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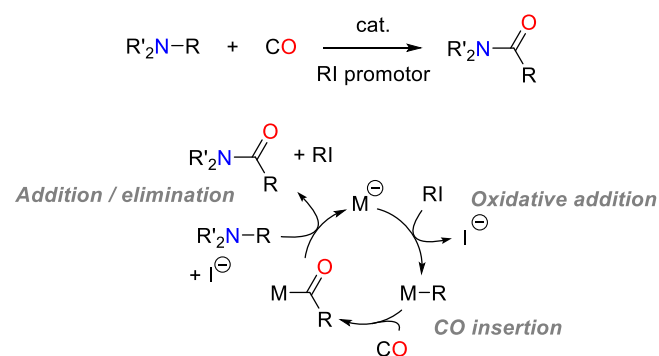
Carbonylation of C–N Bonds in Tertiary Amines Catalyzed by Low Valent Iron Catalysts

Tawfiq Nasr Allah, Solène Savourey, Jean-Claude Berthet, Emmanuel Nicolas, and Thibault Cantat*^[a]

Abstract: The first iron catalysts able to promote the formal insertion of CO into the C–N bond of amines are reported. Using low valent iron complexes, including $K_2[Fe(CO)_4]$, amides are formed from aromatic and aliphatic amines, in the presence of an iodoalkane promoter. Inorganic Lewis acids, such as $AlCl_3$ and $Nd(OTf)_3$, have a positive influence on the catalytic activity of the iron salts, enabling the carbonylation at a low pressure of CO (6 to 8 bars).

Carbon monoxide is a convenient carbon building block and its importance in the chemical industry is illustrated in major processes, such as the Fisher-Tropsch synthesis of hydrocarbons from syngas, the production of acetic acid at the megaton scale and the conversion of olefins to alcohols and aldehydes (Aldox and Oxo processes).^[1] Because CO can be produced from the gasification of waste biomass or the electroreduction of CO_2 , it could be regarded as a renewable carbon source in the future.^[2] The exploration of carbonylation reactions hence remains a very active field of research.^[3] In fact, the carbene character of the CO molecule offers a unique reactivity and the possibility to insert CO in covalent sigma bonds to form carbonyl derivatives with an ideal atom efficiency. The success of this approach is clearly highlighted in the Monsanto process for the synthesis of acetic acid by CO insertion in the O–CH₃ bond of methanol,^[4] or in the production of phosgene from CO and Cl_2 .^[5] By extension, the carbonylation of a C–N bond in an amine would afford an attractive route to amides. Although amides are efficiently synthesized through metal-catalyzed amino-carbonylation reactions of aryl-halides,^[6] these procedures also generate by-products in stoichiometric quantities and this drawback could be advantageously circumvented with catalysts able to promote the insertion of CO in existing C–N bonds. This strategy is hampered by the difficulty to activate amines, as the heterolytic cleavage of a C–N bond is ca. 20 kcal.mol⁻¹ more endothermic than a C–O bond.^[7] Because of this limitation, very few carbonylation reactions of amines have been developed. Strained amines, such as aziridines, have been successfully carbonylated, in a reaction that mimics the carbonylation of epoxides to β -lactones.^[8] Only a handful of catalysts are known to carbonylate linear amines.^[9] Utilizing palladium(II) salts, Li and co-authors successfully prepared *N,N'*-dimethylacetamide by carbonylation of a mixture of trimethylamine and tetramethylammonium iodide at 200 °C with 30 bars of CO.^[10] Reasoning that the palladium catalyst plays the role of a metal nucleophile, the authors reported in 2013 the use

of $Na[Co(CO)_4]$ as an efficient catalyst for the carbonylation of trimethylamine at >180 °C and 30 bars of CO, with CH_3I as a promoter.^[11] Following a different approach, Hu, Huang *et al.* used I_2 to induce charge-transfer complexes and weaken the C–N bond in benzylamines and promote their carbonylation with nickel(II) catalysts.^[12] To realize the potential of the carbonylation of amines, novel catalysts are needed that enable insertion of CO in C–N bonds under a low pressure of CO, for a variety of substrates. To achieve this goal, iron complexes are ideal candidates. Indeed, low valent iron complexes are capable of coupling nucleophiles and electrophiles with CO in stoichiometric as well as catalytic reactions,^[13] and we report herein the first iron catalysts able to carbonylate aliphatic amines to tertiary amides.



Scheme 1. Mechanistic proposal for the carbonylation of amines to amides using nucleophilic low valent metal complexes.

