Rhodium-NHC Hybrid Silica Materials as Recyclable Catalysts for [2+2+2] Cycloaddition Reactions of Alkynes

Martí Fernández,[a] Meritxell Ferré,[b] Anna Pla-Quintana,[a] Teodor Parella,[b,c] Roser Pleixats*[b] and Anna Roglans*[a]

Abstract: Bis-silylated dihydroimidazolium salt **1** and monosilylated imidazolium salt **2** are transformed to (NHC)RhCl(COD) complexes **3** and **4**, which allow the preparation of hybrid silica materials either by sol-gel or grafting processes. After a full characterization of the materials by means of solid state NMR, N_2-sorption measurements, thermogravimetric analysis (TGA) and elemental analysis, the catalytic activity is evaluated in the [2+2+2] cycloaddition of alkynes. Excellent yields of the cycloadducts are obtained for up to six consecutive cycles with the grafted material, using a simple filtration to recover the catalyst. Both conventional and microwave heating prove to be effective for the process described.

Introduction

The transition-metal catalysed [2+2+2] cycloaddition reaction of unsaturated substrates is a very simple and atom-economic strategy to obtain polysubstituted six-membered carbo- and heterocyclic molecules.[1] Many examples of [2+2+2] cycloadditions catalyzed by different transition metals have been described.[1] With regards to the rhodium-catalyzed [2+2+2] cycloaddition of three alkynes to afford highly substituted and/or annulated benzenes, two catalytic systems have proved to be particularly efficient: the Wilkinson complex, which was first used in this reaction by Grigg et al.[2] and which is now used as a neutral rhodium complex,[3] and the combination of a cationic rhodium complex and a BINAP-type ligand, which has been extensively explored by the groups of Tanaka and Shibata[4] and forms a highly active and versatile cationic catalyst.

Given that phosphine ligands are prone to oxidation, resulting in catalyst deactivation and the hampering of the purification of the product, other stabilizing ligands, such as *N*-heterocyclic carbenes (NHC), are increasingly used as alternatives for stabilizing transition-metal catalysts.[5] Furthermore, this type of ligands can have a dramatic influence on both reactivity and selectivity. Rh-NHC complexes have only been described by our group as efficient catalysts for intra- and partially intramolecular [2+2+2] cycloaddition reactions of alkynes,[6] although NHC-complexes of other metals such as ruthenium, cobalt, nickel and iron have been proved to be efficient catalysts in [2+2+2] cycloaddition reactions by other groups.[7]

The recovery and reuse of the catalytic system, especially when this is based on transition metals, is an important challenge in organic synthesis both from an economical and environmental point of view. In the field of [2+2+2] cycloaddition reactions, few examples of the recyclability of catalytic systems have been reported. Among them, several strategies have been tested for the recovery of catalysts: i) the anchoring of a metal complex to a polystyrene resin;[8] ii) the use of molten salts as immobilizing agents;[9] iii) the use of a water soluble catalyst;[10] iv) the immobilization of the ligand at the surface of a dendrimer,[11] and v) the recovery of air stable complexes by column chromatography.[12] In this field, the formation of hybrid silica materials is attractive as a means of achieving supported catalysts based on metal complexes. These materials combine the advantages of a silica matrix, such as high surface area, thermal and mechanical stability and chemical inertness, with the properties of the organometallic precursor.[13] Indeed, the sol-gel hydrolytic condensation of organo-alkoxysilanes[14] is a convenient method for the preparation of hybrid silica materials with targeted properties.[15,16] Moreover, the surfactant-assisted sol-gel synthesis or the grafting on a mesostructured silica are commonly employed routes for the synthesis of mesostructured hybrid silicas[17] with high surface areas and large pore sizes.

Silica supported catalysts have also been used in [2+2+2] cycloaddition reactions as a recovery strategy. Yu et al.[18] immobilized a Pd(II) complex with a bidentate bis-pyridyl ligand on a range of polysiloxanes with controllable solubility, affording materials which proved to be efficient and recyclable catalysts in the [2+2+2] cyclotrimerization of alkynes. Blümel et al.[19] described the use of carbonylnickel(0) catalysts with mono- and bidentate phosphine ligands immobilized on hybrid silica materials as recyclable catalysts for the cycloaddition of phenylacetylene. More recently, Hapke et al.[20] described that the air-stable cobalt complex they recovered by column chromatography[12a] could be grafted on a silica support through a siloxane linker at the Cp-moiety. The heterogeneous Co-catalyst showed moderate activity in the cycloaddition between 1,6-heptadiyne and benzonitrile to afford a pyridine derivative. However, the catalytic system deactivates upon recycling.

Given our interest in the use of Rh-NHC complexes for the [2+2+2] cycloaddition reaction, we undertook the present project with the idea of immobilizing Rh-NHC complexes on silica materials. In this study imidazolium salts conveniently

[a] M. Fernández, Dr. A. Pla-Quintana, Prof. A. Roglans
Institut de Química Computacional I Catàlisi and Departament de Química
Universitat de Girona
Campus de Montilivi, 17071, Girona, Catalonia, Spain
Fax: (+) 34972418150
E-mail: anna.roglans@udg.edu
[b] M. Ferré, Dr. T. Parella, Prof. R. Pleixats
Departament de Química and Centro de Innovación en Química Avanzada (ORFEO-CINQA)
Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193, Barcelona, Catalonia, Spain
E-mail: roser.pleixats@uab.cat
[c] Dr. T. Parella
Servei de RMN
Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193, Barcelona, Catalonia, Spain

Supporting information for this article is given via a link at the end of the document.

functionalized with trialkoxysilyl groups either in the carbon backbone or in the nitrogen atom will be complexed with Rh and incorporated into hybrid silica materials either by a sol-gel or a grafting process. Some few hybrid silica based Rh-NHC materials have already been synthesized and proved to be efficient catalysts in Rh catalyzed reactions,[21] but to the best of our knowledge they have not been reported as catalysts for the [2+2+2] cycloaddition reaction, which is the aim of the present work.

Results and Discussion

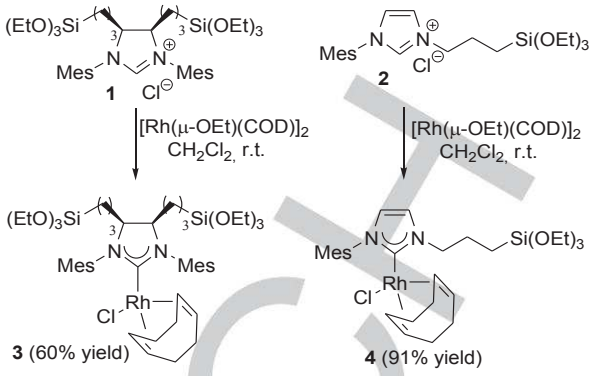
Synthesis and characterization of Rh-NHC

In the last few years, we have made some contributions into recyclable catalysts based on hybrid silica materials. We have described a silica-supported Hoveyda-Grubbs' type complex through the NHC ligand by performing a sol-gel co-gelification process of a silylated NHC-Ru monomer with tetraethoxysilane (TEOS). The new material proved to be an efficient recyclable catalyst for ring-closing metathesis reactions.[22] Furthermore, the sol-gel co-condensation of a silylated Pd-NHC complex with TEOS to afford the corresponding hybrid silica material was also described. This supported palladium complex was efficiently used as a recyclable catalyst in the Heck, Suzuki and Sonogashira coupling reactions.[23] Having developed efficient syntheses for both nitrogen and backbone functionalized imidazolium salts, we decided to evaluate their complexation ability with rhodium. Therefore, we first studied the ability of silylated imidazolium salts **1** and **2** to coordinate rhodium (Scheme 1).

The first attempt to synthesize a Rh-carbene complex from the imidazolium salt **1** followed the procedure reported by Dastgir and Green.[24] This method was based on the treatment of the imidazolium salt with Ag_2O to afford a NHC-Ag(I) complex followed by transmetallation with $[Rh(\mu\text{-Cl})(COD)]_2$. However, in our case only decomposition to elemental silver and the recovery of **1** were observed.

Recently, Esteruelas and Yus[25] have described an alternative method which used the $[Rh(\mu\text{-OMe})(COD)]_2$ complex in the presence of an imidazolium salt to form the corresponding Rh-NHC species directly. The methoxide anion deprotonates the imidazolium ring and releases methanol from the metal centre. Subsequent coordination of the resulting NHC ligand and the chloride anion to the rhodium atom affords the desired Rh-carbene complex.

