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Short communication

Practical (asymmetric) transfer hydrogenation of ketones catalyzed by manganese with (chiral) diamines ligands

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ABSTRACT

The reduction of ketones with 2-propanol as reductant was achieved using an *in-situ* generated catalytic system based on manganese pentacarbonyl bromide, as metal precursor, and ethylenediamine as ligand. The reaction proceeds in high yield at 80 °C, in 3 h, with 0.5 mol% of catalyst. In the presence of chiral (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-diphenylethane-1,2-diamine, as the ligand, sterically hindered alcohols were produced with enantiomeric excess up to 90%.

1. Introduction

Homogeneous catalysis plays an important role in the development of modern environmentally friendly and atom-economical chemistry. While noble transition metal complexes still remain the prominent actors in this area, the search for new alternatives based on their more abundant, inexpensive first row congeners clearly becomes one of the emerging trends of the present century [1]. Compared to iron [2], manganese-based catalysis has remained in the shadow in spite of the natural abundance of this metal, third most abundant transition metal in the Earth's crust after iron and titanium, and its biocompatibility [3].

The rise of manganese catalyzed reduction reactions started recently after the initial work of Beller [4] in hydrogenation and Milstein in hydrogen auto-transfer reaction [5]. The potential of manganese catalysts in such redox reactions was exemplified with various type of tridendate ligands, mainly phosphorus and nitrogen atoms [6–19]. Interestingly, in the case of hydrogen transfer reaction, using isopropanol as hydrogen donor, Beller has shown that tridentate nitrogen ligand, namely di(picolyl)amine, could promote the reduction of ketones, at 70 °C, in 24 h, with a ratio substrate:catalyst of 100:1 [20]. Asymmetric reduction of ketones with manganese is far less developed and the two first example were reported by Clarke [21] and Kirchner [22], using related chiral ferrocenyl based tridentate PNN or PNP' ligands.

In general, tridentate ligands were used in manganese catalyzed reduction, except in one recent case in which bidentate amino-phosphine ligand was efficient for the hydrogenation of esters [23]. In the meantime, most of the ligands used to date, except the dipicolylamine, were phosphine-based ligands. Following our previous contributions on manganese catalyzed hydrosilylation [24–26], hydrogenation and hydrogen borrowing reactions [15,27,28], we were looking for simple, sustainable and practical catalytic systems to promote hydrogen transfer reactions. We found that well-defined nitrogen-based bidendate manganese catalysts, featuring a picolylamine ligand, were highly efficient for the reduction of ketones and aldehydes by hydrogen transfer reactions [29]. Inspired by the breakthrough of Noyori, introducing chiral diamines as ligands in ruthenium catalyzed asymmetric reduction of ketones [30,31], we envisioned that simple diamines could be suitable for manganese-catalyzed reduction of ketones using isopropanol as the hydrogen donor, and that eventually asymmetric reduction of ketones could be achieved with chiral diamines.

In the present contribution, we demonstrate that diamines, as simple as ethylenediamine, can promote hydrogen transfer reaction with manganese, and that the catalytic system can be generated *in-situ*. Besides, we have extended the reactivity to asymmetric hydrogen

