Catalytic Hybrid Materials

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# A Tailored Organometallic–Inorganic Hybrid Mesostructured Material: A Route to a Well-Defined, Active, and Reusable Heterogeneous Iridium-NHC Catalyst for H/D Exchange**

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Tailored functional materials with specific physical or chemical properties have become an important research area due to their wide range of applications in fields such as electronics, optics, or catalysis. The most commonly used methodology for their preparation consists of grafting organosilane precursors onto oxide surfaces.[1] However, although this method provides a convenient way of introducing all kinds of organic moieties into solids, it does not permit control of either their distribution in the final material or the nature of the surface species (formation of mono-, di-, and tripodal species; Figure 1 a). This lack of control during the grafting step is a major problem in the synthesis of homogeneous functionalized materials and could explain the poorer activity of supported homogeneous catalysts prepared by this method with respect to their homogeneous homologues.

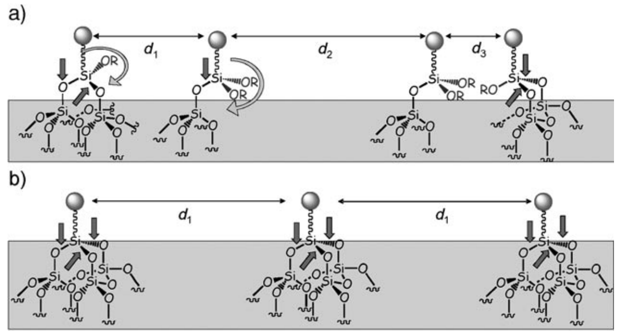

***Figure 1.*** a) Classical supported homogeneous catalysts. b) Mesostructured hybrid materials.

Recent advances in materials chemistry have provided new methodologies and synthetic pathways for the generation of highly mesostructured functionalized materials containing regularly distributed organic moieties along their channel pores. These materials are obtained by cocondensation of tetraethylorthosilicate (TEOS) and an organotriethoxysilane ($RSi(OEt)_3$) in a hydrolytic sol–gel process in the presence of a structure-directing agent (i.e. a surfactant).[2,3] The interactions between the surfactant and the organosilane precursors ensure the structuration of the pore arrays and the regular distribution of the organic fragments in the final materials (Figure 1 b).[4] Moreover, the functional groups are attached via a silicon atom fused into the silica matrix ($T^3$ substructures in the $^{29}$Si solid-state NMR spectra; Figure 1 a).

While these tailored mesostructured materials have found many applications[5] in fields such as separation, optics, encapsulation ion binding, and chemical sensing, only a few examples have been used as catalysts.[6] This is probably due to the fact that one of the main challenges in this chemistry is anchoring highly sensitive organometallic complexes in materials, which requires a high level of understanding, control, and characterization of all the steps, from the tailored mesostructured material synthesis to the selective coordination of complexes onto the desired organic functionalities of the material.

Herein we have chosen to focus on generating a tailored mesostructured material containing N-heterocyclic carbene ligands (NHC) along their channel pores as this type of ligand has already led to major breakthroughs in homogeneous catalysis in fields such as alkene metathesis, C–C coupling, and telomerization.[7] These ligands have also been used to stabilize reactive complexes, for instance in the area of C–H bond activation[8] for incorporation of deuterium into organic molecules,[9] with the ultimate goal being the functionalization of alkanes. However, all these homogeneous systems typically still suffer from deactivation as well as problems related to catalyst recovery and metal separation from the organic substrates. We describe 1) methodologies for the generation of imidazolium-containing mesostructured materials (**M′-Im**) and the corresponding Ir-NHC containing materials **M′-Ir** (Scheme 1), 2) the characterization of these systems at a molecular level, and 3) the use of these catalysts for H/D

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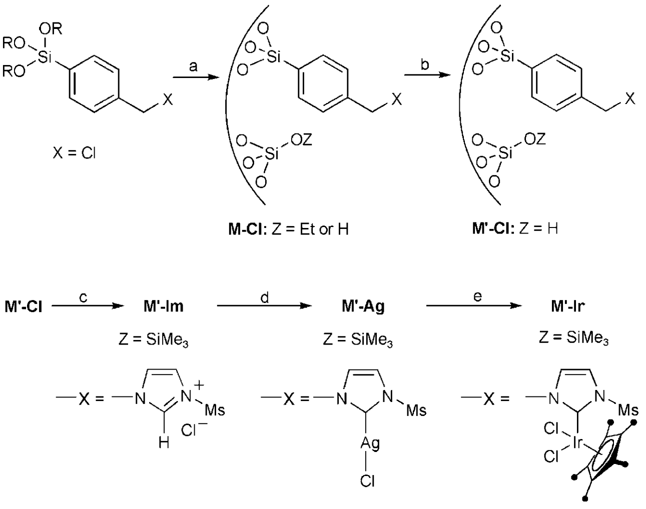

