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Direct *N*-formylation of nitroarenes with CO_2†

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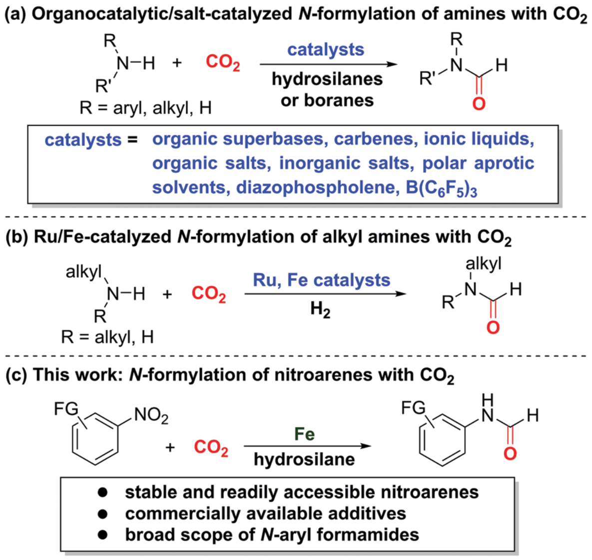
Herein we describe a straightforward *N*-formylation of nitroarenes with CO_2 to access *N*-aryl formamides exclusively in the presence of iron and hydrosilane as additives. This protocol showcases a good tolerance of a wide range of nitroarenes and nitroheteroarenes.

Carbon dioxide (CO_2) constitutes an ideal C1 source in organic synthesis owing to its abundance and stability.[1] In particular, CO_2 serves as the best-suited substitute of more reactive C1 building blocks, such as carbon monoxide (CO), methyl iodide, and phosgene.[2] Despite its high activation barrier and thermodynamic stability,[2] CO_2 has been widely exploited for decades to access a diverse array of functionalized compounds *via* carboxylation,[3] carbonylation,[4] or C–H bond construction.[5] In this context, the incorporation of amines and CO_2 towards synthesis of value-added nitrogen-containing compounds,[6] especially *N*-formylation of amines with CO_2,[7–13] is among the most important chemical transformations due to the versatility of nitrogen-based compounds in academia and industry. Taking the advantage of commercially available hydrosilanes as activating and hydrogenating agents along with various catalysts, such as organic superbases,[7] carbenes,[8] ionic liquids and organic salts,[9] inorganic salts,[10] polar aprotic solvents,[11] diazophospholene,[12] and $B(C_6F_5)_3$,[13] a variety of formamides can be accessed based on amines and CO_2 (Scheme 1a). Additionally, the Ding[14] and Bernskoetter[15] groups described the seminal Ru- and Fe-catalyzed *N*-formylation of alkylamines based on the CO_2/H_2 system, respectively (Scheme 1b). On the other hand, nitroarenes prove to be reliable aminating agents for direct synthesis of amines[16] and amides[17] without preforming the more reactive anilines *via* hydrogenation. Recently, Beller,[17a] Driver,[17b] Hu,[17c] Mankad,[17f] Wu,[17d,e] as well as our group[17g] disclosed the aminocarbonylation reactions to access aryl amides, a class of important compounds in chemical, pharmaceutical, and agrochemical industries, based on nitroarenes and CO or its surrogates. To our knowledge, the merger of CO_2 and nitroarenes for straightforward amide synthesis remains unexplored. We envisioned that the use of suitable and compatible reductants and activating agents could induce the integration of both CO_2 and nitroarenes for amide formation. Herein, we unveil the direct *N*-formylation of nitroarenes with CO_2 in the presence of iron powder and hydrosilane additives (Scheme 1c). This alternative and complementary method would open a conceptually novel avenue for more step-economic and expedient access to formamides without the need of conventional anilines.



Scheme 1 Developments of *N*-formylation based on CO_2.

