Journal Pre-proofs

Selective Mono-*N*-methylation of Nitroarenes with Methanol Catalyzed by Atomically Dispersed NHC-Ir Solid Assemblies

Jiaquan Wang, Jiajie Wu, Zhe-Ning Chen, Daheng Wen, Jiangbo Chen, Qingshu Zheng, Xin Xu, Tao Tu

Selective Mono-*N*-methylation of Nitroarenes with Methanol Catalyzed by Atomically Dispersed NHC-Ir Solid Assemblies

Jiaquan Wang[a], Jiajie Wu[a], Zhe-Ning Chen[c], Daheng Wen[a], Jiangbo Chen[a], Qingshu Zheng[a], Xin Xu[c,*], Tao Tu[a,b,*]

[a] *Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, China*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[c] *Collaborative Innovation Center of Chemistry for Energy Materials, MOE Laboratory for Computational Physical Science, Fudan University, 2005 Songhu Road, Shanghai 200438, China*

* Corresponding author.
E-mail addresses: xxchem@fudan.edu.cn (X. Xu), taotu@fudan.edu.cn (T. Tu).

ABSTRACT

A series of *N*-heterocyclic carbene-iridium (NHC-Ir) coordination assemblies based on bis-pyrenoimidazolium salts are prepared, and shown to function as efficient solid molecular catalysts in selective mono-*N*-methylation of nitroarenes with methanol under mild conditions. The atomically dispersed active Ir(I) centers and the large π-conjugation rings endow the solid catalysts with an exceptionally high activity and selectivity for a broad substrate scope. Such solid NHC-Ir coordination assemblies are robust, which can be easily recovered and reused more than 10 runs without significant loss of their catalytic activity and selectivity. When combined with a

subsequent formylation using the same solid catalysts under ambient conditions, this novel protocol can afford diverse formamides in excellent yields, further highlighting the applicability of the present solid catalysts for an efficient diversification of nitroarenes to a broad number of functional amines.

1. Introduction

As one of the most important building blocks for the synthesis of dyes, surfactants, agrochemicals, pharmaceuticals and natural products [1,2], N-methylamines have attracted a broad interest from both academic community and industry. In contrast to the conventional synthetic methodologies involving stoichiometric toxic reagents (e.g. methyl halides, Me_2SO_4, or Me_2CO_3) [3], N-methylation of primary amines with green and readily available feedstocks, such as methanol, is more appealing [4-6]. However, it is challenging to selectively synthesize mono-N-methylamines via this route, as the mono-N-methylamine products are usually more reactive than the starting primary amines and can readily be transformed into N,N-dimethylated derivatives. It is only up to the last few years that several homogeneous and heterogeneous catalysts based on Ag [7] Ru [8-10], Re [11], Ir [6,12,13], Mn [14-16], Fe [17-19] or Co [20] have been reported for selective mono-N-methylation of primary amines with methanol.

Meanwhile, nitroarenes are also the common N source in the various transformations [21-23]. For example, anilines are generally produced by the reduction of nitroarenes under a high pressure of hydrogen or with stoichiometric metal-hydrides, which can then undergo N-methylation to N-methylanilines (Fig. 1) [24-26]. However, from an environmental point of view, straightforward N-methylation of nitroarenes with methanol is considered as a much more efficient and attractive protocol for the synthesis of diverse N-methylanilines.
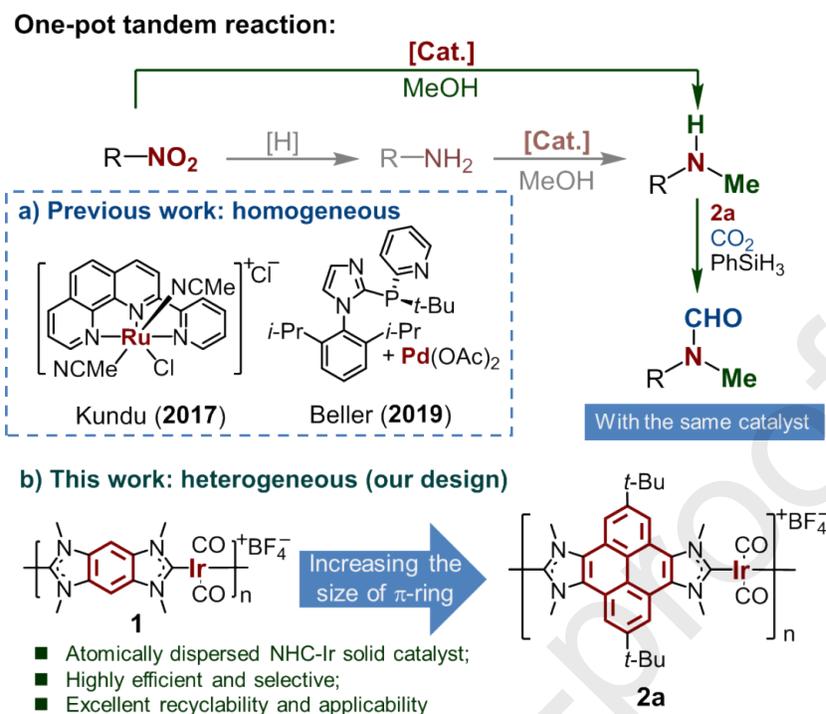
Fig. 1. Direct and selective catalytic mono-*N*-methylation of nitroarenes with methanol: (a) reported homogenous catalysts; (b) our newly designed recyclable NHC-Ir solid molecular catalyst and its applicability in further transformation explored in this work.

Nonetheless, to the best of our knowledge, there are only a limited number of examples on the *N*-methylation of nitroarenes with methanol up to date [27-34], which mainly focused on the N,N-dimethylation of nitroarenes [27,28]. However, the selective mono-N-methylation of nitroarenes is more chanllenging and is thus of great interest. The recent advances of the latter are compiled in Fig.1a. By using the "hydrogen borrowing" strategy [35,36], Kundu and co-workers realized the first tandem reductive amination of nitro compounds with methanol to various *N*-methylamines [33] in the presence of a Ru^{II}-N^N^N pincer-type catalyst [37-39]. Very recently, Beller and co-workers reported a Pd-catalyzed *N*-methylation of nitroarenes with methanol using a imidazole-substituted monophosphine as the ligand [34]. Despite these notable advances, the use of nonrecyclable homogeneous catalysts and the tedious nature of product purification processes may impede further industrial application of these protocols.

Recently, *N*-heterocyclic carbene-iridium (NHC-Ir) complexes have been shown to display an excellent catalytic activity toward dehydrogenation [40], hydrogenation [41], reductive amination,

formylation and C-H functionalization [42,43]. Meanwhile, by using the "self-supporting" strategy [44-47], we have developed a series of NHC-metal coordination assemblies [48-50], which have been successfully applied as solid molecular catalysts in various transformations [51-55]. Among them, NHC-Ir coordination assembly **1** was shown to exhibit excellent activity and recyclability toward selective mono-*N*-methylation of amines [52]. In this work, we sought to design new NHC-Ir coordination assemblies as catalysts in direct and more challenging tandem mono-*N*-methylation of nitroarenes with methanol (Fig. 1b). Considering that the strong σ-donating ability of the NHC ligands can enhance the catalytic activity in the homogenous catalytic systems [56-62], we envisioned that NHC-Ir coordination assemblies **2** with NHCs containing large π-extended rings may also increase their σ-donating ability to further inprove their cataltic activity. Such a design has been barely studied in the heterogenous system. Furthermore, in light of the observation that, for complexes including NHC-Ir **6b**, inactive species are readily formed due to the possible di-/polymerization or cluster formation under the reaction conditions [51-55,63,64], we presumed that bulky NHCs may prevent the possible di-/polymerization due to the isolation ability of their bulkiness. Pleasingly, we show here that NHC-Ir coordination assemblies designed accordingly indeed display excellent catalytic activity, selectivity and recyclability towards direct mono-*N*-methylation of nitroarenes under mild reaction conditions, they also exhibit excellent activity in the formylation reaction with CO_2, phenylsilane and the resultant mono-*N*-methylanilines, affording diverse formamides in good to excellent yields with high selectivity. The present protocol opens a viable way for future production of mono-*N*-methylanilines of various functionalities.