In order to avoid side-etherification reactions with the triethoxysilyl groups of our salts **1** and **2**, we used the analogous non-commercially available ethoxy-complex, $[Rh(\mu\text{-OEt})(COD)]_2$, which was prepared from $[Rh(\mu\text{-Cl})(COD)]_2$ by a nucleophilic substitution of the chloride ligands by ethoxide. When bis-silylated imidazolium salt **1** was mixed with $[Rh(\mu\text{-OEt})(COD)]_2$ in anhydrous dichloromethane at room temperature for 15 hours, the desired rhodium complex **3** was obtained in a 60% isolated yield. Applying the same procedure to the imidazolium salt **2**, a 91% yield of the monosilylated rhodium complex **4** was obtained in 4 hours (Scheme 1).



Scheme 1. Synthesis of Rh-NHC complexes **3** and **4**. Mes: 2,4,6-trimethylphenyl.

Both complexes **3** and **4** were fully characterized by ESI-HRMS, ^{1}H and ^{13}C-NMR. ESI-HRMS spectra of complex **3** showed a peak at *m/z* = 925.4470, corresponding to $[M\text{-Cl}]^+$. The same behaviour was observed for complex **4**, which showed a peak at *m/z* = 601.233, which also corresponded to the same chloride loss. As a result of hindered rotation around the carbene carbon-rhodium bond, two different sets of signals in a 4:1 ratio are observed in the ^{1}H and ^{13}C NMR spectra of complex **3**. Six different signals corresponding to the methyl groups in the aromatic ring can be seen in the ^{1}H-NMR spectrum: the major isomer presented three signals at 2.26, 2.30 and 2.63 ppm whereas the signals corresponding to the minor isomer appeared at 2.29, 2.36, and 2.52 ppm. The ^{13}C-NMR spectrum displays two sets of doublets: at 67.1 ppm ($J_{Rh\text{-}C}$ = 14.5 Hz, major isomer) and 68.3 ppm ($J_{Rh\text{-}C}$ = 14.0 Hz, minor isomer), corresponding to the methylene carbons of the COD ligand, and at 96.8 ppm ($J_{Rh\text{-}C}$ = 6.9 Hz, major isomer) and 96.5 ppm ($J_{Rh\text{-}C}$ = 7.0 Hz, minor isomer), corresponding to the olefinic carbons of the COD ligand. The carbene carbon atom of the NHC ligand coordinated to Rh appeared as a doublet at 213.2 ppm with a coupling constant of $J_{Rh\text{-}C}$ = 48.0 Hz. High-temperature ^{1}H-NMR experiments at up to 95ºC were carried out in an unsuccessful attempt to observe the interconversion between the two isomers. The formation of two diastereoisomers has previously been described by Köhler et al.[26] in the synthesis of a Rh complex derived from 4,5-diallyl-1,3-dimesityl-4,5-dihydroimidazolium chloride, which in our case is a precursor of the synthesis of **1** (see Supporting Information). In this study, the authors also found that no dynamic process was observed by variable-temperature ^{1}H NMR experiments up to 70ºC. In an attempt to identify the relative geometry of the two rotamers, NOESY experiments were planned. Since Rh complex **3** containing triethoxysilyl groups is prone to be hydrolyzed under air conditions, the NMR study was performed with the already described Rh-carbene complex derived from the allylic precursor of imidazolium salt **1** (named **3**-allyl), which analogously gives a double set of signals with a 4:1 isomers ratio. The square planar rhodium complexes feature the carbene ligand in a perpendicular orientation to the square-plane of the complex and *cis* to the chlorine atom. Both diastereoisomers have a plane of symmetry corresponding to the square-plane of the complex. The NOESY data reveal that the two allyl chains of the major isomer point to the Cl atom while in the minor isomer they point to the COD ligand (Figure 1). Whereas in the major isomer both the olefin

COD proton and the H of the NHC core give a cross-peak with the same *ortho* methyl of the mesityl, in the minor isomer both protons correlate to a different *ortho* methyl of the mesityl which is perpendicular to the dihydroimidazole ring. These results can be extrapolated to allow us to conclude that the same type of structures would be found in complex **3**.

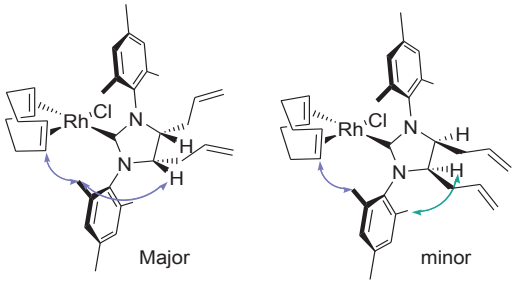


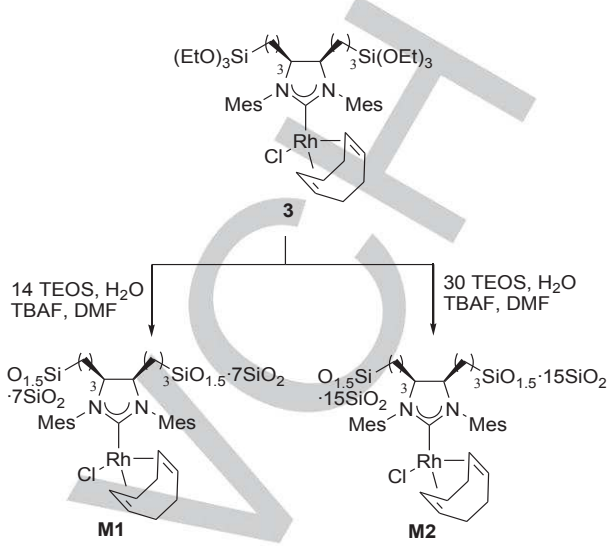
Figure 1. Representation of the two isomers of **3**-allyl showing the major NOESY correlations observed.

In the ^{1}H-NMR spectra of complex **4**, three different methyl and two aromatic signals corresponding to the mesityl ring were observed. The methylene group attached to the second nitrogen atom of the NHC ligand appeared overlapped with COD ligand signals at around 2 ppm. Overlapping was also found at 1.5 ppm between the signals of the central CH_2 unit of the silylated chain and protons of the cyclooctadiene ligand. The CH_2 group next to the Si atom appeared at 0.77 ppm as a triplet. In the ^{13}C NMR spectrum, two doublets at 96.7 and 96.9 ppm corresponded to the olefinic carbons of the COD ligand (Rh-C coupling constants of 7.3 Hz and 7.1 Hz, respectively). Two additional doublets at 67.4 and 68.3 ppm were attributed to the methylene carbons of the COD ligand (Rh-C coupling constants of 14.7 and 14.2 Hz). The carbene carbon atom of the NHC ligand coordinated to Rh appeared at 181.6 ppm as a doublet with a Rh-C coupling constant of 51.5 Hz.

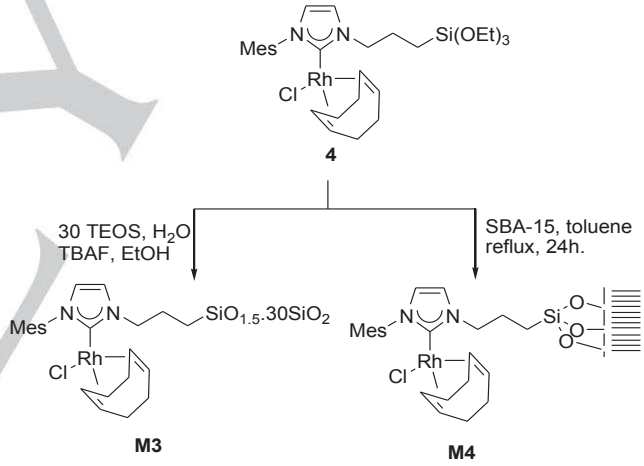
*Synthesis and characterization of organic-inorganic hybrid silica materials **M1-M4***

Two different materials **M1** and **M2** were prepared from complex **3** by cogelification with different amounts of tetraethoxysilane (molar ratios **3**:TEOS of 1:14 and 1:30, respectively). The reactions were performed under nitrogen atmosphere in anhydrous DMF at room temperature under nucleophilic conditions using a stoichiometric amount of water (with respect to the ethoxy groups) and tetrabutylammonium fluoride as the catalyst (1 mol% with respect to Si). Both solutions gelified after one hour and were aged for six days at room temperature under nitrogen atmosphere. They were then filtered and the solid was washed successively with ethanol, acetone and anhydrous diethyl ether. The resulting powders were dried overnight under vacuum at 40°C to afford both materials as an orange powder (Scheme 2).

With complex **4** two different materials were also prepared using two different methodologies. Whereas hybrid silica **M3** was prepared by cogelification with tetraethoxysilane (molar ratio 1:30), as previously described for complex **3**, the material **M4** was obtained by grafting to the mesostructured silica SBA-15 under standard conditions (in refluxing anhydrous toluene under nitrogen atmosphere for 24 hours) (Scheme 3).