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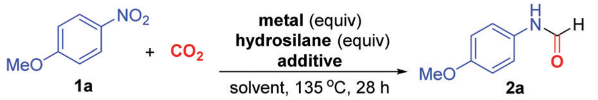
We commenced the study on *N*-formylation of CO_2 using 4-nitroanisole (**1a**) as the model substrate (Table 1). In the presence of 3 equivalents of Zn powder as reductant and 3 equivalents of phenylsilane as additive, **1a** reacted with CO_2 under balloon pressure in dimethylformamide (DMF) solvent at 110 °C to give *N*-4-methoxyphenyl formamide **2a** exclusively in 49% yield (entry 1). In the absence of Zn or hydrosilane, no formylation took place, indicating that both metal reductant and hydrosilane are essential for reaction (entries 2 and 3). When triethoxysilane was used in place of phenylsilane, formylation underwent at 135 °C to offer **2a** in 56% yield (entry 4). Further, when Fe powder was employed instead of Zn, **2a** was also obtained in 51% yield (entry 5). Noteworthily, the yield could be enhanced to 63% when 10 mol% of KI was added as additive in the Fe-mediated reaction (entry 6). Subsequently, 1,1,3,3-tetramethyldisiloxane (TMDSO) was found to be the superior additive, giving **2a** in 75% yield (entries 7–9). Intriguingly, the use of Fe nano powder allowed the reduction of loadings of both Fe and TMDSO to 2 equivalents in association with the yield enhancement to 83% yield (entries 10–12). Such promoting effect would be attributed to the more efficient reduction process provided by the more soluble and finely powdered Fe. In the presence of other polar aprotic solvents such as dimethylacetamide (DMA) and *N*-methylpyrrolidine (NMP), **2a** was formed in similar yields without other side products (entries 13 and 14). Furthermore, no formamide was formed when CO_2 was omitted (entry 15). These control experiments suggested that the carbonyl group of **2a** originates from CO_2 rather than solvent.

The optimized protocol (Table 1, entry 11) proved to be general in *N*-formylation of nitroarenes (Scheme 2). Electron-rich (**1a–1f**), electron-neutral (**1g**), and electron-deficient (**1h–1m**) nitroarenes all reacted with CO_2 to form the corresponding *N*-aryl formamides in moderate to high yields. Additionally, both mono- (**1a-2i**, **1l**) and di-substituted (**1j**, **1k**, **1m–1o**) nitroarenes could be incorporated into the formamide products **2a–2o.** The sterically encumbered 1-nitro-2,4-dimethylbenzene (**1o**) was also suitable reaction partner. Notably, a wide range of nitro-substituted heterocycles could be utilized for formylation, including benzodioxole (**1p**), pyrrole (**1q**), pyridine (**1r**), *N*-alkylated indole (**1s**, **1t**), benzofuran (**1u**), benzothiophene (**1v**), and benzoxazole (**1w**), delivering the corresponding *N*-heteroaryl formamides **2p–2w** in 43–85% yields. Noteworthily, the employment of 3 equivalents of Fe metal (Table 1, entry 10) could improve remarkably the formylation of electron-rich nitro(hetero)arenes **1c**, **1o** and **1s**, affording the corresponding formamides **2c**, **2o** and **2s** in 80%, 60% and 63% yields, respectively. On the contrary, the reactions of electron-deficient nitroarenes with the additional equivalent of Fe led to substantial diminishment of yields. Gratifyingly, by adding $FeCl_2$ (2 equiv.) and slightly increasing the loadings of TMDSO and KI, electron-deficient nitroarenes such as **1j–1m** could react more efficiently to afford the formamides in higher yields (48–68%). This protocol was also amenable to multigram synthesis of **2a** in synthetically useful yield.