2. Experimental

2.1. Chemicals

All commercial reagents were used directly without further purification, unless otherwise stated.
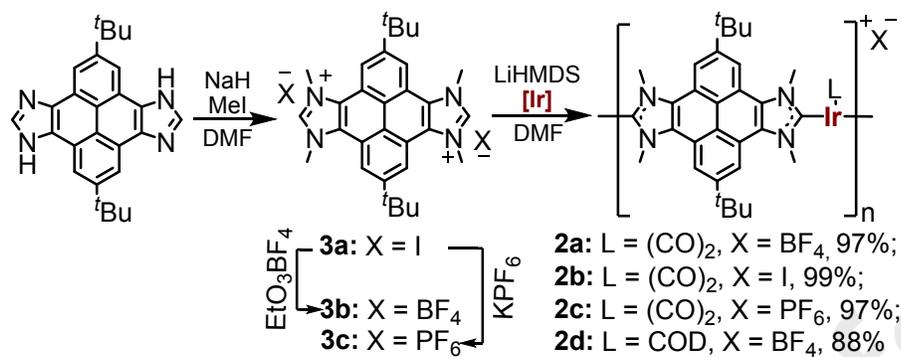
2.2. Synthesis of catalysts

Fig. 2. Syntheses of NHC-Ir assemblies **2a-d**.

With our previous experience [51-55], a series of pyrene analogues **2a-d** were prepared (Fig. 2). 2,7-di-*tert*-butylpyrene imidazole and the bis-pyrenoimidazolium iodide **3a** were synthesized according to the literature report [65]. The **3a** was readily converted to the corresponding BF_4^- and PF_6^- salts (**3b** and **3c**) in good yields by anion-exchange. Treatment of these Janus type ditopic NHC precursors with lithium bis(trimethylsilyl)amide (LiHMDS) led to the formation of bis-NHC species, with two carbene sites geometrically well-constrained and opposite to each other in orientation, which helped to further generate structurally defined coordination assemblies **2a-d** in *N,N*-Dimethylformamide (DMF) with selected iridium salts in very good yields (88-99%).

3b: A Schlenk tube was charged with salt **3a** (184 mg, 0.26 mmol), triethyloxonium tetrafluoroborate (117 mg, 1.04 mmol), dry CH_2Cl_2 (5 mL), and stirred for 12 hours at ambient temperature, methanol (3 mL) was then added. The resulting reaction mixture was stirred for an additional hour and then poured into excess diethyl ether (50 mL). After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder.

3c: To a solution of salt **3a** (184 mg, 0.26 mmol) in 5 mL H_2O was added KPF_6 (191 mg, 1.04 mmol) and reaction mixture was stirred for 3 hours at ambient temperature. After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder.

2a-d: salts **3** (0.5 mmol) and corresponding iridium precursor (0.5 mmol) were dissolved in DMF under N_2 at room temperature, LiHMDS (1 mmol) solution in THF was added dropwise.

The resulting mixture was stirred at 80 °C for 12 h. The dark brown solids were isolated after filtration and washed with deionized water for three times. The solids were then dried over vacuum.

2.3. Catalysts characterization

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. GC-MS spectra were recorded on Agilent technologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector. ESI-MS spectra were recorded on a Bruker microTOF II instrument. IR spectra were recorded on AVATAR FT-IR 360 instrument. Powder XRD studies were performed on a Bruker AXS D8. SEM experiments were carried out on a Philips XL30 microscope operated at 20 kV. TEM experiments were carried out on a JEOL JEM-2010 transmission electron microscope. Gel permeation chromatography (GPC) system was equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3, HR4, and HR5, 7.8 mm × 300 mm) and calibrated with linear polystyrene standards.

2.4. General procedure for the mono-N-methylation of nitroarenes with methanol

Nitroarenes (1.0 mmol), **2a** (7.9 mg, 1 mol %), KO^{t}Bu (112 mg, 1.0 equiv.) were charged in a 15 mL pressure tube with magnetic bar. Then, 3.5 mL of methanol was added into the mixture. The reaction tube was closed with the Teflon stopper and was heated to the desired temperature (130 °C) under stirring. After the desired reaction time, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and then the product was purified by column chromatography and the product was analyzed by NMR spectroscopy.

2.5. General procedure for the formylation of mono-N-methylanilines

Under an inert atmosphere (N$_2$), a 50 mL Schlenk flask equipped with a stir bar was charged successively with *N*-methylanilines (0.5 mmol), phenylsilane (54.1 mg, 1.0 equiv.), **2a** (3.9 mg, 1 mol %) and CH$_3$CN (2 mL). Then, the reaction mixture was stirred at room temperature for 6 h under 1 atmosphere of CO$_2$ (99.999%, balloon). After 6 h, the reaction was concentrated and purified by column chromatography and the product was analyzed by NMR spectroscopy.

3. Results and discussion

3.1. Morphological and structural characterization

Morphologies of solid assemblies **2a-d** were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), as well as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Typical SEM and TEM images, as shown in Fig. 3a and 3b for solid **2a**, revealed that these solid assemblies were nanosized irregular particles. The powder X-ray diffraction (XRD) patterns further confirmed their amorphous nature, and no obvious diffraction peaks were discernible (Figs. S11 and S12). Energy dispersive X-ray (EDX) mapping indicated that the iridium centers and other elements including C, N, O, B and F were uniformly dispersed in the solid matrixes of **2a**, whereas, no obvious iridium nanoparticles, aggregates or clusters were found (Fig. 3c). Moreover, magnified HAADF-STEM further confirmed that the iridium sites were atomically dispersed in the matrix of solid **2a** (Fig. 3g). Similar morphologies and spectra were also observed for solids **2a-d** (Figs. S1-S5, S8, S9, S11 and S12).

In light of their virtual insolubility in all common solvents (including water), the coordination assemblies were further characterized by solid-state ^{13}C-NMR spectroscopy, infrared spectroscopy (FT-IR), and elemental analysis (Figs. S14-S18), etc. In the solid-state ^{13}C NMR spectra of solid **2a,** broad signals at 182 and 170 ppm were assigned to C_{NHC} and C_{CO}, respectively, similar to those observed in the spectra of NHC-Ir complex **4** (180 and 172 ppm, respectively, Fig. 3j), further suggesting their similar coordination environments. In the FT-IR spectrum of solid **2a**, the absorption band at 1955 cm^{-1} corresponding to the auxiliary CO ligand attached to the iridium center [66] was found, which is also similar to that of complex **4** (Fig. S15 vs. S20). In addition, using X-ray photoelectron spectroscopy (XPS), peaks (at binding energies of 65.3 and 62.3 eV, assigned to Ir(I) $4f_{7/2}$ and $4f_{5/2}$) were observed (Fig. 3h), which are also consistent with those of molecular complex **4**. All these outcomes clearly indicated, after the recursive assembly of the geometrically well-constrained Janus type NHC ditopic ligands with the iridium centers via NHC-Ir coordination bonds, the resultant NHC-Ir coordination assemblies **2a-d** have a well defined structure as illustrated in Fig. 2.
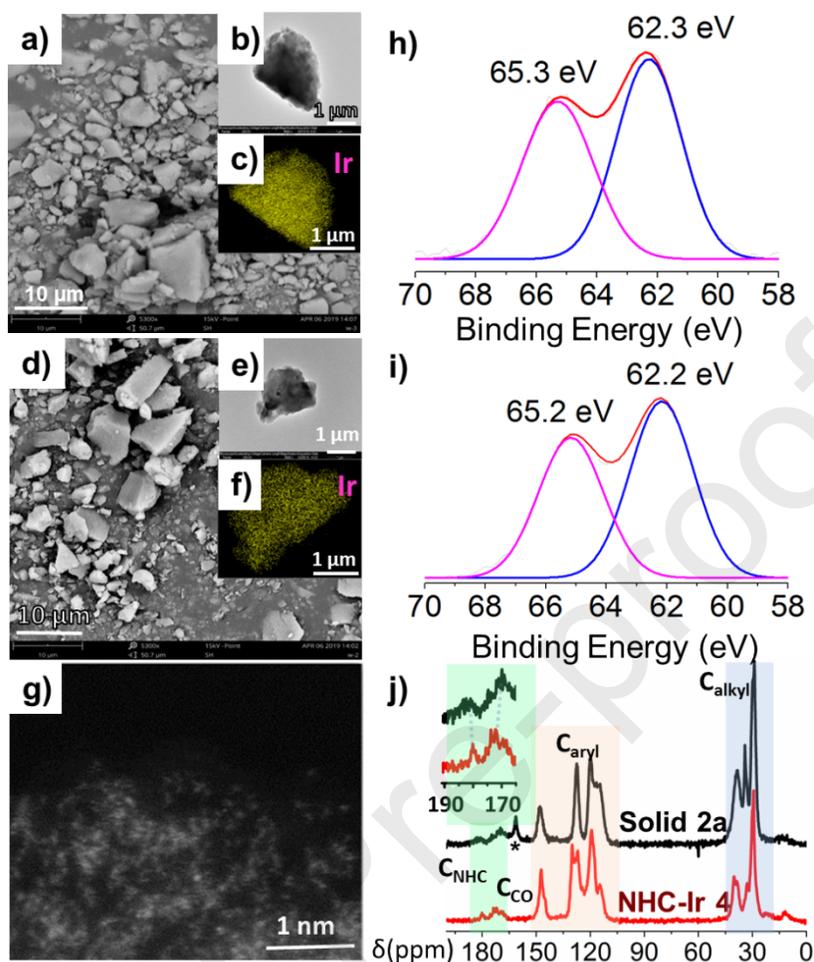
Fig. 3. (a) SEM, (b) TEM, (c) EDX, (g) HAADF-STEM images and (h) XPS spectrum for the freshly prepared NHC-Ir coordination assembly of solid **2a**; (d) SEM, (e) TEM, (f) EDX and (i) XPS spectrum of the recovered solid **2a** after the 12th run; (j) Solid ^{13}C NMR spectrum of solid **2a** and NHC-Ir complex **4** (* indicates the C signal of DMF trapped in the matrix of coordination assembly of solid **2a**) [67].