Scheme 2. Synthesis of hybrid silica materials **M1** and **M2**.



Scheme 3. Synthesis of hybrid silica materials **M3** and **M4**.

The materials were characterized by solid state ^{29}Si NMR and ^{13}C NMR (only for **M1**), N_2-sorption measurements, thermogravimetric analysis (TGA) and elemental analysis, and the amount of rhodium was determined by inductively coupled plasma (ICP). Some analytical and textural data are summarized in Table 1. The TGA curves of all materials (Supporting Information) showed a weight decrease of less than 5% below 200 °C attributed to the loss of the physisorbed water and the remaining uncondensed ethoxy groups. A more significant weight loss was then found in the 250-500 °C range, assigned to the decomposition of the organometallic constituent. We obtained a molar ratio Rh/N of 0.4 for material **M4** from the analytical data, which was close to the expected 0.5 value.

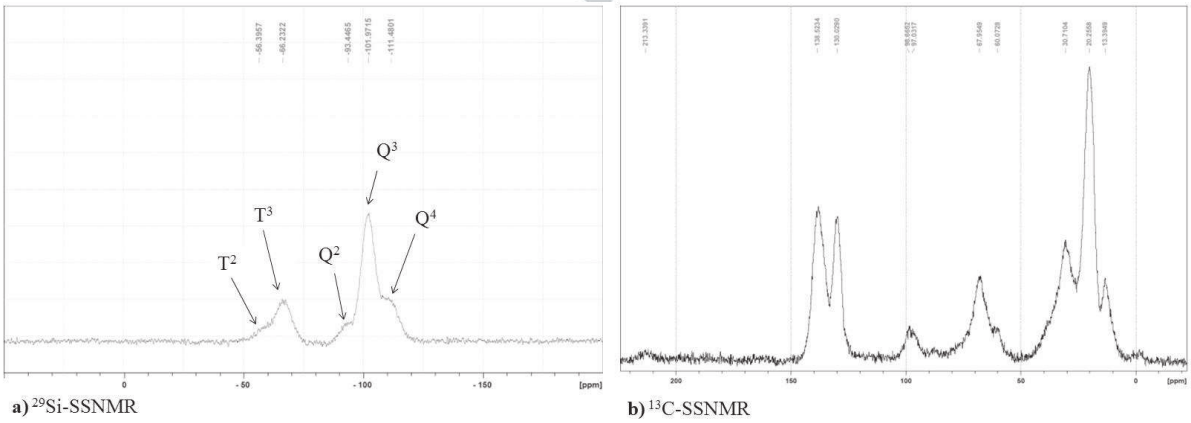
Lower experimental molar ratios for the other materials **M1-M3** were found, indicating that partial decomplexation had occurred in the formation of materials by the sol-gel process. The covalent

incorporation of the organosilane in the hybrid materials was ascertained by ^{29}Si CP MAS solid-state NMR. The ^{29}Si spectra of **M1-M3** showed two sets of chemical shifts: T units at around -55 to -67 ppm, resulting from the hydrolysis-condensation of monomers **3** and **4**, and Q units ranging from -90 to -112 ppm, corresponding to the condensed TEOS, as exemplified by the ^{29}Si solid-state NMR of **M1** (Figure 2, a)**.** Only the solid-state ^{13}C NMR of **M1** was performed (Figure 2, b). Significant absorptions appeared at 13.3 ppm (CH_2-Si), which confirmed the covalently bonded ligand to silica, and at 213.3 ppm, attributable to the carbenic carbon of the NHC ligand coordinated to the rhodium (C-Rh). In the case of the other materials, **M2-M4,** the high dilution of the organic moiety in the inorganic matrix precluded the observation of the corresponding absorptions in ^{13}C solid-state NMR. N_2-sorption measurements revealed a significant porosity for all the materials and high surface areas ranging from 325 to 512 m^2 g^{-1} were obtained. The functionalized mesostructured silica **M4** prepared by grafting exhibited the highest surface area, with a rather sharp pore size distribution centred at around 59 Å and a type IV isotherm typical for mesoporous materials (Figure 3). A powder X-ray diffractogram of **M4** confirmed that the original 2D hexagonal mesostructure of the parent silica had not been affected by the grafting (see Supporting Information). However, the BET surface area decreased significantly from 732 m^2 g^{-1} for parent SBA-15-type silica to 512 m^2 g^{-1} for **M4**, in a clear indication that the precursor **4** had been successfully grafted to the parent silica and had partially filled the pores. For the case of materials derived from sol-gel methodologies, whereas **M1** was found to be a microporous solid (type I isotherm), **M2** exhibited a type IV isotherm and the mesoporous material **M3** presented a type II isotherm according to the IUPAC rules.[27] In the case of **M3** the large amount of nitrogen adsorbed at p/p° > 0.8 arise from nitrogen that condenses in the voids between particles (see Supporting Information).

Table 1. Some analytical and textural data of materials **M1-M4**.

	^{29}Si CP MAS NMR					TGA[a]%	% Rh	mmol Rh/g	S_{BET} (m^2g^{-1})	$Ø_{pore}$ [Å]	V_{pore} [b] (cm^3g^{-1})
	T^2	T^3	Q^2	Q^3	Q^4						
M1	-56.3	-66.2	-93.4	-101.9	-111.4	77.06	4.47	0.435	453	[c]	0.230 (0.209)
M2	-55.7	-65.6	-92.5	-101.7	-110.2	80.66	2.93	0.285	493	20-30[d]	0.280 (0.088)
M3	--	-65.1	-91.6	-101.8	-111.3	75.98	3.15	0.306	325	[e]	0.232 (0.071)
M4	--	--	--	--	--	84.30	1.03	0.100	512	58.8	0.774 (0.044)

[a] Residual mass measured in the TGA analysis. [b] Total pore volume at p/p^0 0.99 (p/p^0 0.8 for **M3**); in brackets contribution of micropores to the V_{pore}. [c] Micropores, type I isotherm. [d] Type IV isotherm, see ESI. [e] Type II isotherm, see text and ESI.



a) ^{29}Si-SSNMR **b)** ^{13}C-SSNMR

Figure 2. Solid state NMR spectra for **M1**.

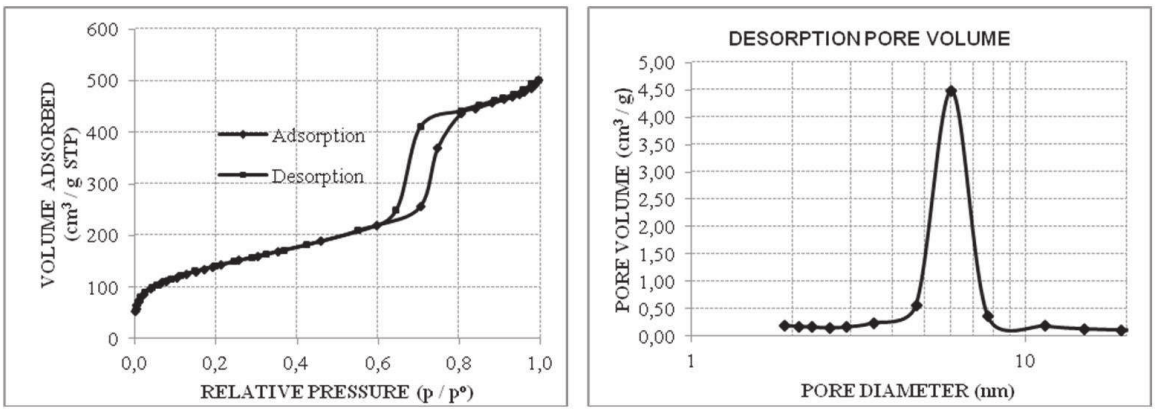
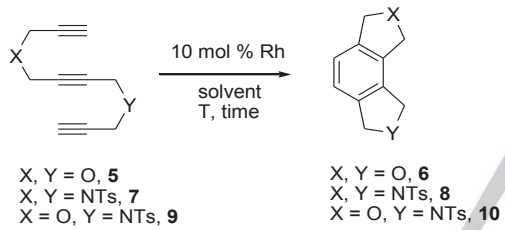


Figure 3. N_2 adsorption-desorption isotherm and pore volume distribution of **M4**.

Catalytic activity of the supported catalysts in [2+2+2] cycloaddition reactions

Once the rhodium hybrid silica materials were prepared and characterized, their catalytic activity in the [2+2+2] cycloaddition reaction of alkynes and their recovery and reuse was evaluated.