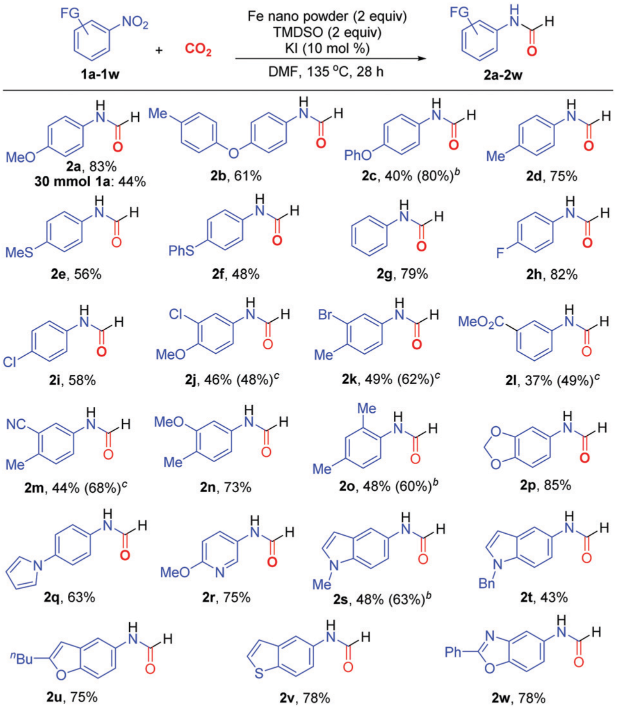
In the course of reaction, nitroarene can be transformed to nitrosoarene, *N*-aryl hydroxylamine, azoxyarene, azoarene, 1,2-diaryl hydrazine, and aniline under reductive conditions.[18] Thus, the reactions of these nitrogen-based species under otherwise

Table 1 Optimization of *N*-formylation of nitroarenes with CO_2[a]

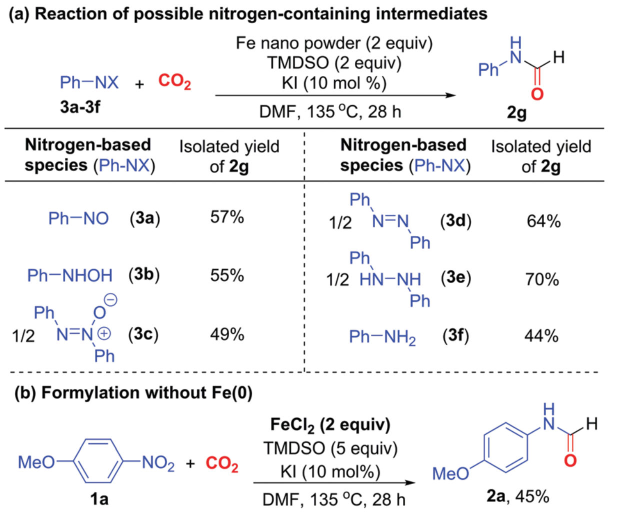


Entry	Metal (equiv.)	Hydrosilane (equiv.)	Additive (mol%)	Solvent	Yield[b] (%)
1[c]	Zn (3)	$PhSiH_3$ (3)	None	DMF	49
2[c]	None	$PhSiH_3$ (3)	None	DMF	0
3[c]	Zn (3)	None	None	DMF	0
4	Zn (3)	$(EtO)_3SiH$ (3)	None	DMF	56
5	Fe (3)	$(EtO)_3SiH$ (3)	None	DMF	51
6	Fe (3)	$(EtO)_3SiH$ (3)	KI (10)	DMF	63
7	Fe (3)	$Me(EtO)_2SiH$ (3)	KI (10)	DMF	25
8	Fe (3)	PMHS (3)	KI (10)	DMF	32
9	Fe (3)	TMDSO (3)	KI (10)	DMF	75
10[d]	Fe (3)	TMDSO (2)	KI (10)	DMF	83
11[d]	Fe (2)	TMDSO (2)	KI (10)	DMF	83
12[d]	Fe (1)	TMDSO (2)	KI (10)	DMF	35
13[d]	Fe (2)	TMDSO (2)	KI (10)	DMA	83
14[d]	Fe (2)	TMDSO (2)	KI (10)	NMP	75
15[d,e]	Fe (2)	TMDSO (2)	KI (10)	DMF	0

