ARTICLE

Effective N-methylation of nitroarenes with methanol catalyzed by a functionalized NHC-based iridium catalyst: a green approach to N-methyl amines

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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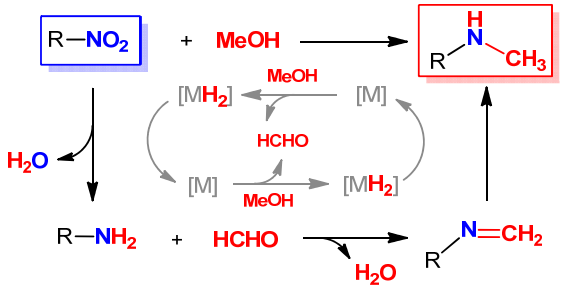
Compound [IrBr(CO)$_2$(κC-tBuImCH$_2$PyCH$_2$OMe)] featuring a flexible pyridine/OMe functionalized NHC ligand κ^{1}C coordinated efficiently catalyzes the selective N-monomethylation of nitroarenes using methanol as both the reducing agent and the C1 source. A range of functionalized nitroarenes including heterocyclic or sterically hindered derivatives have been efficiently converted to the corresponding N-monomethyl amines in good yields at low catalyst loadings using sub-stoichiometric amounts of Cs_2CO_3 as base. Mechanistic investigations support a borrowing-hydrogen mechanism in which methanol acts as hydrogen source and methylating agent. Further the hydrogen transfer reduction of nitrobenzene to aniline under optimized reaction conditions should proceed through a direct mechanism involving nitrosobenzene and N-phenylhydroxyamine intermediates.

Introduction

N-methyl amines are high valuable chemical products as building blocks in the synthesis of fine chemicals, pharmaceuticals, agrochemicals, dyes and natural products.[1] Traditional synthetic methodologies require toxic and dangerous stoichiometric reagents as methyl halides, dimethyl sulphate or diazomethane, produce large waste amounts and generally exhibit low selectivities due to the formation of overalkylated products.[2] On the other hand, reductive amination involving formic acid, formaldehyde or carbon dioxide, or the use of dimethyl carbonate are more sustainable alternatives that still require harsh reaction conditions and excess reducing agents.[3] Alternatively, the use of methanol as a sustainable and atom economical C1 source has emerged as a greener approach to methylation of amines because water is the unique by-product generated and methanol is readily accessible from abundant sources.[4] Remarkably, being based on the borrowing-hydrogen strategy this methodology involves the challenging oxidation of methanol to formaldehyde.[5] The first example of N-methylation of amines with methanol was reported by Grigg et al. at the beginning of 1980s.[6] Since then, a number of transition metal-based homogeneous and heterogeneous catalysts have been developed, being ruthenium and iridium among the most active metals.[7]

On the other hand, although a conventional method to synthesize aromatic amines is the hydrogen transfer reduction of inexpensive and ready available nitroarenes,[8] the one-pot synthesis of N-alkyl amines, entailing the reduction and methylation of nitro derivatives in the presence of alcohols remained unexplored until recent years.[9] The straightforward conversion of nitroarenes into N-methyl amines by using methanol is as appealing as challenging because methanol has to serve as both hydrogen source (for the reduction of the nitro derivative) and methylation agent (of the in situ formed amine), and the catalyst has to perform the consecutive redox reactions typical of a borrowing-hydrogen mechanism (Scheme 1). In this context, it is worth noting that the dehydrogenation energy of methanol is greater than that of higher alcohols such as ethanol or isopropanol.[10]

Despite the fact that a number of transition metal-based catalysts are able to promote the methylation of amines via



Scheme 1 Stepwise borrowing hydrogen mechanism for the synthesis of N-methyl amines from nitro compounds using methanol as a C1 source (IrH_2 represents the result of the formal abstraction of two hydrogen atoms by the catalyst).

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Electronic Supplementary Information (ESI) available: NMR spectra for compounds **1**-**4** and N-methylated derivatives. See DOI: 10.1039/x0xx00000x

hydrogen borrowing (vide supra), only a few catalytic systems have been reported for this tandem catalytic transformation and most of them are based on heterogeneous photocatalysts that yield dimethylated amines as major products.[10,11] Regarding homogeneous catalysts, Kundu et al. reported in 2017 a N,N,N-pincer ruthenium complex, based on a 6-methoxypyridin-2-yl functionalized phenanthroline scaffold, that efficiently catalyzes the N-methylation of aromatic and vinyl nitro compounds to the mono-methylated amine derivatives and nitroalkane substrates to dimethylated amines.[12] Recently, two efficient ruthenium[13] and palladium-based[14] catalytic systems for this tandem transformation have been reported. In both cases, the catalysts were in situ generated from commercial metal precursors, $[RuCl_2(p\text{-cymene})_2]_2$ and $Pd(OAc)_2$, and elaborate NNN amine-pyridine-imine pincer or imidazole-substituted hemilabile phosphine ligands, respectively. In addition, relatively high catalyst loadings, stoichiometric amount of base, excess of auxiliary ligand and long reaction times were generally required. Thus, the development of more efficient homogeneous catalysts is still highly desirable in order to make this methodology more sustainable.

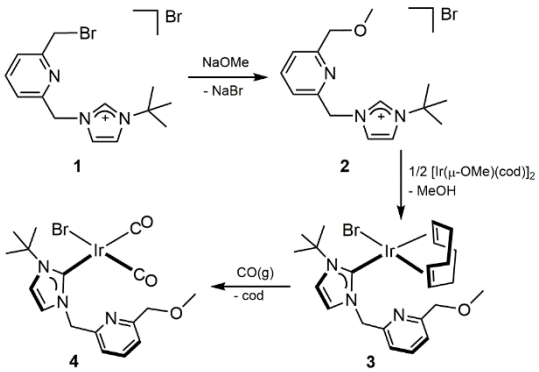
We have recently shown the efficiency of iridium(I) complexes featuring O- and N-donor functionalized NHC ligands as catalysts for the β-alkylation of alcohols and N-alkylation of amines with alcohols via a borrowing hydrogen mechanism.[15] Inspired by the positive influence of the O/N-donor function on the catalytic activity, we have now designed a new type of iridium(I) complexes incorporating a flexible lutidine-derived polydentate ligand, having NHC and -OMe as side donor functions. We foresee that the combination of two very different strong donor functions, such as pyridine and NHC, and a labile methoxy fragment as well as the flexibility imparted by the methylene linkers, could have an impact on the catalyst performance. As reported herein, these iridium(I) complexes have proved to be efficient catalysts for the direct transformation of nitroarenes and methanol into N-methyl anilines.