Scheme 4. Rh-catalysed [2+2+2] cycloaddition reactions of triynes.

The supported catalysts were tested in the completely intramolecular version of the [2+2+2] cycloaddition reaction of triynes, using the O-tethered triyne **5** (Scheme 4) as a benchmark reaction to establish the best operating conditions. Different solvents and temperatures were tested with this substrate under catalysis by material **M2** (Table 2).

First, catalyst loading was set at 10 mol% and the reactions were carried out at room temperature using three different solvents (toluene, dichloroethane and ethanol), but no evolution was observed after three hours of reaction (entries 1-3, Table 2). When the reaction temperature was increased to 80°C for all solvents, the reactions were completed after 3-5 hours (entries 4, 6, 8, Table 2). It can be seen that ethanol was clearly the best solvent as the cyclized product **6** was obtained in an almost quantitative yield (entry 8, Table 2). In addition, using ethanol as the solvent, it was possible to recover the catalyst by filtration and highly pure cycloadduct **6** was afforded by evaporation of the organic phase, eliminating the need to use column chromatography. The heterogeneous Rh-complex was then washed with dichloromethane and diethyl ether and used in a subsequent cycle. With this simple methodology, the catalytic system could be reused for four cycles affording good isolated yields of **6**, although after longer reaction times (entries 8-11, Table 2). Reusability was also tested using DCE and toluene as the reaction solvents. However the reaction yield dropped in the second cycle (entries 5, 7, Table 2). When a decrease of the catalyst loading to 5 mol% was attempted under the same conditions of entry 8 (EtOH, 80 ºC), incomplete conversion was observed after 30 hours of reaction. We therefore decided to use EtOH as the solvent at 80 ºC and 10 mol % of catalyst for further studies with the other supported catalysts (Table 3).

Table 2. Catalytic performance of hybrid silica material **M2** in the [2+2+2] cycloaddition of triyne **5**.

Entry	Solvent	Temp. (ºC)	Cycle	Reaction time (h)	Yield of **6** (%)[a]
1	Toluene	25	1	3	0
2	DCE	25	1	3	0
3	EtOH	25	1	3	0
4	Toluene	80	1	5	61
5	Toluene	80	2	30	16[b]
6	DCE	80	1	3	69
7	DCE	80	2	30	10[b]
8	EtOH	80	1	3	98
9	EtOH	80	2	22	84
10	EtOH	80	3	28	92
11	EtOH	80	4	33	95

[a] Isolated yield. [b] Calculated by ^{1}H-NMR spectroscopy.

When the other materials were tested in the cycloaddition reaction of triyne **5**, **M1** gave the lowest yield (entry 1, Table 3) whereas **M3** and **M4** showed similar activities (entries 2-3, Table 3). The recyclability of **M4** was then assessed. Material **M4** was reused successfully for 6 cycles, although increasing reaction

times were required upon recycling to achieve full conversions (entries 3-8, Table 3).

The rhodium leaching was determined for the four materials. After complete conversion of **5** in the first cycle, the rhodium content in the crude product **6** was determined by ICP-MS analysis and a loss of 5.7% for **M1**, 12.2% for **M2**, 8.4% for **M3** and 12.15% for **M4** was found with respect to the initial amount of rhodium added as catalyst. In the case of material **M4** the rhodium content was also measured after the second cycle and the loss was found to be 9.76%. A hot filtration test was performed with catalyst **M4** in the cycloaddition of triyne **5**. **M4** was filtered off from the hot reaction mixture under the conditions detailed in Table 3 after 4 minutes of reaction (17% GC conversion of **5**) and the remaining filtrate was made to react under the same conditions. After 2.5 h the GC conversion increased to 56% suggesting that a homogeneous pathway plays also a role in the cycloaddition reaction and that homogeneous Rh species released from the immobilized rhodium system are, at least in part, responsible for the catalysis.

Table 3. Catalytic performance of hybrid silica materials **M1**, **M3** and **M4** in the [2+2+2] cycloaddition of triyne **5** [a]

Entry	Material	Cycle	Reaction time (h)	Yield of **6** (%)[b]
1	**M1**	1	4	77
2	**M3**	1	3	85
3	**M4**	1	2.5	85
4	**M4**	2	16	85
5	**M4**	3	19	92
6	**M4**	4	23	93
7	**M4**	5	24	89[c]
8	**M4**	6	48	95

[a] All reactions were carried out in EtOH at 80ºC. [b] Isolated yield. [c] Yield calculated by ^{1}H-NMR spectroscopy.

In order to explore the scope of the reaction, the cycloaddition of the *N*-tosyl-tethered triyne **7** and triyne **9** bearing two different tethers (N-Ts and O) were tested with **M4** under the optimized conditions (EtOH, 80ºC). The results are shown in Table 4.

For both substrates **7** and **9, M4** showed high activity and good recyclability. Almost quantitative yields of **8** and **10** were obtained, respectively, in five successive cycles (Entries 1-5 for **7**, entries 6-10 for **9**, Table 4), although reaction times substantially increased after the first run.

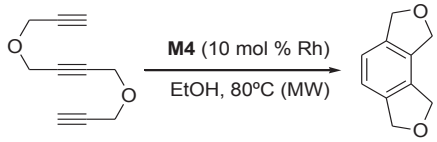
Table 4. Catalytic performance of hybrid silica material **M4** in the [2+2+2] cycloaddition of triynes **7** and **9**[a]

Entry	Substrate	Cycle	Reaction time (h)	Product, (yield (%)[b])
1	**7**	1	4	**8** (99)
2	**7**	2	16	**8** (96)
3	**7**	3	23	**8** (98)
4	**7**	4	25	**8** (98)
5	**7**	5	55	**8** (81)[c]
6	**9**	1	3	**10** (99)
7	**9**	2	19	**10** (96)
8	**9**	3	24	**10** (97)
9	**9**	4	31	**10** (99)
10	**9**	5	42	**10** (98)

[a] All reactions were carried out in EtOH at 80ºC. [b] Isolated yield. [c] Yield calculated by ^{1}H-NMR spectroscopy.

In order to shorten the reaction times, especially after the first cycle, we decided to carry out the cycloaddition under microwave irradiation, whose applications in organic synthesis and catalysis as an alternative to conventional heating has increased considerably in recent years.[28] We used this heating system in the cycloaddition of triyne **5** to afford tricyclic derivative **6** using catalyst **M4** in EtOH at 80ºC (Table 5).

Table 5. Catalytic performance of hybrid silica material **M4** under microwave irradiation.



5 **6**

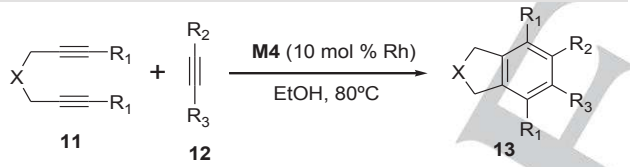
Cycle	Reaction time (min.)	Yield of **6** (%)[a]
1	15	77
2	45	84
3	80	88
4	120	80

[a] Isolated yield.

As shown in Table 5 microwave heating efficiently promotes the cycloaddition reaction of triyne **5** giving excellent yields of **6** in significantly shorter reaction times compared with conventional heating. As an example, when comparing Entry 6 of Table 3 with Entry 4 of Table 5, we observe that the reaction time is reduced from 1 day to just 120 minutes in the fourth cycle. In contrast, the rhodium leaching after the first and second run was 14.94% and 12.57% respectively, slightly higher than with conventional heating.

Finally, we wanted to test the catalytic activity of material **M4** in the partially intramolecular version of the [2+2+2] cycloaddition reaction between several diynes **11** and monoalkynes **12**. We used the same optimized reaction conditions as for the cycloaddition of triynes. Both terminal (Entries 1-4, Table 6) and non-terminal (Entries 5-6, Table 6) diynes with different tethers were active in this process. However, with non-terminal diynes it was necessary to heat the reaction at 110ºC using *n*-BuOH as the solvent as they are less reactive than terminal diynes. Both monosubstituted and disubstituted alkynes **12** also gave good yields of the cycloadducts. In addition, the reusability of **M4** was assessed in the reaction of Entry 1 giving an 85% yield of cycloadduct **13aa** in 4.5 hours.

Table 6. Catalytic performance of hybrid silica material **M4** in the [2+2+2] cycloaddition between diynes **11** and monoalkynes **12**.



