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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]}

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Bis-silylated dihydroimidazolium salt **1** and monosilylated imidazolium salt **2** are transformed to (NHC)RhCl(COD) complexes **3** and **4**, allowing the preparation of hybrid silica materials either by sol-gel or grafting processes. Full characterization of the materials by means of solid state NMR, N₂sorption measurements, thermogravimetric analysis (TGA)

Introduction

The transition-metal catalyzed [2+2+2] cycloaddition reaction of unsaturated substrates is a very simple and atomeconomic 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 rhodiumcatalyzed [2+2+2] cycloaddition of three alkynes to afford highly substituted and/or annulated benzenes, two catalytic systems have proven 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. This latter system 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 leading to catalyst deactivation and complicated product purifications, other stabilizing ligands, such as *N*-heterocyclic carbenes (NHC), are increasingly used as alternatives for stabilizing transition-metal catalysts.^[5] Furthermore, this type of ligand can have a dramatic influence on both and elemental analysis was followed by evaluation of catalytic activity 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 simple filtration to recover the catalyst. Both conventional and microwave heating prove effective for the process described.

reactivity and selectivity. Rh-NHC complexes have only been described by our group as efficient catalysts for intraand 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 shown to be efficient catalysts in [2+2+2] cycloaddition reactions by other groups.^[7]

The recovery and reuse of the catalytic system, especially when 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 solgel hydrolytic condensation of organoalkoxysilanes^[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]

 [[]a] Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain E-mail: anna.roglans@udg.edu http://iqcc.udg.edu

[[]b] 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 http://www.uab.cat/departament/química

[[]c] Servei de RMN, Universitat Autônoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Catalonia, Spain

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immobilized a Pd^{II} complex with a bidentate bipyridyl ligand on a range of polysiloxanes with controllable solubility, affording materials that proved to be efficient and recyclable catalysts in [2+2+2] cyclotrimerization of alkynes. Blümel et al.^[19] described the use of carbonyl nickel(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 onto a silica support through a siloxane linker at the Cp-moiety. The heterogeneous cobalt catalyst showed moderate activity in the cycloaddition of 1,6-heptadiyne with benzonitrile to afford a pyridine derivative. However, the catalytic system was found to undergo inactivation upon recycling.

Given our interest in the use of Rh-NHC complexes for the [2+2+2] cycloaddition reaction, we sought to immobilize Rh-NHC complexes onto silica materials. In this study imidazolium salts conveniently functionalized with trialkoxysilyl groups either in the carbon backbone or in the nitrogen atom were complexed with Rh and incorporated into hybrid silica materials either by a sol-gel or a grafting process. A few hybrid silica-based Rh-NHC materials have been previously synthesized and shown to be efficient catalysts in Rh-catalyzed reactions.^[21] However, to the best of our knowledge, these systems have not been reported as catalysts for [2+2+2] cycloadditions, the aim of the present work.

Results and Discussion

Synthesis and Characterization of Rh-NHC

In the last few years, we have made a number of advances in the area of recyclable catalysts based on hybrid silica materials. We have described a silica-supported Hoveyda-Grubbs' type complex in which the NHC ligand played a key tethering role by performing a sol-gel co-gelification process of a silvlated NHC-Ru monomer with tetraethoxysilane (TEOS). The new material proved to be an efficient recyclable catalyst for ring-closing metathesis reactions.^[22] Furthermore, sol-gel co-condensation of a silvlated 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 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 silvlated 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 treatment of the imidazolium salt with Ag₂O to afford the NHC-Ag^I complex followed by transmetallation with [Rh(μ -Cl)(COD)]₂. However, in our case, only decomposition to elemental silver and the recovery of 1 were observed.