Results and discussion

Synthesis and structure of iridium(I) complexes.

The imidazolium salt precursor for the lutidine-based NHC/OMe ligand was prepared in two steps starting from the commercially available 2,6-bis(bromomethyl)pyridine. Reaction of 2,6-bis(bromomethyl)pyridine with 1-(tert-butyl)-1*H*-imidazole, following the synthetic procedure previously described for related functionalized imidazolium salts,[16] afforded the bromomethyl functionalized lutidine-derived imidazolium salt **1** which was obtained as a white solid in 43% yield. The functionalized imidazolium salt **2**, precursor of Ir-NHC complexes, was prepared by reaction of **1** with sodium methoxide and isolated as a pale yellow powder in 81% yield. The iridium(I) complex [IrBr(cod)(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**3**) was synthesized from the free NHC ligand generated in situ by deprotonation of the imidazolium salt **2** by the methoxo ligands in the dinuclear complex $[Ir(\mu\text{-OMe})(cod)]_2$, and isolated as a yellow powder in 85% yield. Finally, carbonylation of **3** in dichloromethane gave a pale yellow solution from which the carbonyl complex [IrBr(CO)$_2$(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**4**) was isolated as a pale yellow-greenish powder in 75% yield (Scheme 2). The compounds have been fully characterized by elemental analysis, mass spectra and multinuclear NMR spectroscopy. The formation of the Ir–NHC bond is confirmed by the absence of the ^{1}H signal of the C2H group of **2** and the presence of a ^{13}C singlet resonance at δ 180.7 (**3**) and 172.1 ppm (**4**), assigned to the carbenic carbon atom. On the other hand, the neutral character of both complexes was confirmed by conductivity measurements in acetone thereby suggesting the presence of an uncoordinated pyridine fragment in the complexes. The protons of the methylene linker Im-C*H$_2$*-Py in both complexes are diastereotopic affording two well-separated doublets in the ^{1}H NMR spectra with $J_{H\text{-}H} \approx 15$ Hz. In addition, the four distinct resonances for the =CH of the cod ligand in both the ^{1}H and ^{13}C{^{1}H} NMR of **3** suggest restricted rotation about the Ir-C_{NHC} bond. The presence of two carbonyl ligands in a cis disposition in **4** is confirmed by the observation of two strong stretching ν(CO) bands at 2056 and 1969 cm^{-1} in the ATR-IR spectrum and two ^{13}C resonances at δ 180.2 and 167.7 ppm.

The κ^{1}C coordination mode of the ligand in complexes [IrBr(cod)(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**3**) and [IrBr(CO)$_2$(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**4**) was established by an X-ray diffraction analysis (Fig. 1). Both complexes exhibit a slightly distorted square planar geometry at the metal centre with a *cis* disposition of the NHC moiety and the bromido ligand. The C(1)-N(2)-C(3)-C(4)-N(5) ring lies almost perpendicular to the coordination plane [N(2)-C(1)-Ir-Br: 92.6(3)° (**3**); 91.7(6)° (**4**)], and adopts an almost ideal arrangement with respect to the Ir-C(1) bond with pitch (θ) and yaw (ψ) angles of 1.5° and 5.2°,[17] respectively, for both complexes. Notably the higher trans influence of the NHC moiety compared to that of the bromido ligand makes the Ir-Ct1 distance (2.06107(11) Å) longer than Ir-Ct2 (1.98557(12) Å) in **3** as well as the bond length Ir-C(22) (1.901(6) Å) longer than Ir-C(20) (1.875(7) Å) in **4**. Selected



Scheme 2 Synthetic pathway for the preparation of iridium(I) complexes bearing a lutidine-based NHC/OMe functionalized ligand.

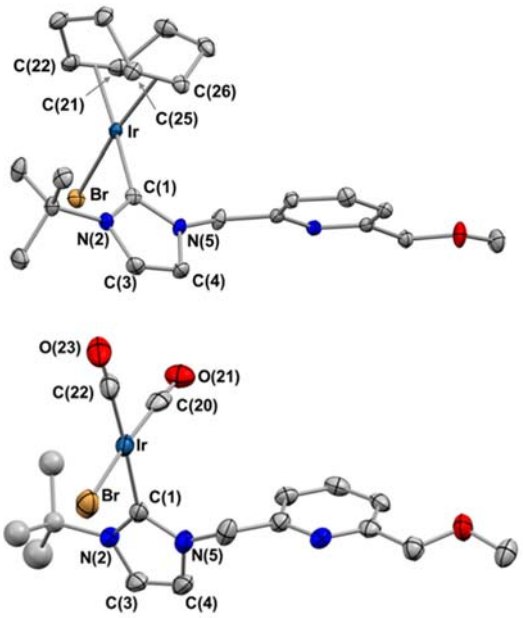


Fig. 1 ORTEP view of the crystal structures of **3** (top) and **4** (bottom). For clarity, hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°) for **3**: Ir-C(1) 2.050(3), Ir-Br 2.5054(3), Ir-Ct1 2.06107(11), Ir-Ct2 1.98557(12), Ct1-Ir-Ct2 87.211(5), Ct1-Ir-C(1) 177.97(8), Ct2-Ir-C(1) 93.77(8), C(1)-Ir-Br 87.15(8), N(2)-C(1)-Ir-Br –92.6(3). Ct1: centroid of C(21)-C(22); Ct2: centroid of C(25)-C(26). Selected bond lengths (Å) and angles (°) for **4**: Ir-C(1) 2.084(5), Ir-Br 2.4670(7), Ir-C(20) 1.875(7), Ir-C(22) 1.901(6), C(20)-O(21) 1.073(8), C(22)-O(23) 1.130(7), C(20)-Ir-C(22) 92.2(2), C(20)-Ir-C(1) 91.0(2), C(22)-Ir-C(1) 176.8(2), C(1)-Ir-Br 89.21(14), N(2)-C(1)-Ir-Br 91.7(6).

