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# Silica hybrid material containing Pd–NHC complex as heterogeneous catalyst for Mizoroki–Heck reactions

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**Abstract**—A silica hybrid material containing palladium-*N*-heterocyclic carbene complexes was prepared by the sol–gel transformation of a molecular triethoxysilylated Pd–NHC complex. The material showed high activity as heterogeneous catalyst in Mizoroki–Heck reaction of aryl bromides and -iodides with styrene and methyl acrylate and could be re-used in at least five reaction cycles with unchanged catalytic properties.

*N*-Heterocyclic carbenes (NHC) attracted considerable interest in the last few years. Firstly described by Wanzlick and Öfele in the late 1960s,[1] NHCs were recognized to be versatile transition metal ligands since Arduengo et al. reported the first stable and crystalline NHC in 1991.[2] Due to their strong σ-donating and low π-accepting abilities,[3] NHCs can efficiently replace phosphine ligands in transition metal complexes, and especially Pd–NHC complexes appeared as versatile catalysts for a multitude of cross coupling reactions.[4] Furthermore, the stability of Pd–carbenes has been exploited for catalyst immobilization on organic polymer[5] and inorganic[6] support, and also for their immobilization in ionic liquid phases.[7]

In continuation on our work concerning silica supported transition metal catalysts,[8] we focused on heterogeneous metallic NHC complexes. We recently reported nanostructured silica bearing imidazolium substructures.[9] These ionic species are versatile precursors for the generation of NHC complexes.[10] Here, we report the first silica hybrid supported Pd–NHC complex.

We synthesized the bis-silylated imidazolium precursor **1**, which was prepared by coupling 3-iodopropyl-triethoxysilane with *N*-(3-triethoxysilylpropyl)-1*H*-imidazole (Scheme 1).[11] The tetrasilylated Pd–NHC complex **2** was subsequently synthesized by reacting precursor **1** and palladium(II) acetate in THF (Scheme 2). This compound was isolated as an orange solid and characterized by NMR and mass spectroscopy.[12]

Compound **2** was directly used for the synthesis of organic–inorganic hybrid silica by the sol–gel process. However, it appeared necessary to adapt the hydrolysis polycondensation conditions to the chemical stability of

**1**

**Scheme 1.** Synthesis of the bis-silylated imidazolium precursor **1**.

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*Keywords*: Silica hybrid materials; NHC-catalyst; Heck-reaction.

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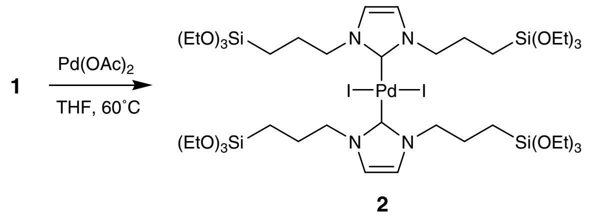
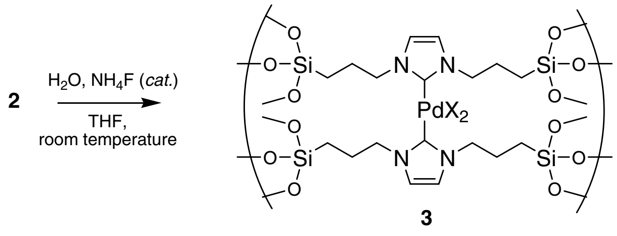


**Scheme 2.** Synthesis of the silylated Pd–NHC complex **2**.

the carbene complex, which rapidly decomposed in basic reaction media, leading to the formation of palladium black. Fortunately, the hydrolysis polycondensation in tetrahydrofurane medium under nucleophilic catalysis of fluoride ions[13] led to the formation of the desired amorphous silica hybrid material **3** as an orange powder (Scheme 3).[14]

The hybrid silica **3** was characterized by solid state NMR, nitrogen adsorption desorption experiments and elemental analysis. The $^{13}$C CP-MAS NMR spectrum of **3** shows the signals of the saturated Pd–NHC complex. Chemical shifts of the propyl chains and the imidazolium rings were similar to those obtained for precursor **2** in a $^{13}$C NMR experiment in solution, indicating a successful incorporation of the Pd–NHC complex in the hybrid silica network (Fig. 1). However, sharp signals at 18 and 58 ppm reveal non-hydrolyzed ethoxy groups, and a small signal at 136 ppm indicates the presence of free imidazolium rings, probably formed by partial C–Pd bond cleavage during the hydrolysis-polycondensation.