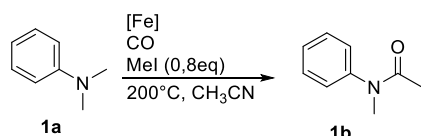
Collman's reagent $Na_2[Fe(CO)_4]$ and its congener $Na[CpFe(CO)_2]$ are strong iron-based nucleophiles, able to react with alkylhalides to generate carbonyl groups by CO migratory insertion.^[14] In fact, the $[CpFe(CO)_2]^-$ anion is about $70 \cdot 10^6$ times more nucleophilic than the $[Co(CO)_4]^-$ anion.^[15] We hence reasoned that low valent iron carbonyl complexes could advantageously replace $Na[Co(CO)_4]$ in a catalytic sequence where the metal nucleophile is alkylated with an iodoalkane promoter to generate an alkyl complex that is carbonylated and further trapped by the amine nucleophile (Scheme 1).^[16] The carbonylation of *N,N*-dimethylaniline (**1a**) was first undertaken using 6 mol% $Fe(CO)_5$, with 55 bars CO and 0.8 equiv. CH_3I as a promoter. After 15 h at 200 °C in acetonitrile, the selective carbonylation of the N–CH₃ linkage was observed and *N*-methylacetanilide **1b** was formed in 40 % yield. This reaction represents the first example of the use of an iron catalyst in the carbonylation of amines. $Fe_3(CO)_{12}$ and $[CpFe(CO)_2]_2$ exhibit a similar catalytic activity (Entries 2-5 in Table 1), and a prolonged reaction time of 60 h was necessary to accomplish a quantitative carbonylation of the amine starting material to **1b** (Table 1, Entries 1 and 5). Interestingly, the potassium salt of Collman's reagent, $K_2[Fe(CO)_4]$, was more

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active and it afforded **1b** in >99 % yield after 15 h at 200 °C. It is notable that the carbonylation reaction is highly chemoselective and only proceeds through the activation of the N–C(sp³) bond, leaving the stronger N–C(sp²) linkage of the aniline backbone untouched. In addition, the resulting amide is unreactive under the applied reaction conditions so that only a single N–CH₃ linkage in **1a** is carbonylated.

Table 1. Screening of iron catalysts for the carbonylation of *N,N*-dimethylaniline **1a**.



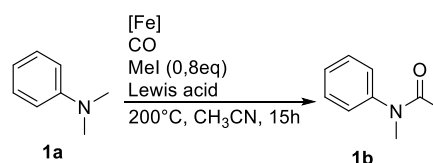
Entry	Cat. (mol%)	CO (bar)	GC Yield (%)
1	Fe(CO) ₅ (6)	55	40 (>99) ^b
2	Fe ₃ (CO) ₁₂ (6)	55	72
3	Fe ₃ (CO) ₁₂ (2)	55	49
4	[CpFe(CO) ₂] ₂ (6)	55	45
5	[CpFe(CO) ₂] ₂ (3)	55	40 (>99) ^b
6	K ₂ [Fe(CO) ₄] (6)	55	>99
7	Fe(CO) ₅ (6)	8	42
8	Fe ₃ (CO) ₁₂ (6)	8	17
9	[CpFe(CO) ₂] ₂ (6)	8	57
10	K ₂ [Fe(CO) ₄] (6)	8	58

[a] Reaction conditions : Dimethylaniline (0.98 mmol), cat (2-6 mol%), Mel (0.8 eq.), 15h, MeCN [b] after 60h of reaction

Capitalizing on this reactivity, the carbonylation of **1a** was attempted at a low pressure of 8 bar CO. Although a decrease in catalytic activity could be noted for all the catalysts, **1b** was formed in 58 % yield after 15 h in the presence of 6 mol% K₂[Fe(CO)₄] and 0.8 equiv. CH₃I (Entries 7-10 in Table 1). In order to overcome the lower carbonylation efficiency under low CO pressure, we investigated the influence of Lewis acids on the reaction. Indeed, the latter are well known promoters in carbonylation steps, having a positive impact both on the kinetics and the thermodynamics of CO migratory insertion reactions.^[17] Several Lewis acids have been tested for the carbonylation of **1a**, (Table 2) including calcium, scandium and neodymium triflate as well as aluminium trichloride. While Ca(OTf)₂ has a deleterious influence on the reaction, 60 mol% AlCl₃ somewhat improved the production of **1b**. More satisfyingly, Sc(OTf)₃ and Nd(OTf)₃ enable the carbonylation of **1a** in a quantitative yield after 15 h at 200 °C, whereas its conversion is limited to 58 % in the absence of the Lewis acid additive. The positive influence of a Lewis acid on the catalytic activity of the low valent iron system can be rationalized from the previous work of Collman, Shriver and others which

demonstrated, *via* stoichiometric reactions, that the migratory insertion of CO into the iron-alkyl bond of a low valent iron carbonyl complex is highly sensitive to the pressure of CO and is accelerated by Lewis acids able to coordinate a ligated CO molecule.^[17b, 18] Interestingly, this strategy enables the quantitative carbonylation of **1a** to amide **1b** using only 8 bars CO at 200 °C (Entry 10 in Table 1). The need for a rather large quantity of the Lewis acid (60 mol%) likely results from the progressive poisoning of this co-catalyst by the amide product. As the reaction proceeds, a strong donor is produced, in the form of amide **1b**, which can coordinate to the Lewis acid. In fact, the reaction was completely inhibited when *N*-methyl-2-pyrrolidinone was used as a solvent. This cyclic amide is indeed known to solvate Lewis acids and form solvent separated species.^[19]

