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Ir(I)-NHC Hybrid Materials: Surface-Stabilization of Low-Valent Iridium Species for High Catalytic Hydrogenation Performances

Iuliia Romanenko,^[a] David Gajan,^[b] Reine Sayah,^[a] Delphine Crozet,^[a] Erwan Jeanneau,^[c] Christine Lucas,^[a] Lénaïc Leroux,^[b] Laurent Veyre,^[a] Anne Lesage,^[b] Lyndon Emsley,^{[b],[d]} Emmanuel Lacôte,^{[a],*} Chloé Thieuleux^{[a],*}

Abstract: An Ir(I)-NHC based hybrid material was prepared using a synthetic methodology allowing the precise positioning and isolation of the Ir-centers along the pore-channels of a silica framework. The full characterization of the material by solid state NMR spectroscopy showed that the supported Ir-sites were stabilized by the silica surface as low-coordinated single-site complexes. The material was found to be extremely efficient for the hydrogenation of functional alkenes. The catalytic performances (TOF and TON) are one to two orders of magnitude higher than those of their molecular Ir-analogues, which could be related to the prevention of bi-molecular deactivation processes of Ir-complexes observable under homogeneous conditions

Catalytic hydrogenation is one of the most important reactions for both bulk and fine chemical production.^[1] As a consequence, the quest for ever more active and selective catalytic systems is essential. Late transition metal complexes stand out among the numerous options because their coordination sphere can be fine tuned for better efficiency, selectivity and stereoselectivity. That is especially true for iridium, one of the most active metals for catalytic hydrogenations.^[2] However, in solution iridium complexes tend to rapidly form inactive polymeric hydride clusters via bimolecular processes, leading to deactivation.^[3]

One strategy to prevent this deactivation path is to slow down the oligomerization of the iridium hydrides in solution by modifying the coordination sphere of the iridium^[4a] or using weakly coordinating anions (for cationic Ir(I) catalysts).^[4b,c] Another option is to graft or intercalate the Ir(I) sites on a solid support, to physically prevent them from assembling into inactive clusters.^[5] The latter is appealing because heterogeneous catalysts are easier to remove from products. However, the

“heterogeneized” catalysts prepared by grafting or intercalation approaches usually exhibit low to similar activity in comparison with their homogeneous equivalents.^[6a-d] We hypothesized that this decrease of activity was due to a lack of control of the metal distribution on the solid supports, and that hybrid materials containing strongly coordinated and precisely positioned supported Ir(I)-sites would be much more efficient hydrogenation catalysts.

In this respect, we proposed a general strategy for the preparation of late transition metal-based catalytic materials which relies on a two-step approach.^[6] The first step is the preparation of hybrid mesostructured silica matrices containing regularly distributed L-type ligands by a sol-gel process using a templating route.^[7] The L-ligand of the platform material is then *in-situ* converted into the targeted supported organometallic complex by Surface Organometallic Chemistry (SOMC).^[8]

The hybrid silica material is prepared by co-hydrolysis and co-condensation of an organotrialkoxysilane precursor and a tetra-alkoxysilane in the presence of a structure directing agent in order to control the loading and organic groups homogeneity along the silica pore-channels. This control is mandatory to ensure that the catalytically active sites in the final material are well isolated from each other.

Using this methodology, we have investigated the immobilization on silica matrices of reactive Pd^{II},^[6c] Ru^{IV[6d-e]} and Ir^{III[6b]} species as their N-heterocyclic carbene (NHC) complexes. The resulting materials are as active as their molecular equivalents.

Here, we coordinate Ir(I) centers to a silica-supported NHC ligand, because the Ir-NHC bond is strong^[9] and NHCs also offer a good alternative to phosphine ligands classically used in iridium-catalyzed hydrogenation.^[2a] A flexible propyl tether was chosen to allow Ir/silica interactions. Such a metal/support interaction was found to be the key for increasing the lifetime of Ru-NHC active species by stabilizing low-valent species^[6e] and we felt that it might be extended to stripped-down Ir-NHC complexes, leading to even more active catalysts (see **M-Ir** on Scheme 1).

