PAPER

Gold nanoparticle-catalysed functionalization of carbon-hydrogen bonds by carbene transfer reactions

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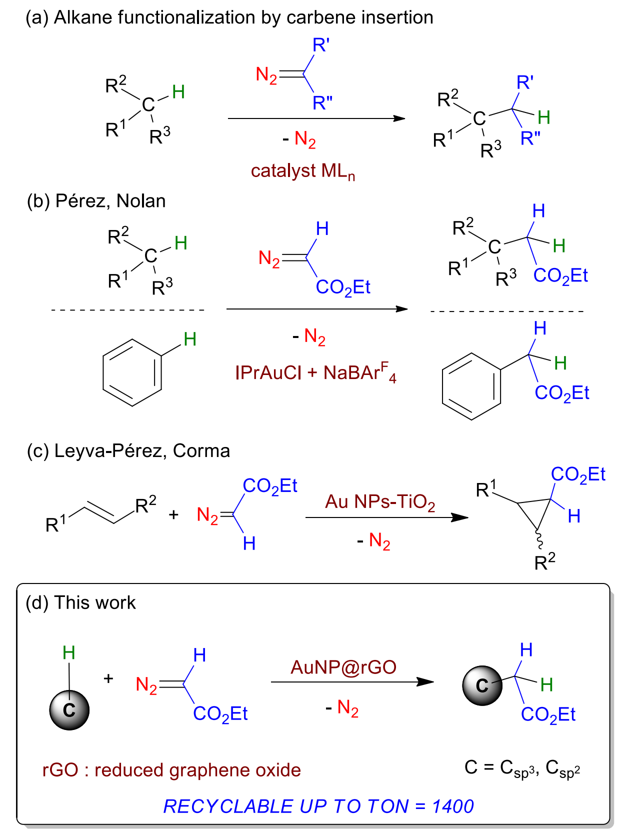
Gold nanoparticles stabilized by NHC ligands and supported onto reduced graphene oxide (rGO) catalyse the functionalization of cyclohexane and benzene C-H bonds upon insertion of carbene $CHCO_2Et$ (from $N_2{=}CHCO_2Et$) groups. This is the first example in which such C_{sp3} or C_{sp2} bonds are functionalized with this strategy with nanoparticulated gold. This Au-NP@rGO material shows an exceptional activity, providing TON values 5-10 times higher than those already reported for molecular gold catalysts. Recyclability is also effective, reaching an accumulate TON value of 1400 after six consecutive uses.

Introduction

Gold nanocatalysts used under heterogeneous conditions are expected to provide new or alternative reactivity or selectivity compared to molecular catalysts, in addition to easier separation of products and recycling.[1] However, there are many catalytic transformations that are yet under-developed toward that end, despite the use of molecular catalysts is well-established. It is the case of the metal-catalyzed carbene transfer diazo compounds, which has been widely studied for the functionalization of a broad variety of substrates.[2] Most examples correspond to either the addition of the carbene unit to unsaturated bonds or its insertion into X–H bonds (X = C, N, O, S, Si, halide, B).[3] Particularly, the functionalization of low reactive C–H bonds of alkanes (Scheme 1a), discovered in the early 80s,[4] has significantly emerged from the beginning of this century,[5] leading to catalytic systems capable of regioselective transformations[6] or even of modification of the most inert alkanes (methane, ethane),[7] among others. Common catalysts



Scheme 1 (a) Alkane functionalization by carbene insertion reactions catalysed by transition-metal complexes using diazo compounds as carbene source; (b) First example of gold-catalysed carbene transfer reactions; (c) Gold nanoparticles-catalysed cyclopropanation of alkenes by carbene transfer reactions; (d) Gold nanoparticles-catalysed functionalization of carbon-hydrogen bonds by carbene insertion reactions.