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

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

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

Both complexes 3 and 4 were fully characterized by ESI-HRMS, ¹H and ¹³C-NMR spectroscopy. ESI-HRMS spectra of complex 3 showed a peak at m/z = 925.4470, corresponding to [M - Cl]⁺. The same behaviour was observed for complex 4, which showed a peak at m/z = 601.233, corresponding to the same chloride loss observed with 3. As a result of hindered rotation around the carbene carbonrhodium bond, two different sets of signals in a 4:1 ratio are observed in the ¹H and ¹³C NMR spectra of complex 3. Six different signals corresponding to the methyl groups in the aromatic ring can be seen in the ¹H-NMR spectrum: the major isomer presented three signals at $\delta = 2.26, 2.30$ and 2.63 ppm whereas the signals corresponding to the minor isomer appeared at δ = 2.29, 2.36, and 2.52 ppm. The ¹³C-NMR spectrum displays two sets of doublets at δ = 67.1 ppm ($J_{\text{Rh-C}}$ = 14.5 Hz, major isomer) and 68.3 ppm $(J_{\text{Rh-C}} = 14.0 \text{ Hz}, \text{ minor isomer})$, corresponding to the methylene carbons of the COD ligand, and at δ = 96.8 ppm $(J_{\rm Rh-C} = 6.9 \, \text{Hz}, \text{ major isomer})$ and 96.5 ppm $(J_{\rm Rh-C} =$ 7.0 Hz, minor isomer), corresponding to the olefinic carbons of the COD ligand. The carbone carbon atom of the

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NHC ligand coordinated to Rh appears as a doublet at δ = 213.2 ppm with a coupling constant of J_{Rh-C} = 48.0 Hz. High-temperature ¹H-NMR experiments at temperatures up to 95 °C 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-dihydroimid-azolium chloride, which, in our case, is a precursor to 1 (see Supporting Information). In this study, the authors also found that no dynamic process was observed by variable-temperature ¹H NMR experiments at temperatures up to 70 °C.

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 hydrolysis when subjected to air, 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 in a 4:1 isomer ratio. The square planar rhodium complexes feature the carbene ligand in a perpendicular orientation relative 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 whereas in the minor isomer they point to the COD ligand (Figure 1). 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. We expect the same type of structures to be formed for complex 3.



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

In the ¹H-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 CH₂ unit of the silylated chain and protons of the cyclooctadiene ligand. The CH₂ group next to the Si atom appeared at $\delta = 0.77$ ppm as a triplet. In the ¹³C NMR spectrum, two doublets at $\delta = 96.7$ 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 $\delta = 67.4$ 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 carbone carbon atom of the NHC ligand coordinated to Rh appeared at $\delta = 181.6$ 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 co-gelification with different amounts of tetraethoxysilane (molar ratios of **3**/TEOS of 1:14 and 1:30, respectively). The reactions were performed under an atmosphere of N_2 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 an N_2 atmosphere. The solids were then filtered and 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 orange powders (Scheme 2).



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

Using complex 4, two different materials were also prepared using two different methodologies. Whereas hybrid silica M3 was prepared by co-gelification with tetraethoxysilane (molar ratio 1:30), as described previously for complex 3, material M4 was obtained by grafting to the mesostructured silica SBA-15 under standard conditions (in refluxing anhydrous toluene under N_2 atmosphere for 24 h) (Scheme 3).



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

The materials were characterized by solid state ²⁹Si NMR and ¹³C NMR (only for M1), N₂-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 found in the 250–500 °C range, assigned to the decomposition of the organometallic constituent. We obtained a molar ratio Rh/

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

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 during the formation of materials by the solgel process. The covalent incorporation of the organosilane into the hybrid materials was ascertained by ²⁹Si CP MAS solid-state NMR spectroscopy. The ²⁹Si 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 ²⁹Si solid-state NMR of M1 (Figure 2, a). Only the solid-state ¹³C NMR of M1 was performed (Figure 2, b). Significant absorptions appeared at $\delta = 13.3$ ppm (CH₂-Si), confirming the covalency of the ligand to silica association, and at $\delta = 213.3$ 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 ¹³C solid-state NMR spectroscopy. N₂-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. Functionalized mesostructured silica M4 prepared by grafting exhibited the highest surface area, with a rather sharp pore size distribution centered at around 59 Å and a type IV isotherm typical for mesoporous materials (Figure 3). Powder X-ray diffraction of M4 confirmed that the original 2D hexagonal mesostructure of the parent silica

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



Figure 2. Solid state NMR spectra for M1.