*Scheme 1.* Preparation of **M′-Im** and **M′-Ir**: a) TEOS, HCl, Pluronic P123, room temperature; b) 2 M $HCl/H_2O$, 45 °C; c) mesitylimidazole, toluene, reflux, 2 days, then TMSBr, $Et_3N$, toluene, room temperature, 48 h; d) $AgOC(CF_3)_3$, $CH_3CN$, 14 h, room temperature; e) $[\{Cp^*IrCl_2\}_2]$, 24 h, 60 °C.

exchange reactions between [D$_4$]methanol and acetophenone, where they display activities similar to their homogeneous homologues combined with the widely recognized advantages of heterogeneous catalysts (recycling and separation of products).

The nanostructured hybrid material **M-Cl**, which contains benzyl chloride functionalities, was prepared first. The rigid benzyl tether was chosen to prevent the active site from interacting with the silica surface. **M-Cl** was obtained by cohydrolysis and co-polycondensation of *p*-(chloromethyl)-phenyltrimethoxysilane (1 equiv) and 30 equivalents of tetraethoxysilane in the presence of Pluronic P123 as the structure-directing agent under acidic conditions.[3] Elemental analysis of **M-Cl** was consistent with the presence of 0.5 mmol g$^{-1}$ of functionalities (1.8% Cl, 36.9% Si). The integrity of the functional groups was confirmed by $^{13}$C solid-state NMR spectroscopy (Figure S1 in the Supporting Information). Moreover, the $^{29}$Si NMR spectrum of **M-Cl** (Figure S2 in the Supporting Information) showed the high degree of condensation of the material (two main signals at $\delta = -101$ and $-111$ ppm associated with $Q^3$ and $Q^4$ substructures, respectively) and that the organic units are bonded to the matrix mainly via three Si–O bonds (main signal at $\delta = -79$ ppm associated with a $T^3$ substructure). The material also exhibits an $N_2$ adsorption-desorption isotherm at 77 K of type IV, which is characteristic of mesoporous materials, with a large BET specific surface area of 1146 m$^2$ g$^{-1}$, a pore volume ($V_p$) of around 1.4 cm$^3$ g$^{-1}$, and a mean pore diameter ($D_{pBJH}$) of 5.7 nm (Figure S3 in the Supporting Information). The TEM and powder XRD measurements are consistent with a material having a long-range structuration of the pore network with a 2D hexagonal array (Figures S4 and S5 in the Supporting Information). This material was subsequently treated with mesitylimidazole to generate the corresponding imidazolium functionalities and then with $Me_3SiBr/NEt_3$ to transform the surface silanol groups into trimethylsiloxane moieties (Si-O-Z with $Z = SiMe_3$). This process yielded **M′-Im**, which was fully characterized by X-ray diffraction, elemental analysis, $N_2$ adsorption/desorption, and $^1$H, $^{13}$C, and $^{29}$Si solid-state NMR spectroscopy (Figures S6–S9 in the Supporting Information). All these data are consistent with the quantitative formation of imidazolium functionalities with no degradation of the material.

