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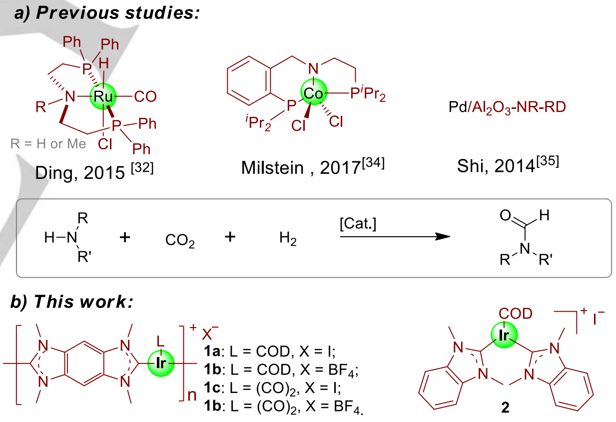
# *N*-Formylation of Amines with $CO_2$ and $H_2$ by Using NHC-Iridium Coordination Assemblies as Solid Molecular Catalysts

Yang Zhang,[a] Jiaquan Wang,[a] Haibo Zhu[a] and Tao Tu*[a,b]

**Abstract:** One of the NHC-iridium coordination assemblies containing 1,5-Cyclooctadiene (COD) and iodide ion has been demonstrated as robust, efficient, recyclable solid molecular catalyst for *N*-formylation of diverse primary and secondary amines with $CO_2$ and $H_2$ under mild reaction conditions. Remarkably, in the case of *N,N*-dimethyl-formamide production, even at 0.1 mol% catalyst loading under solvent free conditions, the solid catalyst can be readily recovered by simply filtration and reused more than 10 runs without obviously loss of activity, highlighting the feasibility in industry.

As one of the most inexpensive, renewable and abundant C1 resource, the utilization of carbon dioxide ($CO_2$) for syntheses of feedstock and value-added chemicals has attracted intensive attentions from both laboratory and industry.[1-9] Therefore, in recent years, great efforts have been devoted to explore and develop efficient catalysts for this purpose. Among all diverse direct transformations of $CO_2$, *N*-formylation of amines with $CO_2$ and $H_2$ constitutes a straightfoward, atom-economic and sustainable approach, in which water is the only by-product.[10] Remarkably, valued-added formamides are usually considered as useful chemicals and precursors for syntheses of a number of biological active compounds.[11-14] For instance, *N,N*-dimethylformamide (DMF) is not only one of the most important solvents, but also considered as a key precursor to access many adhesives, pesticides, preservatives and drugs.[15,16] In contrast with the conventional industrial protocols by carbonylation of dimethylamine ($NHMe_2$) with toxic CO,[17] the direct *N*-formylation of $NHMe_2$ with safe $CO_2$ and $H_2$ for DMF syntheses is challenging and less-studied,[6] probably due to the high thermodynamic stability of $CO_2$ and the possible further reduction of formamides.[18]

The first example of catalytic *N*-formylation of dimethylamine with $CO_2$ and $H_2$ gas was reported by Haynes and co-workers, which provided a sustainable and general approach to access DMF.[19] After this seminal work, a number of homogeneous and heterogeneous catalytic systems have been reported.[20-37] In general, homogeneous complexes are more efficient catalysts and exhibit higher selectivity in a number of transformations. In 2015, in the presence of 0.002 mol% Ru-PNP pincer complex, Ding and co-workers have realized the efficient straightforward and practical *N*-formylation of dimethylamine in DMF at 120 °C under $CO_2/H_2$ atmosphere (35 atm for each, Scheme 1a).[32] Remarkably, a TON of up to 599000 has been attended with high selectivity for DMF production. In addition, even as a homogenous case, the pincer catalyst could be reused for 12 runs without significant loss of activity by a simple recycling process. In 2017, Milstein and coworkers realized the selective *N*-formylation of amines with $CO_2$ and $H_2$ using Co-PNP pincer complex as catalyst. A number of amines were converted to their corresponding formamides at 150 °C.[34] Despite of these achievements, air-sentive luxury phosphine ligands, high reaction temperature and high gas pressure are still hampered their pratical application in industry. As heterogeneous catalytic system is more suitable for the industrial DMF manufacturing,[35-37] in 2014, Shi and coworkers demonstrated $Pd/Al_2O_3$-NR-RD catalyst by depositing palladium on a shape controllable $Al_2O_3$ support exhibiting good activity in the catalytic N-formylation of amines with $CO_2$ and $H_2$ (1 MPa $CO_2$ and 2 MPa $H_2$, Scheme 1a) at 130 °C. And the $Pd/Al_2O_3$-NR-RD catalysts are readily seperated via centrifugation, and 83% yield was maintained after reused for three times.[35]