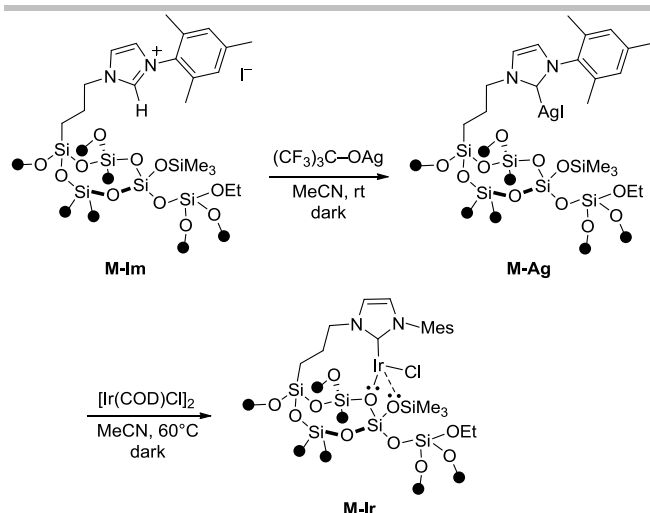
The preparation of the materials relies on the incorporation of iridium onto our previously described NHC-based material **M-Ir** (Scheme 1).^[6b]

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Scheme 1. Scheme for the preparation of the hybrid catalyst **M-Ir**

Passivated platform material **M-Im** (390 m²/g surface area) was first metallated to the silver-carbene containing material **M-Ag** with 1.5 equivalents of AgOC(CF₃)₃ in MeCN at 25 °C in the absence of light. Transmetalation with 7 equiv. of [IrCl(COD)]₂ at 60 °C in MeCN delivered **M-Ir** as a brown powder containing 2.57 wt% Ir (0.13 mmol/g) corresponding to 49% silver to iridium conversion. **M-Ir** was characterized by XRD (Fig. S1), TEM (Fig. S2), and conventional ¹³C, ²⁹Si MAS-NMR (Fig. S3-4) as well as DNP SENS (*vide infra*). We also prepared the ¹³C-labeled material **M*-Ir** from the corresponding **M-Im***, where the carbene carbon was isotopically enriched. Finally, the complex [IrCl(COD)(MesImPr)] **1** was synthesized *via* a known route^[10] and characterized by HRMS, ¹H, ¹³C and ¹H-¹³C HMQC NMR (Fig. S5). The XRD structure of **1** was also elucidated (Fig. S6).^[11] This complex was prepared as a molecular standard for both materials characterization and for sake of comparison in the catalytic study.

The most important feature in **1** is that the iridium complex loses symmetry upon transmetalation because of its square planar structure and the dissymmetry of the NHC ligand. Thus, all carbons of the 1,5-cyclooctadiene ligand (COD) are inequivalent. The methylene ¹³C signals in C₆D₆ appear at 29.4, 29.1, 33.3 and 34.9 ppm, while the sp² carbons are at 50.3, 51.1 (*trans* to Cl) and 83.1 and 83.2 (*trans* to NHC).

²⁹Si CPMAS NMR of **M-Ir** shows the presence of the expected four main peaks: 13 (M), -65 (T₃), -100 (Q₃), -109 ppm (Q₄) (Fig. S3). The first peak corresponds to the SiMe₃ surface groups and shows that passivation was successful, while the presence of a T₃ peak shows that the organosilane residue is completely fused within the silica network leading to a fully condensed tetrahedral Si surface site. In the ¹³C CPMAS NMR spectrum (Fig. S4), the expected signals arising from the propyl tether and the NHC ligand were observed around 9 ppm (Si-CH₂), 18-20 ppm (methyl groups of the mesityl substituent and Si-CH₂-CH₂), 52 ppm (CH₂-N) and 120-140 ppm (aryl and NHC sp² carbons). Interestingly, the ¹³C peaks corresponding to the COD ligand were not detected (*vide infra*).