Furthermore, in order to probe the possible porosities of solid **2a**, nitrogen adsorption measurements were carried out, which showed barely adsorption of N_2 with a Brunauer-Emmett-Teller (BET) surface area of 45 m^2/g (Fig. S23). This result is also consistent with the desired one-dimensional linear structure of solid **2a** [51]. Thermo-gravimetric analysis revealed a good thermal stability (Fig. S21) with a decomposition temperature of around 200 °C. Due to its good thermal stability and insensitive towards air and moisture, the self-supported catalyst has been stored under ambient conditions for more than one year with maintained properties.

3.2. Catalytic performance

As a preliminary assessment of catalytic activities of solid assemblies **2a-d**, mono-*N*-methylation of nitrobenzene with methanol to amine **5** was selected as a benchmark reaction. For comparison, their analogues **1**, **4**, **6a-b** and pincer complexes **7a-b** were also evaluated (Fig. 4a). A careful survey (Table S1) indicated that at 1 mol %, solid **2a** exhibited the highest catalytic activity. When the reaction was carried out at 1 mmol scale with 1 equiv. KO^{t}Bu and 3.5 mL MeOH at 130 ^{o}C for 24 h, amine **5** was isolated in 96% yield, no other possible by-products like nitrosobenzene, aniline, azobenzene or azoxybenzene were detected, highlighting its excellent selectivity. By contrast, a slightly lower yield (89%) of product **5** was observed with solid analogue **1** [51-55], which further supported our concept that increasing the σ-donating ability of the NHC ligands could efficiently enhance the activity of the resulting catalyst [56-62], even in the heterogeneous system. The influence of counter ions and ancillary ligands, e.g., carbon monoxide (CO) or 1,5-cyclooctadiene (COD), were also investigated. Only small differences on the yields were observed for solid molecular catalysts **2a-c** with different counterions, BF_4^- (96%) > I^- (93%) > PF_6^- (92%). Hence, even though these counterions have different structures and neocleophilicities[68], the chemcial environment of the active Ir center is only slightly affected in our cases. While solid **2d** bearing the COD ligand and the BF_4^- counter ion, gave an inferior yield as compared to that of solid **2a** (96% vs 67%, Fig. 4a), indicating the significant impact of the ancillary ligand. Subsequently, NHC-Ir complexes **4** and **6a-b** were also examined. Even with the same compositions of counter ion (BF_4^-) and ancillary ligand (CO) as those in **2a**, obvious decreases in yields (10~30% lower, Fig. 4a) were observed. These results were probably caused by the possible di-/polymerization of molecular NHC-Ir species under the reaction conditions [63,64], further confirming the advantageous isolation effects of bulky ligands in solid **2a**. In addition, pincer complexes **7a-b**, which exhibited excellent activity in various transformations [69], also resulted in only moderate yields (70% and 60% respectively, Fig. 4a). When the catalyst loading of solid **2a** was further decreased to 0.1 mmol %, turnover numbers (TONs) of 650 were achieved.
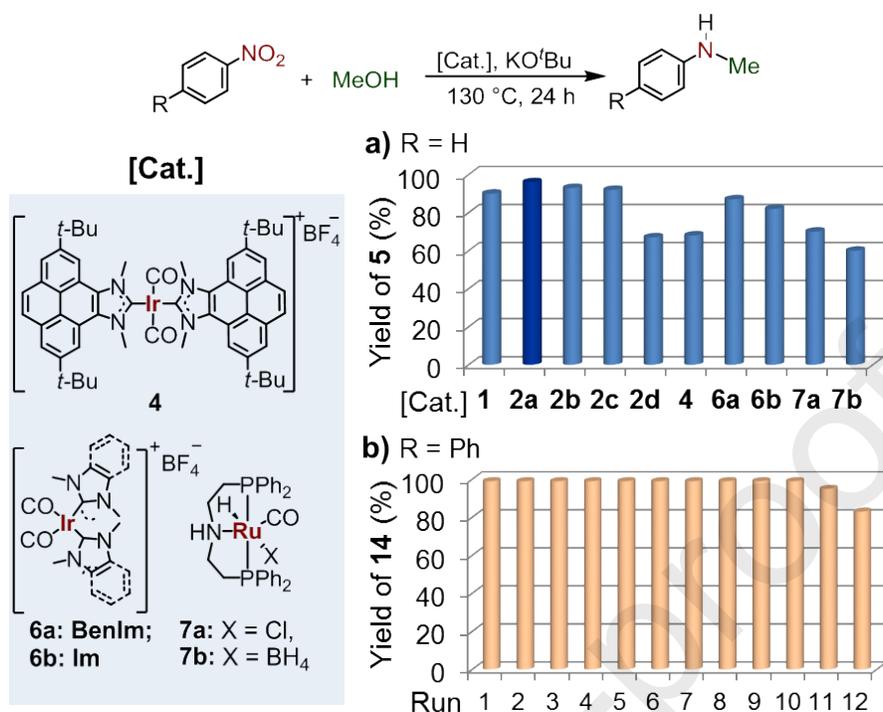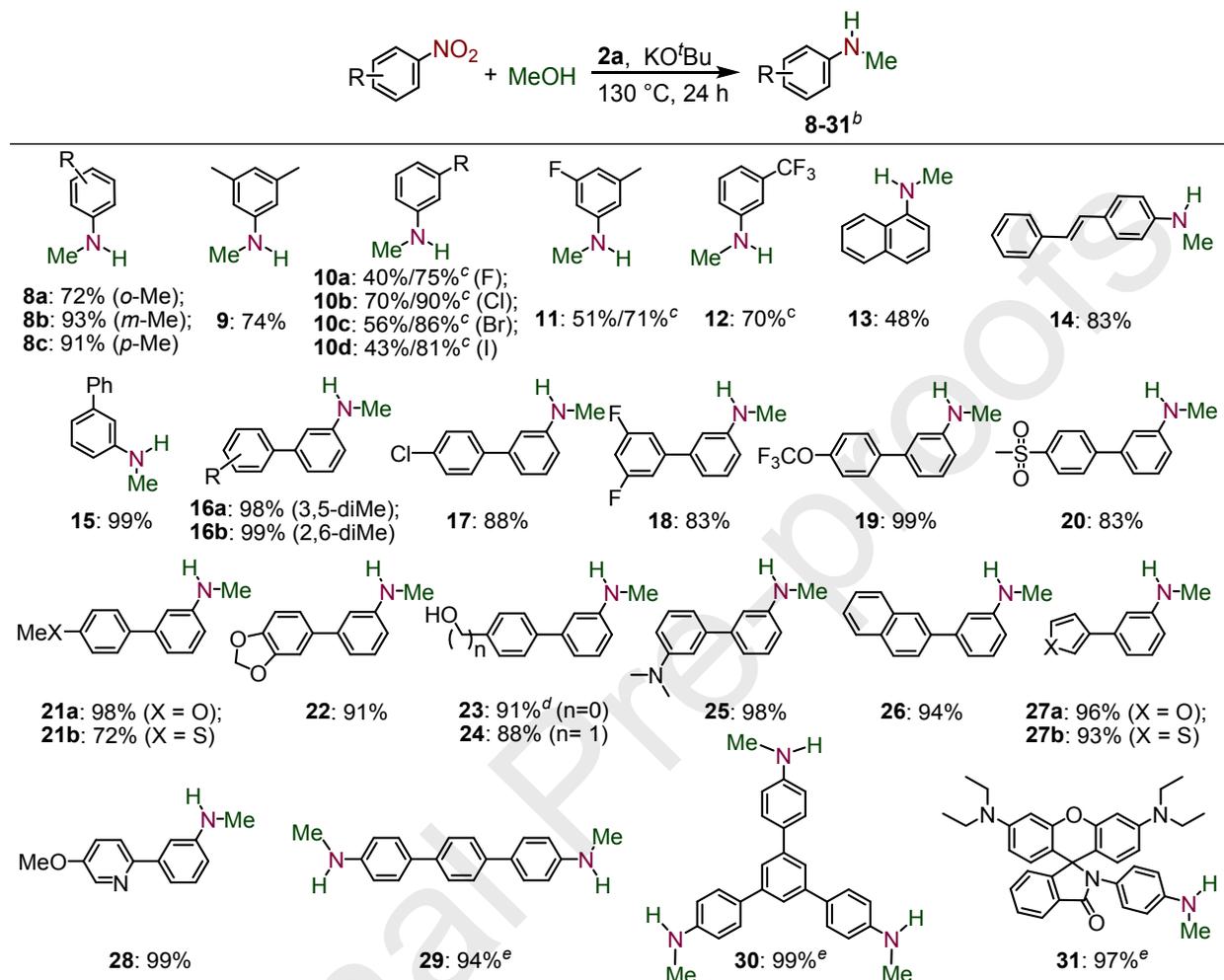
Fig. 4. (a) Catalytic activities of NHC-Ir coordination assemblies **1**, **2a-d** and their molecular analogues **4** and **6a-b**, as well as pincer complexes **7a-b** towards mono-*N*-methylation of nitrobenzene. (b) Recyclability and reusability of NHC-Ir coordination assembly **2a** in the catalytic mono-*N*-methylation of 3-nitrobiphenyl. (Reactions were carried out in 1 mmol scale with 1 mol% solid **2a** with 1 equiv. KO*t*Bu in 3.5 mL methanol at 130 °C for 24 h).