Figure 3. N₂ adsorption-desorption isotherm and pore volume distribution of M4.

had not been affected by the grafting (see Supporting Information). However, the BET surface area decreased significantly from 732 m²g⁻¹ for parent SBA-15-type silica to 512 m²g⁻¹ for **M4**, in a clear indication that 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, **M1** was found to be a microporous solid (type I isotherm), whereas **M2** exhibited a type IV isotherm and the mesoporous material **M3** presented a type II isotherm according to IUPAC rules.^[27] In the case of **M3**, the large amount of nitrogen adsorbed at $p/p^0 > 0.8$ appears to arise from nitrogen that condenses in the voids between particles (see Supporting Information).

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 reactions of alkynes and their amenabilities to recovery and reuse were evaluated.

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





First, the catalyst loading was set at 10 mol-% and 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

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

Entry	Solvent	Temp. [°C]	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 ¹H-NMR spectroscopy.

(Table 2, Entries 1-3). When the reaction temperature was increased to 80 °C for all solvents, the reactions were completed after 3-5 hours (Table 2, Entries 4, 6, 8). It can be seen that ethanol was clearly the best solvent as cyclized product 6 was obtained in almost quantitative yield (Table 2, Entry 8). 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 for 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 longer reaction times were needed (Table 2, Entries 8-11). Reusability was also tested using DCE and toluene as reaction solvents. However, the reaction yield dropped in the second cycle (Table 2, Entries 5, 7). When catalyst loading was reduced to 5 mol-% under the same conditions as shown in Entry 8 [(EtOH, 80 °C) (Table 2, Entry 8)], incomplete conversion was observed even after 30 hours of reaction. Consequently, we decided to use EtOH as the solvent at 80 °C and 10 mol-% of catalyst for further studies with the other supported catalysts (Table 3).

When the other materials were tested in the cycloaddition reaction of triyne 5, M1 gave the lowest yield (Table 3, Entry 1) whereas M3 and M4 showed similar ac-

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 80 °C. [b] Isolated yield. [c] Yield calculated by ¹H-NMR spectroscopy.

tivities (Table 3, Entries 2, 3). The recyclability of **M4** was then assessed. Material **M4** was reused successfully for 6 cycles, although longer reaction times were required upon recycling to achieve full conversions (Table 3, Entries 3–8).

The extent of 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 losses of 5.7% for M1, 12.2% for M2, 8.4% for M3 and 12.15% for M4 were found with respect to the initial amount of rhodium added as catalyst. In the case of 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 trivne 5. Catalyst M4 was filtered off from the hot reaction mixture under the conditions detailed in Table 3 after 4 min of reaction (17% GC conversion of 5) and the remaining filtrate was made to react under the same conditions. After 2.5 h, the conversion, as determined by GC analysis, increased to 56% suggesting a role for a homogeneous pathway in addition to the M4catalyzed reaction. We hypothesize that homogeneous Rh species released from the immobilized rhodium system are, at least in part, responsible for catalytic generation of 6from 5.

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

For both substrates 7 and 9, M4 proved to have high activity and good recyclability. Almost quantitative yields of 8 and 10 were obtained, respectively, in five successive cycles (Table 4, Entries 1–5 for 7 and Entries 6–10 for 9), although reaction times did require substantial increases after the first run.

In order to shorten the reaction times, especially after the first cycle, we carried out cycloadditions under microwave irradiation conditions. The application of microwaves 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 80 °C (Table 5).

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 80 °C. [b] Isolated yield. [c] Yield calculated by ¹H-NMR spectroscopy.

Table 5. Catalytic performance of hybrid silica material M4 under

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	M4 (10 mol-% Rh) ► EtOH, 80 °C (MW)	
Cycle	 eaction time [min]	Yield of 6 [%] ^[a]
1	15	77
2	45	84
3	80	88
4	120	80

[a] Isolated yield.

microwave irradiation.

As shown in Table 5 microwave heating efficiently promoted the cycloaddition reaction of triyne **5** giving excellent yields of **6** in significantly shorter reaction times relative to conventional heating. For instance, when comparing Entry 6 of Table 3 with Entry 4 of Table 5, we observe that the reaction time for cycle four is reduced from 1 day to just 120 min. In contrast, 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 (Table 6, Entries 1–4) and non-terminal (Table 6, Entries 5, 6) diynes with different tethers were active in this process. However, the use of non-terminal diynes made it necessary to heat the reaction to 110 °C using *n*BuOH as the solvent. Non-terminal diynes are clearly less reactive than terminal diynes under these reaction conditions. Both mono- and disubstituted alkynes **12** gave desired cycloadducts in good yields. In addition, the reusability of **M4** was assessed in the Entry 1 reaction (Table 6, Entry 1); cycloadduct **13aa** was generated in 85% yield after 4.5 h.