TEM micrographs and EDX analyses **showed** the presence of silver aggregates arising from production of the silver halide salt during the transmetalation process. **TEM micrographs do not indicate the presence of any Ir nanoparticle, while EDX performed on several zones of the material provided**

similar Ir loadings, suggesting a homogeneous distribution of the Ir throughout all the material (see Figure S7). These observations suggest that iridium is present as a supported coordination complex, not as metal nanoparticles.

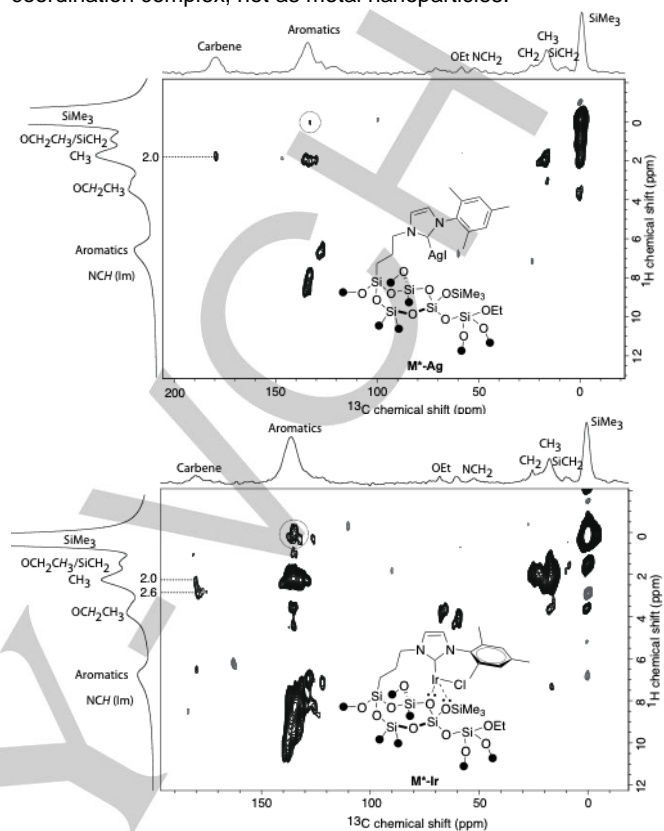


Figure 1. 2D ¹H-¹³C HETCOR NMR spectra of **M*-Ag** and **M*-Ir** recorded on a 800 MHz with a long contact time (2 ms). **The top traces are the corresponding 1D ¹³C CPMAS spectra and the left traces the corresponding 1D ¹H Hahn echo spectra.** (See SI for experimental details).

To shed light on the nature of the iridium species, and their possible interaction with the silica surface, we compared the 2D HETCOR NMR spectra of the labeled materials **M*-Im**, **M*-Ag** and **M*-Ir** at long (Figure 1 and S10) and short (Fig. S11) contact times to discriminate directly bonded ¹H and ¹³C vs. spatially close ¹H and ¹³C atoms. At a long contact time, correlation spots were found between the protons of the surface trimethylsilyl (TMS) groups and the aromatic carbons of the mesityl for all materials, suggesting that the NHC is folded toward the surface. More interestingly, the sole crosspeak assigned to the carbene in the ¹H-¹³C HETCOR of **M*-Ag** (Fig. 1, top) is split after Ir transmetalation (Fig. 1, bottom). This is attributed to the formation of the Ir-NHC along with residual Ag-NHC species. This observation is consistent with a splitting of the NMR signal of the same methyl groups in **1**. Here again, no signal attributed to COD was detected, strongly suggesting its absence in the Ir coordination sphere. Taking into account that the NHC folds toward the surface, one may hypothesize that the Ir sites are stabilized by surface Si-O-Si groups after decoordination of 1,5-cyclooctadiene. In order to discard any possible uncertainty due to the limited sensitivity of conventional MAS NMR, we implemented advanced dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) experiments.^[12] The samples were prepared by impregnation of the materials with a solution of 16 mM TEKPOL in 1,1,2,2-

tetrachloroethane and the spectra were recorded on a 400 MHz/263 GHz gyrotron DNP NMR system. In this setup, EPR transitions of the radical are saturated at 100 K by microwaves which induces transfer of the electron spin polarization to nuclei of interest at the silica surface, resulting in large NMR signal enhancement.

