



Selective mono *N*-methylation of anilines with methanol catalyzed by rhenium complexes: An experimental and theoretical study[☆]



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ABSTRACT

The selective mono-*N*-methylation of anilines using methanol as an alkylating reagent was achieved with high efficiency under the catalysis of well-defined rhenium complexes bearing tridentate diphosphinoamino ligands and in the presence of a base. The reaction proceeds well for a large scope of anilines (32 examples) with low loadings of both the catalyst (down to 0.5 mol%) and the base (Cs₂CO₃, down to 5 mol%). The mechanism of the reaction was investigated by DFT (PBE0-D3) calculations.

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1. Introduction

In the context of green and sustainable development, the utilization of non-toxic, inexpensive, renewable and readily available reagents is highly desirable. As such, the replacement of hazardous and waste-generating reactants embraces several of the 12 principles of green chemistry, especially when coupled with catalysis [1,2]. In this respect and considering the importance of *N*-methylated amines as key intermediates and building blocks in synthetic chemistry, the development of methylation reagents greener than classical formaldehyde, methyl iodide, methyl triflate, or dimethyl sulfate is a topical challenge. For selective mono-*N*-methylation of amines, sustainable sources of “methyl” group were investigated [3,4], including carbon dioxide [5–15], dialkylcarbonate [16–18] and formic acid [19–21]. Methanol, the simplest alcohol, can also be used as a green and renewable C1 source for methylation reactions [22] using the hydrogen borrowing method-

ology [23–35]. Actually, “Methanol Economy” identifies and promotes methanol as a substitute for petroleum oil in the field of energy and chemistry [36,37]. Methanol is a biodegradable liquid, easy to handle and a safe chemical to produce, compared to, for example, formaldehyde, acetic acid, or ethylene [38]. In addition, due to the plurality of its supply, including renewable sources [39–45], methanol is a sustainable building block.

The first methylations of amines with methanol as an alkylating reagent were developed using group 8–10 transition metal-based catalysts [46–58]. By contrast, group 7 transition metals remained in the shadows regarding catalyst design for hydrogen borrowing reactions and related hydrogenations [59,60]. Manganese was recently disclosed as a suitable metal for promoting (de)-hydrogenation reactions [61,62]. Along with hydrogenation catalysts [63–76], a few manganese catalysts were able to promote hydrogen borrowing reactions [77–84]. In particular, the activation of methanol [85] allowed mono-*N*-methylation of amines [86–88], formylation of amines [89], and amino-methylation of aromatic compounds [90].

With rhenium-based catalysts, hydrogen auto-transfer reactions are quite rare. Rhenium polyhydride phosphine complexes catalyzed acceptorless dehydrogenative coupling of alcohols with carbonyl derivatives [91], amines or alcohols [92], and amination

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of alcohols [93]. Heterogeneous rhenium catalysts promoted the N-methylation of amines with CO₂ and H₂ [94]. During the course of the present study, α -alkylation of ketones with alcohols via hydrogen auto-transfer reactions catalyzed by rhenium complex **1** (*vide infra*), was also reported [95].

In line with our interest in developing group 7 metals based catalysts [65–67,75,87,96–99], we have recently demonstrated that bis(di-isopropylphosphinoethane)amine rhenium catalyst **1** (Scheme 1) efficiently promotes the hydrogenation of carbonyl derivatives with low catalyst loading [100]. DFT calculations suggested that hydrogen transfer from the catalyst to the ketone is a two-step process starting with hydride transfer from Re to C followed by proton transfer from N to O. However, the rate-determining step of the transformation has been found to be the heterolytic cleavage of H₂ across the Re–N bond. Kinetic modeling highlighted the importance of the H₂ concentration required to induce full conversion.

Pursuing our investigations of this class of rhenium complexes, we decided to investigate the challenging methylation of amines with MeOH. Hereafter, we describe the first example of methylation of aromatic amines with methanol catalyzed by rhenium catalysts with the exclusive and selective formation of mono-N-methylated products.