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

x	^{——} R ₁ + ——R ₁ +	R ₂ M4 (10 mol-9 EtOH, 80 °	$\frac{6 \text{ Rh}}{C} \times 1$	R_1 R_2 R_3 R_1 R_3
Entry	11 (X, R ¹)	12 (R ² , R ₃)	Reaction time [h]	Yield of 13 $[\%]^{[a]}$
1	11a (O, H) 11a (O, H)	12a (CH ₂ OH, H) 12a (CH ₂ OH, H)	2 4.5	13aa (100) 13aa (85) ^[b]
2	11a (O, H)	12b (Ph, H)	1	13ab (50)
3	11b (NTs, H)	12a (CH ₂ OH, H)	3	13ba (100)
4	11b (NTs, H)	12b (Ph, H)	5	13bb (72)
5 ^[c]	11c (O, CH ₃)	12a (CH ₂ OH, H)	2.5	13ca (100)
6 ^[c]	11c (O, CH ₃)	12c (CH ₂ OH, CH ₂ OH)	5	13cc (71) ^[d]

[a] Isolated yield. [b] Second round of catalyst use. [c] Reaction run in *n*BuOH at 110 °C. [d] Yield calculated by ¹H-NMR spectroscopy.

Conclusions

Rhodium(I) complexes bearing an N-heterocyclic carbene ligand functionalized with either two silvlated groups at the saturated carbon backbone (complex 3) or one silvlated group at the nitrogen (complex 4) were synthesized by reacting the corresponding imidazolium salts with [Rh(u-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 onto mesostructured silica SBA-15 giving material M4. The materials obtained were fully characterized with the standard solid state techniques, making it possible to verify that the structure of the catalytic site was maintained in the solid. Furthermore, the rhodium content of the materials was determined by ICP. Catalytic activities of the new materials were evaluated in [2+2+2] cycloaddition reactions of trivne substrates, which afforded tricvclic polysubstituted benzene derivatives. After screening the reaction conditions, ethanol at 80 °C 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 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. Cycloadducts were obtained in good purity after simple filtration of the catalyst and evaporation of the solvent.

Experimental Section

General: Imidazolium chlorides 1 (see Supporting Information) and $2^{[23]}$ were prepared as described previously. [Rh(μ -OEt)-(COD)]₂,^[29] triynes 5^[2b] and 7^[30] were prepared by published meth-