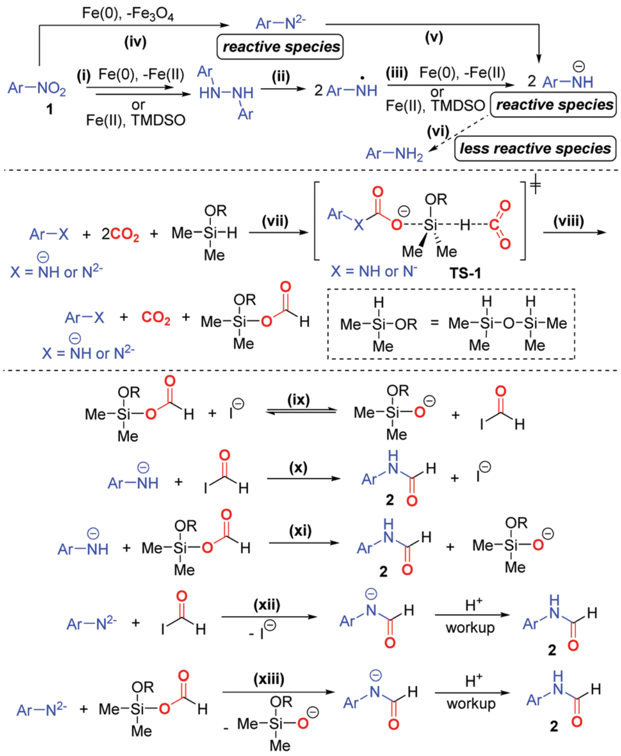
[a] General procedure: **1a** (0.5 mmol), CO_2 (balloon), metal powder (1–1.5 mmol), hydrosilane (1–1.5 mmol), additive (10 mol%), solvent (1.5 mL), 135 °C, 28 h. [b] Isolated yield. [c] Reaction conducted at 110 °C. [d] Fe nano powder used. [e] Argon atmosphere without CO_2.



Scheme 2 Substrate scope of nitroarenes in *N*-formylation.[a] [a] Reaction conditions: nitroarene (0.5 mmol), CO_2 (balloon), nano Fe (1 mmol), TMDSO (1 mmol), KI (0.05 mmol), DMF (1.5 ml), 135 °C, 28 h. Isolated yields were shown. [b] 3 equiv. of Fe. [c] Modified conditions: nitroarene (1 equiv.), CO_2 (balloon), nano Fe (2 equiv.), $FeCl_2$ (2 equiv.), TMDSO (3 mmol), KI (30 mol%), DMF (3 ml), 135 °C, 28 h.



Scheme 3 Control experiments for *N*-formylation.



Scheme 4 Proposed mechanism of *N*-formylation.

identical conditions were examined to probe their roles in formylation (Scheme 3a). Nitrosobenzene (**3a**), *N*-phenyl hydroxylamine (**3b**), azoxybenzene (**3c**) and azobenzene (**3d**) all reacted to give formamide **2g** in 49–64% yields. Particularly, diphenyl hydrazine (**3e**) reacted most efficiently to afford **2g** in 70% yield. Presumably, nitrobenzene is sequentially reduced to **3a**, **3b**, **3c**, **3d**, and finally **3e**,[18] which acts as the ultimate intermediate to participate in the formylation reaction. Aniline **3f** also reacted to give **2g** in 44% yield, suggesting that it is likely the minor intermediate to induce the formylation. Furthermore, when Fe(0) was omitted, the addition of Fe(II) salt, which is a viable oxidized Fe species, could enable the formylation of nitroarene **1a** in the presence of excess TMDSO to give formamide **2a** in 45% yield. We surmised that hydrosilane can also act as a reductant and a hydrogen source for the reduction of nitroarene *via* the action of Fe-hydride species,[16a,b] apart from its conventional application as CO_2-activating agent.[6h]

