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DOI: 10.1039/C8CC02833H

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COMMUNICATION

Ruthenium nanoparticles ligated by cholesterol-derived NHCs and their application in the hydrogenation of arenes †

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Herein we present ruthenium nanoparticles (Ru-NPs) stabilized with two rigid NHC ligands derived from cholesterol. The obtained nanoparticles were fully characterized and applied in the hydrogenation of various aromatic compounds under mild conditions. Interestingly, the more bulky ligand gives a slightly lower ligand coverage and a faster catalyst.

N-Heterocyclic carbenes (NHCs) are well established stabilizers in transition metal catalysis exhibiting attractive characteristics such as their electron-donating nature, strong bond to metals and broad structural variation.[1] The benefits of these ligands are also of high interest for the stabilization and functionalization of metal nanoparticles (MNPs).[2] Indeed, as for molecular complexes, it has been shown that the characteristics of the MNPs can be tuned by the NHCs. In this regard, structural variability of the ligands can range from simple NHCs such as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) or (N,N'-di(tert-butyl)imidazol-2-ylidene) (ItBu),[3] to the introduction of long alkyl chains,[4] additional binding motives,[5] hydrophilic groups[6] or chiral motives.[7] In addition to other potentially interesting parameters, the integration of a natural product into a ligand is attractive due to the diversity of the compounds, the readily accessible functional complexity and the possibility to act as a recognition unit. Very recently, we synthesized two imidazolium salts derived from cholesterol (**1**·HOMs and **2**·HI) (Figure 1) and examined them in biophysical and cellular studies, identifying compound **2**·HI as a functional analogue of natural cholesterol in a cellular environment.[8] Unlike imidazolium salts bearing long alkyl chains these molecules contain a rigid, lipophilic moiety either as the N-substituent or in the backbone of the imidazolium core. For this study, we wanted to generate the NHCs of the steroidal-based imidazolium salts for the first time and test if they could act as stabilizing ligands for NPs and if the rigid moiety influences the properties of the obtained NPs.

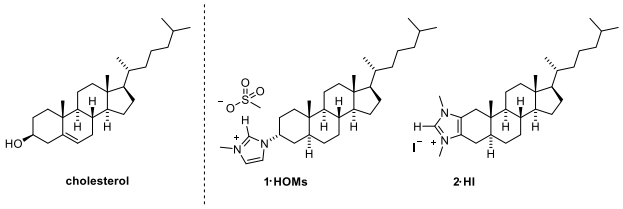
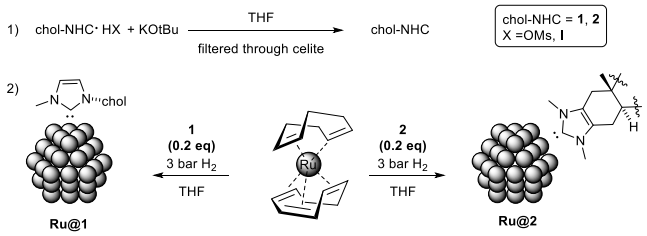


Figure 1: Cholesterol (left) and cholesterol-based imidazolium salts **1**·HOMs and **2**·HI (right).

The hydrogenation of aromatic substrates is of great interest from a synthetic organic and an industrial point of view[9] since the generated cyclohexanes and cyclohexenes can serve as precursors for further functionalization[10] or as motifs in functional materials like pharmaceuticals.[11] The high stability of arenes due to their aromaticity makes their reduction difficult and catalysts in forcing conditions are usually required.[12] As ruthenium nanoparticles (Ru-NPs) proved to be efficient materials to probe NP surface properties[13] and feature interesting catalytic activities[14] including the hydrogenation of arenes[3c] we investigated the rigid ligands **1** and **2** in the synthesis of Ru-NPs. The characteristics and catalytic performances of the obtained NPs (Ru@**1** and Ru@**2,** respectively) were examined to establish the influence of the ligand.