**Scheme 1**. *N*-Formylation of Amines with $CO_2$ and $H_2$.

*N*-heterocyclic carbenes (NHCs) constitute one of robust and environmental-benign ligands,[38,39] which have been widely applied in the diverse transition-metal-catalyzed reactions due to their high reactivity.[40,41] To our best knowledge, there is no example on *N*-formylation of amines with $CO_2$ and $H_2$ involving NHC ligands. Recently, we have demonstrated a series of NHC-Ir coordination assemblies functioned as highly efficient solid molecular catalysts in the oxidative hydrogenation of glycerol to potassium lactate,[42] hydrogenation of levulinic acid to γ-valerolactone[43] and selective monomethylation of anilines via reductive amination pathway.[44] Remarkably, these solid molecular catalysts could be reused dozens of runs without obviously loss of activity and selectivity under mild conditions. Following our recent research interests in the development of molecular assemblies based on functional organometallic

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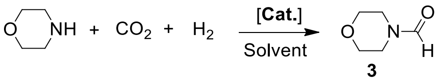
Supporting information for this article is given via a link at the end of the document.(Please delete this text if not appropriate) complexes and their potential applications in sensor and catalysis,[45-48] herein, we would like to explore their catalytic activity and reusability in *N*-formylation of diverse primary, secondary and even chiral amines with $CO_2$ and $H_2$ (Scheme 1b), especially, at low temperature, low gas pressure and solvent-free or base-free reaction conditions.