ods. Details for the synthesis of triyne **9**, performed here for the first time, are given in the Supporting Information. SBA-15-type mesostructured silica was synthesized as described previously.^[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 N2 atmosphere and dissolved in anhydrous CH₂Cl₂ (50 mL). The reaction mixture was stirred at room temperature for 15 h (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). ¹H NMR (400 MHz, CDCl₃): δ = 0.49 (t, ${}^{3}J_{H,H}$ = 8.2 Hz, 4 H, major + minor, CH₂Si), 1.142 (t, ${}^{3}J_{H,H}$ = 7.0 Hz, 18 H, major, OCH₂CH₃), 1.147 (t, ${}^{3}J_{H,H}$ = 7.0 Hz, 18 H, minor, OCH₂CH₃), 1.37-1.76 (m, 16 H, major + minor, CH₂CH₂CH₂Si, CH₂CH₂CH₂Si, COD-CH₂), 2.26 (s, 6 H, major, CH₃), 2.30 (s, 6 H, minor, CH₃), 2.30 (s, 6 H, major, CH₃), 2.36 (s, 6 H, minor, CH_3), 2.53 (s, 6 H, minor, CH_3), 2.63 (s, 6 H, major, CH₃), 3.02 (br. signal, 2 H, major, COD-CH), 3.32 (br. signal, 2 H, minor, COD-CH), 3.683 (q, ${}^{3}J_{H,H} = 7.0$ Hz, 12 H, major, OCH_2CH_3), 3.687 (q, ${}^{3}J_{H,H}$ = 7.0 Hz, 12 H, minor, OCH_2CH_3), 4.01-4.09 (m, 2 H, major + minor, NCH), 4.43 (br. signal, 2 H, major + minor, COD-CH), 6.90 (s, 2 H, major, Ar), 6.93 (s, 2 H, minor, Ar), 6.94 (s, 2 H, minor, Ar), 7.00 (s, 2 H, major, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 10.6 (*C*H₂Si, major), 10.7 (*C*H₂Si, minor), 18.2 (OCH₂CH₃, major + minor), 19.1 (CH₃, major), 19.8 (CH₃, minor), 20.2 (CH₃, minor), 20.6 (CH₂, minor), 20.7 (CH₂, major), 20.9 (CH₃, major), 21.0 (CH₃, minor), 21.7 (CH₃, major), 27.9 (CH₂, major), 28.0 (CH₂, minor), 30.8 (COD-CH₂, minor), 31.2 (COD-CH₂, major), 32.5 (COD-CH₂, major), 32.7 (COD-CH2, minor), 58.2 (OCH2CH3, major + minor), 65.3 (NCH, minor), 66.1 (NCH, major), 67.1 (d, ¹J_{Rh,C} = 14.5 Hz, COD-CH, major), 68.3 (d, ¹J_{Rh-C} = 14.0 Hz, COD-CH, minor), 96.5 (d, ${}^{1}J_{\text{Rh-C}} = 7.0 \text{ Hz}, \text{ COD-}C\text{H}, \text{ minor}), 96.9 (d, {}^{1}J_{\text{Rh,C}} = 6.9 \text{ Hz}, \text{ COD-}C\text{H}, \text{ minor})$ CH, major), 128.3 (CH-Ar, minor), 128.5 (CH-Ar, major), 129.9 (CH-Ar, minor), 130.0 (CH-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, ${}^{1}J_{Rh,C}$ = 48.0 Hz, Rh- $C_{carbene}$, minor + major) ppm. ESI-HRMS (m/z): calculated for [C47H78O6N2RhSi2]+: 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(u-OEt)-(COD)]₂ (1.95 mmol), anhydrous CH₂Cl₂ (25 mL), work up with anhydrous diethyl ether. Yellow solid (2.24 g, 91% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.77$ (t, ${}^{3}J_{H,H} = 8.4$ Hz, 2 H, CH₂Si), 1.25 (t, ${}^{3}J_{H,H} = 7.0 \text{ Hz}$, 9 H, OCH₂CH₃), 1.46–1.70 (m, 2 H, CH₂CH₂CH₂ + 2 H, COD-CH₂), 1.82 (s, 3 H, CH₃), 1.96-2.20 (m, 4 H, COD-CH₂ + 2 H, NCH₂), 2.37 (s, 3 H, CH₃), 2.43 (s, 3 H, CH₃), 2.96 (m, 1 H, COD-CH₂), 3.43 (m, 1 H, COD-CH₂), 3.86 $(q, {}^{3}J_{H,H} = 7.0 \text{ Hz}, 6 \text{ H}, \text{ OC}H_2\text{CH}_3), 4.19 \text{ (m, 1 H, COD-CH)},$ 4.76-4.88 (m, 2 H, COD-CH), 5.29 (m, 1 H, COD-CH), 6.73 (d, ${}^{3}J_{H,H}$ = 1.8 Hz, 1 H, imidazole), 6.90 (br. s, 1 H, Ar), 7.03 (d, ${}^{3}J_{H,H}$ = 1.8 Hz, 1 H, imidazole), 7.09 (br. s, 1 H, Ar) ppm. ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3): \delta = 7.83 (CH_2Si), 17.7, 18.3 (OCH_2CH_3), 19.7,$ 21.0, 24.6, 27.9 (COD-CH₂), 29.1 (COD-CH₂), 31.5 (COD-CH₂), 34.0 (COD-CH₂), 54.0 (NCH₂), 58.5 (OCH₂CH₃), 67.4 (d, ¹J_{Rh,C} = 14.7 Hz, COD-CH), 68.3 (d, ${}^{1}J_{Rh,C}$ = 14.2 Hz, COD-CH), 96.7 (d, ${}^{1}J_{Rh,C}$ = 7.3 Hz, COD-CH), 96.9 (d, ${}^{1}J_{Rh,C}$ = 7.1 Hz, COD-CH), 120.9 (CH-imidazole), 122.8 (CH-imidazole), 128.0 (CH-Ar), 129.5 (CH-Ar), 134.3 (C-Ar), 136.2 (C-Ar), 137.2 (C-Ar), 138.5 (C-Ar), 181.6 (d, ${}^{1}J_{\text{Rh,C}}$ = 51.5 Hz, Rh- C_{carbene}) ppm. 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 1 M 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 N₂ atmosphere. The reaction mixture was stirred at room temperature for 5 min. A gel was formed within 1 h and was left to age at room temperature under N₂ atmosphere for 6 days. This gel was pulverized, filtered and washed with EtOH ($3 \times 10 \text{ mL}$), acetone ($3 \times$ 10 mL) and anhydrous Et_2O (3 × 10 mL). In order to completely remove residual DMF, the powder obtained was left in a soxhlet apparatus for 48 h with chloroform. The powder was dried overnight at 40 °C under vacuum to afford material M1 as an orange powder (1.25 g). ²⁹Si-CP-MAS NMR (79.5 MHz): $\delta = -111.4$ (Q⁴), -101.9 (Q³), -93.4 (Q²), -66.2 (T³), -56.3 (T²) ppm. ¹³C-CP-MAS NMR (100.6 MHz): $\delta = 13.3, 20.2, 30.7, 60.0, 67.9, 97.0, 98.6,$ 130.0, 138.5, 213.3 ppm. BET S_{BET}: 453 m²/g; type I sorption isotherm; TGA (air, 30 to 700 °C) residual mass 77.06%. EA calculated for C35H48N2ClRh·2SiO15·14SiO2 (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). ²⁹Si-CP-MAS NMR (79.5 MHz): $\delta = -110.2 \text{ (Q}^4)$, $-101.7 \text{ (Q}^3)$, $-92.5 \text{ (Q}^2)$, $-65.6 \text{ (T}^3)$, $-55.7 \text{ (T}^2)$ ppm. BET S_{BET}: 493 m²/g; type IV sorption isotherm; TGA (air, 30 to 700 °C) residual mass 80.66%. EA calculated for C₃₅H₄₈N₂ClRh·2SiO_{1.5}·30SiO₂ (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). ²⁹Si-CP-MAS NMR (79.5 MHz): $\delta = -111.3$ (Q⁴), -101.8 (Q³), -91.6 (Q²), -65.1 (T³) ppm. BET S_{BET}: 325 m²/g; type II sorption isotherm; TGA (air, 30 to 700 °C) residual mass 75.98%. EA calculated for C₂₃H₃₁N₂ClRh·SiO_{1.5}·30SiO₂ (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 h. The resulting suspension was filtered and the powder obtained was washed with EtOH (3×20 mL), acetone (3×20 mL) and anhydrous Et₂O (3×20 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 m²/g; pore diameter (BJH): 58.8 Å (desorption); type IV sorption isotherm; pore volume (BJH): 0.692 cm³/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 80 °C (external temperature). When there was no presence of starting material (TLC or GC monitoring), the stirring was stopped and the reaction mixture was cooled down. The solution was then filtered. The recovered catalyst was washed with CH_2Cl_2 (3 × 3 mL) and Et_2O (2 × 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. ¹H NMR (400 MHz, CDCl₃): δ = 5.03 (br. s, 4 H, CH₂O), 5.12 (br. s, 4 H, CH₂O), 7.14 (s, 2 H, Ar) ppm.