The $^{29}$Si CP-MAS spectra (Fig. 2) shows signals at −60 ppm and −66 ppm characteristic for $T^2$ and $T^3$ sites of $RSiO_3$ units with different condensation degrees. The absence of signals in the region around −100 ppm confirms that no Si–C bond cleavage took place during the hydrolysis polycondensation procedure. Elemental analysis gave a Pd/Si ratio of 1/5, indicating that a small part of the palladium leached out during the hydrolysis-polycondensation. This result also confirms the limited stability of the Pd–NHC complex under the hydrolysis polycondensation conditions. In nitrogen adsorption–desorption experiments, hybrid material **3** showed low porosity with a specific surface area of approx. 5 $m^2\,g^{-1}$.



**Scheme 3.** Sol–gel transformation of precursor **2** leading to the silica hybrid material **3**.

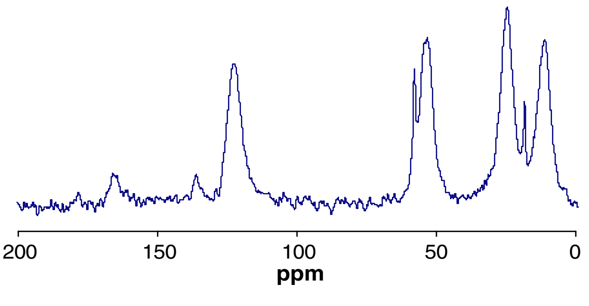


**Figure 1.** $^{13}$C CP-MAS NMR spectrum of material **3**.

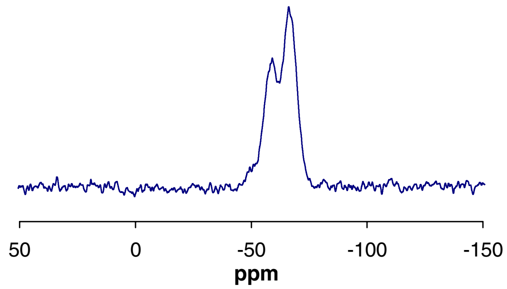
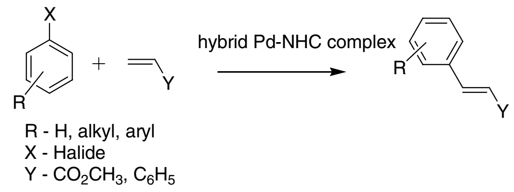


**Figure 2.** $^{29}$Si CP-MAS NMR spectrum of material **3**.

We used this material as a heterogeneous catalyst for Mizoroki–Heck coupling reactions (Scheme 4). Initial trials were performed to optimize reaction conditions for the coupling reaction of iodobenzene and methyl acrylate. After screening a range of usual inorganic and organic bases and exploring the scope of various solvents, we found that the hybrid NHC catalyst is efficient for Mizoroki–Heck reaction in refluxing DMF in the presence of triethylamine. Using these optimized reaction conditions, the efficiency of the hybrid catalyst was studied for the coupling reaction of various aryl halides and alkenes. The results are summarized in Table 1.