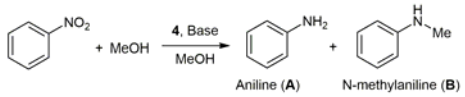
intermolecular contacts in both compounds are discussed in the ESI.

N-Methylation of nitroderivatives catalyzed by [IrBr(CO)$_2$(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)]

We investigated the catalytic applicability of the iridium(I) compounds **3** and **4** in N-alkylation reactions by studying the N-methylation of nitrobenzene with methanol as a model reaction. In an initial screening we used a catalyst loading of 2.5 mol%, 1 equiv of KO^{t}Bu as base, and 2.5 mL of methanol at 383 K for 15 h. Under these experimental conditions both complexes gave full conversion of nitrobenzene with selectivities to N-methylaniline higher than 90%. However, catalyst **4** is the most efficient in terms of selectivity (96%). In addition, the reaction does not take place in the absence of **3** or **4**, and the dimer [Ir(μ-Cl)(cod)]$_2$ gave a selectivity of only 27% (see ESI). After these preliminary tests, the reaction conditions for catalyst **4** were optimized evaluating different bases, the influence of the temperature and the loading of base and catalyst (Table 1). While bases such as KO^{t}Bu, KOH, NaOMe, NaH or KHMDS promoted the reaction providing full nitrobenzene conversion in 5 h and 60-70% selectivities in N-methylaniline (entries 1-6), Cs_2CO_3 was much more effective giving 84% of selectivity (entry 7). Temperature has a strong influence on the catalytic performance: increasing the temperature to 403 K raised the selectivity up to 95% (entry 9). Under these catalytic conditions, the amount of base can be lowered to 0.75 equiv while maintaining the selectivity (entry 12). Decreasing the catalyst loading to 1% had a negative impact on the selectivity that drops to 83% (entry 17). On the other hand, neither increasing the reaction time to 7 h nor increasing the concentration of the reactants by decreasing the amount of methanol had a positive impact on the selectivity (entries 18-20). Finally, the reaction in the presence of mercury (4 equiv) under optimized conditions gave similar results confirming that the catalytic reaction proceeds in homogeneous phase (entry 21).[18] We have also examined the performance of **4** at milder temperatures or lower catalyst loadings. Although only 86% selectivity was attained after 48 h at 333 K at 2.5 mol% catalyst loading, gratifyingly, the catalyst loading can be lowered up to 0.5 mol% at 403 K giving full selectivity to N-methylaniline in 24 h (see ESI).

In order to explore the substrate scope of this transformation, the N-methylation of a range of substituted nitrobenzene

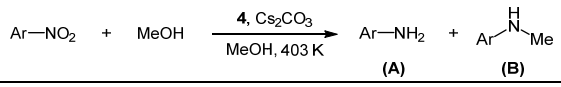
Table 1 Optimization of reaction conditions for the N-methylation of nitrobenzene with methanol catalyzed by [IrBr(CO)$_2$(κ-*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (4).[a]

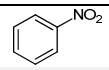
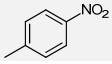
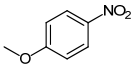
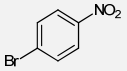
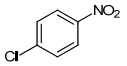
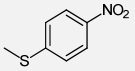
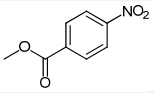
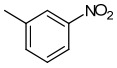
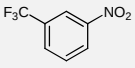


	T (K)	Base (mol%)	4 (mol%)	t (h)	Selectivity (%)[b] A	B
1	383	KO^{t}Bu (100%)	2.5	15	4	96
2	383	KO^{t}Bu (100%)	2.5	5	28	72
3[c]	383	KOH (100%)	2.5	5	32	68
4	383	NaOMe (100%)	2.5	5	43	57
5	383	NaH (100%)	2.5	5	33	67
6	383	KHMDS (100%)	2.5	5	38	62
7	383	Cs_2CO_3 (100%)	2.5	5	16	84
8	413	Cs_2CO_3 (100%)	2.5	5	4	96
9	403	Cs_2CO_3 (100%)	2.5	5	5	95
10	363	Cs_2CO_3 (100%)	2.5	5	65	35
11	403	Cs_2CO_3 (125%)	2.5	5	4	96
12	403	Cs_2CO_3 (75%)	2.5	5	5	95
13	403	Cs_2CO_3 (50%)	2.5	5	23	77
14	403	Cs_2CO_3 (25%)	2.5	5	41	59
15	403	Cs_2CO_3 (75%)	3	5	5	95
16	403	Cs_2CO_3 (75%)	2	5	15	85
17[c]	403	Cs_2CO_3 (75%)	1	5	17	83
18	403	Cs_2CO_3 (75%)	2.5	7	5	95
19	403	Cs_2CO_3 (75%)	2.5	3	14	86
20[d]	403	Cs_2CO_3 (75%)	2.5	5	29	71
21[e]	403	Cs_2CO_3 (75%)	2.5	5	9	91

[a] Reaction conditions: nitrobenzene (0.5 mmol, catalyst 4 (mol%), base (mol%) in methanol (2.5 mL). Conversion: 100%; based on the consumption of nitrobenzene. [b] Selectivity determined by GC using mesitylene as internal standard. [c] Conversion: 94%; based on the consumption of nitrobenzene. [d] Reaction carried out in 1.25 mL of methanol. [e] Reaction performed in the presence of 4 equiv of Hg.