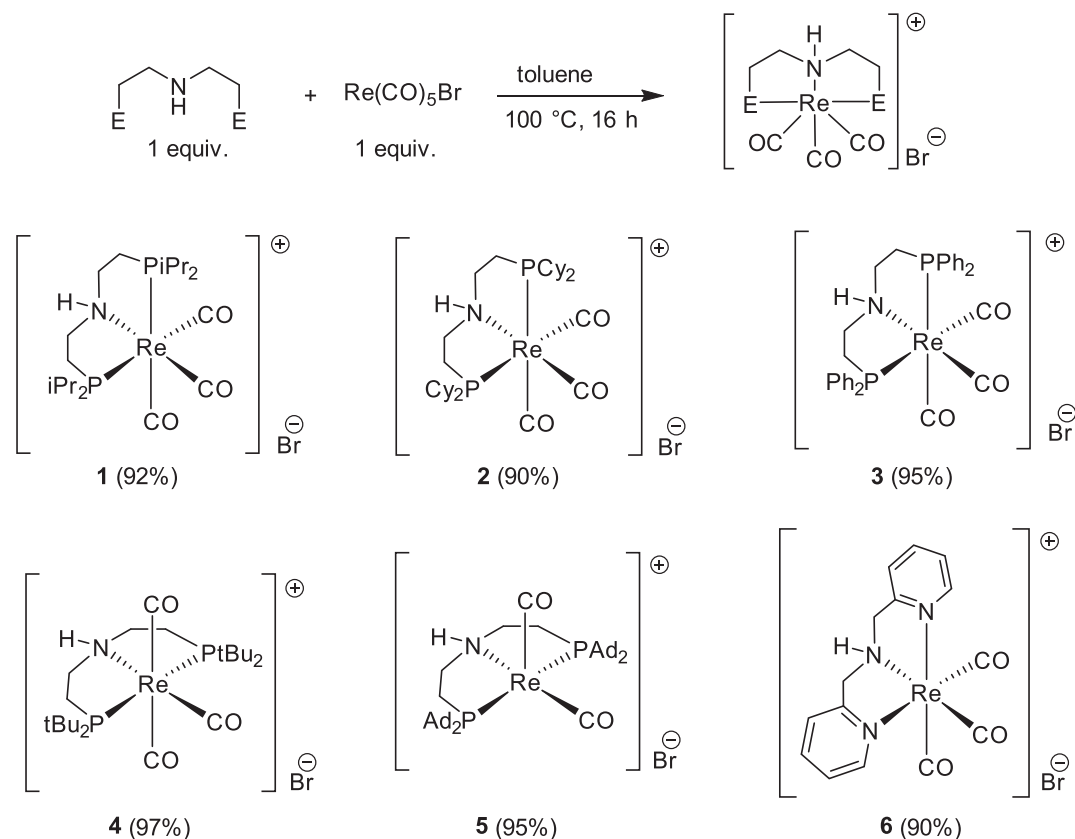
2. Results and discussion

A new series of cationic tricarbonyl Re(I) complexes bearing tridentate PNP [101–112] based on NH(CH₂CH₂PR₂)₂ ligands with different alkyl or aryl substituents on the phosphorus atoms (**2**, R = Cy; **3**, R = Ph; **4**, R = *t*Bu; **5**, R = Ad), was prepared following the methodology previously developed for complex **1**, *i.e.* upon reaction of one equivalent of ligand with one equivalent of [ReBr(CO)₅] in toluene at 100 °C overnight. For comparative purposes,

the **1–5** series of complexes was complemented with the dipicolylamine analogue **6**, prepared following the same procedure from [ReBr(CO)₅] and dipicolylamine. Complexes **1–6** were thus obtained in excellent yield (90–97% yield, see Scheme 1 and S.I). It must be noted that complex **6** has been previously prepared starting from the [NEt₄]₂[Re(CO)₃Br₃] cationic precursor [113]. All the new complexes **2–5** were characterized by NMR, elemental analysis, IR, HR-MS and X-ray diffraction studies. The coordination mode of the tridentate ligand evolved from facial for **1–3** to meridional for **4–5** when the size of the substituent on the phosphorus atom increased (Figs. 1 and 2). According to our previous calculations [100], mer-isomers correspond to the thermodynamically stable geometry, and thus isolated fac-isomers are kinetic products of the reaction.

In the case of the bulkiest adamantyl derivative, complex **5** was obtained as an orange solid, in sharp contrast with the white color of all the other complexes. The ¹³C{¹H} NMR displays only two signals of seemingly equal intensity for the carbonyl ligands, while complexes **1–4** and **6** typically displayed three distinct signals. In the IR spectrum, only two equally intense CO stretching bands are present, while three are present for complexes **1–4** and **6** (Table 1). Finally, the X-ray structure confirmed the sole presence of two carbonyl coordinated to the rhenium center (Fig. 2, right), along with the PNP ligand, thus highlighting the unsaturated coordination sphere of the metal.

Initial screening of the catalytic activity of the complexes focused on the methylation of aniline with methanol (Table 2), using similar conditions as those optimized for manganese catalysts, *i.e.* in the presence of *t*BuOK (25 mol%) as the base, at 130 °C for 48 h (Table 2, entries 1–7), and in a 1:1 (v:v) mixture of methanol and toluene as solvent. Gratifyingly, catalysts **1–3** were active, **3** giving the highest yield (75%), whereas **4–6** and Re(CO)₅Br were totally inactive. It is worth noting that in all the reactions,



Scheme 1. Synthesis and structures of the rhenium complexes used in our investigation.

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