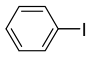
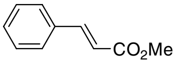
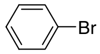
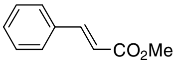
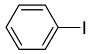
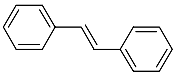
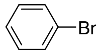
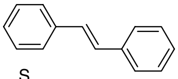
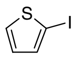
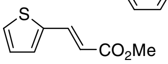
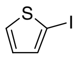
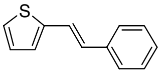
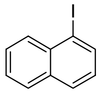
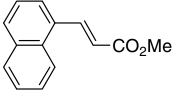
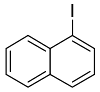
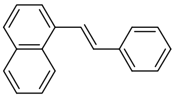
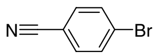
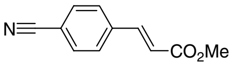
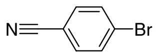
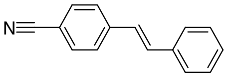
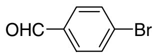
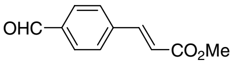
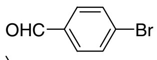
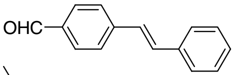
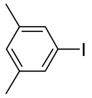
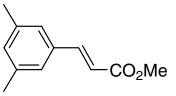
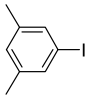
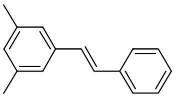
Despite the low porosity of the material, we observed high catalytic activity in Heck reactions. Aromatic iodo and activated bromo compounds were efficiently coupled with methylacrylate and styrene to give the corresponding 1,2 substituted alkenes in good to excellent yields. The reactions with 2-iodothiophene were successfully achieved (entries 5 and 6), which provide a useful way for introduction of unsaturated group on the thiophene ring. However, reactivity toward chloroarenes, which was observed by others,[15] was not achieved with our catalyst system.

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are important factors. To clarify this issue, we performed a set of experiments using the recycled catalyst. We found that the catalyst showed excellent recyclability in the Heck coupling reaction of iodobenzene with



**Scheme 4.** Heck coupling reaction using Pd–NHC containing hybrid silica catalyst **3**.

**Table 1.** Heck reaction of aryl halides and alkenes using catalytic hybrid material **3**[a]

| Entry | Aryl halide | Product | Yield[b] (%) |
|---|---|---|---|
| 1 |  |  | 95 |
| 2 |  |  | 82 |
| 3 |  |  | 77 |
| 4 |  |  | 70 |
| 5 |  |  | 94 |
| 6 |  |  | 69 |
| 7 |  |  | 94 |
| 8 |  |  | 86 |
| 9 |  |  | 83 |
| 10 |  |  | 65 |
| 11 |  |  | 77 |
| 12 |  |  | 59 |
| 13 |  |  | 93 |
| 14 |  |  | 86 |

[a] Reaction was carried out using 1 mmol of aryl halide, 1.5 mmol of alkene, 2 mmol of triethylamine and 16 mg (0.013 mmol Pd) catalyst in refluxing DMF (5 ml).

[b] Yield was determined by GC with dodecane as internal standard with respect to aryl halide, and was confirmed by $^1$H NMR spectroscopy.

methyl acrylate (Table 2). All runs were carried out under similar conditions in refluxing DMF. After the first reaction giving methyl cinnamate in 95% yield, the catalyst was recovered by filtration, washed with dichloromethane and acetone and finally dried at 100 °C for 1 h. A new reaction was then performed with fresh solvent and reactants under similar conditions. The silica hybrid catalyst showed unchanged catalytic activity in at least five reaction cycles. No catalyst deterioration was observed, confirming the high stability of the heterogeneous Pd–NHC catalyst under the reaction conditions.

**Table 2.** Recyclability of catalytic hybrid material **3** in the Heck coupling reaction of iodobenzene with methyl acrylate

| Run | Reaction condition (°C/h) | Conversion (%) |
|---|---|---|
| 1 | 130/12 | 95 |
| 2 | 130/12 | 94 |
| 3 | 130/14 | 96 |
| 4 | 130/14 | 94 |
| 5 | 130/15 | 93 |

Pd leaching of this catalyst was also examined in the Heck reaction of iodobenzene and methyl acrylate by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). This study revealed that the supernatant part of the Heck reaction of iodobenzene and methyl acrylate contained 22 ppm of palladium. This value, higher than those we already observed for other heterogenous catalysts for Mizoroki–Heck reactions,[16] may be due to the relatively high reaction temperatures. However, this leaching did not affect the catalytic activity of the recovered solid.