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are soluble transition metal complexes of groups 8-12.[5] Among them, gold-based catalysts have received increasing attention accordingly to the diverse reactivity that they exhibit: the formation of gold-carbene species can take place not only from diazo compounds[8] but also upon activation of alkyne carbon-carbon bonds,[9] leading to a plethora of transformations. The discovery of gold for carbene transfer reactions from diazo compounds was disclosed in 2005 from a collaboration between one of our laboratories and Nolan's group, employing NHC-containing gold complexes as catalyst precursors (Scheme 1b).[10] These compounds catalysed the insertion of carbene groups into the C_{sp3}–H bonds of alkanes[11] and C_{sp2}–H bonds of arenes.[10,12] Since then, this strategy has been expanded with notable success in a number of transformations.[8]

At variance with those successful soluble systems, scarce examples can be found regarding the use of heterogenous systems for C–H bond modification by carbene insertion, and more specifically with nanocatalysts, which have only proven to be moderately efficient with Ru.[13] Regarding the use of gold, an outstanding advance was disclosed by Leyva-Pérez and Corma,[14] that described the capabilities of gold nanoparticles on TiO_2 for the transfer of the carbene $CHCO_2Et$ from ethyl diazoacetate ($N_2{=}CHCO_2Et$, EDA) to olefins (Scheme 1c). However, at variance with the soluble gold catalysts previously reported, no modification of C_{sp3}–H or C_{sp2}–H bonds was accomplished. This could be the result of the electronic density of the gold-carbene intermediates at those nanoparticles, which were proposed to be as electron-rich. It is well-known that for low reactive C–H bonds, electron-deficient metal-carbene species are required. Similar nanoparticles were later described as catalyst for Si–H bond functionalization with diazo reagents by Stratakis.[15]

In the recent times, it is worth noting the importance of gold complexes bearing N-heterocyclic carbene (NHC) ligands,[16] and particularly IPr (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) in several catalytic processes. As mentioned above, this was the ligand providing the best results in carbene transfer reactions from diazo compounds in terms of C–H functionalization processes.[8,11] Unfortunately, a literature survey reveals that the preparation of stable Au-NPs stabilized with IPr (or other NHC ligand having an N–C_{aryl} bond) is yet unknown, since aryl-containing NHCs leads to the formation of the corresponding gold hydride complexes instead of Au-NPs,[17] and therefore the extrapolation of the molecular catalysts IPrAuCl to IPrAu-NPs has not been yet disclosed.

We have now targeted the use of gold nanoparticulated materials, yet unreported, toward the modification of alkane and arene carbon-hydrogen bonds by this methodology. Such Au-NP have been tested both free as well as supported on reduced graphene oxide (rGO).[18] Herein we describe the first example of such NP systems for C–H bond functionalization by carbene insertion, where the nanoparticles are stabilized with N-heterocyclic carbene groups. The most efficient catalyst is supported on rGO, favouring separation and recycling in such manner that turnover numbers surpass by one order of magnitude those already described with soluble, molecular catalysts.

Results and discussion

Gold nanoparticles and their fixation onto reduced graphene oxide. One of our groups has reported the preparation and catalytic properties of gold complexes and gold nanoparticles (Au-NPs) containing NHC ligands with pyrene tails responsible for their support onto reduced graphene oxide (rGO) through π-π stacking interactions (Figure 1)[19], or metal nanoparticles as active sites.[20] The key point in designing these hybrid materials consists in the use of metal complexes with ligands containing polyaromatic handles which allow the formation of multiple π-stacking interactions with graphene type surfaces. Among others, the pyrene tag, which contain four benzene fused units, forms strong interactions that avoid deactivation by leaching of metal nanoparticles under catalytic conditions. In the preparation of AuNPs toward their testing as catalysts for C-H bond functionalization by carbene transfer reaction, we have used two different NHC ligands with a pyrene tag and alkyl or 1,3-bis(diisopropylphenyl) N-substituent groups (IPr^{pyr} and IMe^{pyr}, Figure 1). Catalyst **1** contains AuNPs functionalized with IPr^{pyr} immobilized on rGO. The synthesis employs a well-defined gold complex whose decomposition is induced by the rGO. As commented before, non-supported AuNPs functionalized with NHC ligands containing aryl substituents are not known. For comparative purposes and with aiming to analyse the influence of rGO in catalysis, we prepared the hybrid material **2** and its non-supported version **3**. Catalysts **2** and **3** were prepared by decomposition of NHC-Au complexes using reducing agents. The hybrid materials were fully characterized by microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) (Figure 2 and ESI for details). XPS analysis of Au(4f) region for catalyst **2** confirms the presence of Au(I) and Au(0) oxidation states. The spectrum after deconvolution shows two doublets, due to the spin-orbit splitting effect ($4f_{7/2}$ and $4f_{5/2}$) at binding energies of 88.9 and 85.2 eV at 87.9 and 84.3 eV attributed to Au(I) and Au(0) respectively.