After catalyst screening, the scope and the limitation of the protocol were then explored (Table 1). To our delight, a variety of nitroarenes bearing electron-donating (**8a-c** and **9**), electron-withdrawing (**10a** and **12**) substituents or sterically hindered ones (**13**) were all well tolerated, and moderate to excellent yields with good selectivity were obtained (up to 93%, Table 1). The position of substituents on the nitroarenes exhibited obvious impacts on the transformation; a *meta*-substituted substrate **8b** produced a higher yield than its *ortho*- and *para*- isomers (**8a** and **8c**). Therefore, inferior yields were also observed with *ortho*-substituted and bulky substances (**8a** and **13**). For the reactions with *meta*-halo-nitroarenes (**10a-d**), good to excellent yields were obtained by prolonging reaction times (48 h), in which *cholo*-nitroarene gave out the best isolated yield (90%). Moreover, C=C double bonds (**14**) could also be well tolerated (83%), indicating the high chemoselectively of the protocol.

10

Table 1. Mono-*N*-methylation of Nitroarenes[a].

R⟨ring⟩NO₂ + MeOH →[2a, KO^{t}Bu / 130 °C, 24 h] R⟨ring⟩N(H)Me   **8-31**[b]

8a: 72% (*o*-Me);
8b: 93% (*m*-Me);
8c: 91% (*p*-Me)

9: 74%

10a: 40%/75%[c] (F);
10b: 70%/90%[c] (Cl);
10c: 56%/86%[c] (Br);
10d: 43%/81%[c] (I)

11: 51%/71%[c]

12: 70%[c]

13: 48%

14: 83%

15: 99%

16a: 98% (3,5-diMe);
16b: 99% (2,6-diMe)

17: 88%

18: 83%

19: 99%

20: 83%

21a: 98% (X = O);
21b: 72% (X = S)

22: 91%

23: 91%[d] (n=0)
24: 88% (n= 1)

25: 98%

26: 94%

27a: 96% (X = O);
27b: 93% (X = S)

28: 99%

29: 94%[e]

30: 99%[e]

31: 97%[e]

[a] Reactions were generally carried out on 1 mmol of the nitroarenes with 1 mol % solid catalyst **2a** and 1 equiv. KO^{t}Bu in 3.5 mL methanol at 130 °C for 24 h; [b] isolated yield; [c] After 48 h; [d] With 2 equiv. KO^{t}Bu; [e] 0.5 mmol scale, 48 h.

Presumably, owing to the presence of the strongly electron-withdrawing nitro group, several *ortho-*, *para*-substituted substrates (Scheme S3) tended to undergo the S$_N$Ar reactions [70] rather than *N*-methylation, which led to low conversions in some cases. Therefore, a series of biphenyl substrates were explored, in which electron-donating or electron-withdrawing and heterocyclic substituents were all well compatible. Good to excellent yields with high selectivity were obtained (**15-28**, 72-99%, Table 1). Pleasingly, when a methyl-sulfonyl substituted substance was applied, mono-*N*-methylaniline with unchanged sulfone group was produced in good yield (**20**, 83%, Table

1). For the substrates bearing free hydroxyl groups, the desired products were also isolated in good yields (91% and 88% for **23** and **24**, respectively), while the hydroxyl groups remained untouched, further confirming the selectivity of the present protocol. In light of the crucial role of heterocyclic *N*-methylamines in pharmaceutical and material sciences [1,2], heterocyclic substrates containing O, S, N atoms were also tested and excellent yields were obtained (**27a**,**b** and **28**, 93-99%, Table 1). Unfortunately, aliphatic nitro compounds were incompatible to this protocol.

Remarkably, dinitro and trinitro-arenes were also found to be suitable substrates for mono-*N*-methylation. Under the otherwise identical conditions, the multiple-nitiro groups were all mono-*N*-methylated, and no *N,N*-dimethylated products were detected, despite that the corresponding secondary anilines were more nucleophilic. By extending reaction time to 48 h, *di*-mono-*N*-methylaniline **29** was obtained in 94% yield, and almost quantitative yield was observed for *tri*-mono-*N*-methylaniline **30**. The protocol was further extended to synthesize mono-*N*-methylated rhodamine derivative **31** and an excellent yield was obtained (97%, Table1). The rhodamine core structure was not affected during the methylation, highlighting the potential applications for modification of drugs and structurally elaborated molecules.

3.3. recyclable performance

In consideration of its insolubility of solid **2a** in methanol, the solid catalyst was readily recovered when the reaction mixture was simply centrifuged and washed with fresh methanol. The recovered solid **2a** was applied as the catalyst directly in the next cycle without additional activation or treatment. Taking account of low boiling point of mono-*N*-methylaniline, we thus selected 3-nitrobiphenyl as the substrate for the catalyst-recycling test. To our delight, catalyst **2a** could be reused for more than 10 runs while maintaining quantitative yields (Fig. 4b). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was applied to monitor the potential iridium leaching in each run (Table S2). Only trace amount of leaching (< 0.09 mg/L) was observed with the initial three runs, which might be the unreactive iridium precursors or low-molecular weight polymers trapped in the solid matrix of **2a** during the coordination assembly. By using Gel permeation chromatography (GPC), a NHC-Ir dimer **2a'** could be detected with molecular weight of 1090 (Fig. S24), which supported that the possible leaching may be aroused by the trace amount of the low-molecular weight assemblies.