In conclusion, we report the first silica hybrid material incorporating Pd–NHC species. This material appears as an efficient heterogeneous catalyst in Mizoroki–Heck coupling reactions of aryl halides with styrene and methyl acrylate. However, the reaction only occurs at high temperatures and therefore requires a high boiling solvent such as DMF. We are currently investigating supported Pd–NHC catalysts which allow to perform coupling reactions under milder reaction conditions which may allow to reduce metal leaching.

## Acknowledgment

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## Supplementary data

Full characterization of the organic precursor molecule and the nanostructured heterogeneous catalyst. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.029.

## References and notes

1. (a) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, 42–43; (b) Wanzlick, H. W.; Schönherr, H. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141–142.
2. Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
3. Süßner, M.; Plenio, H. *Chem. Commun.* **2005**, 5417–5420.
4. Kantchev, E. A. B.; O’Brian, C. J.; Organ, M. G. *Aldrichim. Acta* **2006**, *39*, 97–111, and references therein.
5. (a) Buyn, J. W.; Lee, Y. S. *Tetrahedron Lett.* **2004**, *45*, 1837–1840; (b) Steel, P. G.; Teasdale, C. W. T. *Tetrahedron Lett.* **2004**, *45*, 8977–8980; (c) Schönfelder, D.; Nuyken, O.; Weberskirch, R. *J. Organomet. Chem.* **2005**, *690*, 4648–4655; (d) Kim, J. H.; Kim, J. W.; Shokouhimehr, M.; Lee, Y. S. *J. Org. Chem.* **2005**, *70*, 6714–6720.
6. (a) Aksin, Ö.; Türkmen, H.; Artok, L.; Çetinkaya, B.; Ni, C.; Büyükgüngör, O.; Özkal, E. *J. Organomet. Chem.*

