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Heterogenized Gold(I)–Carbene as a Single-Site Catalyst in Continuous Flow

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Catalytically active gold(I)–carbene complexes on a polystyrene backbone were synthesized by treating metal-coordinated isocyanides with the nitrogen nucleophile of a piperazine group bonded to the polystyrene. The local environment of the metal was readily tuned by variation of the functional group. This versatile synthesis procedure is not restricted to gold and can easily be extended to other metals such as Pd and Pt. The gold carbene complexes were extensively characterized, and resonant inelastic X-ray scattering identified the +1 oxidation state of the supported gold. This single-site catalyst catalyzed the synthesis of oxazoles, and the system could be used in continuous flow.

Gold catalysis has emerged as a hot topic in organic chemistry. The unique reactivity and the mild reaction conditions that can be used make this metal attractive for a number of different applications, such as cycloisomerization and C–C bond-formation reactions.^[1–10] Most of the reactions are performed in the homogeneous phase, which makes separation of products and catalyst difficult. We introduce a versatile and simple procedure to heterogenize metal carbene complexes and illustrate that Au¹–carbene-catalyzed oxazole synthesis can be performed in continuous flow. Metal-coordinated isocyanides react with the nitrogen nucleophile of a piperazine group attached to a polystyrene backbone. The local environment of the metal can be readily tuned by variation of the functional groups, and the method is not restricted to gold.

The uniqueness of gold catalysts is mostly explored in the homogeneous phase.^[1-10] Because of their straightforward separation, heterogeneous processes are attractive. However, in general heterogeneous catalysts lack the versatility that characterizes homogeneous ones. Moreover, performing a reaction in continuous mode has clear advantages above doing it in batch

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styrene mode. Here, we show the synthesis, characterization, and catated isolytic reactivity of a heterogenized acyclic Au¹-carbene complex that can be applied in a continuous process. We characterized

that can be applied in a continuous process. We characterized the immobilized complexes by using IR spectroscopy, electron microscopy, and X-ray absorption spectroscopy (XAS).^[11] Heterogenized phosphine Au^I and salen-type Au^{III} complexes have been synthesized before.^[12-18] Reports dealing with Au^l are relatively scarce, probably because of the delicate synthesis of these metal complexes.^[19-21] Instead of frequently used ordered mesoporous silica, such as SBA-15 and MCM-41,^[22,23] we used modified polystyrene beads as a support. Polystyrene is an often-used material in Merrifield solid-phase synthesis and in heterogeneous catalysis.^[24-26] Modified polystyrene polymers, that is, JendaJel and TentaGel, are used as scavengers in organic chemistry and continuous flow processes. They can be tailor-made for different applications and can be produced in large quantities at low cost. We chose a polystyrene modified with piperazine. Attack of the nitrogen nucleophile to a metalcoordinated isocyanide yields an acyclic carbene (Schemes 1



Scheme 1. Formation of acyclic carbenes starting from metal-coordinated isocyanides.

and 2).^[27-33] In a subsequent reaction, the carbene gold complex can react with an alkyne group to form a gold–acetylide complex. By treating these compounds with an acid such as HNTf₂ (Tf=trifluoromethanesulfonyl), the acetylide is released, which enables silver-free activation.^[34] A silver salt is generally needed to remove halogens, which is not possible in the heterogeneous system.^[35-37] The chemical surrounding of the metal can be modified by changing loading and type of the modifier.

Combining only 3 polymers and 4 isocyanides leads to 12 distinct materials. (Figure S1, Supporting Information), which uniquely enables libraries of materials to be built up in a relatively simple manner. We prepared half of the possible materials by using gold¹. Moreover, we successfully tested some of the materials in the well-known synthesis of oxazoles. In this reaction, a propargyl amide rearranges into the corresponding oxazole derivative by Au¹ or Au^{III} complexes under homogeneous conditions.



Scheme 2. Synthesis of the acyclic Au¹-carbene complexes onto piperazine-modified polystyrene to yield Au@PS6_Y (Y is the second ligand attached to gold).

We characterized the synthesized materials by a variety of methods, including resonant inelastic X-ray scattering (RIXS), which combines X-ray absorption and X-ray emission spectroscopy (XAS and XES).^[38] RIXS yields the exact local geometry and electronic structure in an element-specific manner. Because hard X-rays are used, measurements can readily be performed under catalytically relevant conditions.^[11,39]

Figure 1 shows the yield as a function of time in the rearrangement of a propargyl amide into the oxazole derivative over Au@PS6_AC. Homogeneous Au¹ catalysts yield oxazolidene derivative A,^[40,41] which isomerizes into the aromatic compound either in the presence of acid or AuCl₃. All heterogeneous catalysts yielded **B** directly in a cascade reaction, most likely because any residual amine site that acts as a base for the formation of the acetylide complex becomes protonated and acts as the acid site. We observed this site by using IR spectroscopy (see below). A higher amount of acid (HNTF₂) during catalyst activation, while keeping all other conditions constant, yielded higher catalytic activity. Thus, increasing the amount of acid increases the number of activated centers,

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Figure 1. Reaction profile of the oxazole synthesis by using different amounts of HNTF₂ during activation of Au@PS6_AC. The yield was determined by GC by using dodecane as an internal standard. Conditions: starting material (1.00 mmol), catalyst (5.00 mol%), CH₂Cl₂ (2.00 mL), RT.