**Table 1.** Optimization of reaction conditions for *N*-formylation of morpholine with $CO_2$ and $H_2$[a]

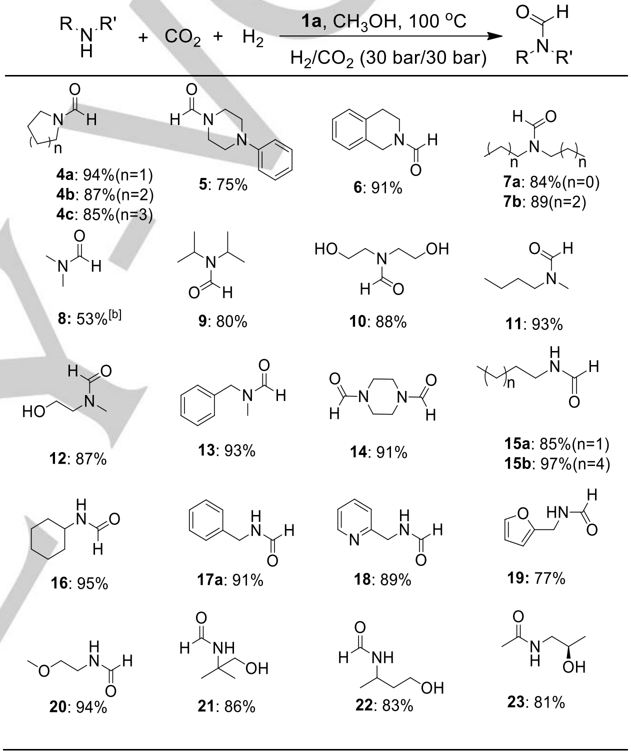


| Entry | [Cat.] | Solvent | Base | *T* (°C) | Yield (%)[b] | TON |
|---|---|---|---|---|---|---|
| 1 | **1a** | THF | *t*-BuOK | 120 | 23 | 230 |
| 2 | **1a** | MeOH | *t*-BuOK | 120 | 26 | 260 |
| 3 | **1a** | EtOH | *t*-BuOK | 120 | 21 | 210 |
| 4 | **1a** | *i*-PrOH | *t*-BuOK | 120 | 23 | 230 |
| 5 | **1a** | MeOH | / | 120 | 41 | 410 |
| 6 | **1a** | MeOH | / | 100 | 40 | 400 |
| 7 | **1a** | MeOH | / | 100 | 76[c] | 760 |
| **8** | **1a** | **MeOH** | **/** | **100** | **99[d]** | **990** |
| 9 | **1b** | MeOH | / | 100 | 45[d] | 450 |
| 10 | **1c** | MeOH | / | 100 | 33[d] | 330 |
| 11 | **1d** | MeOH | / | 100 | 37[d] | 370 |
| 12 | **2** | MeOH | / | 100 | 80 [d] | 800 |

[a] Reaction was carried out with 0.1 mol% catalyst, 10 mmol morpholine in 2 mL solvent at $P_{H2} = P_{CO2}$ = 30 bar for 2 hrs. [b] Yield was determined by GC-MS with tridecane as an internal standard and 0.1 mol% *t*-BuOK was used. [c] For 10 hrs. [d] For 20 hrs.

Initially, *N*-formylation of morpholine with $CO_2$ and $H_2$ was selected as a model reaction to optimize the reaction conditions. In the presence of 0.1 mol% NHC-Ir coordination assemblies **1a** and 0.1 mol% *t*-BuOK, the reactions were carried out in 10 mmol scale under 40 bar pressure (20 bar for $CO_2$ and $H_2$, respectively) at 120 °C for 2 hours. When THF, MeOH, EtOH and *i*-PrOH were selected as solvents, similar but low yields of product **3** were usually obtained (21-26%, Table 1, entries 1-4). Other inorganic and organic bases hardly enhanced yields (Table S1, see the Supporting Information). When the total pressure was increased to 60 bar, a 41% yield was presented without external base addition (Table 1, entry 5). At 100 °C, a similar yield was still obtained (40%, entry 6). Further decreasing the reaction temperature, inferior outcomes were obtained (Table S1, see the Supporting Information). A good yield could be achieved by extending the reaction time to 10 hours (76%, Table 1, entry 7). Finally, a quantitative yield with 990 TON was obtained by extending the reaction time to 20 hours (Table 1, entry 8). With the optimized reaction conditions in hand, the catalytic activity of other solids **1b-d** was then investigated (Table 1, entries 11-13). Disappointingly, assemblies **1b-d** all exhibited lower catalytic activity; inferior yields with lower TONs were presented even with extended reaction time (37-45%, Table 1, entries 9-11), which clearly indicated auxiliary ligands (COD and CO) and counter-ions ($I^-$ and $BF_4^-$) affected the transformation. For direct comparison, a homogeneous analogue, NHC-Ir complex **2** was also involved in the model reaction under otherwise identical reaction conditions. However, only a 80% yield with 800 TON was obtained (Table 1, entry 14), which may be caused by possible inactive Ir species formed by dimerization of NHC-Ir **2** during the reaction,[46] highlighting the advantage of solid assemblies **1a**.

**Table 2.** NHC-Ir-catalyzed *N*-formylation of amines with $H_2$ and $CO_2$[a]



[a] Conditions: amines (10 mmol), **1a** (0.1 mol %), $P_{H2} = P_{CO2}$ = 30 bar, MeOH (2 mL), 100 °C, 20 h, isolated yield. [b] $[Me_2NH_2]^+•[Me_2NCOO]^-$ was used.