2,7-Bis(*p*-tolylsulfonyl)-1,3,6,8-tetrahydro-2,7-diaza-*as*-indacene (8):^[30] Colourless solid. ¹H NMR (300 MHz, CDCl₃): δ = 2.40 (s, 6 H, *CH*₃), 4.45 (s, 4 H, *CH*₂), 4.57 (s, 4 H, *CH*₂), 7.04 (s, 2 H, Ar), 7.31 [d, ³*J*(H,H) = 8.0 Hz, 4 H, Ts], 7.74 (d, ³*J*_{H,H} = 8.0 Hz, 4 H, Ts) ppm.

7-(*p***-Tolylsulfonyl)-2-oxa-7-aza-1,3,6,8-tetrahydro-***as***-indacene (10): Colourless solid, m.p. 142–144 °C (dec.). ¹H NMR (300 MHz, CDCl₃): \delta = 2.40 (s, 3 H, CH₃), 4.50 (br. s, 2 H, CH₂-NTs), 4.62 (br. s, 2 H, CH₂-NTs), 4.97 (br. s, 2 H, CH₂-Q), 5.06 (br. s, 2 H, CH₂-Q), 7.05–7.12 (m, 2 H, CH-Ar), 7.31 (d, ³J_{H,H} = 8.1 Hz, 2 H, Ar-Ts), 7.76 (d, ³J_{H,H} = 8.1 Hz, 2 H, Ar-Ts) ppm. ¹³C NMR (75 MHz, CDCl₃): \delta = 21.8 (CH₃-Ts), 52.6 (CH₂-NTs), 53.7 (CH₂-NTs), 72.3 (CH₂-Q), 73.7 (CH₂-Q), 120.7 (CH-Ar), 121.9 (CH-Ar), 127.9 (CH-Ts), 129.7 (C-Ar), 130.2 (CH-Ts), 133.9 (C-Ar), 134.0 (C-Ar), 135.9 (C-Ts), 139.5 (C-Ar), 144.1 (C-Ts) ppm. IR (ATR): \tilde{v} = 2857, 1340, 1156 cm⁻¹. ESI-MS (***m***/***z***): 316 [M + H]⁺, 338 [M + Na]⁺, 653 [2M + H]⁺. ESI-HRMS (***m***/***z***): calculated for [C₁₇H₁₇O₃NS + Na]⁺: 338.0809, found 338.0821.**

5-Hydroxymethylphthalan (13aa):^[32] Colourless solid. ¹H NMR (300 MHz, CDCl₃): δ = 4.69 (s, 2 H, CH₂OH), 5.09 (s, 5 H, CH₂O + OH), 7.19–7.27 (m, 3 H, CH-Ar) ppm.

5-Phenylphthalan (13ab):^[32] Colourless solid. ¹H NMR (300 MHz, CDCl₃): δ = 5.17 (s, 4 H, CH₂O), 7.29–7.60 (m, 8 H, CH-Ar) ppm.

5-Hydroxymethyl-2-(*p***-tolylsulfonyl)-1,3-dihydroisoindole** (13ba):^[33] Colourless solid. ¹H NMR (300 MHz, CDCl₃): δ = 2.39 (s, 3 H, CH₃), 4.56 (s, 4 H, CH₂-NTs), 4.64 (s, 2 H, CH₂OH), 7.11–7.23 (m, 3 H, CH-Ar), 7.30 (d, ³J_{H,H} = 8.1 Hz, 2 H, Ts), 7.74 (d, ³J_{H,H} = 8.1 Hz, 2 H, Ts) ppm.

5-Phenyl-2-(*p*-tolylsulfonyl)-1,3-dihydroisoindole (13bb):^[32] Colourless solid. ¹H NMR (300 MHz, CDCl₃): δ = 2.43 (s, 3 H, *CH*₃), 4.69 (br. signal, 4 H, *CH*₂-NTs), 7.25 (d, ³*J*_{H,H} = 8.1 Hz, 1 H, *CH*-Ar), 7.30–7.56 (m, 9 H), 7.80 (d, ³*J*_{H,H} = 8.3 Hz, 2 H, Ts) ppm.

5-Hydroxymethyl-4,7-dimethylphthalan (13ca):^[2b] Colourless solid. ¹H NMR (300 MHz, CDCl₃): δ = 2.21 (s, 6 H, CH₃), 4.69 (s, 3 H, CH₂OH), 5.11 (s, 4 H, CH₂O), 7.07 (s, 1 H, CH-Ar) ppm.

5,6-Dihydroxymethyl-4,7-dimethylphthalan (13cc):^[2b] Colourless solid. ¹H NMR (400 MHz, [D₆]DMSO): δ = 2.18 (s, 6 H, *CH*₃), 4.56 (d, ³*J*_{H,H} = 5.2 Hz, 4 H, *CH*₂OH), 4.71 (t, ³*J*_{H,H} = 5.2 Hz, 2 H, *OH*), 5.01 (s, 4 H, *CH*₂O) ppm.

Supporting Information (see footnote on the first page of this article): Experimental procedures for the synthesis of 1, 3-allyl and 9; NMR spectra for all of the products synthesized; characterization of materials M1–M4.

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