Table 2 N-methylation of nitroarenes with methanol catalyzed by compound **4.**[a]



Entry	Substrate	4 (mol%)	t (h)	conv. (%)[b]	A/B ratio (%)[c]
1		2.5	5	100	4/96 (92)
2		2.5	5	100	-/100 (97)
3		2.5	5	100	-/100 (92)
4		2.5	5	80	11/35[d]
5[e]		2.5	15	100	-/90[d,f]
6		2.5	5	100	-/76[g]
7[e]		2.5	15	100	12/75[f,g]
8		2.5	5	100	30/70
9		2.5	15	100	20/80
10		5	15	100	-/100 (94)
11		2.5	5	100	59/41
12		2.5	15	100	17/83
13		2.5	24	100	1/99 (93)
14		2.5	5	98	46/54
15		2.5	15	100	16/84
16		5	15	100	8/92 (86)
17		2.5	5	100	53/47
18		2.5	15	100	19/81
19		2.5	24	100	10/90 (80)
20		2.5	5	100	60/40
21		2.5	15	100	40/60
22		5	15	100	15/85
23		5	20	100	6/94 (90)
24		2.5	5	100	53/47
25		2.5	15	100	19/81
26		2.5	24	100	11/89 (90)
27		2.5	5	100	38/62
28		2.5	15	100	23/77
29		2.5	24	100	14/86 (82)

[a] Reaction conditions: nitroarene (0.5 mmol), Cs_2CO_3 (0.375 mmol, 75 mol%) in methanol (2.5 mL) at 403 K. [b] Conversion, based on nitroarene, and selectivity determined by GC using mesitylene as internal standard. [c] Isolated yield (%) in parenthesis. [d] p-anisidine and 4-methoxy-N-methylaniline observed. [e] Reaction performed at 383 K. [f] Not isolable by column chromatography. [g] 1-methoxy-4-nitrobenzene and p-anisidine detected.

derivatives with methanol was carried out under the following standard reaction conditions: [nitroarene] = 0.2 M, 2.5 mol% of **4**, 75% of Cs_2CO_3 as base in 2.5 mL of methanol at 403 K for 5 h (Table 2). Substrates having electro-donating groups at the *para* position were quantitatively transformed into the mono-methylated derivatives (entries 2 and 3). Halogen-substituted derivatives underwent nucleophilic aromatic substitution resulting in the formation the methoxy-derivatives with the subsequent reduction of the selectivity for the desired N-methylaniline derivatives (entries 4 and 6). However, the selectivity for 4-halo-N-methylaniline derivatives was considerably improved by lowering the temperature at 383 K (entries 5 and 7). The thioether-substituted derivative required 5 mol% catalyst to get the full conversion to N-methyl-4-(methylthio) aniline in 15 h (entries 8-10). Substrates with electro-withdrawing groups are somewhat less reactive, though methyl 4-nitrobenzoate was almost quantitatively transformed into the corresponding methyl 4-(methylamino)benzoate derivative in 24 h (entries 11-13). In case of *ortho* and *meta* substituted nitrobenzene derivatives, longer reaction times and/or higher catalyst loadings are required to attain selectivities higher than 90% in the desired N-methylaniline derivatives (entries 14-23). Heterocyclic or sterically hindered substrates, such as 3-nitropyridine and 1-nitronaphthalene, were efficiently transformed into the corresponding N-methylated derivatives in 24 hours with selectivities close to 90% (entries 24-29). The N-methylated amine derivatives, except those derived from halo-derivatives, have been isolated as yellow or colorless oils in 80–95% yield after purification by column chromatography.

Mechanistic investigations.

Reaction profile of the N-methylation of nitrobenzene under optimized conditions shows the immediate consumption of nitrobenzene with formation of N-methylaniline with a conversion of 25% in 30 min (Fig. 2). In the early stage of the reaction azobenzene is detected up to a maximum of 4% at 30 min. Aniline is slowly accumulated, reaching a maximum of 10% at 2.5 h, and nitrobenzene is totally consumed in 3 h. Subsequently, aniline is progressively transformed into N-methylaniline, which is in agreement with the selectivity observed.

Remarkably, N-methyleneaniline was not detected suggesting fast hydrogenation to N-methylaniline. On the other hand, the use of methanol-d_4 or methanol-d_1 as solvent resulted in the formation of N-(methyl-d_3)aniline-*d* and N-(methyl)aniline-*d*, respectively, which supports a borrowing-hydrogen mechanism in which methanol acts as hydrogen source and methylating agent (Fig. 3).

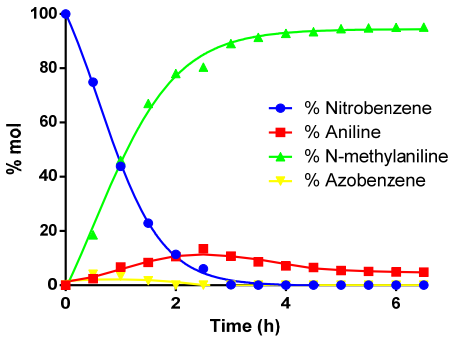


Fig. 2 Time-dependence of the N-methylation of nitrobenzene with methanol catalyzed by compound **4**. Reaction conditions: nitrobenzene (0.5 mmol), **4** (2.5 mol%) and Cs_2CO_3 (75 mol%) in methanol (2.5 mL) at 403 K monitored by GC.

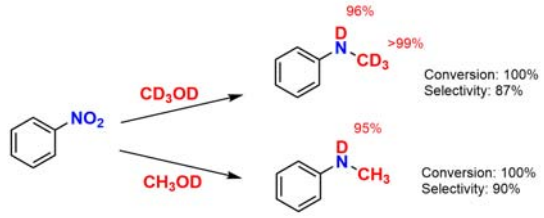


Fig. 3 N-Methylation of nitrobenzene with methanol-d_4 (top) and methanol-d_1 (bottom) catalysed by **4** (2.5 mol%) in the presence of Cs_2CO_3 (75 mol%) at 403 K, 5 h

According to the reported data, the hydrogen transfer reduction of nitrobenzene to aniline can occur through two reaction pathways (Fig. 4).[8c,8d,19] In the direct route the stepwise hydrogen transfer reduction of nitrobenzene to N-phenylhydroxyamine, via the intermediate nitrosobenzene, is followed by hydrogen transfer reduction and dehydration to aniline. On the other hand, in the indirect route, reductive coupling of the intermediates nitrosobenzene and N-phenylhydroxyamine affords azoxybenzene. This species is reduced via hydrogen transfer and dehydrated to azobenzene that is further reduced to aniline through the intermediate 1,2-diphenylhidrazine.