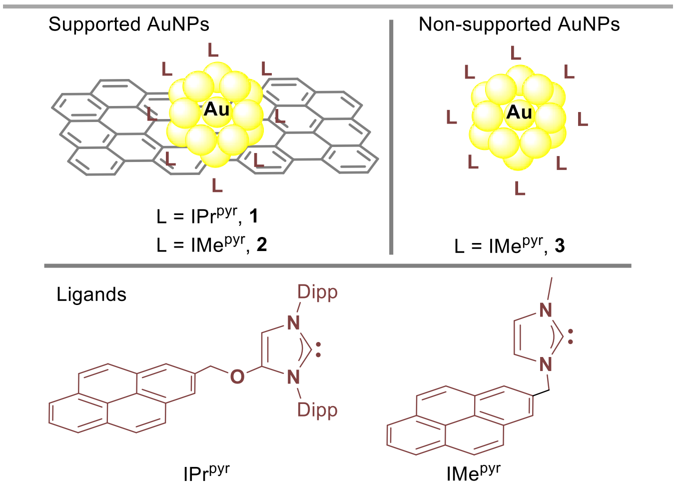


Figure 1 rGO-supported (**1**, **2**) and non-supported (**3**) Au-NPs stabilized by the NHC ligands IPr^{pyr} and IMe^{pyr} employed in this work.

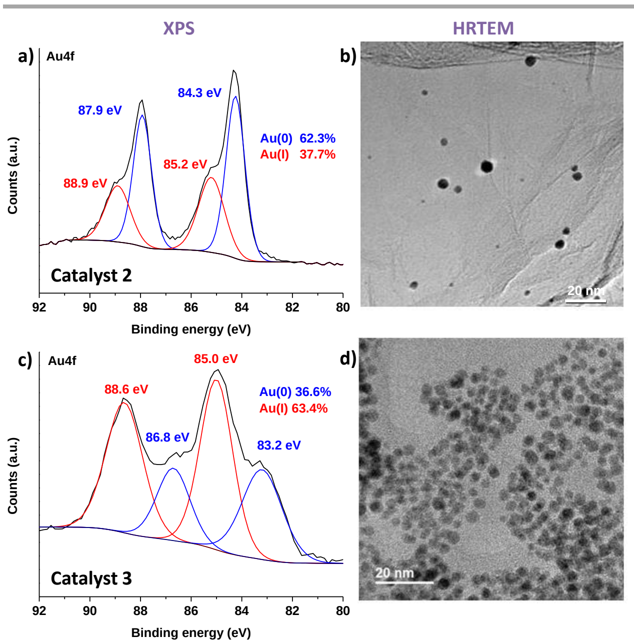


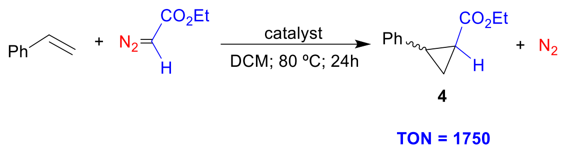
Figure 2 Characterization of catalysts **2** and **3**. XPS analysis of the core-level peaks (eV) for the Au4f region and HRTEM micrographs showing the spherical morphology of AuNPs.

Microscopic characterization by HRTEM confirmed the presence of small spherical AuNPs (average size 3.0 ± 1.0 nm). In the case of catalysts **1** and **2**, the characteristic layered structure of rGO it is also observed. The AuNPs are homogeneously distributed all over the surface of rGO and not only located at the edges, wrinkles, or defects. The non-supported AuNPs corresponding to catalyst **3** are homogeneous in size: EDX compositional analysis confirms the presence of organic ligands. According to these techniques, AuNPs are composed of a core of Au(0) atoms surrounded of Au(I) and covered by the NHC ligands that in the case of catalysts **1** and **2** act as binding motifs for immobilization onto rGO.