Subsequently, the scope of various amines was then explored under the optimized reaction conditions. As compiled in Table 2, diverse secondary and primary amines were selected for this purpose. Cyclic amines including pyrrole, piperidine, azepane and 1,4-piperazine were all well tolerated to produce corresponding formamides in good to excellent yields (85-94%, **4a-c**). Similar as cyclic cases, acyclic symmetric and asymmetric secondary amines are also compatible and readily converted into the desired products in good to excellent yields (75-93%, **5-13**). In the case of volatile dimethylamine (for safety reason, $[Me_2NH_2]^+•[Me_2NCOO]^-$ was applied instead), a moderate yield was still presented to produce DMF (53%, **8**). Other dialkyl secondary amines with higher boiling points, good to excellent yields were usually observed even with bulky substitutes and unprotected OH groups (80-93%, 7-13). In the case of primary amines, even better outcomes were presented (77-97%, **15-23**), whenever bearing aliphatic acyclic and cyclic chains, aromatic and heterocyclic substitutes, further highlighting the protocol efficiency. Heterocyclic substrate, such as 2-picolylamine and furan-2-ylmethanamine still delivered the corresponding products in excellent yields (77-89%, **18-19**). Aminoalcohols are very important building blocks, which are also suitable substrates for the N-formylation with $CO_2$ and $H_2$ under the standard reaction conditions and excellent yields are observed both for protected and unprotected aminoalcohols (81%-94%, **20-23**). It was notable that when the chiral aminoalcohol was involved, unprotected chiral amide **23** was produced in 81% yield.

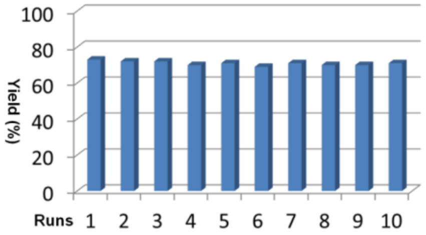


**Figure 1.** Recycling and reuse of the solid NHC-Ir catalyst **1a** in the DMF production (20 mmol scale at 0.1 mol% catalyst loading under the optimized reaction conditions; the average yields of two parallel recycling sequences are provided).

In light of the crucial role of DMF in industry, the reaction conditions for the *N*-formylation of $[Me_2NH_2]^+ \cdot [Me_2NCOO]^-$ was then fully investigated (Table S2, see the Supporting Information). To our surprise, solvents hardly show any impacts on the transformation, similar outcomes were observed under the standard reaction conditions, which is unlike Ding's Ru-PNP catalytic system.[33] In addition, solvent-free conditions led to a higher yield (57%, Table S2, entry 6), which could be further enhanced to 73% by increasing the pressure to 70 bar ($P_{H_2} = P_{CO_2}$ = 35 bar, Table S2, entry 7). When the catalyst loading was decreased to 0.05 mol%, a 72% yield was still achieved (Table S2, entry 12). No obvious change was found by extending the reaction time to 30 hrs (72% vs. 71%, Table S2, entries 12 vs 13). Again, inferior yields were observed with other NHC-Ir assemblies **1b-d** under such reaction conditions (Table S2, entries 16-18).

Due to insolubility of solid NHC-Ir **1a** in DMF, after reaction completion, the solid is readily recovered via simple centrifugation and decantation. Remarkably, the recovered solid **1a** could be directly used in the next run without any activation operation. And up to 10 runs could be recycled for the solid **1a** without any obvious loss in DMF production (Figure 1), highlighting the feasibility of NHC-Ir solid molecular catalyst **1a.** In order to further understand the catalytic nature of catalyst **1a** in the reaction and corresponding recycling process, the content of iridium in the filtrate after each run was analyzed by inductively coupled plasma emission spectroscopy (ICP-AES). The original Ir content in the NHC-Ir coordination assemblies **1a** was 24.4 % determinded by ICP-AES, which was consistent with the theoretical value (24.0%) of $(IrC_{23}H_{33}IN_5O \cdot DMF \cdot H_2O)_n$, wheraes, the amount of leaching iridium species in the recycling process was negligible. Notably, no iridium nanoparticles or nanoclusters were found in the filtrate and recovered solid catalysts, which may highlight NHC-Ir coordination assemblies **1a** act as a molecular catalyst in the reaction. In addition, no obvious changes were observed in the SEM and TEM morphologies of freshly prepared and recovered (after 10 runs) solid catalyst **1a** (Figure 2 a, b vs d, e). Energy dispersive X-ray spectroscopy (EDS) mapping images of fresh and recovered solids **1a** indicated no alternation of distribution of Ir species in the polymer matrix (Figure 2 c vs f), further confirming the stability of the solid molecular catalyst.