12

For the recovered solid **2a** after the 12th run, similar SEM and TEM images as those freshly prepared amorphous samples were observed (Figs. 3d and 3e). EDX mapping indicated that the iridium sites were still uniformly dispersed in the solid matrix without the formation of nanoparticles (Figs. 3f, S6 and S7). The unchanged XPS pattern (Fig. 3i) further supported the structural robustness of the NHC-Ir(I) assembly of solid **2a**. As shown in Fig. 5a, by using complex **6a** as a catalyst model, density functional theory (DFT) calculations [71-73] showed a strong binding strength between the NHC ligand and the Ir center, in which the dissociation free energy is as high as 36.4 kcal/mol. Whereas, the dissociation of the CO ligand is much more feasible, with an observably smaller dissociation free energy of 14.2 kcal/mol. These findings demonstrated that the NHC ligands are firmly bonded to the Ir center, supporting the structural stability of the solid assembles observed in experiments. Instead, the dissociation of the CO ligand is a viable route to provide the reactive site for the catalytic reactions.

3.4. Catalytic mechanism

To probe the plausible reaction mechanism, several control experiments were carried out (Scheme S5). The reaction between 3-nitrobipenyl and CD_3OD under the standard conditions produced deuterated mono-*N*-methylaniline **15a** in 75% yield (Scheme S5a), suggesting that methanol served as both a hydrogen source and a methylation reagent. Further reaction with CD_3OH gave a mixture of N-methylated products **15b** (61%) and **15b-d2** (39%) in an overall yield of 90% (Scheme S5a). The slightly lower yield with CD_3OD than that with CD_3OH suggests that the activation of the O-H bond in methanol can have an impact on the transformation. When formaldehyde was used instead of methanol in *tert*-butanol, no product was observed (Scheme S5b), revealing that the dehydrogenation of methanol and the produced hydrogen were crucial for the reduction of nitroarenes. In addition, when the possible intermediates, including nitrosobenzene, azobenzene and aniline were subjected to the reaction, respectively, under the standard conditions, the *N*-methylaniline was obtained in moderate to good yields in each case (Scheme S5c). Meanwhile, we also successfully detected the formation of azobenzene in the reaction. Whereas, azobenzene was isolated as a side-product in Beller's system [34] but not found by Kundu and coworkers [33]. Consequently, azobenzene or its derivatives were thought to be hardly converted into the corresponding N-methyl anilines in the previous reports. Therefore, all the information may indicate a completely new reduction pathway for N-methylation of

nitroarenes catalyzed by solid **2a**, in which the direct transfer hydrogenation of nitrobenzene to aniline could be excluded [39,74]. Additionally, to investigate the excellent selectivity in the mono-*N*-methylation, *N*-methylaniline was subjected to the standard conditions at 120, 130 and 160 ºC respectively. Only 9% yield of *N,N*-dimethylaniline was detected at 160 ºC, indicating the effectiveness of this catalytic system to the mono-*N*-methylation of nitroarenes, while showing that further methylation of the secondary amines could be kinetically prevented under the standard conditions. (Scheme S5d).
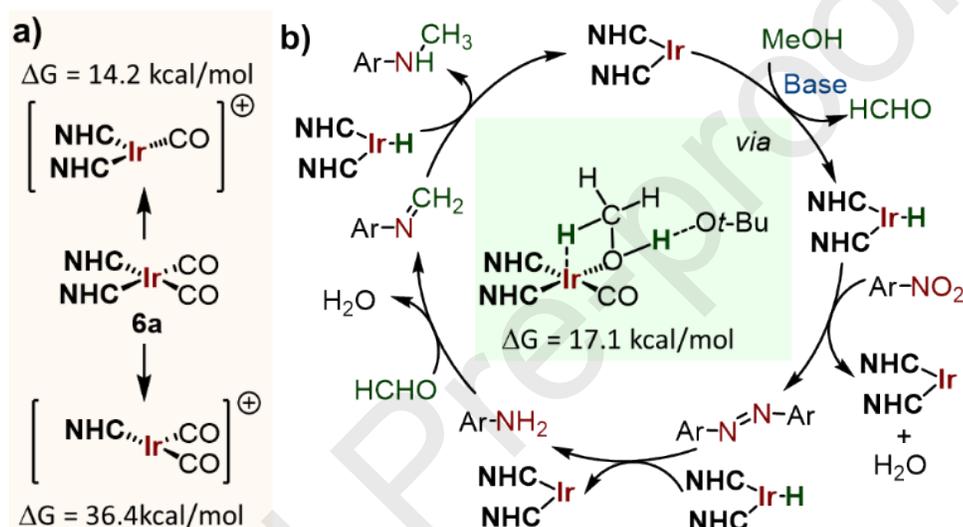

Fig. 5. (a) The DFT calculated free energy changes for the ligand detachment from NHC-Ir complex **6a**. (b) Proposed reaction mechanism. The DFT calculated value for dehydrogenation transition state represents the relative free energy with respect to NHC-Ir complex **6a** and methanol.

Based on aforementioned results and our previous work [51-55], a plausible mechanism is proposed in Fig. 5b. Firstly, oxidative dehydrogenation of methanol is mediated by the NHC-Ir catalyst and the base, giving formaldehyde with the simultaneous generation of a NHC-Ir-H species. Nitroarenes are reduced by the latter to anilines via an azoarene intermediate. Condensation of anilines with formaldehyde gives rise to *N*-methylated imines accompanied by water liberation. The resulting imines are hydrogenated by the NHC-Ir-H species and *t*BuO-H to produce the mono-*N*-methylated product, and regenerate the catalyst. In the middle of Fig. 5b, we illustrate the structure of the dehydrogenation transition state. DFT calculations confirmed that the

NHC-Ir catalyzed dehydrogenation reaction of methanol occurs after a CO ligand dissociation from the Ir center, with the participation of the solvated base (^{t}BuO-), to generate formaldehyde. Intriguingly, such a dehydrogenation step proposed here is a redox-neutral Ir(I)/Ir(I) process without changing the apparent valence of the Ir center. This process is indeed feasible with an apparent activation free energy of 17.1 kcal/mol only.

3.5. Further N-formylation with the same catalyst

Table 2. Further formylation of *N*-methylanilines with the same catalyst[a].
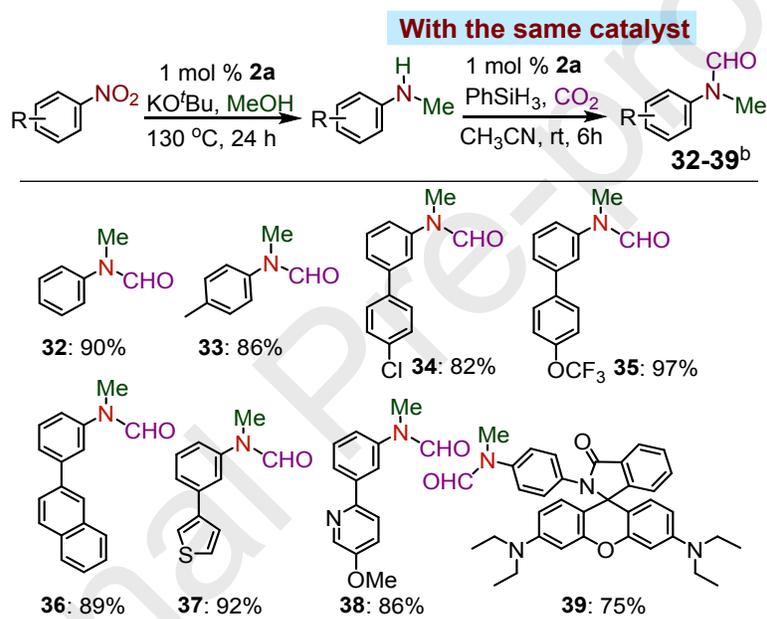
[a] Reactions were carried out in 0.5 mmol scale with 1 mol % solid catalyst **2a** and 1.0 equiv. PhSiH$_3$ in 2 mL CH$_3$CN under 1 atm CO$_2$ (balloon) at room temperature for 6h; [b] isolated yield.