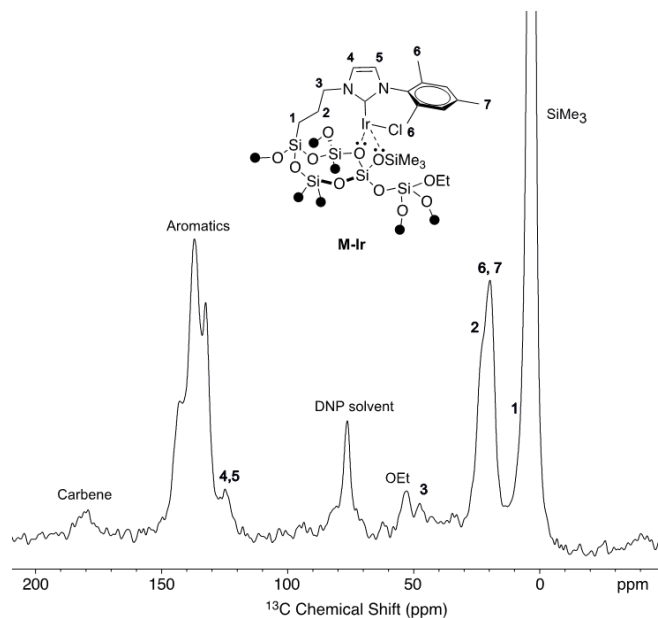


Figure 2. ^{13}C CP MAS solid echo DNP SENS spectrum of **M-Ir** recorded on a 400MHz DNP NMR system with an echo time of 40 rotor periods (see SI for details).

Again, no signal in the COD region was detected in the ^{13}C DNP SENS experiments (Fig. 2 and S12). Similarly, no correlation signal involving a COD was observed in 2D DNP SENS ^1H - ^{13}C HETCOR spectra (Fig S13). However, 2D DNP SENS ^1H - ^{29}Si HETCOR (Fig. S14a) showed a correlation between Q signals at -100 ppm and the NHC backbone and mesityl protons even with short contact times. At longer contact times (Fig. S14b), crosspeaks between the SiMe_3 and the aromatics appeared in addition. As this method assesses the spatial proximity of protons to the silicon centers,^[12b] this further suggests that the spacer folds toward the surface to stabilize a COD-free Ir species.

We finally attempted to prove the absence/presence of COD by a chemical method. We exposed a C_6D_6 suspension containing **M-Ir** and toluene as an internal standard to hydrogen in a pressure-stable NMR tube without an olefinic substrate, and monitored the reaction by solution ^1H NMR. We were able to detect trace amount of cyclooctane, whose quantification against toluene (Figure S15–S16) revealed that only 8 % of Ir sites contain COD.^[13]

To conclude, we have shown that surface-metal interactions stabilize a supported low-coordinated iridium complex, whose structure we tentatively assign in Figure 1. *This has to our knowledge never been observed before in Ir-chemistry.* A similar phenomenon between supported Ru complexes and the surface was already suggested, but not directly observed for the surface metal complex.^[6e]