The detection of azobenzene in the N-methylation of nitrobenzene with methanol catalyzed by **4** (Figure 2) suggests that the indirect route is operative.[8c] Nonetheless it cannot be ruled out that the direct route is operative, as well. In order to better understand the nitrobenzene reduction step, additional experiments at lower temperature were performed and the resulting reaction mixtures analyzed at a reaction time of 2 h. (Table 3). It is worth noting that both reduction of nitrobenzene and formation of N-methylaniline occur even at 333 K. In addition, the accumulation of azoxybenzene (16%) and azobenzene (30%) was observed at this temperature (entry 1). Interestingly, the progressive increase of the temperature (entries 2-4) resulted in a steady decrease of the amount of both intermediates which eventually were not

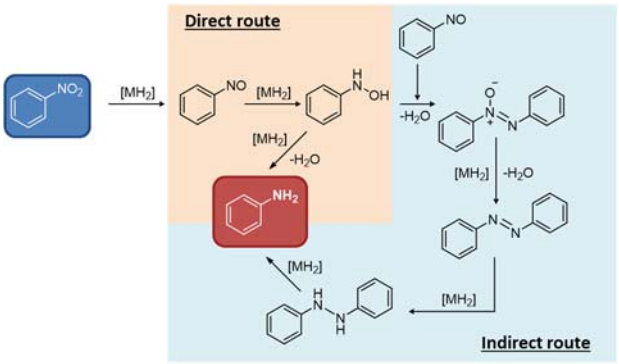


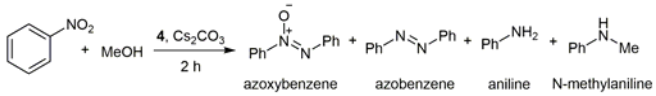
Fig. 4. Mechanistic pathways for the transfer hydrogenation reduction of nitrobenzene to aniline using methanol as hydrogen source. Methanol dehydrogenation by the catalyst produces MH_2 and formaldehyde after each hydrogenation step (not shown).

observed at 403 K (entry 4). At the same time, the amount of N-methylaniline increased gradually, the selectivity being 88% at 403 K (entry 4).

The reaction of azobenzene, an intermediate product of the indirect route, with methanol in the presence of catalyst **4** under the optimized reaction conditions has been studied as well (Table 4). A 36% conversion of azobenzene was attained in 5 h to give a mixture in which the azobenzene reduction products, 1,2-diphenylhydrazine and aniline, are obtained with selectivities of 30% and 60%, respectively, with only an 8% of the final product N-methylaniline. Additionally, azoxybenzene, the oxidation/hydration product of azobenzene is also present at 2%. As expected, the presence of water (0.5 mmol) inhibits the conversion (28%) and results in an increase in the proportion of azoxybenzene (14%) and unexpectedly, an increase in the selectivity to the product N-methylaniline (17%) (Table 4).

Comparing the conversion and selectivity to N-methylaniline attained in the N-methylation of azobenzene (Table 4, entry 1) with those for the N-methylation of nitrobenzene, i.e. full conversion and 95% selectivity (Table 1, entry 1), it can be inferred that the mechanism operating in the reduction of

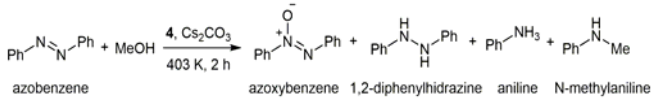
Table 3 Influence of the temperature on the N-methylation of nitrobenzene with methanol catalyzed by [IrBr(CO)$_2$(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**4**).[a]



	T (K)	Conv. (%)[b]	Selectivity (%)[b]			
			azoxybenzene	azobenzene	aniline	N-methylaniline
1	333	32	16	30	21	33
2	353	34	14	26	21	39
3	373	57	7	3	28	62
4	403	87	-	-	12	88

[a] Reaction conditions: nitrobenzene (0.5 mmol), **4** (2.5 mol%), and Cs_2CO_3 (75 mol%) in MeOH (2.5 mL) for 2 h. [b] Conversion, based on nitrobenzene, and selectivity determined by GC using mesitylene as internal standard.

Table 4 N-methylation of azobenzene with methanol catalyzed by [IrBr(CO)$_2$(κ-*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**4**).[a]



	Conv. (%)[b]	Selectivity (%)[b]			
		azoxybenzene	1,2-diphenylhidrazine	aniline	N-methylaniline
1	36	2	30	60	8
2[c]	28	14	13	56	17

[a] Reaction conditions: azobenzene (0.5 mmol), catalyst **4** (2.5 mol%), Cs_2CO_3 (75 mol%) in methanol (2.5 mL) at 403 K for 5 h. [b] Conversion, based on the consumption of azobenzene, and selectivity determined by GC using mesitylene as internal standard. [c] In the presence of H_2O (0.5 mmol, 0.2 M).

nitrobenzene by hydrogen transfer under optimized conditions (403 K) cannot follow the indirect route and that direct route should account for the observed outcome. This finding contrast with the observed in the literature as the hitherto reported iridium complexes seem to follow the indirect route.[8c,20] However, the detection at 333 K of significant amounts of azoxybenzene and azobenzene suggests that the indirect route could be operative at low temperature or even at 403 K to an extent.