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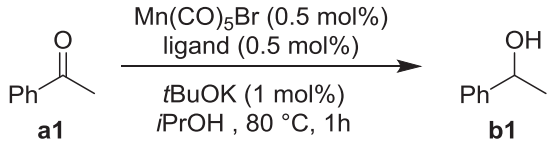
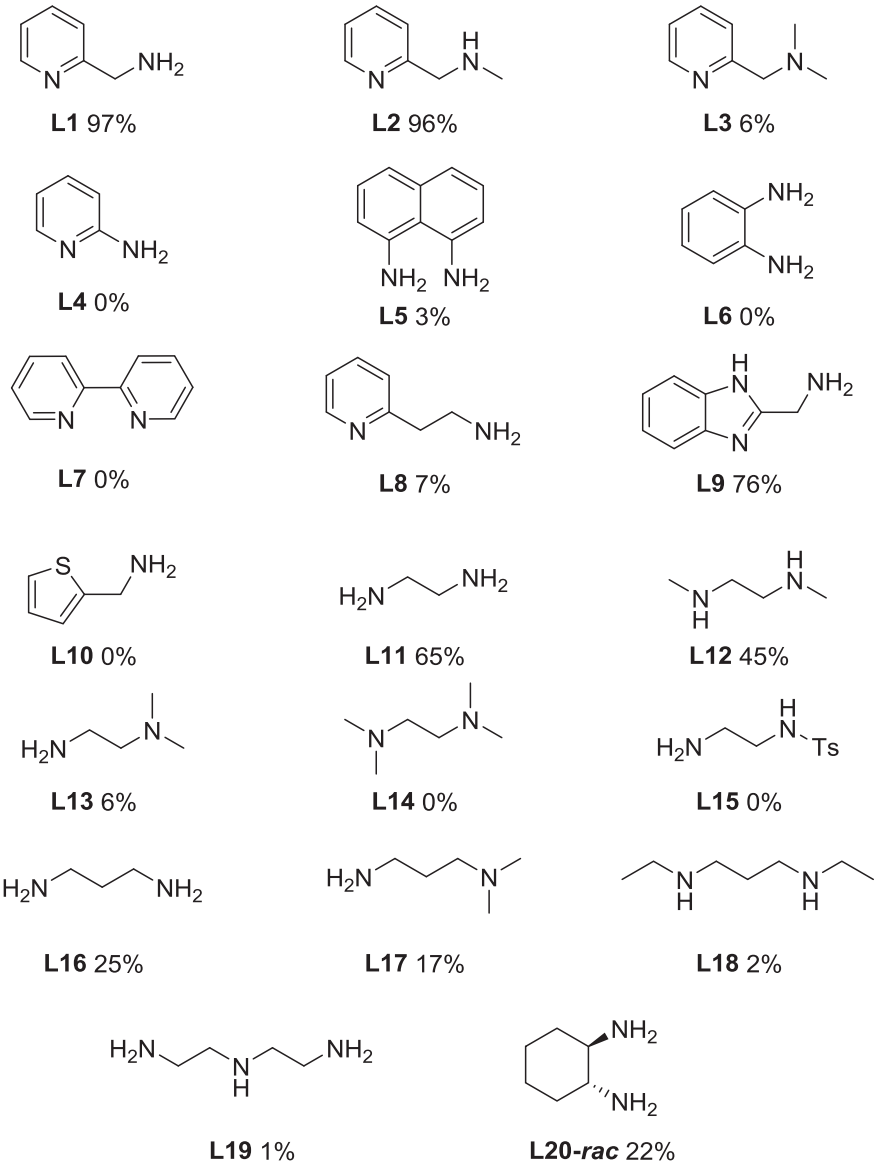


Scheme 1. Screening of bidentate nitrogen based ligands for the reduction of acetophenone in the presence of $Mn(CO)_5Br$ and *t*BuOK in 2-propanol.[a] [[a]Typical conditions: acetophenone **a1** (2 mmol), 2-propanol (8 mL). Conversions were determined by ^1H NMR.]



transfer reaction, with ee up to 90%, employing symmetrical chiral diamines as ligands.

2. Experimental

2.1. Representative procedure for transfer hydrogenation reaction of acetophenone

To a solution of acetophenone (58 μL, 0.5 mmol) in 2-propanol (0.5 mL) was added a stock solution of manganese pentacarbonyl bromide (0.5 mL, 0.005 mol·L^{-1}; 2.7 mg, 0.010 mmol, in 2 mL 2-propanol) followed, in this order, by a stock solution of ethylenediamine (0.5 mL, 0.005 mol·L^{-1}; 1.0 μL, 0.0125 mmol, in 2.5 mL 2-propanol) and *t*BuOK (0.5 mL, 0.010 mol·L^{-1}; 2.4 mg, 0.020 mmol, in 2 mL 2-propanol). The reaction mixture was stirred for 3 h at 80 °C in an oil bath. The solution was then filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the conversion was determined by ^1H NMR. The crude residue was then purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate or dietyl ether as eluent.

Enantiomeric excesses were determined by GC analyses performed on GC-2014 (Shimadzu) 2010 apparatus equipped with Supelco beta-DEX 120 column (30 m × 0.25 mm). The determination of the absolute configuration was done by comparison with (*S*)-alcohol obtained by kinetic resolution of racemic alcohols with Novozym 435 (Candida Antarctica Lipase B) and by comparison of the retention times with the literature [32–34].