Table 2. Screening of Lewis acids for the carbonylation of *N,N*-dimethylaniline **1a**.

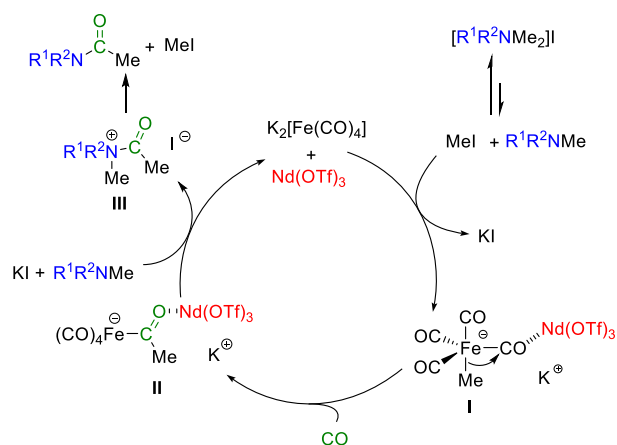


Entry ^a	Lewis acid (mol%)	Temperature	GC Yield (%)
1	-	200	58
2	Ca(OTf) ₂ (60)	200	17
3	Sc(OTf) ₃ (60)	200	>99
4	AlCl ₃ (60)	200	78 ^b
5	Nd(OTf) ₃ (60)	200	>99
6	Nd(OTf) ₃ (30)	200	77
7	Nd(OTf) ₃ (6)	200	19
8	Nd(OTf) ₃ (60)	180	35
9	Nd(OTf) ₃ (60)	160	1
10 ^b	Nd(OTf) ₃ (60)	200	>99

[a] Reaction conditions : K₂Fe(CO)₄ (6 mol%), dimethylaniline (0.98 mmol), Mel (0.8 eq.), CO (8bar) 15h, 6 mL MeCN, 200°C [b] Average of two runs

The carbonylation of **1a** was found to depend on the reaction temperature and the yield of **1b** dropped to 35 % and 1 %, when the temperature is lowered to 180 and 160 °C, respectively (Table 2). This finding is consistent with the proposal from Li *et al.* that the catalytic cycle involves an equilibrium between the free amine and its quaternary salt [PhNMe₃]⁺.^[10-11] This equilibrium must be reversed at high temperature to increase the concentration of the free and reactive amine and iodomethane. Altogether, these observations and data support the mechanistic proposal depicted in Scheme 2: Alkylation of Collman's reagent with iodomethane (involved in a deleterious equilibrium with the amine reagent) affords the anionic alkyl complex [Fe(CH₃)(CO)₄]⁻

I. The subsequent CO migratory insertion is facilitated by the coordination of the Lewis acid co-catalyst to yield an acylferrate intermediate II. Nucleophilic addition of the free amine on the acyl ligand forms, after elimination, a quaternarized amide product III that subsequently decomposes to the amide product and regenerates iodomethane. Importantly, this mechanism circumvents the problematic activation of the strong C–N bond, by generating an electrophilic acyl moiety, able to react with the amine reagent, so that the C–C bond between the alkyl residue and CO is formed prior to the C–N bond cleavage.



Scheme 2. Proposed mechanism for the carbonylation of **1a** catalysed by $K_2[Fe(CO)_4]$ + $Nd(OTf)_3$, in the presence of Mel.

Motivated by the catalytic activity of the low valent iron catalysts, we were interested in exploring the scope of reactive amine substrates in this carbonylation reaction. $Nd(OTf)_3$ was selected as the Lewis acidic additive, because it exhibits an enhanced stability and a greater resilience to hydrolysis, compared to $AlCl_3$. To assess the electronic influence of the amine reagent, substituted *N,N*-dimethylaniline derivatives were first tested. Aniline **4a**, bearing –CN electron withdrawing group (EWG) at the *para* position, was carbonylated in moderate yield of 55 % after 15 h at 200 °C (Table 3, Entry 1). The lower conversion likely stems from the decreased nucleophilicity of the nitrogen atom resulting in a slower transfer of the acyl group from iron to the amine. In fact, replacing the cyano EWG with the weaker fluoride EWG enabled the near-quantitative carbonylation of **3a** to **3b**. This result is consistent with the high selectivity of this reaction: only a single N–CH₃ group can undergo a carbonylation event because the resulting amide has a nucleophilicity much lower than the amine starting material.