Scheme 1: Synthesis of Ru@**1** and Ru@**2**.

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†Electronic supplementary information (ESI) available. See DOI: DOI: 10.1039/x0xx00000x
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According to a previous procedure for the synthesis of Ru-NPs with non-isolable NHCs,[15] the preparation of the NPs was achieved by controlled decomposition of Ru(cyclooctadiene) (cyclooctatriene) [Ru(COD)(COT)] at 3 bar of H_2 [room temperature (r.t.) in THF] in the presence of 0.2 equivalent (equiv.) of each NHC (Scheme 1). In situ deprotonation of the imidazolium salts studied by NMR demonstrated the possibility to generate the free NHCs **1** and **2** by the above mentioned conditions (ESI, Figure S14 and S15).

Both samples, Ru@**1** and Ru@**2**, contain spherical and well-distributed NPs with a mean diameter of ca. 1.5 (0.3) nm and ca. 1.4 (0.3) nm, respectively. High-resolution TEM (HRTEM) analysis revealed for both systems crystalline NPs with a hexagonal close-packed (hcp) structure, as for bulk Ru (ESI, Figures S1 and S2). Analysis via Wide-Angle X-Ray Scattering (WAXS) confirmed the HRTEM observations by showing a pattern consistent with small NPs of metallic Ru in the hcp structure and a coherence length of ca. 1.6 nm with no sign of oxidation (ESI, Figure S3). Evidence for the presence of the NHCs on the NPs could be found by ^{13}C magic angle spinning solid-state NMR (MAS-NMR) (ESI, Figures S4 and S6). MAS $^{13}C\{^1H\}$ NMR spectra of Ru@**1** and Ru@**2** performed with ^1H-^{13}C cross-polarization (CP) presented a signal at *ca.* 55 ppm corresponding to the CH_3-group attached to the nitrogen atoms and a group of resonances between 40 and 10 ppm which belongs to the steroidal body of the NHC. The amount of ruthenium in the NPs was determined by Atomic Absorption Spectroscopy (AAS) displaying a metal content of ca. 50% (51% Ru@**1**, 47% Ru@**2**) and a Ru/ligand ratio of 4.8:1 for Ru@**1** and 4.0:1 for Ru@**2** (ESI, Table S1). As one might expect the ligand with the bulky N-substituent (**1**) needs more room for coordination to the Ru surface, and as a result, Ru@**1** has a higher metal/ligand ratio than Ru@**2**. Consequently, given the similar mean sizes of the NPs Ru@**1** is expected to have slightly more free available Ru sites than Ru@**2**.

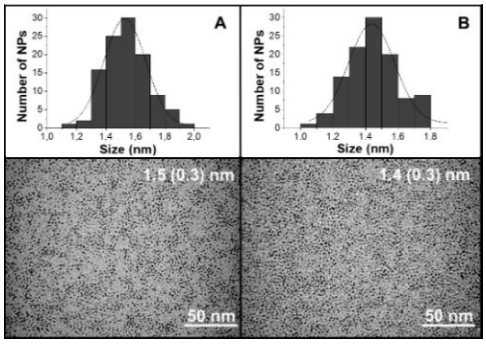


Figure 2: TEM micrographs and the corresponding size histograms of Ru@**1** (A) and Ru@**2** (B).