Catalytic studies with nanoparticles and their fixation onto reduced graphene oxide.

We have employed the above materials as catalyst precursors for the catalytic carbene transfer from a diazo compound, first studying the benchmark reaction of styrene cyclopropanation to verify their capabilities toward that end. Table 1 contains the results of this first array of catalytic experiments with **1**-**3** using ethyl diazoacetate (EDA) as carbene source (see ESI for optimization conditions). The results are conclusive: only the Au-NP@rGO **1** induced the transfer of the CHCO$_2$Et group from the diazo compound in an efficient manner, with total consumption of this reagent, and 70% yield into cyclopropanes. Similarly to the homogeneous system, the aryl-N-substituted NHC ligand is the right choice, whereas the alkyl-counterpart is significantly less effective toward the C-H bond fucntionalization. Moreover, at variance with homogeneous systems based on IPrAu cores, where usually 1-5 mol% catalyst loadings are employed, this system uses a material with a very low gold incorporation. Thus, the use of 25 mg of **1** in these experiments corresponds to only 4 x 10^{-5} mmol of Au, and a 0.04 mol% catalyst loading with respect to the limiting reagent EDA. Another important advantage compared to homogeneous systems is that catalyst **1** does not require the NaBAr$^F_4$ or any other halide scavenger for activation. Therefore, the observed 70% yield, EDA-based, into cyclopropanes, correspond to a TON value of 1750, which finds no precedent in the chemistry of gold-mediated carbene transfer. It is also worth mentioning that the previously described AuNP@TiO$_2$ system provides moderate cyclopropanation yields (10-35%).[14]

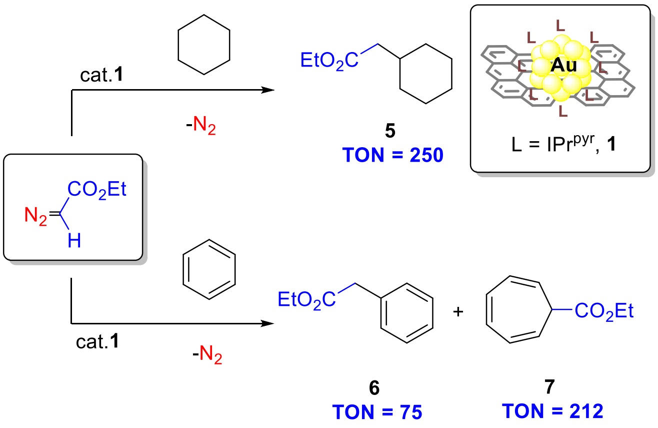
Table 1 Cyclopropanation of styrene with EDA under optimized reaction conditions.[a]



Entry	Catalyst	EDA conversion (%)	Yield (%)[b]
1	**1**	100	70
2	**2**	20	9
3	**3**	20	9
4[c]	rGO	20	10
5	none	16	9

[a]Reaction conditions: styrene (1 mmol), EDA (0.1 mmol), catalyst (4 x 10^{-5} mmol Au, 0.04 mol% referred to EDA), dichloromethane (DCM; 10 mL) under inert atmosphere. [b]Yields were determined by ^{1}H NMR employing 1,2,3-trimethoxybenzene as internal standard. Diethyl fumarate/maleate and products derived from carbene oligomerization accounted for initial EDA. See ESI for full description. [c]25 mg of pure rGO were employed.

Other by-products were diethyl fumarate and diethyl maleate, resulting from carbene dimerization, and low-mass EDA oligomers (see ESI for details), accounting for the initial



Scheme 2 Cyclohexane and benzene functionalization by carbene insertion using catalyst **1**. Reaction conditions: substrate = solvent (10 mL), EDA (0.1 mmol), catalyst (8 x 10^{-5} mmol, 0.08 mol% referred to EDA) under inert atmosphere, temperature 80 °C, 24 h. Yields were determined by GC and ^{1}H NMR employing 1,2,3-trimethoxybenzene as internal standard (see ESI).