Entry	**11** (X, R_1)	**12** (R_2, R_3)	Reaction time (h)	Yield of **13** (%)[a]
1	**11a** (O, H)	**12a** (CH_2OH, H)	2	**13aa** (100)
	11a (O, H)	**12a** (CH_2OH, H)	4.5	**13aa** (85)[b]
2	**11a** (O, H)	**12b** (Ph, H)	1	**13ab** (50)
3	**11b** (NTs, H)	**12a** (CH_2OH, H)	3	**13ba** (100)
4	**11b** (NTs, H)	**12b** (Ph, H)	5	**13bb** (72)
5[c]	**11c** (O, CH_3)	**12a** (CH_2OH, H)	2.5	**13ca** (100)
6[c]	**11c** (O, CH_3)	**12c** (CH_2OH, CH_2OH)	5	**13cc** (71)[d]

[a] Isolated yield. [b] Second batch. [c] Reaction run in *n*-BuOH at 110ºC. [d] Yield calculated by ^{1}H-NMR spectroscopy.

Conclusions

Rhodium(I) complexes bearing an *N*-heterocyclic carbene ligand functionalized with either two silylated groups at the saturated carbon backbone (complex **3**) or one silylated group at the nitrogen (complex **4**) were synthesized by reacting the corresponding imidazolium salts with [Rh(μ-OEt)(COD)]$_2$. Hybrid silica materials were obtained by cogelification of complexes **3** and **4** with different amounts of tetraethoxysilane, effectively affording hybrid silica materials **M1**-**M3**. Monosilylated rhodium complex **4** was also grafted on to the mesostructured silica SBA-15 giving material **M4**. The materials obtained were fully characterized with the standard solid state techniques, making it possible to check that the structure of the catalytic site was maintained in the solid. Furthermore, the rhodium content of the materials was determined by inductively coupled plasma. Their catalytic activity was evaluated in the [2+2+2] cycloaddition reaction of triyne substrates, which afforded tricyclic polysubstituted benzene derivatives. After screening the reaction conditions, ethanol at 80ºC was found to be optimal for the catalytic system giving excellent yields of cycloadducts. It is possible to separate the catalytic system from the reaction mixture by simple filtration affording an analytically pure product. The catalyst can be reused up to six times without loss of yield of the cycloadducts. The catalytic activity of material **M4** was also tested in the cycloaddition reaction between diynes and monoalkynes resulting in good yields of the corresponding cycloadducts. These compounds were obtained with enough purity after filtration of the catalyst and evaporation of the solvent.

Experimental Section

Imidazolium chlorides **1** (see Supporting Information) and **2**[23] were prepared as described previously by some of us. [Rh(μ-OEt)(COD)]$_2$[29], triynes **5**[2b] and **7**[30] were prepared by published methods. Details for the synthesis of triyne **9**, performed here for the first time, are given in the supplementary material. Mesostructured silica of SBA-15 type was synthesized as previously described.[31]

*Synthesis of bis-silylated Rh-NHC complex **3**.*

Imidazolium salt **1** (2.32 mmol) and [Rh(μ-OEt)(COD)]$_2$ (1.17 mmol) were transferred into a Schlenk tube under nitrogen atmosphere and dissolved in anhydrous CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temperature for 15 hours (TLC monitoring). The solvent was evaporated under vacuum and the residue was treated with anhydrous hexanes until the filtrate was colorless. The combined filtrates were then concentrated under vacuum to give Rh complex **3** as an orange gum (1.33 g, 60% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 0.49 (t, $^3J_{H,H}$ = 8.2 Hz, 4H, major + minor, CH_2Si), 1.142 (t, $^3J_{H,H}$ = 7.0 Hz, 18H, major, OCH_2CH_3), 1.147 (t, $^3J_{H,H}$ = 7.0 Hz, 18H, minor, OCH_2CH_3), 1.37-1.76 (m, 16H, major + minor, $CH_2CH_2CH_2Si$, $CH_2CH_2CH_2Si$, COD-CH_2), 2.26 (s, 6H, major, CH_3), 2.30 (s, 6H, minor, CH_3), 2.30 (s, 6H, major, CH_3), 2.36 (s, 6H, minor, CH_3), 2.53 (s, 6H, minor, CH_3), 2.63 (s, 6H, major, CH_3), 3.02 (br abs, 2H, major, COD-CH), 3.32 (br abs, 2H, minor, COD-CH), 3.683 (q, $^3J_{H,H}$ = 7.0 Hz, 12H, major, OCH_2CH_3), 3.687 (q, $^3J_{H,H}$ = 7.0 Hz, 12H, minor, OCH_2CH_3), 4.01-4.09 (m, 2H, major + minor, NCH), 4.43 (br abs, 2H, major + minor, COD-CH), 6.90 (s, 2H, major, Ar), 6.93 (s, 2H, minor, Ar), 6.94 (s, 2H, minor, Ar), 7.00 (s, 2H, major, Ar). ^{13}C NMR (75MHz,

$CDCl_3$) δ (ppm): 10.6 (CH_2Si, major), 10.7 (CH_2Si, minor), 18.2 (OCH_2CH_3, major + minor), 19.1 (CH_3, major), 19.8 (CH_3, minor), 20.2 (CH_3, minor), 20.6 (CH_2, minor), 20.7 (CH_2, major), 20.9 (CH_3, major), 21.0 (CH_3, minor), 21.7 (CH_3, major), 27.9 (CH_2, major), 28.0 (CH_2, minor), 30.8 (COD-CH_2, minor), 31.2 (COD-CH_2, major), 32.5 (COD-CH_2, major), 32.7 (COD-CH_2, minor), 58.2 (OCH_2CH_3, major + minor), 65.3 (N*C*H, minor), 66.1 (N*C*H, major), 67.1 (d, $^1J_{Rh,C}$ = 14.5 Hz, COD-*C*H, major), 68.3 (d, $^1J_{Rh-C}$ = 14.0 Hz, COD-*C*H, minor), 96.5 (d, $^1J_{Rh-C}$ = 7.0 Hz, COD-*C*H, minor), 96.9 (d, $^1J_{Rh,C}$ = 6.9 Hz, COD-*C*H, major), 128.3 (*C*H-Ar, minor), 128.5 (*C*H-Ar, major), 129.9 (*C*H-Ar, minor), 130.0 (*C*H-Ar, major), 134.9 (*C*-Ar, major), 136.1 (*C*-Ar, minor), 136.1 (*C*-Ar, major), 136.5 (*C*-Ar, minor), 137.2 (*C*-Ar, major + minor), 138.2 (*C*-Ar, minor), 139.3 (*C*-Ar, major), 213.2 (d, $^1J_{Rh,C}$ = 48.0 Hz, Rh-$C_{carbene}$, minor + major). ESI-HRMS (m/z): calculated for $[C_{47}H_{78}O_6N_2RhSi_2]^+$: 925.4448; found: 925.4470.

*Synthesis of monosilylated Rh-NHC complex **4**.*

Prepared according to the method described for complex **3** with the following specific conditions: Imidazolium salt **2** (3.87 mmol), [Rh(μ-OEt)(COD)]$_2$ (1.95 mmol), anhydrous CH_2Cl_2 (25 mL), work up with anhydrous diethyl ether. Yellow solid (2.24 g, 91% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 0.77 (t, $^3J_{H,H}$ = 8.4 Hz, 2H, CH_2Si), 1.25 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, OCH_2CH_3), 1.46-1.70 (m, 2H $CH_2CH_2CH_2$ + 2H COD-CH_2), 1.82 (s, 3H, CH_3), 1.96-2.20 (m, 4H COD-CH_2 + 2H NCH_2), 2.37 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.96 (m, 1H, COD-CH_2), 3.43 (m, 1H, COD-CH_2), 3.86 (q, $^3J_{H,H}$ = 7.0 Hz, 6H, OCH_2CH_3), 4.19 (m, 1H, COD-*C*H), 4.76-4.88 (m, 2H, COD-*C*H), 5.29 (m, 1H, COD-*C*H), 6.73 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, imidazole), 6.90 (br s, 1H, Ar), 7.03 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, imidazole), 7.09 (br s, 1H, Ar). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm): 7.83 (CH_2Si), 17.7, 18.3 (OCH_2CH_3), 19.7, 21.0, 24.6, 27.9 (COD-CH_2), 29.1 (COD-CH_2), 31.5 (COD-CH_2), 34.0 (COD-CH_2), 54.0 (NCH_2), 58.5 (OCH_2CH_3), 67.4 (d, $^1J_{Rh,C}$ = 14.7 Hz, COD-*C*H), 68.3 (d, $^1J_{Rh,C}$ = 14.2 Hz, COD-*C*H), 96.7 (d, $^1J_{Rh,C}$ = 7.3 Hz, COD-*C*H), 96.9 (d, $^1J_{Rh,C}$ = 7.1 Hz, COD-*C*H), 120.9 (*C*H-imidazole), 122.8(*C*H-imidazole), 128.0 (*C*H-Ar), 129.5 (*C*H-Ar), 134.3 (*C*-Ar), 136.2 (*C*-Ar), 137.2 (*C*-Ar), 138.5 (*C*-Ar), 181.6 (d, $^1J_{Rh,C}$ = 51.5 Hz, Rh-$C_{carbene}$). ESI-HRMS (m/z): calculated for $[C_{29}H_{46}O_3N_2RhSi]^+$: 601.2327; found: 601.2333.