As is well known, formamides are versatile chemicals and important building blocks, which can be prepared by formylation of amines [75,76]. In order to extend the applicability of our newly developed NHC-Ir coordination assembly catalysts, we explored the feasibility of *N*-methylamines in further transformation. We used the direct formylation to demonstrate this concept, in which the selected products obtained by mono-*N*-methylation of nitroarenes were readily functionalized to the corresponding formamides using CO$_2$ and phenylsilane in the presence of 1 mol % solid **2a** at

15

room temperature within 6 h (Table 2). Broad substrate scope was observed with this new catalytic formylation approach. Substrates bearing electron-donating and electro-withdrawing substituents, as well as heterocyclic (**37**, **38**) substrates, were all compatible. Good to excellent yields were achieved. Moreover, rhodamine derivative **39** was produced in 75% isolated yield, further attesting the broad catalytic applicability of the NHC-Ir coordination assemblies.

4. Conclusions

A series of robust NHC-Ir coordination assemblies based on bis-pyrenoimidazolium salts have been prepared, which can function as solid single-site catalysts with atomically dispersed iridium centers, having a similar coordination environment as their molecular analogues. These catalysts have been shown to exhibit a high catalytic activity and selectivity in the mono-*N*-methylation of nitroarenes with methanol. Besides a broad substrate scope, the robust NHC-Ir assemblies have been found to be readily recovered and reused for more than 10 runs without loss of their catalytic activity and selectivity. DFT calculations have disclosed a redox-neutral Ir(I)/Ir(I) process with a synergetic participation of the solvated base in support of the observed robustness, reusability, but extremely high catalytic activity of the catalytic system. In addition, this protocol has been shown here to be readily extended with further formylation using the same solid molecular catalyst under the ambient reaction conditions. The direct and selective mono-*N*-methylation of nitroarenes to amines using our recyclable solid molecular catalysts may pave the way to future industrial production of various bioactive or fluorescent mono-*N*-methylanilines.

Declaration of competing interest

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: XXXXX

References

[1] A. Corti, A. M. Gasparri, M. Ghitti, A. Sacchi, F. Sudati, M. Fiocchi, V. Buttiglioe, L. Perani, A. Gori, S. Valtorta, Glycine *N*-methylation in NGR-tagged nanocarriers prevents isoaspartate formation and integrin binding without impairing CD13 recognition and tumor homing, Adv. Funct. Mater. 27 (2017) 1701245, https://doi.org/10.1002/adfm.201701245.

[2] P. Ruiz-Castillo, S. L. Buchwald, Applications of palladium-catalyzed C-N cross-coupling reactions, Chem. Rev. 116 (2016) 12564-12649, https://doi.org/10.1021/acs.chemrev.6b00512.

[3] Y. Chen, Recent advances in methylation: a guide for selecting methylation reagents, Chem. Eur. J. 25 (2019) 3405-3439, https://doi.org/10.1002/chem.201803642 and reference therein.

[4] T. Yan, B. L. Feringa, K. Barta, Direct *N*-alkylation of unprotected amino acids with alcohols, Sci. Adv. 3 (2017) eaao6494, https://doi.org/10.1126/sciadv.aao6494.

[5] K. Natte, H. Neumann, M. Beller, R. V. Jagadeesh, Transition-metal-catalyzed utilization of methanol as a C1 source in organic synthesis, Angew. Chem. Int. Ed. 56 (2017) 6384-6394, https://doi.org/10.1002/anie.201612520.

[6] R. Liang, S. Li, R. Wang, L. Lu, F. Li, *N*-methylation of amines with methanol catalyzed by a Cp*Ir complex bearing a functional 2, 2'-bibenzimidazole ligand, Org. Lett. 19 (2017) 5790-5793, https://doi.org/10.1021/acs.orglett.7b02723.

[7] V. N. Tsarev, Y. Morioka, J. Caner, Q. Wang, R. Ushimaru, A. Kudo, H. Naka, S. Saito, N-methylation of amines with methanol at room temperature, Org. Lett. 17 (2015) 2530-2533, https://dx.doi.org/10.1021/acs.orglett.5b01063.

[8] G. Choi, S. H. Hong, Selective monomethylation of amines with methanol as the C1 source, Angew. Chem. Int. Ed. 57 (2018) 6166-6170, https://doi.org/10.1002/anie.201801524.

[9] O. Ogata, H. Nara, M. Fujiwhara, K. Matsumura, Y. Kayaki, *N*-monomethylation of aromatic amines with methanol via PN(H)P-pincer Ru catalysts, Org. Lett. 20 (2018) 3866-3870, https://doi.org/10.1021/acs.orglett.8b01449.

[10] T. T. Dang, B. Ramalingam, A. M. Seayad, Efficient ruthenium-catalyzed *N*-methylation of amines using methanol, ACS Catal. 5 (2015) 4082-4088, https://doi.org/10.1021/acscatal.5b00606.

[11] D. Wei, O. Sadek, V. Dorcet, T. Roisnel, C. Darcel, E. Gras, E. Clot, J.-B. Sortais, Selective mono N-methylation of anilines with methanol catalyzed by rhenium complexes: An experimental and theoretical study, J. Catal. 366 (2018) 300-309, https://doi.org/10.1016/j.jcat.2018.08.008.

[12] D. Deng, B. Hu, M. Yang, D. Chen, Methylation of amines and ketones with methanol catalyzed by an iridium complex bearing a 2-hydroxypyridylmethylene fragment, Organometallics 37 (2018) 3353-3359, https: //doi.org/10.1021/acs.organomet.8b00575.

[13] J. Campos, L. S. Sharninghausen, M. G. Manas, R. H. Crabtree, Methanol dehydrogenation by iridium *N*-heterocyclic carbene complexes, Inorg. Chem. 54 (2015) 5079-5084, https://doi.org/10.1021/ic502521c.

[14] J. Neumann, S. Elangovan, A. Spannenberg, K. Junge, M. Beller, Improved and general manganese-catalyzed *N*-methylation of aromatic amines using methanol, Chem. Eur. J. 23 (2017) 5410-5413, https://doi.org/10.1002/chem.201605218.

[15] S. Elangovan, J. Neumann, J. B. Sortais, K. Junge, C. Darcel, M. Beller, Efficient and selective *N*-alkylation of amines with alcohols catalysed by manganese pincer complexes, Nat. Commun. 7 (2016) 12641-12648, https://doi.org/10.1038/ncomms12641.

[16] A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, N-methylation of anilines with methanol catalyzed by a manganese pincer-complex, J. Catal. 347 (2017) 57-62, http://dx.doi.org/10.1016/j.jcat.2017.01.004.

[17] K. Polidano, B. D. W. Allen, J. M. J. Williams, L. C. Morrill, Iron-catalyzed methylation using the borrowing hydrogen approach, ACS Catal. 8 (2018) 6440-6445, https://doi.org/10.1021/acscatal.8b02158.

[18] A. Lator, S. Gaillard, A. Poater, J.-L. Renaud, Well-defined phosphine-free iron-catalyzed *N*-ethylation and *N*-methylation of amines with ethanol and methanol, Org. Lett. 20 (2018) 5985-5990, https://doi.org/10.1021/acs.orglett.8b02080.

[19] K. Natte, H. Neumann, R. V. Jagadeesh, M. Beller, Convenient iron-catalyzed reductive aminations without hydrogen for selective synthesis of *N*-methylamines, Nat. Commun. 8 (2017) 1344-1352, https://doi.org/10.1038/s41467-017-01428-0.

[20] Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao, Z. Liu, Efficient cobalt-catalyzed methylation of amines using methanol, Adv. Synth. Catal. 359 (2017) 4278-4283, https://doi.org/10.1002/adsc.201701044.

[21] C. W. Cheung, N. Shen, S.-P. Wang, A. Ullah, X. Hu, J.-A. Ma, Manganese-mediated reductive amidation of esters with nitroarenes, Org. Chem. Front. 6 (2019) 756-761, https://doi.org/10.1039/C8QO01405A.

[22] C. W. Cheung, M. Leendert Ploeger, X. Hu, Amide synthesis *via* nickel-catalysed reductive aminocarbonylation of aryl halides with nitroarenes, Chem. Sci. 9 (2018) 655-659, https://doi.org/10.1039/C7SC03950F.

[23] C. W. Cheung, J. A. Ma, X. Hu, Manganese-mediated reductive transamidation of tertiary amides with nitroarenes, J. Am. Chem. Soc. 140 (2018) 6789-6792, https://doi.org/10.1021/jacs.8b03739.