To learn whether the free surface sites are accessible for substrates, the coordination of CO onto Ru@**1** and Ru@**2** was examined by MAS-NMR and infrared spectroscopy (FT-IR). CO can coordinate to the metal surface in two different modes: a bridging mode (CO_b), the sites of which are located on the faces of the NPs, and a terminal binding mode (CO_t), the sites of which are located on apexes and edges.[16] For this purpose, the Ru-NPs were reacted with ^{13}CO (1 bar, r.t., 20 h) and analysed by $^{13}C\{^1H\}$ NMR spectroscopy (ESI, Figures S5 and S7). In both cases, a broad peak at δ ≈ 220 ppm and a sharp one at δ ≈ 190 ppm were observed which could be attributed to CO_b and CO_t, respectively. The FT-IR spectra of Ru@**1** and Ru@**2** (ESI, Figures S12 and S13) indicated the presence of a CO absorption band (ca. 1920 cm^{-1} for both NPs) already before the reaction with CO, which indicates the decarbonylation of THF during the NP synthesis demonstrating the high reactivity of the NPs, as previously observed.[17] After the reaction with CO (bubbling CO into a THF solution during 5 min), the absorption band showed a higher intensity as well as a shift to ca. 1970 cm^{-1}. An additional band appeared at ca. 2030 cm^{-1}, that may correspond to CO coordinated in a multi-terminal mode $Ru(CO)_2$ as was previously observed for rhodium NPs.[18]

Thanks to the high solubility of the NPs, liquid NMR studies could be performed and confirmed the existence of the NHC on the NP surface (Figure 3 and ESI, Figures S8 and S9). From previous studies on NPs, it is known that groups closely located to the particles suffer from a peak broadening or even a peak disappearance in ^1H and ^{13}C NMR.[19] In ^1H NMR spectra of Ru@**1** and Ru@**2** the methyl groups of the N-substituents (ca. 4.1 ppm for **1**·HOMs and ca. 4.0 ppm for **2**·HI), the NHC-backbone protons (ca. 7.5 ppm for ppm for **1**·HOMs) and the proton of the cholesterol ring in direct neighbourhood to the NHC core (ca. 4.5 ppm for **1**·HOMs) vanished.

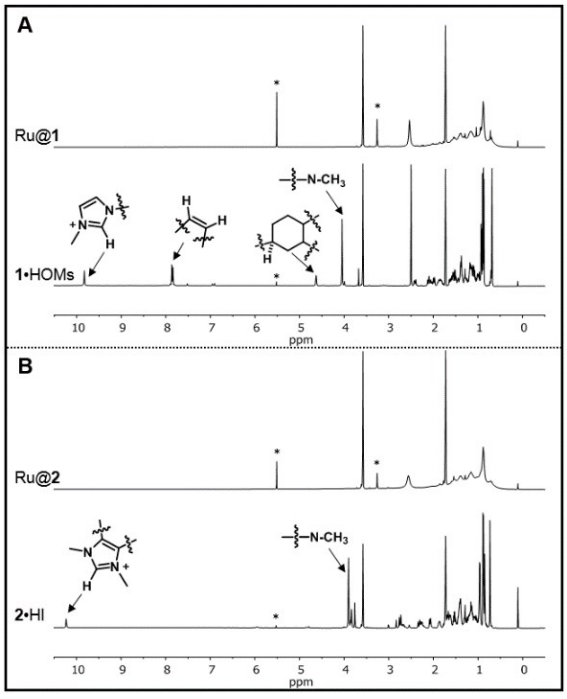


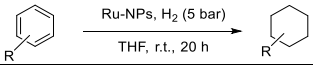
Figure 3: ^1H liquid-NMR spectra (in d_8-THF) of Ru@**1** and **1**·HOMs (**A**) and Ru@**2** and **2**·HI (**B**). Peaks that correspond to protons at or close to the imidazolium core are labelled. Peaks marked with an asterisk (*) correspond to CH_2Cl_2 (δ 5.5 ppm), which comes from the purification step of the ligands, and MeOH (δ 3.2 ppm), which arises from the purification of Ru@**1** and Ru@**2**.

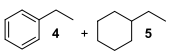
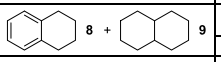
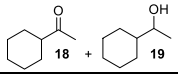
Thus, as expected, line broadening and peak disappearance was observed for most of the ligand signals, indicating not only the

coordination of the NHCs on the NP surface, but also a full rigidity of the ligands and absence of dynamical exchange between the surface of the NP and the solution. The lack of mobility of the ligands and their strong coordination to the Ru surface makes these NPs perfect candidates to become chemioselective and stable catalysts.