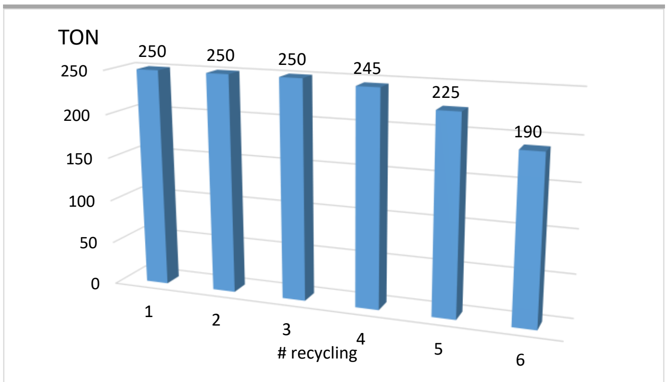


Figure 3 Recycling studies of **1** in the C–H functionalization of cyclohexane. Yields were determined by GC (referred to initial EDA). TONs are referred to compound **5**.

EDA. The use of the catalysts employing IMe^{pyr}, either supported on rGO (**2**) or as free NPs (**3**), was not productive (entries 2, 3), since the reaction outcome was similar to the experiment carried out in the absence of any catalyst (entry 5). The support rGO itself was also tested, proving no activity (entry 4) beyond that of the blank experiment. These results reinforce the importance of ligand design in the preparation of Au-NPs and the increase stability induced by the rGO support as previously observed.[19a]

Once demonstrated the catalytic capabilities of **1** to transfer the carbene $CHCO_2Et$ group from EDA, we focused on C–H bonds, given the lack of examples employing Au-NPs toward that end. Cyclohexane and benzene have been employed as prototypical examples of C_{sp^3}–H and C_{sp^2}–H bonds (Scheme 2), the experiments leading to the formation of the products derived from the insertion of the carbene group in such those bonds (**5**, **6**). In the case of benzene, the product derived from the Buchner reaction, the cycloheptatriene **7**, has also been obtained. These results constitute the first examples of gold-nanoparticles as catalyst for C–H bond functionalization by carbene insertion. In addition, the catalyst activity is quite remarkable, surpassing by far the results previously found with IPrAu-based homogeneous catalysts. Thus, the formation of **5** corresponds to a TON value of 250, one order of magnitude higher than that for the IPrAuCl soluble catalyst (TON = 17).[8] Similarly, the 75 TON value for the formation of **6** is of note, an activity five times higher than that of IPrAuCl. Despite this remarkable behaviour, most of the initial EDA was converted into the previously mentioned by-products. This is the result of a very high concentration of EDA around the gold nanoparticles, which could not even be improved by slow addition devices. Such concentration favours non-desired side reactions, a drawback to be solved in the future. In any case, our aim is not focussed onto synthetic routes for these compounds but to the fact of the excellent activity of the catalyst. The IPrAu core is now present in the NP (free nanoparticles of this type are not known) which are stabilized by the rGO. Moreover, recent work from our laboratories have demonstrated a beneficial role of the rGO in this type of transformations, due to electronic draining caused by the rGO from the metal, thus enhancing electrophilicity.[21]

The recyclability of **1** was tested in the carbene transfer reaction of EDA with cyclohexane (Figure 2) for six cycles. A global ca. 1400 TON was provided by **1** overall the six cycles, with all EDA being consumed in each cycle. This TON value is, by far, the highest described for a gold-based catalyst for this type of transformation with an alkane. Hot filtration test was also performed (see ESI for details), the filtrate obtained being not active towards additional EDA, indicating that this **1**-catalysed carbene transfer reactions takes place only under heterogeneous catalytic conditions.