[24] M. Orlandi, D. Brenna, R. Harms, S. Jost, M. Benaglia, Recent developments in the reduction of aromatic and aliphatic nitro compounds to amines, Org. Process Res. Dev. 22 (2018) 430-445, https://doi.org/10.1021/acs.oprd.6b00205.

[25] R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, Nanoscale Fe_2O_3-based catalysts for selective hydrogenation of nitroarenes to anilines, Science 342 (2013) 1073-1076, https://doi.org/10.1126/science.1242005.

[26] D. Formenti, F. Ferretti, F. K. Scharnagl, M. Beller, Reduction of nitro compounds using 3d-non-noble metal catalysts, Chem. Rev. 119 (2019) 2611-2680, https://dx.doi.org/10.1021/acs.chemrev.8b00547.

[27] L. Xu, X. Li, Y. Zhu, Y. Xiang, One-pot synthesis of N,N-dimethylaniline from nitrobenzene and methanol, New J. Chem. 33 (2009) 2051-2054, https://doi.org/10.1039/b905656d.

[28] L. Zhang, Y. Zhang, Y. Deng, F. Shi, Light-promoted N,N-dimethylation of amine and nitro compound with methanol catalyzed by Pd/TiO_2 at room temperature, RSC Adv. 5 (2015) 14514-14521, https://doi.org/10.1002/adsc.201701044.

[29] V. Goyal, J. Gahtori, A. Narani, P. Gupta, A. Bordoloi, K. Natte, Commercial Pd/C-catalyzed N-methylation of nitroarenes and amines using methanol as both C1 and H2 source, J. Org. Chem. 84 (2019) 15389-15398, https://dx.doi.org/10.1021/acs.joc.9b02141.

[30] A. Fu, Q. Liu, M. Jiang, G. Xu, Selective N-monomethylation of amines and nitroarenes using methanol over an encapsulated iridium nanocatalyst, Asian J. Org. Chem. 8 (2019) 487-491, https://doi.org/10.1002/ajoc.201900140.

[31] S. Zhang, J. J. Ibrahim, Y. Yang, A pincer ligand enabled ruthenium catalyzed highly selective N-monomethylation of nitroarenes with methanol as the C1 source, Org. Chem. Front. 6 (2019) 2726-273, https://doi.org/10.1039/c9qo00544g.

[32] B. G. Reed-Berendt, N. Mast, L. C. Morrill, Manganese-catalyzed one-pot conversion of nitroarenes into N-methylarylamines using methanol, Eur. J. Org. Chem. 2020 (2020) 1136-1140, https://doi.org/10.1002/ejoc.201901854.

[33] B. Paul, S. Shee, K. Chakrabarti, S. Kundu, Tandem transformation of nitro compounds into *N*-methylated amines: greener strategy for the utilization of methanol as a methylating agent, ChemSusChem 10 (2017) 2370-2374, https://doi.org/10.1002/cssc.201700503.

[34] L. Wang, H. Neumann, M. Beller, Palladium-catalyzed methylation of nitroarenes with methanol, Angew. Chem. Int. Ed. 58 (2019) 5417-5421, https://doi.org/10.1002/anie.201814146.

[35] C. Gunanathan, D. Milstein, Application of acceptorless dehydrogenation and related transformations in chemical synthesis, Science 6143 (2013) 1229712, https://doi.org/10.1126/science.1229712.

[36] Q. Yang, Q. Wang, Z. Yu, Substitution of alcohols by N-nucleophiles via transition metal-catalyzed dehydrogenation, Chem. Soc. Rev. 44 (2015) 2305-2329, https://doi.org/10.1039/c4cs00496e.

[37] K. Chakrabarti, A. Mishra, D. Panja, B. Paul, S. Kundu, Selective synthesis of mono-and di-methylated amines using methanol and sodium azide as C1 and N1 sources, Green Chem. 20 (2018) 3339-3345, https://doi.org/10.1039/C8GC00863A.

[38] B. Paul, S. Shee, D. Panja, K. Chakrabarti, S. Kundu, Direct synthesis of *N, N*-dimethylated and β-methyl *N, N*-dimethylated amines from nitriles using methanol: experimental and computational studies, ACS Catal. 8 (2018) 2890-2896, https://doi.org/10.1021/acscatal.8b00021.

[39] K. Chakrabarti, S. Shee, M. Maji, A. Mishra, S. Kundu, A simple and efficient in situ generated ruthenium catalyst for chemoselective transfer hydrogenation of nitroarenes: kinetic and mechanistic studies and comparison with iridium systems, RSC Adv. 6 (2016) 100532-100545, https://doi.org/10.1039/C6RA22221H.

[40] M. Iglesias, L. A. Oro, A leap forward in iridium-NHC catalysis: new horizons and mechanistic insights, Chem. Soc. Rev. 47 (2018) 2772-2808, https://doi.org/10.1039/C7CS00743D.

[41] I. Romanenko, D. Gajan, R. Sayah, D. Crozet, E. Jeanneau, C. Lucas, L. Leroux, L. Veyre, A. Lesage, L. Emsley, E. Lacote, C. Thieuleux, Iridium(I)/*N*-heterocyclic carbene hybrid materials: surface stabilization of low-valent iridium species for high catalytic hydrogenation performance, Angew. Chem. Int. Ed. 54 (2015) 12937-12941, https://doi.org/10.1002/anie.201505867.

[42] T. K. Maishal, M. Boualleg, M. Bouhrara, C. Copéret, E. Jeanneau, L. Veyre, C. Thieuleux, Domination of local environment over pore confinement effects on the catalytic performances of single-site Cp*Ir^{III}-NHC heterogeneous *vs*. homogeneous H/D exchange catalysts, Eur. J. Inorg. Chem. 2010 (2010) 5005-5010, https://doi.org/10.1002/ejic.201000679.

[43] T. K. Maishal, J. Alauzun, J. M. Basset, C. Coperet, R. J. Corriu, E. Jeanneau, A. Mehdi, C. Reye, L. Veyre, C. Thieuleux, A tailored organometallic-inorganic hybrid mesostructured material: a route to a well-defined, active, and reusable heterogeneous iridium-NHC catalyst for H/D exchange, Angew. Chem. Int. Ed. 47 (2008) 8654-8656, https://doi.org/10.1002/anie.200802956.

[44] B. Karimi, P. F. Akhavan, A study on applications of *N*-substituted main-chain NHC-palladium polymers as recyclable self-supported catalysts for the Suzuki-Miyaura coupling of aryl chlorides in water, Inorg. Chem. 50 (2011) 6063-6072, https://doi.org/10.1021/ic2000766.

[45] Z. Wang, G. Chen, K. Ding, Self-supported catalysts, Chem. Rev. 109 (2009) 322-359, https://doi.org/10.1021/cr800406u.

[46] K. Ding, Z. Wang, X. Wang, Y. Liang, X. Wang, Self-supported chiral catalysts for heterogeneous enantioselective reactions, Chem. Eur. J. 12 (2006) 5188-5197, https://doi.org/10.1002/chem.200501387.

[47] L. X. Dai, Chiral metal-organic assemblies-a new approach to immobilizing homogeneous asymmetric catalysts, Angew. Chem. Int. Ed. 43 (2004) 5726-5729, https://doi.org/10.1002/anie.200460301.

[48] K. Y. Wan, F. Roelfes, A. J. Lough, F. E. Hahn, R. H. Morris, Iridium and rhodium complexes containing enantiopure primary amine-tethered *N*-heterocyclic carbenes: synthesis, characterization, reactivity, and catalytic asymmetric hydrogenation of ketones, Organometallics 37 (2018) 491-504, https://doi.org/10.1021/acs.organomet.7b00915.

[49] N. Sinha, F. E. Hahn, Metallosupramolecular architectures obtained from poly-*N*-heterocyclic carbene ligands, Acc. Chem. Res. 50 (2017) 2167-2184, https://doi.org/10.1021/acs.accounts.7b00158.

[50] N. Sinha, T. T. Y. Tan, E. Peris, F. E. Hahn, High-fidelity, narcissistic self-sorting in the synthesis of organometallic assemblies from poly-NHC ligands, Angew. Chem. Int. Ed. 56 (2017) 7393-7397, https://doi.org/10.1002/anie.201702637.