Furthermore, diffusion-ordered spectroscopy (DOSY) NMR yielded the diffusion coefficients of the Ru-NPs in comparison to those of the free ligands (ESI, Figures S10 and S11). As expected, diffusion of the surface coordinated ligand is slower than that of the free ligand in solution: 2.4 x 10^{-10} m^2s^{-1} for Ru@**1** against 5.0 x 10^{-10} m^2s^{-1} for **1**·HOMs; 2.5 x 10^{-10} m^2s^{-1} for Ru@**2** against 6.0 x 10^{-10} m^2s^{-1} for **2**·HI. These results confirm once again the coordination of the ligands to the NP surface (further details are given in the ESI).

Table 1: Application of Ru-NPs in the mild hydrogenation of arenes.[a]



No	cat	starting materials	products[b]	conv./product ratios[c]
1	Ru@**1**	 **3**	 **4** + **5**	100%/**4**:**5** = 100:0[a] 100%/**4**:**5** = 100:0[d]
	Ru@**2**			100%/**4**:**5** = 100:0[a] 100%/**4**:**5** = 0:100[d]
2	Ru@**1**	 **6**	 **5**	100%
	Ru@**2**			100%
3	Ru@**1**	 **7**	 **8** + **9**	100%/**8**:**9** = 60:40
	Ru@**2**			100%/**8**:**9** = 87:13
4	Ru@**1**	 **10**	Ph—Cy + Cy—Cy **11** **12**	100%/**11**:**12** = 60:40[a] 91%/**11**:**12** = 74:26[e]
	Ru@**2**			70%/**11**:**12** = 75:25[a] 56%/**11**:**12** = 75:25[e]
5	Ru@**1**	 **13**	 **14**	100%
	Ru@**2**			100%
6	Ru@**1**	 **15**	 **16**	100%
	Ru@**2**			100%
7	Ru@**1**	 **17**	 **18** + **19**	100%/**16**:**17** = 0:100
	Ru@**2**			100%/**18**:**19** = 20:80

a: Reaction conditions: substrate (0.2 mmol), Ru-NPs (2 mg, 0.01 mmol Ru assuming ≈ 50% Ru from AAS), THF (1 mL), hydrogen (5 bar), r.t., 20 h; b: products were identified by GC-MS analysis; c: conversions and ratios were determined by GC-FID analysis with mesitylene (0.2 mmol) as internal standard; d: substrate (2 mmol); e: hydrogen (1 bar).