Preparation of materials

*Material **M1***: A mixture of TBAF (0.16 mL of 1M solution in anhydrous THF, 0.160 mmol) and doubly deionized water (milliQ) (0.745 mL, 41.3 mmol) in anhydrous DMF (3 mL) was added to a stirred solution of complex **3** (0.64 g, 0.6 mmol) and TEOS (1.70 mL, 8.57 mmol) in anhydrous DMF (10 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 minutes. A gel was formed within 1 hour and was left to age at room temperature under nitrogen atmosphere for 6 days. This gel was pulverized, filtered and washed with EtOH (3 x 10 mL), acetone (3 x 10 mL) and anhydrous Et_2O (3 x 10 mL). In order to completely remove residual DMF, the powder obtained was left in a soxhlet apparatus for 48 hours with chloroform. The powder was dried overnight at 40°C under vacuum to afford material **M1** as an orange powder (1.25 g). ^{29}Si-CP-MAS NMR (79.5 MHz) δ (ppm): -111.4 (Q^4), -101.9 (Q^3), -93.4 (Q^2), -66.2 (T^3), -56.3 (T^2). ^{13}C-CP-MAS NMR (100.6 MHz) δ (ppm): 13.3, 20.2, 30.7, 60.0, 67.9, 97.0, 98.6, 130.0, 138.5, 213.3. BET S_{BET}: 453 m^2/g; type I sorption isotherm; TGA (air, 30 to 700°C) residual mass 77.06%. EA calculated for $C_{35}H_{48}N_2ClRh{\cdot}2SiO_{1.5}{\cdot}14SiO_2$ (considering complete condensation): 1.77% N, 26.60% C, 3.06% H, 6.51% Rh; found: 1.01% N, 15.45% C, 2.65% H, 4.47% Rh.

*Material **M2***: Prepared according to the method described for material **M1** with the following specific conditions: TBAF (0.215 mL, 0.215 mmol), *milliQ* water (1.5 mL, 83.3 mmol), complex **3** (0.64 g, 0.6 mmol), TEOS (4.6 mL, 20.1 mmol). **M2** was obtained as an orange powder (1.91 g). ^{29}Si-CP-MAS NMR (79.5 MHz) δ (ppm): -110.2 (Q^4), -101.7 (Q^3), -92.5 (Q^2), -65.6 (T^3), -55.7 (T^2). BET S_{BET}: 493 m^2/g; type IV sorption isotherm; TGA (air, 30 to 700°C) residual mass 80.66%. EA calculated for $C_{35}H_{48}N_2ClRh{\cdot}2SiO_{1.5}{\cdot}30SiO_2$ (considering complete condensation): 1.10% N, 16.54% C, 1.90% H, 4.05% Rh; found: 0.83% N, 10.65% C, 2.33% H, 2.93% Rh.

*Material **M3***: Prepared according to the method described for material **M1** with the following specific conditions: TBAF (0.350 mL, 0.350 mmol), *milliQ* water (2.5 mL, 83.3 mmol), EtOH as solvent, complex **4** (0.72 g, 1.13 mmol), TEOS (7.7 mL, 33.9 mmol). **M3** was obtained as a pale-yellow powder (2.64 g). ^{29}Si-CP-MAS NMR (79.5 MHz) δ (ppm): -111.3 (Q^4), -101.8 (Q^3), -91.6 (Q^2), -65.1 (T^3). BET S_{BET}: 325 m^2/g; type II sorption isotherm; TGA (air, 30 to 700°C) residual mass 75.98%. EA calculated for $C_{23}H_{31}N_2ClRh{\cdot}SiO_{1.5}{\cdot}30SiO_2$ (considering complete condensation): 1.20% N, 11.86% C, 1.34% H, 4.42% Rh; found: 1.18% N, 12.19% C, 2.29% H, 3.15% Rh.

*Material **M4***. A mixture of complex **4** (0.21 g, 0.34 mmol) and mesostructured silica SBA-15 (1.96 g, 32.70 mmol) was transferred into a Schlenk tube equipped with a Dean-Stark apparatus in anhydrous toluene (40 mL). The reaction mixture was stirred and refluxed for 24 hours. The resulting suspension was filtered and the powder obtained was washed with EtOH (3 x 20 mL), acetone (3 x 20 mL) and anhydrous Et_2O (3 x 20 mL). The powder was dried overnight at 40°C under vacuum. **M4** was obtained as a white powder (1.76 g). BET S_{BET}: 512 m^2/g; pore diameter (BJH): 58.8 Å (desorption); type IV sorption isotherm; pore volume (BJH): 0.692 cm^3/g (desorption). TGA (air, 30 to 700°C) residual mass 84.30%. EA found: 0.55% N, 5.39% C, 1.00% H, 1.03% Rh.

General procedure for [2+2+2] cycloaddition reactions.

The reactions were carried out in a Carousel multireactor. The alkynes (0.1 mmol), the material (0.01 mmol Rh) and EtOH (3 mL) were transferred into the reaction tubes of the reactor and the reaction mixtures were stirred at 80ºC (external temperature). When there was no presence of starting material (TLC or GC monitoring), the stirring was stopped and the reaction mixture was allowed to cool down. The solution was then filtered. The recovered catalyst was washed with CH_2Cl_2 (3 x 3 mL) and Et_2O (2 x 3 mL), dried under vacuum and directly used in the next cycle. The filtrates were concentrated under reduced pressure to afford the corresponding product.

1,3,6,8-Tetrahydro-2,7-dioxa-as-indacene, ***6***.[2b] Colourless solid. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 5.03 (br s, 4H, CH_2O), 5.12 (br s, 4H, CH_2O), 7.14 (s, 2H, Ar).

2,7-Bis(p-toluenesulfonyl)-1,3,6,8-tetrahydro-2,7-diaza-as-indacene, ***8***.[30] Colourless solid. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.40 (s, 6H, CH_3), 4.45 (s, 4H, CH_2), 4.57 (s, 4H, CH_2), 7.04 (s, 2H, Ar), 7.31 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, Ts), 7.74 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, Ts).

7-(p-toluenesulfonyl)-2-oxa-7-aza-1,3,6,8-tetrahydro-as-indacene, ***10.*** Colourless solid. M.p. 142-144ºC (dec.). ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.40 (s, 3H, CH_3), 4.50 (br s, 2H, CH_2-NTs), 4.62 (br s, 2H, CH_2-NTs), 4.97 (br s, 2H, CH_2-O), 5.06 (br s, 2H, CH_2-O), 7.05-7.12 (m, 2H, *C*H-Ar), 7.31 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, Ar-Ts), 7.76 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, Ar-Ts). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm): 21.8 (CH_3-Ts), 52.6 (CH_2-NTs), 53.7 (CH_2-NTs), 72.3 (CH_2-O), 73.7 (CH_2-O), 120.7 (*C*H-Ar), 121.9 (*C*H-Ar), 127.9 (*C*H-Ts), 129.7 (*C*-Ar), 130.2 (*C*H-Ts), 133.9 (*C*-Ar), 134.0 (*C*-Ar), 135.9 (*C*-Ts), 139.5 (*C*-Ar), 144.1 (*C*-Ts). IR (ATR) ν (cm^{-1}): 2857, 1340, 1156. ESI-MS (m/z): 316 $[M + H]^+$, 338 $[M + Na]^+$, 653 $[2M + H]^+$.

ESI-HRMS (m/z): calculated for $[C_{17}H_{17}O_3NS + Na]^+$: 338.0809; found: 338.0821.

5-hydroxymethylphthalan, ***13aa***.[32] Colourless solid. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 4.69 (s, 2H, CH_2OH), 5.09 (s, 5H, CH_2O + O*H*), 7.19-7.27 (m, 3H, C*H*-Ar).

5-phenylphthalan, ***13ab***.[32] Colourless solid. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 5.17 (s, 4H, CH_2O), 7.29-7.60 (m, 8H, C*H*-Ar).