Experimental section

Synthesis

All experiments were carried out under an atmosphere of argon using Schlenk techniques. Solvents were distilled immediately prior to use from the appropriate drying agents or obtained from a Solvent Purification System (Innovative Technologies). Oxygen-free solvents were employed throughout. $CDCl_3$, and bencene-d_6 were dried using activated molecular sieves. Methanol-d_4 and methanol-d_1 (<0.02% D_2O) were purchased from Eurisotop and used as received. The substrates were obtained from common commercial sources and used as received or recrystallized or distilled prior to use depending on their purity. The iridium starting material [Ir(μ-OMe)(cod)]$_2$ was prepared according to the literature procedure.[21]

Scientific Equipment

C, H, and N analyses were carried out in a PerkinElmer 2400 Series II CHNS/O analyzer. Infrared spectra were recorded on a FT-PerkinElmer Spectrum One spectrophotometer using Nujol mulls between polyethylene sheets. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 300 (300.1276 MHz and 75.4792 MHz). NMR chemical shifts are reported in ppm relative to tetramethylsilane and are referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in hertz. Spectral assignments were achieved by combination of ^1H–^1H COSY, ^{13}C APT, ^1H–^{13}C HSQC and ^1H–^{13}C HMBC experiments. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formate as reference. Conductivities were measured in ca. 5×10^{-4} M nitromethane solutions of the complexes using a Philips PW 9501/01 conductimeter. The catalytic reactions were analyzed on an Agilent 4890D system equipped with an HP-INNOWax capillary column (0.4 μm film thickness, 25 m × 0.2 mm i.d.) using mesitylene as the internal standard. Organic compounds were identified by gas chromatography-mass spectrometry (GC/MS) using an Agilent 6890 GC system with an Agilent 5973 MS detector equipped with an HP-5MS polar capillary column (0.25 μm film thickness, 30 m × 0.25 mm i.d.).

Synthesis of precursors and iridium(I) complexes

Synthesis of [^{t}BuHImCH$_2$PyCH$_2$Br]Br (1). 1-(tert-butyl)-1H-imidazole (937 mg, 7.55 mmol) was slowly added to a solution of 2,6-bis(bromomethyl)pyridine (4.00 g, 15.1 mmol) in toluene (20 mL). The solution was stirred for 3 days at room temperature to give a white suspension. The suspension was filtered and the white solid washed with toluene (2 x 10 mL) and dried under vacuum. The compound was purified by column chromatography (silica gel, MeOH/Et_2O 1:1) obtaining a white oil. The oil was disaggregated by stirring with cold diethyl ether, to give a white solid which was washed with diethyl ether (2 x 10 mL) and dried under vacuum. The pure compound was isolated as a white solid (2.50 g, 43%). Anal. Calc. for $C_{14}H_{19}Br_2N_3$: C, 43.21; H, 4.92; N, 10.80. Found: C, 42.80; H, 4.77; N, 10.15. HRMS (ESI+, MeOH, m/z): 308.0752 $[M]^+$. ^1H NMR (298 K, 300 MHz, $CDCl_3$): δ 11.03 (s, 1H, NCHN), 7.98 (d, $J_{H\text{-}H}$ = 7.7 Hz, 1H, H_m Py), 7.78 (t, $J_{H\text{-}H}$ = 7.5 Hz, 1H, H_p Py), 7.76 (d, $J_{H\text{-}H}$ = 1.7 Hz, 1H, =CH Im), 7.42 (d, $J_{H\text{-}H}$ = 7.7 Hz, 1H, H_m Py), 7.24 (d, $J_{H\text{-}H}$ = 1.9 Hz, 1H, =CH Im), 5.92 (s, 2H, CH_2Im), 4.52 (s, 2H, CH_2Br), 1.74 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (298 K, 75 MHz, $CDCl_3$): δ 156.8, 152.7 (C_o Py), 138,8 (C_p Py), 136.2 (N*C*HN), 124.0, 123.5 (C_m Py), 122.9, 118.3 (=CH, Im), 60.6 (C ^{t}Bu), 53.4 (CH_2Im), 33.4 (CH_2Br), 30.1 (CH_3 ^{t}Bu).

Synthesis of [^{t}BuHImCH$_2$PyCH$_2$OMe]Br (2). Sodium methoxide (266 mg, 4.92 mmol) was added to a solution of [^{t}BuHImCH$_2$PyCH$_2$Br]Br (**1**) (1.60 g, 4.11 mmol) in methanol (10 mL). The solution was stirred for 15 h at room temperature to give an orange solution. The solution was brought to dryness under vacuum and the residue extracted with dichloromethane (10 mL) to give a suspension which was filtered and washed with dichloromethane (2 x 5 mL). The resulting solution was brought to dryness under vacuum to give an orange oil which was disaggregated by stirring with cold diethyl ether to give an orange solid which was washed with diethyl ether (2 x 5 mL) and dried under vacuum. The pure compound was isolated as a pale yellow-orange solid (1.13 g, 81%). Anal. Calc. for $C_{15}H_{22}BrN_3O$: C, 52.95; H, 6.52; N, 12.35. Found: C, 53.27; H, 6.74; N, 12.07. HRMS (ESI+, MeOH, m/z): 260.1757 $[M]^+$. ^1H NMR (298 K, 300 MHz, $CDCl_3$): δ 11.04 (s, 1H, NCHN), 7.86 (d, $J_{H\text{-}H}$ = 7.6 Hz, 1H, H_m Py), 7.74 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, H_p Py), 7.64 (d, $J_{H\text{-}H}$ = 1.9 Hz, 1H, =CH Im), 7.39 (d, $J_{H\text{-}H}$ = 7.8 Hz, 1H, H_m Py), 7.26 (d, $J_{H\text{-}H}$ = 1.9 Hz, 1H, =CH Im), 5.85 (s, 2H, CH_2Im), 4.51 (s, 2H, CH_2OMe), 3.45 (s, 3H, OCH_3), 1.71 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (298 K, 75 MHz, $CDCl_3$): δ 158.8, 152.3 (C_o Py), 138.5 (C_p Py), 136.5 (N*C*HN), 123.5 (C_m Py), 122.7 (=CH Im), 121.8 (C_m Py), 118.4 (=CH Im), 75.5 (CH_2OMe), 60.6 (C ^{t}Bu), 59.0 (OCH_3), 53.9 (CH_2Im), 30.3 (CH_3 ^{t}Bu).