Material	Yield [%]	
Batch mode	180 min	420 min
Au@PS6_AC/HNTF ₂ (2 equiv.)	20	43
Au@PS6_AC/HNTF ₂ (3 equiv.)	31	61
Au@PS6_AC/HNTF ₂ (4 equiv.)	37	76
homogeneous complex ^[40]	79	-
pure PS_c	0	C
PS_c_HNTF ^[a]	0	C
Au@PS6_Cl	0	C
Continuous flow		
Au@PS6_NTf ₂	>95 ^[b]	-

which boosts the activity. In all cases, the reaction went to complete conversion within 24 h.

Table 1 summarizes the catalytic measurements. In the absence of acid activation and in the absence of gold (with acid activation), no catalytic activity was observed. The yield of the homogeneous complex was similar to that of the heterogeneous complex that was activated with the highest amount of acid. Because the polystyrene beads swell to a multiple of their original volume upon immersion in liquid, large pores are present in the polymer beads through which reactants and products can readily diffuse. By using the immobilized catalyst in the continuous flow apparatus and by pumping the oxazole substrate $(0.1 \text{ M} \text{ in } CH_2Cl_2)$ through the reactor by a syringe pump with a flow rate of 1.5 mLh⁻¹, near complete conversion of the propargyl amide into the corresponding oxazole derivative was observed. The amount of catalyst was 10 mol% relative to the whole amount of substrate in each single run. The flow was maintained until the substrate solution was com-

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pletely consumed. The reaction was repeated after flushing the catalyst with CH_2CI_2 , and the reaction was restarted by pumping fresh substrate solution. The reaction was performed five times, which yielded essentially identical results. The constant catalytic performance and the absence of color change, which would indicate gold particle formation, prove that the catalyst is highly stable in flow mode.

There are very few related reports dealing with heterogenized gold complexes,^[15,21] and the support and method of synthesis largely differ. Echavarren used a phosphine-containing polymer that was treated with an already active gold(I) precursor to form a heterogenized gold(I) phosphine complex. Yu and Cao used a heterogenized triazole as a counterion for a preformed gold(I) phosphine complex. In both reports, a substrate scope different from ours was addressed, and they both delivered results with regard to yield and catalyst loading that were comparable to our system.

Highly dispersed gold species were observed by STEM images (Figure S2). Exposure of the catalyst to NaHB(OAc)₃ indicated particle formation and complete removal of the highly dispersed gold species. This treatment caused an instantaneous color change attributed to particle formation. SEM with energy-dispersive X-ray spectroscopic elemental analysis (Figures S3–S5 and Tables S1 and S2) showed that the gold was evenly distributed over the individual polystyrene beads, which were between 40 and 80 μ m in size. Thus, the immobilized gold complexes in the polystyrene are accessible to chemicals, they remain stable during reaction, and they decompose into particles under a strongly reducing environment.

Figure 2a shows the $L_{\alpha 1}$ -RIXS plane of Au@PS6_AC. $L_{\alpha 1}$ -RIXS planes of Au@PS6_Cl and Au@PS6_NTf2 were also measured (not shown). The high selectivity to the 5d orbitals of gold is achieved as a result of the strong $2p_{3/2}{\rightarrow}5d$ resonant excitation, marked by the solid line. The total fluorescence yield (TFY) and high-energy resolution (HR) XAS curves were extracted from the RIXS plane and are plotted in Figure 2a (right panel). The HRXAS spectrum exhibits more pronounced features than the TFY-XAS curve, [42,43] which indicates the enhanced sensitivity of RIXS as a selective probe for the unoccupied d density of states of gold. The HRXAS spectrum shows a distinct white line, which is the first intense feature in the spectrum. This feature is much less pronounced in the TFY-XAS spectrum. A quantitative analysis of the 5d unoccupied states was performed on the basis of the energy-transfer RIXS plane^[44] plotted in Figure 2b. The correlation of the gold oxidation state versus the detected intensities at the 5d resonance was obtained from the integrated counts along constant incident beam energies and constant energy transfer curves, as marked in Figure 2b. The use of gold foil, AuCl, and Au₂O₃ as reference materials for Au⁰, Au¹, and Au^{III} respectively, enabled the oxidation state of gold in the three gold complexes to be determined (Figure 2 c). On the basis of the experimental reference points, a linear dependence of the intensity and oxidation state was assumed. A calibration curve was then employed to determine the gold oxidation state in Au@PS6_AC, Au@PS6_Cl, and Au@PS6_NTf2. Oxidation states of 1.1, 0.9, and 0.9, respectively, were obtained; this indicates that gold is pres-