5-hydroxymethyl-2-(p-toluenesulfonyl)-1,3-dihydroisoindole, ***13ba***.[33] Colourless solid. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.39 (s, 3H, CH_3), 4.56 (s, 4H, CH_2-NTs), 4.64 (s, 2H, CH_2OH), 7.11-7.23 (m, 3H, C*H*-Ar), 7.30 (d, $^3J_{H,H}$= 8.1 Hz, 2H, Ts), 7.74 (d, $^3J_{H,H}$= 8.1 Hz, 2H, Ts).

5-phenyl-2-(p-toluenesulfonyl)-1,3-dihydroisoindole, ***13bb***.[32] Colourless solid. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.43 (s, 3H, CH_3), 4.69 (br abs, 4H, CH_2-NTs), 7.25 (d, $^3J_{H,H}$= 8.1 Hz, 1H, C*H*-Ar), 7.30-7.56 (m, 9H), 7.80 (d, $^3J_{H,H}$= 8.3 Hz, 2H, Ts).

5-hydroxymethyl-4,7-dimethylphthalan, ***13ca***.[2b] Colourless solid. ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.21 (s, 6H, CH_3), 4.69 (s, 3H, CH_2O*H*), 5.11 (s, 4H, CH_2O), 7.07 (s, 1H, C*H*-Ar).

5,6-dihydroxymethyl-4,7-dimethylphthalan, ***13cc***.[2b] Colourless solid. ^{1}H NMR (400MHz, DMSO-d_6) δ (ppm): 2.18 (s, 6H, CH_3), 4.56 (d, $^3J_{H,H}$= 5.2 Hz, 4H, CH_2OH), 4.71 (t, $^3J_{H,H}$= 5.2 Hz, 2H, O*H*), 5.01 (s, 4H, CH_2O).

Acknowledgements

Financial support from MICINN of Spain (CTQ2011-23121, CTQ2009-07881, CTQ2012-32436, CTQ2011-22649, CSD2007-00006) and "Generalitat de Catalunya" (2009SGR637, 2009SGR1441, and a predoctoral grant to M.Fernández) is acknowledged. M. Ferré thanks the Universitat Autònoma de Barcelona for a predoctoral scholarship. We would like to thank Mònica Iglesias and Enriqueta Anticó for ICP measurement and Xavier Cattoën for helpful comments.

Keywords: Rhodium • Carbenes • Supported catalysts • Sol-gel processes • Cycloadditions

[1] For a monography, see: *Transition-Metal-Mediated Aromatic Ring Construction*, (Ed.: K. Tanaka) John Wiley & Sons, Hoboken, **2013**. For recent reviews, see: a) S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901-2915; b) S. Kotha, E. Brahmachary, K. Lahiri, *Eur. J. Org. Chem.* **2005**, 4741-4767; c) Y. Yamamoto, *Curr. Org. Chem.* **2005**, *9*, 503-519; d) V. Gandon, C. Aubert, M. Malacria, *Chem. Commun.* **2006**, 2209-217; e) P.R. Chopade, J. Louie, *Adv. Synth. Catal.* **2006**, *348*, 2307-2327; f) N. Agenet, O. Buisine, F. Slowinski, V. Gandon, C. Aubert, M. Malacria, *Org. React.* **2007**, *68*, 1-291; g) B. Heller, M. Hapke, *Chem. Soc. Rev.* **2007**, *36*, 1085-1094; h) K. Tanaka, *Synlett* **2007**, 1977-1993; i) J.A. Varela, C. Saá, *Synlett* **2008**, 2571-2578; j) T. Shibata, K. Tsuchikama, *Org. Biomol. Chem* **2008**, *6*, 1317-1323; k) K. Tanaka, *Chem. Asian J.* **2009**, *4*, 508-518; l) B.R. Galan, T. Rovis, *Angew. Chem. Int. Ed.* **2009**, *48*, 2830-2834; m) S. Perreault, T. Rovis, *Chem. Soc. Rev.* **2009**, *38*, 3149-3159; n) L. Zhou, S. Li, K.-I. Kanno, T. Takahashi, *Heterocycles* **2010**, *80*, 725-738; o) A. Pla-Quintana, A. Roglans, *Molecules* **2010**, *15*, 9230-9251; p) P.A. Inglesby, P.A. Evans, *Chem. Soc. Rev.* **2010**, *39*, 2791-2805; q) M.R. Shaaban, R. El-Sayed, A.H.M. Elwahy, *Tetrahedron* **2011**, *67*, 6095-6130; r) S. Okamoto, *Heterocycles* **2012**, *85*, 1579-1602; s) K. Tanaka, *Heterocycles* **2012**, *85*, 1017-1043; t) R. Hua, M.V.A. Abrenica, P. Wang, *Curr. Org. Chem.* **2011**, *15*, 712-729; u) G. Domínguez, J. Pérez-Castells, *Chem. Soc. Rev.* **2011**, *40*, 3430-3444; w) N. Weding, M. Hapke, *Chem. Soc. Rev.* **2011**, *40*, 4525-4538; y) D.L.J. Broere, E. Ruijter, *Synthesis* **2012**, 2639-2672.

[2] a) R. Grigg, R. Scott, P. Stevenson, *Tetrahedron Lett.* **1982**, *23*, 2691-2692; b) R. Grigg, R. Scott, P. Stevenson, *J. Chem. Soc. Perkin Trans. 1* **1988**, 1357-1364.

[3] For selected and recent references, see: a) L. Garcia, A. Pla-Quintana, A. Roglans, *Org. Biol. Chem.* **2009**, *7*, 5020-5027; b) L. Severa, L. Adriaenssens, J. Vávra, D. Šaman, I. Císařová, P. Fiedler, F. Teplý, *Tetrahedron* **2010**, *66*, 3537-3552; c) S.B. Suryawanshi, M.P. Dushing, R.G. Gonnade, C.V. Ramana, *Tetrahedron* **2010**, *66*, 6085-6096; d) T. Welsch, H.-A. Tran, B. Witulski, *Org. Lett.* **2010**, *12*, 5644-5647; e) N. Saito, T. Ichimaru, Y. Sato, *Org. Lett.* **2012**, *14*, 1914-1917; f) Y. Li, J. Zhu, L. Zhang, Y. Wu, Y. Gong, *Chem. Eur. J.* **2013**, *19*, 8294-8299; g) A.-F. Tran-Van, S. Götz, M. Neuburger, H.A. Wegner, *Org. Lett.* **2014**, *16*, 2410-2413.

[4] For selected references, see: a) K. Tanaka, K. Toyoda, A. Wada, K. Shirasaka, M. Hirano, *Chem. Eur. J.* **2005**, *11*, 1145-1156; b) T. Shibata, Y.-K. Tahara, *J. Am. Chem. Soc.* **2006**, *128*, 11766-11767; c) T. Shibata, Y.-K. Tahara, K. Tamura, K. Endo, *J. Am. Chem. Soc.* **2008**, *130*, 3451-3457; d) Y. Otake, R. Tanaka, K. Tanaka, *Eur. J. Org. Chem.* **2009**, 2737-2747; e) Y. Komine, A. Kamisawa, K. Tanaka, *Org. Lett.* **2009**, *11*, 2361-2364; f) K. Tanaka, Y. Swada, Y. Aida, M. Thammathevo, R. Tanaka, H. Sagae, Y. Otake, *Tetrahedron* **2010**, *66*, 1563-1569; g) T. Shibata, M. Miyoshi, T. Uchiyama, K. Endo, N. Miura, K. Monde, *Tetrahedron* **2012**, *68*, 2679-2686; h) T. Shibata, M. Fujimoto, H. Hirashima, T. Chiba, K. Endo, *Synthesis* **2012**, 3269-3284; i) K. Murayama, Y. Sawada, K. Noguchi, K. Tanaka, *J. Org. Chem.* **2013**, *78*, 6202-6210.

[5] For selected monographs and reviews, see: a) *N-Heterocyclic Carbenes in Transition Metal Catalysis,* in: *Topics in Organometallic Chemistry,* (Ed.: F. Glorius), Springer, Heildelberg, **2007**, vol. 21; b) *N-Heterocyclic Carbenes in Synthesis,* (Ed.: S.P. Nolan), Wiley-VCH, Weinheim, **2006**; c) S. Díez-González, N. Marion, S.P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676; d) T. Dröge, F. Glorius, *Angew. Chem., Int. Ed.* **2010**, *49*, 6940-6952; e) R. Corberán, E. Mas-Marzá, E. Peris, *Eur. J. Inorg. Chem.* **2009**, 1700-1716; f) N. Imlinger, K. Wurst, M.R. Buchmeiser, *Monatsh. Chem.* **2005**, *136*, 47-57; g) V. César, S. Bellemin-Laponnaz, L.H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619-636; h) T. Weskamp, V.P.W. Böhm, W.A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12-22; i) W.A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162-2187.