As shown in Figure 3, recycled **1** yet exhibited conversions similar to the fresh catalyst after 3 runs. However, a slight decrease in the activity was found after the fourth and next cycles. This decrease can be attributed to a slight loss of Au-NPs from one cycle to another, a proposal which has been confirmed by ICP-MS analysis of the recovered materials, showing the decrease of the metal onto rGO after the six cycles studied (see ESI). Such loss must explain the decay in activity, since XPS analysis revealed that the nature of recycled catalyst **1** remained unaltered along the cycles, no poisoning nor degradation being observed (see ESI, Figure S7).

In conclusion, we have demonstrated that gold nanoparticles stabilized with IPr-like NHC ligands and supported onto reduced graphene oxide (rGO) catalyse the insertion of the carbene $CHCO_2Et$ from ethyl diazoacetate with TON values much larger than those already described homogeneous gold catalysts. For cyclohexane, an increase in one order of magnitude in TON values has been found, whereas for benzene, TON values for the Au-NP based system is five times higher than the soluble catalysts. Ligand design containing aromatic groups at the N positions and electronic draining caused by the rGO are crucial parameters for the observed activity, which is maintained for six cycles with very high accumulated TON values. These findings show the great potential of Au-NP@rGO as catalyst for reactions where an electrophilic nature is required at the metal center, with the additional advantage of high activity at very low loadings.

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Experimental Section

Materials and instrumentation

All air– and moisture–sensitive manipulations were carried out with standard Schlenk techniques under nitrogen atmosphere or in a glovebox (MBRAUN UNILAB) under an atmosphere of purified nitrogen. All reactants were purchased from Sigma-Aldrich and used without further purification. rGO was purchased from Graphenea. Solvents were purchased from Scharlau and dried using standard protocols: cyclohexane and benzene were refluxed over sodium/benzophenone, dichloromethane was refluxed over calcium hydride and separated by distillation under nitrogen. Nuclear magnetic resonance (NMR) spectra were recorded at room temperature from solutions in $CDCl_3$ on Bruker spectrometer operating at 400 MHz (^1H NMR) and were referenced to residual solvent peak (chloroform: 7.26 ppm for ^1H NMR). High-resolution images of transmission electron microscopy (HRTEM) and high-angle annular dark-field (HAADF-STEM) images of the samples were obtained using a Jem-2100 LaB6 (JEOL) transmission electron microscope coupled with an INCA Energy TEM 200 (Oxford) energy dispersive X-ray spectrometer (EDX) operating at 200 kV. Samples were prepared by drying a drop let of a MeOH dispersion on a carbon-coated copper grid. X-ray photoelectron spectra (XPS) were acquired on a KratosAXIS ultra DLD spectrometer with a monochromated AlKaX-ray source (1486.6 eV) using a pass energy of 20 eV. To provide a precise energy calibration, XPS binding energies were referenced to the C1s peak at 284.6 eV. UV/Vis spectra were acquired on a Varian Cary 50 spectrophotometer. GC studies were performed on a Bruker GC-450 gas chromatograph equipped with an FID detector and a 30 m x 0.25 mm CP-Sil 8CB capillary column.

Synthesis of catalysts

The methodology for the synthesis of hybrid materials **1** and **2**) composed of rGO and AuNPs functionalized with NHC ligands has been previously described.[19] Unsupported AuNPs (**3**) have been obtained using general procedures of decomposition of well-defined Au complexes with appropriate reducing agents.

*Synthesis of **1**.* A suspension of 490 mg of rGO in 350 mL of CH_2Cl_2 in a round-bottom flask was immersed in an ultrasounds bath for 30 min to achieve a rGO dispersion. In parallel, the gold complex $iPr^{Pyr}AuCl$ (150 mg, 0.166 mmol) and silver triflate (56.4 mg, 0.184 mmol) were dissolved in 8 mL of dry CH_2Cl_2 and the mixture was stirred at room temperature for 15 min. in a Schlenk flask protected from light. Then, the reaction was filtered through a pad of Celite® to remove the AgCl formed. The solution containing the $iPr^{Pyr}AuOTf$ was concentrated until ca. 5 mL using a rotatory evaporator. Then, this solution was added to the suspension of rGO in CH_2Cl_2 and was stirred at room temperature for 48 h. The black solid was isolated by filtration and washed with 200 mL of CH_2Cl_2 affording the hybrid material **1**. The exact amount of supported gold was determined by ICP-MS analysis. The results accounted for a 0.033 mg Au/100 mg rGO in the hybrid material **1**.