Knowing that NHCs bearing rigid moieties are capable of stabilizing Ru-NPs, the effect of the steroidal body on the catalytic activity should be tested. In former reports, Ru-NPs were recognized as active catalysts for the hydrogenation of various arenes,[3c,14,17] e.g. the selective hydrogenation of the arene moiety in benzoic acid.[14g] Additionally, dependencies of the ligand bulkiness on the selectivities were observed in the hydrogenation of arenes that bear other functional groups.[3c,17] Inspired by the activities of known catalysts we wanted to investigate the catalytic differences of Ru@**1** and Ru@**2** in the mild hydrogenation of arenes to learn about the impact of the rigid moiety (2 mg NPs, 5 bar H_2, r.t., 20 h – table 1). Various aromatic compounds were successfully hydrogenated resulting in a complete hydrogenation of the aromatic moiety (No **1**[a]**, 2, 5**) and the functional group (No **1**[a]**, 2**) illustrating the high activity of the catalysts. Moreover, the hydrogenation of phenol (No **6**) could be performed highlighting the potential of our Ru-NPs for the transformation of lignocellulosic biomass derivatives.[20] TEM analysis performed after the hydrogenation of styrene (ESI, Figures S16 and S17) revealed similar sizes for the NPs as before catalysis thus demonstrating their stability under catalytic conditions. Differences in activity of Ru@**1** and Ru@**2** could be observed for more complex substrates like naphthalene (**7**), biphenyl (**10**) and acetophenone (**17**). Ru@**1** enabled not only their complete conversion but also presented a higher reactivity for the fully hydrogenated compounds. A lower activity was observed for Ru@**2** with these three substrates, since the hydrogenation of the compounds was either not quantitative (No **4**[a]) or the amount of fully hydrogenated products was significantly lower (No **3, 4**[a]**, 7**) leading to moderate selectivities. Lowering the hydrogen pressure (No **4**[e]) in the hydrogenation of biphenyl (**10**) slightly improves selectivity in the case of Ru@**1** but additionally lowers the reactivity for both systems. Interestingly, when the catalytic loading was considerably reduced (from 5% to 0.5%; No **1**[d]), both Ru-NPs presented totally different selectivities for the hydrogenation of styrene (**3**). While Ru@**1** produced the fully hydrogenated product (ethylcyclohexane), Ru@**2** performed a selectivity switch by completing a selective partial hydrogenation process, forming only ethylbenzene. Similar results were observed in a multiple addition test were a new batch of styrene was added to the reaction mixture four times (ESI, S12). During the first reaction run a complete hydrogenation of styrene occurred for both systems resulting in the formation of ethylcyclohexane. Interestingly, the following additions of styrene resulted in its full conversion for both NPs but in the case of Ru@**2** only the partial hydrogenation to ethylbenzene was observed, while Ru@**1** exclusively formed ethylcyclohexane for all additions. These results illustrate once more the superior activity of Ru@**1** compared to Ru@**2.** This difference may result from the ligand structures. Due to the more flexible connection of the steroid to the NHC core in ligand **1**, it possesses a higher steric demand than **2** which results in a lower NHC amount on the Ru@**1** surface (ESI, table S1), and therefore in a higher quantity of free faces. As faces are necessary to hydrogenate aromatic rings, Ru@**1** presents a higher activity in hydrogenation of arenes as was already observed for other stabilized Ru-NPs.[3c,17] In molecular complex catalysts similar phenomena have been reported, i.e. bulky ligands giving more active catalysts.[21] Unfortunately, the selectivity switch by lowering the catalyst loading or changing the conditions (temperature, solvent, pressure, time) could not be applied for other substrates (**7**, **10**, **17**).

Herein, for the first time we report biomimetic NHCs derived from cholesterol and the successful application of these rigid NHCs as stabilizers of Ru-NPs. The particles obtained were fully characterized, including analysis by liquid NMR techniques given their high solubility induced by the NHCs ligands. They were applied as catalysts in the hydrogenation of arenes at r.t. Ru@**1** showed a higher activity than Ru@**2**, especially at lower catalyst loading and in the multi-addition experiments. This difference in activity is attributed to steric differences between the two NHCs which in fact appears as a way to tune the

View Article Online DOI: 10.1039/C8CC02833H

nanocatalyst surface properties. Furthermore, the hydrogenation of phenol was successfully performed showing the interest of these catalysts for the transformation of lignocellulosic biomass derivatives. The application of the rigid ligands without ligand loss not only opens the way to catalysis in the solid state but also offers the possibility to utilize it as a recognition unit for biological systems as well as for substrate interactions in catalysis which we will focus on in the future.

We thank the Deutsche Forschungsgemeinschaft (SFB 858) and CNRS, UPS-Toulouse, INSA, IDEX/Chaires d'attractivité l'Université Fédèrale Toulouse Midi-Pyrénées for generous financial support. We also thank L. Datas for TEM facilities (UMS Castaing), S. Cayez for HRTEM micrographs, Y. Coppel (LCC, CNRS) for NMR measurements and P. Lecante (CEMES, CNRS) for WAXS analysis.

Conflicts of interest

There are no conflicts to declare.

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DOI: 10.1039/C8CC02833H

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