[51] Y. Zhang, J. Wang, H. Zhu, T. Tu, *N*-formylation of amines with CO_2 and H_2 by using NHC-iridium coordination assemblies as solid molecular catalysts, Chem. Asian J. 13 (2018) 3018-3021, https://doi.org/10.1002/asia.201800953.

[52] J. Chen, J. Wu, T. Tu, Sustainable and selective monomethylation of anilines by methanol with solid molecular NHC-Ir catalysts, ACS Sustain. Chem. Eng. 5 (2017) 11744-11751, https://doi.org/10.1021/acssuschemeng.7b03246.

[53] Z. Sun, J. Chen, T. Tu, NHC-based coordination polymers as solid molecular catalysts for reductive amination of biomass levulinic acid, Green Chem. 19 (2017) 789-794, https://doi.org/10.1039/C6GC02591A.

[54] Y. Liu, Z. Sun, C. Huang, T. Tu, Efficient hydrogenation of biomass oxoacids to lactones by using NHC-iridium coordination polymers as solid molecular catalysts, Chem. Asian J. 12 (2017) 355-360, https://doi.org/10.1002/asia.201601537.

[55] Z. Sun, Y. Liu, J. Chen, C. Huang, T. Tu, Robust iridium coordination polymers: highly selective, efficient, and recyclable catalysts for oxidative conversion of glycerol to potassium lactate with dihydrogen liberation, ACS Catal. 5 (2015) 6573-6578, https://doi.org/10.1021/acscatal.5b01782.

[56] H. Zhu, Y. Shen, D. Wen, Z. G. Le, T. Tu, Selective synthesis of ortho-substituted diarylsulfones by using NHC-Au catalysts under mild conditions, Org. Lett. 21 (2019) 974-979, https://doi.org/10.1021/acs.orglett.8b03957.

[57] H. Zhu, Y. Shen, Q. Deng, J. Chen. T. Tu, Acenaphthoimidazolylidene gold complex-catalyzed alkylsulfonylation of boronic acids by potassium metabisulfite and alkyl halides: a direct and robust protocol to access sulfones, ACS Catal. 7 (2017) 4655-4659, https://doi.org/10.1021/acscatal.7b00860.

[58] Q. Deng, Y. Zhang, H. Zhu, T. Tu, Acenaphthoimidazolylidene palladacycles: highly efficient catalysts for the amination of *N*-heteroaryl chlorides, Chem. Asian J. 12 (2017) 2364-2368, https://doi.org/10.1002/asia.201700877.

[59] Q. Deng, Y. Shen, H. Zhu, T. Tu, A magnetic nanoparticle-supported *N*-heterocyclic carbene-palladacycle: an efficient and recyclable solid molecular catalyst for Suzuki-Miyaura cross-coupling of 9-chloroacridine, Chem. Commun. 53 (2017) 13063-13066, https://doi.org/10.1039/C7CC06958H.

[60] H. Zhu, Y. Shen, Q. Deng, J. Chen. T. Tu, Pd (NHC)-catalyzed alkylsulfonylation of boronic acids: a general and efficient approach for sulfone synthesis, Chem. Commun. 53 (2017) 12473-12476, https://doi.org/10.1039/C7CC05851A.

[61] W. Fang, Q. Deng, M. Xu, T. Tu, Highly efficient aminocarbonylation of iodoarenes at atmospheric pressure catalyzed by a robust acenaphthoimidazolyidene allylic palladium complex, Org. Lett. 15 (2013) 3678-3681, https://doi.org/10.1021/ol401550h.

[62] W. Fang, H. Zhu, Q. Deng, S. Liu, X. Liu, Y. Shen, T. Tu, Design and development of ligands for palladium-catalyzed carbonylation reactions, Synthesis 46 (2014) 1689-1708, https://doi.org/10.1055/s-0033-1338635.

[63] J. Campos, L. S. Sharninghausen, R. H. Crabtree, D. Balcells, A carbene-rich but carbonyl-poor $[Ir_6(IMe)_8(CO)_2H_{14}]^{2+}$ polyhydride cluster as a deactivation product from catalytic glycerol dehydrogenation, Angew. Chem. Int. Ed. 53 (2014) 12808-12811, https://doi.org/10.1002/anie.201407997.

[64] L. S. Sharninghausen, J. Campos, M. G. Manas, R. H. Crabtree, Efficient selective and atom economic catalytic conversion of glycerol to lactic acid, Nat. Commun. 5 (2014) 5084-5092, https://doi.org/10.1038/ncomms6084.

[65] S. Ibanez, A. Guerrero, M. Poyatos, E. Peris, Fluorescent pyrene-based bis-azole compounds: synthesis and photophysical analysis, Chem. Eur. J. 21 (2015) 10566-10575, https://doi.org/10.1002/chem.201501179.

[66] M. G. Manas, J. Campos, L. S. Sharninghausen, E. Lin, R. H. Crabtree, Selective catalytic oxidation of sugar alcohols to lactic acid, Green Chem. 17 (2015) 594-600, https://doi.org/10.1039/C4GC01694G.

[67] J. Choi, H. Y. Yang, H. J. Kim, S. U. Son, Organometallic hollow spheres bearing bis(*N*-heterocyclic carbene)-palladium species: catalytic application in three-component strecker reactions, Angew. Chem. Int. Ed. 49 (2010) 7718-7722, https://doi.org/10.1002/anie.201003101.

[68] M. Uchiyama, K. Satoh, M. Kamigaito, Diversifying cationic RAFT polymerization with various counteranions: generation of cationic species from organic halides and various metal salts, ACS Macro Lett. 5 (2016) 1157-1161, https://dx.doi.org/10.1021/acsmacrolett.6b00541.

[69] C. Gunanathan, D. Milstein, Bond activation and catalysis by ruthenium pincer complexes, Chem. Rev. (2014) 114 12024-12087, https://doi.org/10.1021/cr5002782.

[70] M. Chaouchi, A. Loupy, S. Marque, A. Petit, Solvent-free microwave-assisted aromatic nucleophilic substitution-synthesis of aromatic ethers, Eur. J. Org. Chem. 2002 (2002) 1278-1283, https://doi.org/10.1002/1099-0690(200204)2002:7<1278::AID-EJOC1278>3.0.CO;2-B.

[71] I. Y. Zhang, X. Xu, Y. Jung, W. A. Goddard III, A fast doubly hybrid density functional method close to chemical accuracy using a local opposite spin ansatz, Proc. Natl. Acad. Sci. U. S. A. 108 (2011) 19896-19900, https://doi.org/10.1073/pnas.1115123108.

[72] C. T. Lee, W. T. Yang, R. G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785-789, https://doi.org/10.1103/PhysRevB.37.785.

[73] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behaviour, Phys. Rev. A 38 (1988) 3098-3100, https://doi.org/10.1103/PhysRevA.38.3098.

[74] S. Hohloch, L. Suntrup, B. Sarkar, Arene-ruthenium(II) and -iridium(III) complexes with "Click"-based pyridyl-triazoles, bis-triazoles, and chelating abnormal carbenes: applications in catalytic transfer hydrogenation of nitrobenzene, Organometallics 32 (2013) 7376-7385, https://doi.org/10.1021/om4009185.

[75] K. Dong, R. Razzaq, Y. Hu, K. Ding, Homogeneous reduction of carbon dioxide with hydrogen, Top Curr. Chem. 375 (2017) 1-26, https://doi.org/10.1007/s41061-016-0088-1.

[76] J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, Selective catalytic synthesis using the combination of carbon dioxide and hydrogen: catalytic chess at the interface of energy and chemistry, Angew. Chem. Int. Ed. 55 (2016) 7296-7343, https://doi.org/10.1002/anie.201507458.

- Highly efficient and recyclable catalysts with atomically dispersed catalytic sites.

- Selective and effective mono-*N*-methylation of nitroarenes via one pot tandem reaction.

- Using methanol as green carbon source and water is the only byproduct.

- Avoiding the usage of toxic reagents.

Graphical Abstracts

>30 examples, up to 99% yield   up to 97% yield

■ Recyclable NHC-Ir Solid Assemblies
■ Atomically Dispersed
■ Highly selective and efficient
■ Catalyst reuse up to 12 runs