Based on the experimental results, we proposed a plausible mechanism of the formylation protocol (Scheme 4). Nitroarene **1** is sequentially reduced to 1,2-diaryl hydrazine *via* the intermediacy of nitrosoarene, *N*-aryl hydroxylamine, azoxyarene, and/or azoarene[18] (pathway i). 1,2-Diaryl hydrazine then undergoes facile homolysis under heating to give aminyl radicals,[17g] which are then reduced to amide ion $ArNH^-$ (pathways ii and iii). Meanwhile, nitroarene can be reduced to amide dianion ArN^{2-} followed by $ArNH^-$, whereas Fe(0) is oxidized to Fe_3O_4[19] (pathway iv and v). A small amount of aniline can also be generated (pathway vi). In the reduction processes, Fe(0) is likely the major reducing agent, while TMDSO likely acts as both mild reducing agent and hydrogenating agent. Owing to the strong nucleophilicity of $ArNH^-$ and ArN^{2-}, they likely activate both CO_2 and TMDSO *via* the transition state **TS-1**, in which the carbamate ion formed further activates TMDSO to trigger the hydride attack to another CO_2 (pathway vii). Such transition state is regarded as the lowest energy pathway for CO_2 activation.[6h] *Via* **TS-1**, formoxysilane is formed with the concomitant regeneration of amide species (pathway viii). We proposed that iodide ion behaves as a strong nucleophile in polar aprotic solvent DMF, thereby facilitating the deformylation of formoxysilane to form a more reactive formyl iodide in conjunction with silanolate ion (pathway ix). Finally, $ArNH^-$ reacts with both formyl iodide and formoxysilane to deliver the *N*-aryl formamide **2** (pathways x and xi). In the same vein, $ArNH^{2-}$ undergoes nucleophilic substitutions with formyl iodide and formoxysilane to give amidate ion, which furnishes formamide **2** upon acidic workup (pathways xii and xiii). On the other hand, the *N*-formylation based on aniline may proceed but tends to be a minor pathway due to the attenuated nucleophilicity of aniline. The detailed reaction mechanism is subjected to a dedicated study in the future.

Under the standard conditions, electron-rich nitro(hetero) arenes tended to react more efficiently to form higher product yields (∼50–85%) than electron-deficient and sensitive group-bearing nitroarenes (∼40–60%, Scheme 2). We rationalized that the nitrogen-based intermediates derived from the latter are more unstable, especially in the reductive reaction conditions and in the presence of basic by-products (*e.g.* iron oxides, silanolate ions), and likely undergo over-reduction and decomposition at varying degrees in the course of reactions. Additionally, an additional equivalent of Fe(0) was found advantageous in the reactions of electron-rich nitro(hetero)arenes but detrimental for electron-deficient ones. We speculated that the contribution of Fe(0)- and TMDSO-based reduction steps would vary with respect to the electronic effect of nitroarenes. The reduction of electron-rich nitro(hetero)arenes would mainly rely more on highly reducing Fe(0) to deliver more amide ions. Conversely, the excess Fe(0) would over-reduce the electron-deficient nitroarenes to less reactive anilines or other side products, but additional milder reduction given by Fe(II)/TMDSO system would in turn be more productive for formation of amide ions.

In conclusion, we have developed an alternative strategy to access formamides *via* direct *N*-formylation of nitroarenes with CO_2. By using commercially available Fe powder and 1,1,3,3-tetramethyldisiloxane as additives, a variety of *N*-aryl and *N*-heteroaryl formamides are synthesized. Mechanistic study suggests that both Fe metal and hydrosilane can reduce nitroarenes to anionic nitrogen-based intermediates, which then activate CO_2 and hydrosilane for subsequent formylation.

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Conflicts of interest

There are no conflicts to declare.

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