**2006**, *691*, 3027–3036; (b) Karimi, B.; Enders, D. *Org. Lett.* **2006**, *8*, 1237–1240.

7. (a) Albrecht, M.; Stoeckli-Evans, H. *Chem. Commun.* **2005**, 4705–4707; (b) Wang, R.; Twamley, B.; Shreeve, J. M. *J. Org. Chem.* **2006**, *71*, 426–429.
8. (a) Hesemann, P.; Moreau, J. J. E. *Tetrahedron: Asymmetry* **2000**, *11*, 2183–2194; (b) Ciriminna, R.; Hesemann, P.; Moreau, J. J. E.; Carraro, M.; Campestrini, S.; Pagliaro, M. *Chem. Eur. J.* **2006**, *12*, 5220–5224.
9. (a) Gadenne, B.; Hesemann, P.; Moreau, J. J. E. *Chem. Commun.* **2004**, 1768–1769; (b) Gadenne, B.; Hesemann, P.; Polshettiwar, V.; Moreau, J. J. E. *Eur. J. Inorg. Chem.* **2006**, 3697–3702.
10. (a) Xu, L.; Chen, W.; Xiao, J. *Organometallics* **2000**, *19*, 1123–1127; (b) Xiao, J. C.; Twamley, B.; Shreeve, J. M. *Org. Lett.* **2004**, *6*, 3845–3847.
11. The synthesis of a similar bis-trimethoxysilyl-imidazolium precursor was already reported: Cazin, C. S. J.; Veith, M.; Braunstein, P.; Bedford, R. B. *Synthesis* **2005**, 622–626; Synthesis of a bis-silylated dihydroimidazolium precursor: Lee, B.; Im, H. J.; Luo, H.; Hagaman, E. W.; Dai, S. *Langmuir* **2005**, *21*, 5372–5376, *N*-3-Propylimidazole triethoxysilane (**1**) 2.72 g (0.01 mol) and 3-iodopropyl triethoxysilane 4.3 g (0.013 mol) were dissolved in 10 ml of acetonitrile in a Schlenk tube. The reaction mixture was stirred under inert atmosphere at 80 °C for 24 h. After completion, the solvent was evaporated and the product was washed with ether to remove excess of 3-iodopropyl triethoxysilane, yielding 5.8 g (96%) of the pure product. FT-IR (KBr): 3070, 2972, 2922, 2885, 1562, 1445, 1294, 1163, 1076, 956, 783, 639 $\mathrm{cm}^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 0.48 (4H, t, $J = 8$ Hz), 1.07 (t, 18H, $J = 7.2$ Hz), 1.89 (4H, m), 3.67 (12H, q, $J = 7.2$ Hz), 4.24 (4H, t, $J = 7.2$ Hz), 7.33 (2H, s), 9.85 (1H, s) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ 7.1, 18.3, 24.4, 51.8, 58.6, 122.3, 135 ppm; MS (FAB$^+$): (M$^+$) 477; HRMS (FAB$^+$): Calcd for $C_{21}H_{45}N_2O_6Si_2$ (M$^+$) 477.2816; found, 477.2824.
12. To a solution of 0.67 g of $Pd(OAc)_2$ (0.003 mol) in 100 ml dry THF, 3.9 g of 1,3-*N*,*N*-bis(3-(triethoxysilyl)propyl)-imidazolium iodide (**2**) (0.006 mol) was added and the reaction mixture was stirred at room temperature for 1 h and then refluxed for 6 h. The formation of Pd–carbene complex can be checked by in situ NMR. After completion, THF was evaporated to yield the crude oily product which solidified after tituration with pentane, yielding 3.5 g of orange coloured Pd–carbene complex **3** (88%). FT-IR (KBr): 3121, 2974, 2929, 2885, 1458, 1079, 949, 794, 713 $\mathrm{cm}^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 0.6 (8H, m), 1.16 (t, 36H, $J = 7.2$ Hz), 2.1 (8H, m), 3.77 (24H, q, $J = 7.2$ Hz), 4.3 (8H, m), 7.87 (4H, s) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ 7.62, 18.32, 23.5, 53.3, 58.46, 121, 167, ppm; MS (FAB$^+$) (%): 1314 (M$^+$, 3); 1266 (M$-$EtO$^-$, 7); 1184 (M$-$I$^-$, 46); 477 (100).
13. Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217–1224.
14. The catalytic organic silica was synthesized by slightly modified classical conditions. The Pd–carbene complex (**3**) (3.5 g, 2.7 mmol) was dissolved in 5 ml of THF and 0.6 ml of water was added. To this solution, 0.6 ml of 1 N $NH_4F$ was added with stirring at room temperature. Gelification occurred within 10 min. The gel was allowed to stand for 2 days. After this time, the solid was washed with ethanol and acetone and dried under vacuum at 90 °C for 6 h to yield 2.6 g of orange coloured silica (**4**). FT-IR (KBr): 3120, 2930, 2863, 1126, 1001, 876, 691 $\mathrm{cm}^{-1}$; $^{29}$Si CP-MAS: $\delta$ $-59$ (T$^2$), $-66$ (T$^3$) ppm, $^{13}$C CP-MAS: $\delta$ 11, 18, 24 53, 57, 128, 166 ppm; BET: Surface area 5 $\mathrm{m}^2$/g; elemental analysis/% C, 22,40; H, 3.79; N, 4.67; I, 22.08; Pd, 8.62; Si, 11.87.
15. (a) Molnar, A.; Papp, A. *Synlett* **2006**, 3130–3134; (b) Pröckl, S. S.; Kleist, W.; Köhler, K. *Tetrahedron* **2005**, *61*, 9855–9859.
16. Polshettiwar, V.; Hesemann, P.; Moreau, J. J. E. *Tetrahedron* **2007**, *63*, 6784–6790.