The catalytic activity of the **M-Ir** material was tested in the hydrogenation of several functional substrates (styrenes with

various substituents, stilbene and limonene (TableS4)). In a typical catalytic experiment, a solution of *trans*-stilbene in toluene was heated at 40°C in a Fisher-Porter reactor under 3 bar of dihydrogen in the presence of 0.1 mol% **M-Ir** (based on iridium loading given by elemental analysis). The reaction was followed by solution NMR to build its conversion vs. time profile (Figure 3). Full conversion was observed after 18 h. The same reaction using **1** under homogeneous conditions failed to reach full conversion after more than 80 days! Cationic iridium species $[\text{Ir}(\text{COD})(\text{MesImPr})\text{BF}_4]$ *in-situ* generated from $[\text{IrCl}(\text{COD})(\text{MesImPr})]$ with AgBF_4 under homogeneous conditions worked faster, but even then the reaction was not over after 60 days. Moreover, a blank test using the parent material **M-Ag** left the substrate unchanged, showing that catalysis was due to the Ir centers in the material.

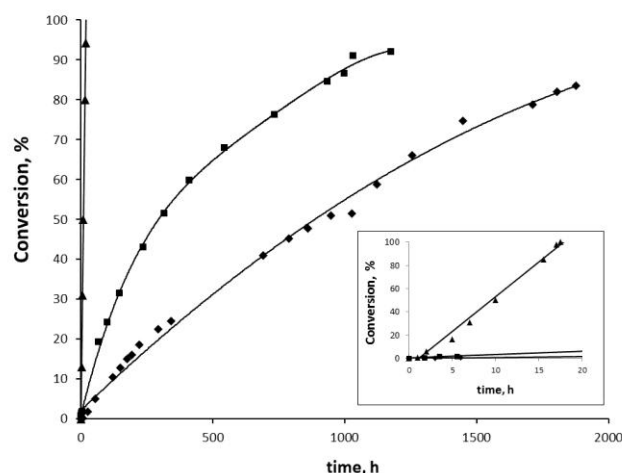


Figure 3. Conversion of *trans*-stilbene hydrogenation as a function of reaction time using: the neutral organometallic complex **1** (◆ diamonds); cationic $[\text{Ir}(\text{COD})(\text{MesImPr})\text{BF}_4]$ (■ squares); **M-Ir** material (▲ triangles). The hydrogenation experiments were carried out in toluene at 40°C under 3 bar of H_2 (0.1 mol% of Ir).

We calculated the initial TOFs (after 5h of reaction) for **M-Ir**, the neutral complex **1** and its cationic form: $\text{TOF} = 38\text{h}^{-1}$ for **M-Ir** vs 1.8h^{-1} for $[\text{Ir}(\text{COD})(\text{MesImPr})\text{BF}_4]$, and 0.75h^{-1} for **1**. The material is thus 50 times faster than **1**, and 20 times faster than $[\text{Ir}(\text{COD})(\text{MesImPr})\text{BF}_4]$, fully validating our hypotheses. Furthermore, the hydrogenation profile of **M-Ir** in Fig. 3 is linear thus suggesting no catalyst deactivation of the catalysts during the catalytic test.

We evaluated the heterogeneous catalyst activity using very high substrate/catalyst ratios (0.01 mol%, Figure 4). While both homogeneous complexes are deactivated and only reach a $\text{TON}_{\text{max}} \leq 1000$ after 700 h (observation of the catalyst deactivation at 89% conversion using 0.1 mol% of **1**), **M-Ir** exhibited a much higher productivity reaching 80% conversion ($\text{TON} = 8000$ using 0.01mol% of **M-Ir**). **After catalysis the solid was analyzed by HRTEM. We did not see any trace of Ir nanoparticles in the recovered catalyst.** Unfortunately, we could not determine the TON_{max} . The trace impurities remaining after purification of the large amounts of solvent and substrate needed for the tests induced side poisoning of the 60mg of catalyst needed for reproducibility at the high substrate/Ir ratios required for TON_{max} determination.