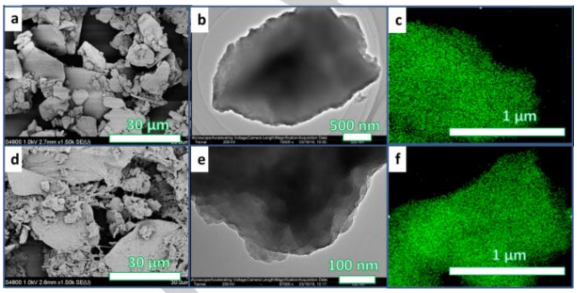
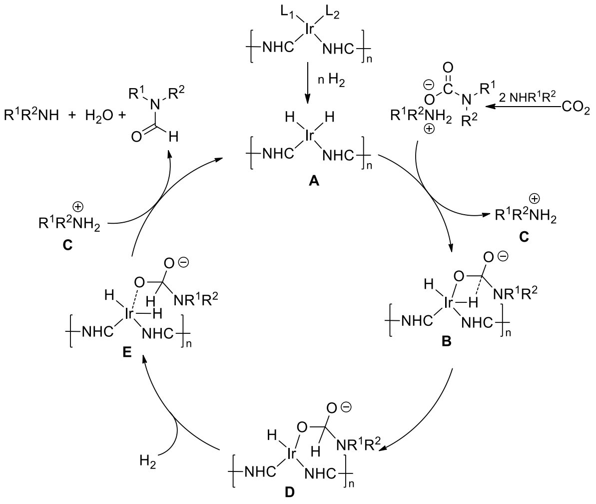


**Figure 2**. a-c): SEM, TEM, EDS images of the freshly prepared NHC-Ir coordination polymer **1a**; d-f): images of the recovered **1a** after the 10th run.

With all these outcomes in hand, a plausible mechanism catalyzed by NHC-Ir coordination assemblies **1a** was the proposed in Scheme 2. Initially, the *cis*-dihydride species **A** was generated from catalyst**,** which may act as the actual catalyst in the subsequent hydrogenation transformations.[49] Amines readily react with $CO_2$ to form internal salts.[50] After direct nucleophilic attacking of the carbonyl group of the salts, and coordinated species **B** was generated along with ammonium ion **C**. After hydride transfer, active intermediate **D** could further reacted with hydrogen to generate intermediate **E**, which could further react with ammonium ion **C** leading to the final formamides formation along with corresponding amine and water production.



**Scheme 2.** Plausible mechanism of *N*-formylation of amines.

In conclusion, one of NHC-iridium coordination assemblies containing COD and iodide ion has been demonstrated as robust, efficient and recyclable solid molecular catalyst for *N*-

formylation of various primary and secondary amines with $H_2$ and $CO_2$ under mild reaction conditions. A number of formamide derivatives could be produced in excellent yields even with chiral unprotected aminoalcohol as substrates at catalyst loadings as low as 0.1 mol%. Furthermore, the DMF production could be performed without external solvents at 0.1 mol% catalyst loading. Remarkably, the catalyst could be readily reused via simple centrifugation and decantation without any activating treatments. No significant loss of activity after 10 runs highlights the potential of protocol in industry.

## Acknowledgements

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## Conflicts of interest

There are no conflicts to declare.

**Keywords:** carbon dioxide transformation • coordination assembly • hydrogenation • iridium • *N*-formylation

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## Entry for the Table of Contents

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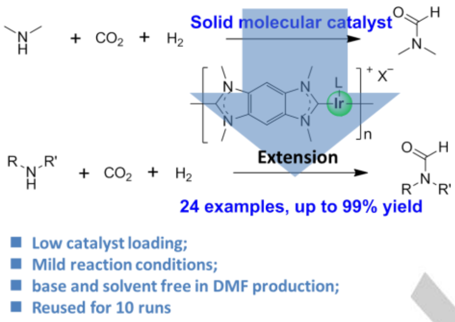

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