*Synthesis of **2**.* A dispersion of rGO in CH_2Cl_2 (475 mg in 50 mL) was sonicated for 30 min. Immediately afterwards, complex $IMe^{Pyr}AuBr$[19b] (25 mg, 0.046 mmol) was added. The mixture was sonicated for 10 min. Then, tertbutylaminoborane (412 mg, 4.6 mmol) was slowly added. The mixture was stirred at room temperature for 48 h. The black solid was isolated by filtration and washed with 200 mL of CH_2Cl_2, 200 mL of water and 200 mL of acetone affording the hybrid material **2**. The exact amount of supported gold was determined by ICP-MS analysis. The results accounted for a 0.1 mg Au/100 mg rGO in the hybrid material **2**. The hybrid material was characterized by HRTEM and XPS.

*Synthesis of **3**.* In a round bottom flask, a solution of $NaBH_4$ (145 mg, 3.8 mmol) in water (58 mL) was added over a stirred solution of gold complex $IMe^{Pyr}AuCl$ (113 mg, 0.148 mmol) in CH_2Cl_2 (150 mL). The two-phase mixture was vigorously stirred at room temperature for 4 h and then filtered over celite®. The remaining solution was washed with water (3 x 20mL) and the organic phase was dried with anhydrous $MgSO_4$. Removal of solvent in the rotatory evaporator afforded AuNPs functionalized with NHC ligands (catalyst **3**) as a dark purple solid.

General procedure for the cyclopropanation of styrene with EDA

In a light-protected 50 mL J-Young ampoule charged with 10 mL of solvent, the corresponding amount of catalyst was added. For graphene-supported catalysts, the mixture was previously sonicated for 10 min. Then, 115 µL of styrene (1.0 mmol, 104 mg) were added and the mixture was stirred for 5 min. Afterwards, 12.5 µL of EDA (0.1 mmol) were added. The resulting mixture was stirred for the desired time and temperature. When the reaction was completed, the solid catalyst was filtered off and washed with 3x5 mL of DCM. The filtrates were collected, and volatiles were removed under vacuum resulting in a yellowish residue. Yields were determined by ^1H NMR analysis employing 1,2,3-trimetoxybenzene as internal standard and identified by its comparison with literature precedents.

General procedure for the reactions of cyclohexane and benzene with EDA

Following the previous procedure, 10 mL of cyclohexane or benzene and 50 mg of catalyst **1** ($8x10^{-5}$ mmol Au; 0.08 mol% referred to EDA) were reacted with 12.5 µL of EDA (0.1 mmol). The resulting mixture was heated for 24 h at 80 °C. Yields were determined by GC or NMR analysis employing 1,2,3-trimetoxybenzene as internal standard, and identified by comparison with literature data.

Recycling studies with 1

Following the previous procedure for cyclohexane, when the reaction was finished, the mixture was allowed to decant, and an aliquot was taken for its analysis by GC. Then, the liquid fraction was filtered off and the resulting solid catalyst was washed with DCM (3x5 mL) and cyclohexane (3x5 mL). Fresh cyclohexane and EDA (10 mL and 12.5 µL, respectively) were added for the second run. The procedure was repeated up to six cycles.

Hot filtration test with 1

To a light-protected, 50 mL J-Young ampoule charged with 10 mL of cyclohexane and 50 mg of catalyst **1** (8×10^{-5} mmol Au; 0.08 mol% referred to EDA), 12.5 µL of EDA (0.1 mmol) were added after 10 min of sonication (see above). The resulting mixture was heated under stirring for 8 h at 80 °C. Then, the mixture was filtered off and an aliquot from filtrate was analysed by GC. At this point, an EDA conversion of ca. 50% was observed. Then, the filtrate was heated at 80 °C for 24 h. After this time, the mixture was analysed by GC, showing a similar value, within experimental error, to that registered before, demonstrating that no catalysis takes place by soluble species.

Conflicts of interest

There are no conflicts to declare.

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