Synthesis of [IrBr(cod)(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (3). [Ir(μ-OMe)(cod)]$_2$ (195 mg, 0.294 mmol) was added to a solution of [^{t}BuHImCH$_2$PyCH$_2$OMe]Br (**2**) (200 mg, 0.59 mmol) in dichloromethane (5 mL). The solution was stirred 15 h at room temperature to give a yellow solution. The solution was brought to dryness under vacuum to give an orange oil which was disaggregated by stirring with cold n-pentane to give a yellow solid which was washed with n-pentane (2 x 5 mL) and dried under vacuum. The compound was isolated as a yellow solid (320 mg, 85%). Anal. Calc. $C_{23}H_{33}BrN_3OIr$: C, 43.19; H, 5.20; N, 6.57. Found: C, 43.56; H, 5.41; N, 6.15. HRMS (ESI+, MeOH, m/z): 560.2248 $[M\text{-}Br]^+$. ^1H NMR (298 K, 300 MHz, C_6D_6): δ 7.54 (d, $J_{H\text{-}H}$ = 7.3 Hz, 1H, H_m Py), 7.22–7.10 (m, 2H, H_m y H_p Py), 6.69 (d, $J_{H\text{-}H}$ = 14.8 Hz, 1H, CH_2Im), 6.55 (d, $J_{H\text{-}H}$ = 2.1 Hz, 1H, =CH Im), 6.38 (d, $J_{H\text{-}H}$ = 2.2 Hz, 1H, =CH Im), 5.86 (d, $J_{H\text{-}H}$

= 14.8 Hz, 1H, CH_2Im), 5.20–5.11 (m, 1H, =CH cod), 5.08–4.98 (m, 1H, =CH cod), 4.51 (ABq, δ_A = 4.53, δ_B = 4.47 J_{A-B} = 5.0 Hz, 2H, CH_2OMe), 3.15 (s, 3H, OCH_3), 3.05–2.97 (m, 2H, =CH cod), 2.30–1.95 (m, 4H, >CH_2 cod), 1.64 (s, 9H, ^{t}Bu), 1.62–1.28 (m, 4H, >CH_2 cod). $^{13}C\{^1H\}$ NMR (298 K, 75 MHz, C_6D_6): δ 180.7 (C_{NCN}), 158.8, 156.2 (C_o Py), 137.6 (C_p Py), 122.4, 120.3 (C_m Py), 120.2, 120.0 (=CH Im), 82.1, 80.0 (=CH cod), 75.8 (CH_2OMe), 58.8 (C ^{t}Bu), 58.5 (CH_2Im), 58.4 (OCH_3), 53.8, 51.8 (=CH cod), 33.9 (>CH_2 cod), 33.0 (>CH_2 cod), 32.4 (CH_3 ^{t}Bu), 30.4 (>CH_2 cod), 30.0 (>CH_2 cod).

Synthesis of [IrBr(CO)$_2$(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (4). Carbon monoxide was bubbled through a solution of [IrBr(cod)(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**3**) (200 mg, 0.31 mmol) in dichloromethane (10 mL) at room temperature to give an orange solution. The solution was brought to dryness under vacuum to give an oily residue which was disaggregated by stirring with cold n-pentane to give a yellow solid which was washed with n-pentane (2 x 5 mL) and dried under vacuum. The compound was isolated as a pale yellow greenish solid (138 mg, 75%). Anal. Calc. for $C_{17}H_{21}BrN_3O_3Ir$: C, 34.76; H, 3.60; N, 7.15. Found: C, 34.39; H, 3.74; N, 7.18. HRMS (ESI+, MeOH, m/z): 508.1215 $[M\text{-}Br]^+$, 480.1266 $[M\text{-}Br\text{-}CO]^+$. IR (ATR, cm^{-1}): 2056, 1969 (ν_{CO}). ^{1}H NMR (298 K, 300 MHz, $CDCl_3$): δ 7.70 (t, J_{H-H} = 7.3 Hz, 1H, H_p Py), 7.37 (d, J_{H-H} = 7.8 Hz, 1H, H_m Py), 7.31 (d, J_{H-H} = 7.6 Hz, 1H, H_m Py), 7.19 (d, J_{H-H} = 1.9 Hz, 1H, =CH Im), 7.15 (d, J_{H-H} = 2.0 Hz, 1H, =CH Im), 5.98 (d, J_{H-H} = 15.0 Hz, 1H, CH_2Im), 5.64 (d, J_{H-H} = 15.0 Hz, 1H, CH_2Im), 4.56 (s, 2H, CH_2OMe), 3.48 (s, 3H, OCH_3), 1.82 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (298 K, 75 MHz, $CDCl_3$): δ 180.2 (CO), 172.1 (C_{NCN}), 167.7 (CO), 158.7, 154.7 (C_o Py), 137.7 (C_p Py), 122.0 (C_m Py), 121.2 (=CH, Im), 120.9 (C_m Py), 120.1 (=CH, Im), 75.6 (CH_2OMe), 59.6 (C ^{t}Bu), 59.0 (OCH_3), 58.2 (CH_2Im), 32.5 (CH_3 ^{t}Bu).

General procedures for the catalytic N-methylation of nitroarenes

The catalytic N-methylation of nitro compounds were carried out under argon atmosphere in thick glass reaction tubes fitted with a greaseless high-vacuum stopcock. In a typical experiment, the reactor was charged inside a glove box with catalyst (0.0125 mmol) and base (0.375 mmol). After that, under argon, methanol (2.5 mL), nitro compound (0.5 mmol) and mesitylene as internal standard (0.25 mmol) were added. The resulting mixture was stirred at room temperature until complete dissolution of the catalyst and base and then placed in a thermostated oil bath at the required temperature, typically 130 °C, for the required time. Conversions and selectivities were determined by gas chromatography analysis under the following conditions: column temperature 80 °C (4 min) to 250 °C at a heating rate of 20 °C min^{-1} by using ultra-pure He as carrier gas. Time-dependence studies on the N-methylation of nitrobenzene with methanol catalyzed by compound **4** under the optimized reaction conditions were carried out by performing a series of identical experiments in parallel, following the outlined procedure, in order to avoid the adverse effects derived from opening the system. The different experiments were analyzed by CG every 30 min for an overall reaction time of 6 h.

