation reactions by Yates and coworkers in 1982 [21], several protocols for the hydrosilylation of polarized double bonds such as ketones [22–27], esters [28, 29], amides [30–32] and acids [33] as well as alkenes [34–36] and alkynes [37] were developed.

Our group recently reported on the chemoselective hydrogenation of aldehydes, catalyzed by a well-defined PNP-Mn(I) complex [15]. We wondered if the same complex is also capable of undergoing hydrosilylation reactions of carbonyl compounds and whether the substrate scope could be extended to ketones (Scheme 1). Here, we describe the chemoselective hydrosilylation of aldehydes and ketones.
catalyzed by well-defined PNP-Mn(I) complexes based upon the 2,6-diaminopyridine scaffold (Scheme 2). As inexpensive silane source polymethylhydrosiloxane (PMHS) is utilized.

Results and discussion

To evaluate the potential use of PNP-based Mn(I) complexes, the hydrosilylation of 4-fluoroacetophenone with phenylsilane was chosen as model reaction utilizing complexes 1–4 as pre-catalysts. Conversions and yields were determined by $^{19}$F{1H} NMR-spectroscopy [13, 18]. While complexes 1, 3, and 4 are capable of metal–ligand bifunctionality, metal–ligand cooperation is blocked in the case of complex 2 due to methylation of the $N$-linker. As shown in Table 1, complexes 1 and 2 gave moderate to good conversion whereas compounds 3 and 4 did not show any reactivity for the hydrosilylation of 4-fluoroacetophenone. The hydride ligand seems to be vital for the activity of the system. Interestingly, complex 1 and 2 gave similar conversions indicating that metal–ligand cooperativity is not crucial for the hydrosilylation of ketones.

According to the results represented in Table 1, catalyst 1 was chosen for further investigations and optimization of the reaction parameters. Since the use of phenylsilane as hydrogen-source is connected to high costs, we wondered if substitution by the inexpensive siloxane polymethylhydrosiloxane (PMHS) is possible. PMHS is a byproduct in industrial siloxane product and, therefore, displays an interesting candidate as hydrogen-source in hydrosilylation reactions [38]. To our delight, the substitution of phenylsilane with PMHS even increased the conversion to 92% (Table 2, entry 1). Increasing the reaction temperature to 110 °C led to full conversion of substrate at only 1 mol% catalyst (Table 2, entry 4). However, the difference between determined conversion and yield was attributed to formation of a hemiacetal as side product.

Therefore, a screening of solvents was done to circumvent the formation of undesired byproduct. Toluene and THF gave low conversion, but no formation of hemiacetal could be detected. Employing isopropanol as solvent led only to traces of product formation. 1,2-Dimethoxyethane (DME) revealed to be the best solvent for this transformation, giving a clean reaction. To achieve good conversions, the catalyst loading was reinvestigated, whereas 2.5 mol% gave the best results (Table 2, entry 10).

Table 1

| Entry | Catalyst | Conversion% | Yield% |
|-------|----------|-------------|-------|
| 1     | 1        | 78          | 65    |
| 2     | 2        | 70          | 63    |
| 3     | 3        | –           | –     |
| 4     | 4        | –           | –     |

Reaction conditions: 0.35 mmol ketone, 2 mol% catalyst, 0.1 mmol PhSiH$_3$, 2 cm$^3$ ACN, 18 h, 80 °C

$^a$Conversion determined via $^{19}$F{1H} NMR-spectroscopy

$^b$Yield determined via $^{19}$F{1H} NMR-spectroscopy and fluorobenzene as standard
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Having established the optimized reaction conditions, the scope and limitation was investigated and a broad variety of different (hetero)aromatic substrates was examined. The introduced procedure tolerated halides (7) as well as coordinating groups such as amine (10), ether (9), and nitrile (11) functionalities. It should be noted, that high chemoselectivity towards the reduction of the keto-group in the presence of a nitro-group could be detected, whereas the nitrile functionality stays unaltered. Lower conversion could be detected in case of dartanal (29) as substrates. Unfortunately, only low conversion could be detected in case of helional (24), citronellal (26), and citral (27) as substrates. The scope of the introduced protocol covered a broad variety of aromatic ketones. In the case of aldehydes, challenging substrates featuring (conjugated) C–C double bonds were chosen which are important in the fragrance industry.

**Conclusion**

In sum, we have described an efficient manganese-catalyzed hydrosilylation of aldehydes and ketones with the inexpensive siloxane PMHS, which is a byproduct in industry. High chemoselectivity for the reduction of carbonyl groups in the presence of (conjugated) C–C double bonds or other reducible groups such as nitro or nitrile functionalities could be reported. The scope of the introduced protocol covered a broad variety of aromatic ketones. In the case of aldehydes, challenging substrates featuring (conjugated) C–C double bonds were chosen which are important in the fragrance industry.

**Experimental**

All manipulations were performed under an inert atmosphere of argon using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures [39]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. Complexes [Mn(PNP-iPr)(CO)₂H] (1), [Mn(PNPMe-iPr)(CO)₂H] (2), [Mn(PNP-iPr)(CO)₂Br] (3), and [Mn(PNP-iPr)(CO)₂(κ¹-O-CHO)] (4) were prepared according to the literature [15, 40, 41]. ¹H NMR spectra were recorded on Bruker AVANCE-250 and 400. ¹H NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethyldisilane (δ = 0 ppm). ¹⁹F{¹H} NMR spectra are reported relative to trichlorofluoromethane (CFCl₃) (δ = 0 ppm).

**General procedure for hydrosilylation reactions**

Inside an Ar-flushed glovebox, an 8 cm³ microwave vial was charged with complex (0.01–0.03 mol%), carbonyl substrate (0.35 mmol), 2 cm³ solvent, and silane (0.035–0.1 mmol) in this order. A stirring bar was added, and the vial was sealed. The closed vial was removed from the glovebox and stirred for 18 h at the indicated temperature in a heated aluminum block. The vial was allowed to reach room temperature and the reaction was quenched by...
exposure to air. In case of screening reactions, fluorobenzene (0.35 mmol) was added and the reaction mixture was analyzed by $^{19}$F-$^1$H NMR.

### Isolation of the product

To the reaction mixture 2 cm$^3$ of a 20 wt% NaOH-solution were added and the solution was stirred for 18 h at room temperature.
temperature. The phases were separated, and the aqueous phase was three times extracted with 2 cm³ diethyl ether. The combined organic phases were filtered over a pad of silica, dried over Na₂SO₄ and the solvent was removed. Spectroscopic data of all isolated products are in line with the literature [11, 42–49].

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