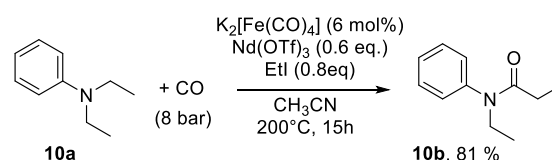
Catalytic tests also revealed that the introduction of electron donating groups (EDGs) somewhat lowers the conversion yield to the amide product. For instance, the *m*-Me and *p*-Me substituted *N,N*-dimethylaniline derivatives were converted to amides **6b**, and **2b** in 99 and 81 % yield, respectively. This trend follows the relative electron donating ability of the substituents, as given by their Hammett sigma constants: -0.07 (*m*-Me) and -0.17 (*p*-Me).^[20] This effect likely results from the enhanced stability of the trimethylammonium cation $[ArNMe_3]^+$, which provides smaller

quantities of the reactive promotor Mel at 200 °C, via the equilibrium depicted in Scheme 2. The presence of a methyl group in the *ortho* position of *N,N*-dimethylaniline does not hamper the catalysis and **5a** was converted to amide **5b** in >99 % yield. Beyond *N,N*-dimethylaniline derivatives, diphenyl-*N*-methyl amine **7a** was found to undergo a carbonylation of the N–CH₃ linkage and, under the same reaction conditions utilized for **1a**, amide **7b** was formed in 56 % yield. Similarly, the trialkylamine *N*-methyl morpholine **9a** gave **9b** in 28% yield after 15 h. The same trend is observed for 1,2,3,4-*N*-methyl tetraisoquinoline **8a** which provided amide **8b** in 22 and 54 % yield after 15 and 60 h, respectively. The lower activity likely stems from the use of aliphatic amines that strongly bind Mel.

Table 3. Screening of tertiary amines.

Entry ^a	Substrates	Products	GC Yield (%)
1			>99 (83) ^c
	1a , R = H	1b , R = H	>99 (83) ^c
	2a , R = Me	2b , R = Me	81
	3a , R = F	3b , R = F	95
2			>99
	5a	5b	>99
3			>99
	6a	6b	>99
5			56
	7a	7b	56
6			22 / 54 ^b
	8a	8b	22 / 54 ^b
7			28 ^b
	9a	9b	28 ^b

[a] Reaction conditions : $K_2[Fe(CO)_4]$ (6 mol%), amine (0.98mmol), $Nd(OTf)_3$ 60mol%, Mel (0.8 eq.), CO (8bar) 15h, 6 mL MeCN [b] After 60h of reaction. [c] Isolated yield



Scheme 3. Carbonylation of **10a** catalysed by $K_2[Fe(CO)_4]$ + $Nd(OTf)_3$, in the presence of EtI.

When the carbonylation of N,N-diethylaniline **10a** was carried out using EtI as a promoter in the presence of 6 mol% $K_2Fe(CO)_4$, 60 mol% $Nd(OTf)_3$ and 8 bar CO, the carbonylation of the $N-CH_2CH_3$ functionality afforded amide **10b** in a very good 81 % yield (Scheme 3). This is an especially interesting result as it demonstrates that the carbonylation is not limited to N–Me functionalities but is also viable for longer alkyl chains.

In summary, we have reported the first iron catalysts able to promote the carbonylation of tertiary amines, by formal insertion of CO into a C–N bond, using low valent iron complexes, such as $K_2[Fe(CO)_4]$. The transformation requires an iodoalkane promoter and inorganic Lewis acids (e.g. $Nd(OTf)_3$) acting as co-catalysts, enabling the carbonylation at a low pressure of CO (8 bars).

Experimental Section

General procedure for the catalytic carbonylation of tertiary amines in autoclaves:

In a glove box the autoclave is charged with the catalyst (2, 3 or 6 mol%), the amine (1 mmol), MeI (0.8 eq.) and a Lewis acid (60mol%). The solvent (6 mL) is added and the autoclave is purged 4 times with 10 bar of CO, then pressurized at the required pressure. The reaction is then allowed to heat at 200°C for 15h or 60h. At the end of the reaction, the autoclave is cooled down to RT and the pressure is released slowly. Finally, the solution is filtrated on a Celite pad before analysis on GC/MS chromatography.

Keywords: Amides • Carbon Monoxide • Iron • Catalysis • Lewis Acids

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