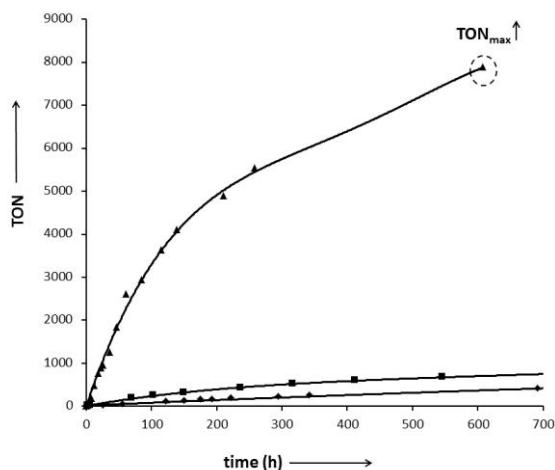


Figure 4. TON of *trans*-stilbene hydrogenation as a function of reaction time using: **1** (◆diamonds); [Ir(COD)(MesImPr)]BF₄ (■ squares); **M-Ir** (▲ triangles). The hydrogenation experiments were carried out in toluene at 40°C under 3 bar of H₂ (0.1 mol% of Ir for **1** and [Ir(COD)(MesImPr)]BF₄; 0.01 mol% of Ir for M-Ir)

Split tests were carried out using **M-Ir** (Fig S19). No conversion was detected, thus showing the absence of any active Ir-species in solution. Finally, no leaching of Ir was detected in the reaction supernatants by ICP measurements. Therefore there is no contribution of any homogeneous pathway. The catalytic hydrogenation takes place on Iridium surface sites of the material.

The behavior of the other substrates (styrene, 4-fluorostyrene, 4-vinylanisole, 4-acetoxystyrene and limonene) is shown in the supporting information. In all cases, the material is better than **1** (Figure S18 and part 7). For limonene, the less hindered bond is fully hydrogenated before the more substituted one started reacting.

In summary, we have prepared a well-defined single-site Ir(I)-NHC based heterogeneous catalyst in which the iridium atoms are homogeneously positioned by design. Using advanced solid state NMR techniques, and a chemical method we showed that the Ir centers are stabilized by the surface as low-coordinated complexes. This catalytic material is one to two orders of magnitude more active and faster than its molecular analogue in the hydrogenation of *trans*-stilbene, and also faster than the corresponding cationic species. This enhanced activity was also observed for other functional olefins. It derives from the isolation of the supported Ir-NHC species, which prevents the bimolecular deactivation processes (hydride cluster formation) usually encountered for Ir complexes in solution. Interactions between the silica surface and the Ir sites, which stabilize a low-valent Ir(I) species were evidenced for the first time in Ir catalysis. They likely also account for the higher catalytic performances of **M-Ir**.^[13]

The strategy whereby more active catalysts are obtained by preventing deactivation of bimolecular processes and using the support to stabilize more reactive species is of interest for many other catalytic systems. Further work will focus on extending this approach towards the preparation of highly selective heterogeneous Ir asymmetric catalysts.

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Keywords: Hydrogenation • Heterogeneous catalysis • Mesoporous materials • Iridium • Carbene ligands

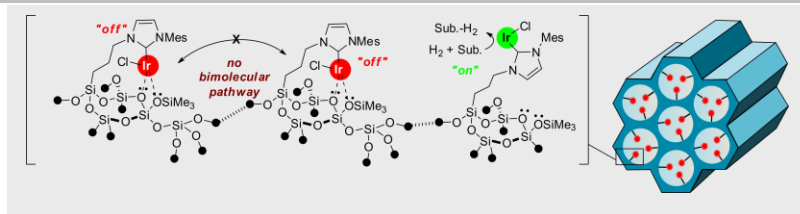
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Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION



Homogeneous positioning of Ir(I) complexes in the pore-channels of a silica framework stabilizes a low-valent Ir(I) species and lead to drastic improved catalyst efficiency. Catalyst decomposition by formation of iridium-hydride clusters is prevented by the attachment on the support.

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Ir(I)-NHC Hybrid Materials: Surface-Stabilization of Low-Valent Iridium Species for High Catalytic Hydrogenation Performances