Isolation of N-methylated amines

The reaction mixture obtained from catalytic reactions of N-methylation of nitroaromatic compounds, following the general procedure, was cooled to room temperature and then silica gel was added. The mixture was dried under vacuum and the residue transferred to a silica gel column and then eluted using the eluent appropriate for each product (see Electronic Supplementary Information).

Isotopic labeling experiments

The reaction of N-methylation of nitrobenzene was carried out in methanol-d_4 or methanol-d_1 following the general procedure for the catalytic N-methylation of nitroarenes: nitrobenzene (0.5 mmol), catalyst **4** (2.5 mol%), Cs_2CO_3 (75 mol%) in methanol-d_n (1 mL) at 403 K for 5 h. The reaction mixture was cooled to room temperature and brought to dryness under vacuum. The residue was extracted with $CDCl_3$ and the solution analyzed by ^{1}H NMR.

Crystal structure determination

Single crystals of [IrBr(cod)(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**3**) and [IrBr(CO)$_2$(κ*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (**4**) for the X-ray diffraction studies were grown by slow cooling of saturated solutions of the complexes in toluene (**3**) and hexane (**4**). X-ray diffraction data were collected at 100(2) K on a Bruker APEX DUO CCD diffractometer with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) using ω rotations. Intensities were integrated and corrected for absorption effects with SAINT–PLUS[22] and SADABS[23] programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-97[24] and refined by full matrix least-squares on F^2 with SHELXL-2014,[25] under WinGX.[26]

Crystal data and structure refinement for [IrBr(cod)(κ-*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (3). $C_{23}H_{33}BrIrN_3O$, M = 639.63 g mol^{-1}, monoclinic, $P2_1/c$, a = 8.5663(3) Å, b = 11.0966(4) Å, c = 24.1272(9) Å, β = 98.5950(10)°, V = 2267.70(14) Å^3, Z = 4, D_{calc} = 1.874 g cm^{-3}, μ = 7.669 mm^{-1}, F(000) 1248, prism, yellow, 0.150 x 0.120 x 0.100 mm^3, $\theta_{min}/\theta_{max}$ 1.707/29.650°, index ranges $-11\le h\le 11$, $-15\le k\le 14$, $-33\le l\le 33$, reflections collected/independent 34038/6081 [R(int) = 0.0451], data/restraints/parameters 6081/4/282, GOF on F^2 1.019, R_1 = 0.0236, [$I>2\sigma(I)$], wR_2 = 0.0514 (all data), largest diff. peak/hole 1.359/–0.609 e Å^{-3}. CCDC deposit number: 1942661.

Crystal data and structure refinement for [IrBr(CO)$_2$(κ-*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] (4). $C_{17}H_{21}BrIrN_3O_3$, M = 587.48 g mol^{-1}, triclinic, $P\bar{1}$, a = 9.2294(9) Å, b = 11.1211(11) Å, c = 11.8920(19) Å, α = 99.1570(10)°, β = 110.946(2)°, γ = 114.3940(10)°, V = 968.3(2) Å^3, Z = 2, D_{calc} = 2.015 g cm^{-3}, μ = 8.978 mm^{-1}, F(000) 560, prism, yellow, 0.250 x 0.200 x 0.180 mm^3, $\theta_{min}/\theta_{max}$ 1.966/26.368°, index ranges $-11\le h\le 11$, $-13\le k\le 13$, $-14\le l\le 14$, reflections collected/independent 11641/3938 [R(int) = 0.0210], data/restraints/parameters 3938/31/230, GOF on F^2 1.061, R_1 = 0.0290 [$I>2\sigma(I)$], wR_2 = 0.0740 (all data), largest diff. peak/hole 2.507/–2.000 e Å^{-3}. CCDC deposit number: 1942666.

Conclusions

A functionalized imidazolium salt precursor of a flexible lutidine-derived polydentate ligand having NHC and -OMe as side donor functions has been prepared from commercially available 2,6-bis(bromomethyl)pyridine in two steps. Deprotonation of the imidazolium salt by $[Ir(\mu\text{-}OMe)(cod)]_2$ affords the diene complex $[IrBr(cod)(\kappa C\text{-}tBuImCH_2PyCH_2OMe)]$ which on its turn reacts with carbon monoxide rendering the the carbonyl compound $[IrBr(CO)_2(\kappa C\text{-}tBuImCH_2PyCH_2OMe)]$ The polydentate ligand in these iridium(I)-NHC compounds exhibits a κ^1C coordination mode with an uncoordinated pyridine fragment.

Compound $[IrBr(CO)_2(\kappa C\text{-}tBuImCH_2PyCH_2OMe)]$ is an efficient pre-catalyst for the selective N-monomethylation of nitroarenes using methanol as both the reducing agent and the C1 source. A range of functionalized nitroarenes having both electron-donating and electron-withdrawing substituents, including heterocyclic or sterically hindered derivatives, have been efficiently converted to the corresponding N-methyl amines in good to excellent yields at low catalyst loadings using sub-stoichiometric amounts of Cs_2CO_3 as base. Mechanistic investigations based on deuterium-labelling experiments support a borrowing-hydrogen mechanism in which methanol acts as hydrogen source and methylating agent. The study of influence of the temperature on the selectivity of the N-methylation of nitrobenzene at a short reaction time and the observed activity and selectivity for the N-methylation of azobenzene suggest that the reduction of nitrobenzene by hydrogen transfer under optimized reaction conditions proceeds through the direct route.

The modular synthetic approach to the lutidine-based NHC/OMe ligand opens the way for finely tuning the catalyst in order to achieve improved performances. Further mechanistic studies in order ascertain the role of the pyridine and methoxy donor functions in the catalyst are currently underway in our laboratory.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Financial support from the Ministerio de Ciencia e Innovación (MICINN/FEDER) under the Project CTQ2016-75884-P and the Regional Government of Aragón/FEDER 2014-2020 “Building Europe from Aragón” (group E42_17R) is gratefully acknowledged. M. G.-L. thanks MINECO for a predoctoral fellowship (BES-2014-069624).

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