[6] I. González, A. Pla-Quintana, A. Roglans, *Synlett* **2009**, 2844-2848.

[7] Selected references of the use of NHC ligands for other metals in [2+2+2] cycloaddition reactions, see: a) N. Saino, D. Kogure, S. Okamoto, *Org. Lett.* **2005**, *7*, 3065-3067; b) A. Geny, S. Gaudrel, F. Slowinski, M. Amatore, G. Chouraqui, M. Malacria, C. Aubert, V. Gandon, *Adv. Synth. Catal.* **2009**, *351*, 271-275; c) R. M. Stolley, H. A. Duong, D. R. Thomas, J. Louie, *J. Am. Chem. Soc.* **2012**, *134*, 15154-15162; d) S. Medina, G. Domínguez, J. Pérez-Castells, *Org. Lett.* **2012**, *14*, 4982-4985; e) S. K. Rodrigo, I. V. Powell, M. G. Coleman, J. A. Krause, H. Guan, *Org. Biomol. Chem* **2013**, *11*, 7653-7657.

[8] a) P. Diversi, G. Ingrosso, A. Lucherini, A. Minutillo, *J. Mol. Catal.* **1987**, *40*, 359-377; b) P. Perkins, K.P.C. Vollhardt, *J. Am. Chem. Soc.* **1979**, 101, 3985-3987.

[9] a) V. Conte, E. Elakkari, B. Floris, V. Mirruzzo, P. Tagliatesta, *Chem. Commun.* **2005**, 1587-1588; b) I. González, S. Bouquillon, A. Roglans, J. Muzart, *Tetrahedron Lett.* **2007**, *48*, 6425-6428; c) Y.-Y. Lin, S.-C. Tsai, S.J. Yu, *J. Org. Chem.* **2008**, *73*, 4920-4928.

[10] Y.-H. Wang, S.-H. Huang, T.-C. Lin, F.-Y. Tsai, *Tetrahedron* **2010**, *66*, 7136-7141.

[11] L. García, A. Roglans, R. Laurent, J.-P. Majoral, A. Pla-Quintana, A. M. Caminade, C*hem. Commun*. **2012**, *48*, 9248-9250.

[12] a) I. Thiel, A. Spannenberg, M. Hapke, *ChemCatChem* **2013**, 2865-2868; b) A. Geny, N. Agenet, L. Iannazzo, M. Malacria, C. Aubert, V. Gandon, *Angew. Chem. Int. Ed.* **2009**, *48*, 1810-1813.

[13] a) A. Corma, H. García, *Adv. Synth. Catal.* **2006**, *348*, 1391-1412; b) A. Zamboulis, N. Moitra, J. J. E. Moreau, X. Cattoën, M. Wong Chi Man, *J. Mater. Chem*. **2010**, *20*, 9322-9338; c) A. Monge-Marcet, R. Pleixats, X. Cattoën, M. Wong Chi Man, *Catal. Sci. Technol*. **2011**, *1*, 1544-1563.

[14] C. J. Brinker, G. W. Scherrer, *Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, **1990**.

[15] K. J. Shea, J. J. E. Moreau, D. Loy, R. J. P. Corriu, B. Boury, *in Functional Hybrid Materials*, ed. P. Gómez-Romero and C. Sanchez, Wiley-VCH, Weinheim, **2004**, pp. 50-8.

[16] a) Q. Yang, J. Liu, L. Zhang, C. Li, *J. Mater. Chem*. **2009**, *19*, 1945-1955; b) C. Sanchez, P. Belleville, M. Popall, L. Nicole, *Chem. Soc. Rev*. **2011**, *40*, 696-753; c) R. Ciriminna, A. Fidalgo, V. Pandarus, F. Béland, L. M. Ilharco, M. Pagliaro, *Chem. Rev*. **2013**, *113*, 6592-6620.

[17] a) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* **2006**, *45*, 3216-3251; b) J. H. Clark, D. J. Macquarrie, S. J. Tavener, *Dalton Trans* **2006**, 4297-4309; c) D. J. Macquarrie, *Top. Catal.* **2009**, *52*, 1640-1650; d) A. Mehdi, C. Reye, R. Corriu, *Chem. Soc. Rev.* **2011**, *40*, 563-574.

[18] Y.-S. Fu, S.J. Yu, *Angew. Chem. Int. Ed.* **2001**, *40*, 437-440.

[19] S. Reinhard, P. Soba, F. Rominger, J. Blümel, *Adv. Synth. Catal.* **2003**, *345*, 589-602.

[20] I. Thiel, M. Hapke, *J. Mol. Cat. A: Chem.* **2014**, *383-384*, 153-158.

[21] For examples of Rh(I)-NHC complexes functionalized with an alkyloxysilyl tail group, further immobilization on silica-based inorganic supports and their applications in catalytic hydrogenation and hydrosilylation, see: a) P. Li, W.A. Herrmann, F.E. Kühn, *ChemCatChem* **2013**, *5*, 3324-3329; b) G. Lázaro, F.J. Fernández-Alvarez, M. Iglesias, C. Horna, E. Vispe, R. Sancho, F.J. Lahoz, M. Iglesias, J.J. Pérez-Torrente, L.A. Oro, *Catal. Sci. Technol.,* **2014**, *4*, 62-70.

[22] A. Monge-Marcet, R. Pleixats, X. Cattoën, M. Wong Chi Man, *J. Mol. Catal. A: Chemical* **2012**, 357, 59-66.

[23] G. Borja, A. Monge-Marcet, R. Pleixats, T. Parella, X. Cattoën, M. Wong Chi Man, *Eur. J. Org. Chem.* **2012**, 3625-3635.

[24] S. Dastgir, K.S. Coleman, M.L.H. Green, *Dalton Trans.* **2011**, *40*, 661-672.

[25] I. Peñafiel, I.M. Pastor, M. Yus, M.A. Esteruelas, M. Oliván, *Organometallics* **2012**, *31*, 6154-6161.

[26] K. Weigl, K. Köhler, S. Dechert, F. Meyer, *Organometallics* **2005**, *24*, 4049-4056.

[27] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem*. **1985**, *57*, 603-619.

[28] a) M. Larhed, C. Möberg, A. Hallberg, *Acc. Chem. Res*. **2002**, *35*, 717-727; b) C. O. Kappe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6250-6284; c) V. Polshettiwar, R. S. Varma, *Acc. Chem. Res*. **2008**, *41*, 629-639; d) B. K. Singh,N. Kaval, S. Tomar, E. Van der Eycken, V. S. Parma, *Org. Process Res. Dev*. **2008**, *12*, 468-474.

[29] a) R. Usón, L.A. Oro, J.A. Cabeza, *Inorg. Synth.* **1985**, *23*, pp 126; b) L.M. Green, D.W. Meek, *Organometallics* **1989**, *8*, 659-666.

[30] I. Ojima, A.T. Vu, J.V. McCullagh, A. Kinoshita, *J. Am. Chem. Soc.* **1999**, *121*, 3230-3231.

[31] J. S. Lettow, Y. J. Han, P. Schmidt-Winkel, P. Yang, D. Zhao, G. D. Stucky, J. Y. Ying, *Langmuir* **2000**, *16*, 8291-8295.

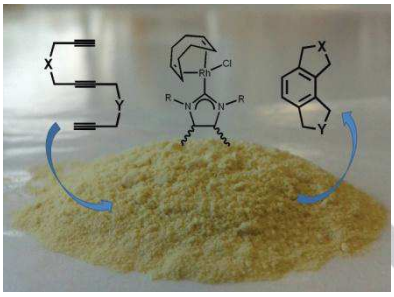
[32] S. Brun, M. Parera, A. Pla-Quintana, A. Roglans, T. León, T. Achard, J. Solà, X. Verdaguer, A. Riera, *Tetrahedron* **2010**, *66*, 9032-9040.

[33] H. Kinoshita, H. Shinokubo, K. Oshima, *J. Am. Chem. Soc.* **2003**, *125*, 7784-7785.

Entry for the Table of Contents

FULL PAPER

Hybrid silica materials derived from rhodium(I) complexes bearing an *N*-heterocyclic carbene ligand are obtained either by sol-gel or grafting processes. The materials are fully characterized by solid state NMR, N_2-sorption measurements, thermogravimetric analysis and elemental analysis. Their catalytic activity and recyclability are evaluated in the [2+2+2] cycloaddition of alkynes.



Martí Fernández, Meritxell Ferré, Anna Pla-Quintana, Teodor Parella, Roser Pleixats, Anna Roglans**

Page No. – Page No.

Rhodium-NHC Hybrid Silica Materials as Recyclable Catalysts for [2+2+2] Cycloaddition Reactions of Alkynes