**M′-Im** was then converted into **M′-Ir**. Thus, treatment of **M′-Im** with 1.5 equivalents of $AgOC(CF_3)_3$[10] at 25 °C for 14 h in the absence of light gave **M′-Ag**, which, upon transmetalation with $[\{Cp^*IrCl_2\}_2]$ (1 equiv) at 60 °C for 24 h, yielded **M′-Ir** as a pale-orange solid containing 6.83 wt.% of Ir (0.35 mmol g$^{-1}$, 1Ir/2N). The $^{13}$C CP-MAS NMR spectrum of **M′-Ir** displays signals corresponding to the benzyl and mesityl groups as well as new signals at $\delta = 7.6$ and 87.8 ppm corresponding to the $CH_3$ and the $C_{sp^2}$ carbon atoms of the Cp* moiety, respectively (Figure S10 in the Supporting Information). The disappearance of the signal at $\delta = 139$ ppm (attributed to C2 of the imidazolium ring) and the Ir/N ratio of 2 are consistent with the quantitative conversion of imidazolium functionalities into Ir-NHC units (greater than 99%). This chemical transformation was further confirmed by preparation of the corresponding $^{13}$C-labeled materials at position 2 (**M′-Im***, **M′-Ag***, and **M′-Ir***, Figures S11–S13 in the Supporting Information) and the homologous molecular complex **C-Ir** (Figure 2). For instance, the strong signal at $\delta = 139$ ppm arising from the labeled imidazolium carbon atom is replaced by an intense signal at $\delta = 181$ ppm upon treatment of $AgOC(CF_3)_3$ with **M′-Im***, which is fully consistent with the quantitative formation of **M′-Ag***. Subsequent treatment of **M′-Ag*** with $[\{Cp^*IrCl_2\}_2]$ yields **M′-Ir***, as evidenced by the replacement of the signal at $\delta = 181$ ppm with one at $\delta = 176$ ppm. These assignments were further confirmed by comparing these data with those obtained for the corresponding homogeneous complex **C-Ir**, which was fully characterized by $^1$H and $^{13}$C NMR spectroscopy, HRMS, and single-crystal X-ray diffraction.[11]

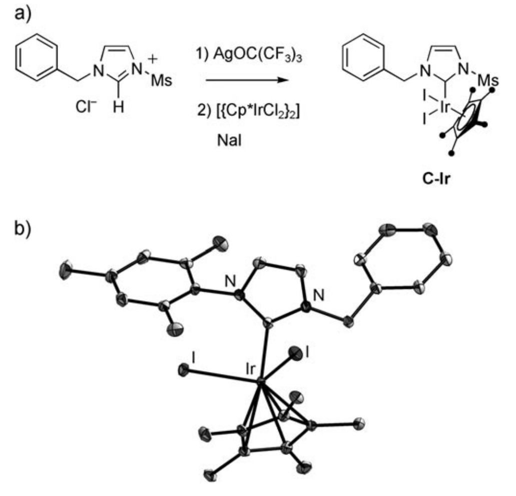

*Figure 2.* a) Preparation of the molecular complex **C-Ir** and b) its X-ray structure.

Finally, we investigated and compared the catalytic efficiency of **M′-Im**, **M′-Ir**, and **C-Ir** in the deuteration of acetophenone with [D$_4$]methanol (2 mol% catalyst and 4 mol% AgOTf at 100 °C).[8b] **C-Ir** and **M′-Ir** were found to display comparable activities under the same reaction conditions, with deuteration occurring selectively at the methyl substituent of acetophenone to yield PhCOCD$_3$ (Table 1, entries 1 and 3). In contrast, the parent material **M′-Im**, which does not contain an IrCp*Cl$_2$ moiety, shows no activity (Table 1, entry 2). We also performed recycling tests and found, for instance, that **M′-Ir** can be reused three times without significant loss of activity (Table 1, entries 3–5).

***Table 1:*** H/D exchange reaction with **C-Ir** and **M′-Ir** as catalyst to yield PhCOCD$_3$.

| Entry | Catalyst | Substrate/Cat. | Conversion [%] | *t* [min] |
|---|---|---|---|---|
| 1 | **C-Ir** | 50 | 98.5 | 5 |
| 2 | **M′-Im** | 50 | < 0.1 | 15 |
| 3 | **M′-Ir** | 50 | 93.8 | 15 |
| 4[a] | **M′-Ir** | 50 | 94.0 | 15 |
| 5[b] | **M′-Ir** | 50 | 92.0 | 15 |

[a] Second cycle. [b] Third cycle.

In summary, we have prepared a well-defined single-site Ir-based heterogeneous catalyst from tailored hybrid organic–inorganic materials and characterized it at a molecular level. The control, understanding, and characterization of all the reaction steps—passivation of the oxide surface, the generation of Ag-NHC units in situ by addition of a soluble silver source, and transmetalation of the Ag-NHC units into Ir-NHC complexes—each of which is quantitative according to NMR spectroscopy, provided the final heterogeneous catalyst. This strategy thus bridges the gap between homogeneous and heterogeneous catalysis by providing single-site heterogeneous catalysts based on Ir-NHC units perfectly distributed within the pores of the material. Considering the importance of organic ligands, and more specifically NHCs, in catalysis, this methodology opens up new routes for the design of novel heterogeneous catalysts where all the sites are equivalent and regularly distributed within a material.

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[11] CCDC 669229 (**C-Ir**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.