Figure 2. a) RIXS plane of Au@PS6_AC, b) RIXS plane of Au@PS6_AC transferred to the energy-transfer scale, and c) dependence of constant incidence energy (CIE) and constant energy transfer (CET) along the 5d resonance on gold oxidation state [the points of Au@PS6_CI and Au@PS6_NTf₂ overlap]; d) HRXAS spectra extracted from the RIXS planes.

ent as Au¹ in the complexes. The chemical sensitivity of RIXS to the local environment can be further observed in the HRXAS curves (Figure 2d). The intensity of the white line is similar in all three spectra, and this is indicative of the Au¹ oxidation state. The distinct differences in the edge position and local features at energies higher than that of the white line reveal that the electronic structure and geometric environment are probed. A shift in the edge position is caused by a different Fermi level energy. The bands at energies higher than that of the white line originate from the d component in the antibonding states between gold and the ligand. Their differences are reminiscent of the different geometry and electronic structure in the first few coordination spheres; however, these features were not further analyzed.

FTIR spectroscopy identified the characteristic vibrational spectra of the supported complexes. The spectral features of the heterogenized complexes were similar to those of the homogeneous analogues, which is indicative of a very similar local structure. The frequency of the carbene group changed significantly with variation of the ligand structure (Figure S6 and Table S3). In contrast to materials prepared from aromatic isocyanides, Au@PS3_AC showed a hypsochromic shift in the absorption of the carbene, which is in agreement with earlier

reports. Interestingly, the material containing the carbene complexes derived from the perfluorinated isocyanide showed an even stronger hypsochromic shift, which revealed the strong electronic influence of the perfluorinated moiety on the ligand. The same trend was observed on going from Au@PS6_Cl to Au@PS6_NTf₂. Because the chloro ligand is a stronger donor than the trifluorimidato group, the carbene moiety experiences a less-electron-rich metal surrounding, and this results in a shortening of the C-N bond. Treatment of the polymer with HNTf₂ leads to protonation of the alkyne; this is indicated by the disappearance of the absorption at 2110 cm⁻¹ and to the formation of the Brønsted acid site by protonation of the basic centers in the polymer, which results in an intense absorption at approximately 3312 cm⁻¹ (Figure S6). As mentioned above, the use of Au^I as a catalyst requires the presence of an acid to form the oxazole.

In conclusion, we reported a new method to prepare stable acyclic Au¹-carbene complexes that are highly dispersed on a polystyrene support. Within a single step, heterogenization and ligand formation was achieved, and simple variation of the starting compounds, the isocyanide, and the polymer modifier allowed electronic tuning of the metal complex. This on-support synthesis of metal-carbene complexes is not restricted to

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gold; it is versatile and can be extended to other metals. The catalytic experiments revealed activity in oxazole synthesis from propargyl amide that is comparable to the corresponding complexes in homogeneous catalysis. The presence of the Brønsted acid sites catalyzed the direct formation of the oxazoles. The use of polystyrene beads enabled reuse of the catalyst and the stable operation of the catalyst in continuous flow. HRXAS, RIXS, and IR spectroscopy of the immobilized complex unequivocally identified the gold structure to be Au¹. Electron microcopy showed that gold is well distributed over the individual polystyrene beads and that no structural changes occurred during the reaction.

Experimental Section

Synthesis of the materials

See the Supporting Information.

Synthesis of the catalysts

Au@PS6_Cl (Figure 1): The polymer PS_c (1.00–1.50 mmol_{amine} g⁻¹) was suspended in CH₂Cl₂ (10.0 mL), and the suspension was magnetically stirred at 150 rpm. (tht)AuCl (tht = tetrahydrothiophene; 200 mg, 624 µmol) and IC_d (200 µL) were added. The suspension was stirred for 24 h at RT and then filtered through a glass frit. The solid was washed with CH₂Cl₂ (3×60.0 mL) and dried under vacuum. The wash solution was analyzed by FTIR to detect unreacted metal isocyanide complex.

Au@PS6_AC: The polymer PS_c (1.00–1.50 mmol_{amine}g^{-1}) was suspended in CH₂Cl₂ (10.0 mL), and the suspension was magnetically stirred at 150 rpm. (tht)AuCl (200 mg, 624 µmol), IC_d (200 µL), phenylacetylene (500 µL), and NEt₃ (1.00 mL) were added. The suspension was stirred for 72 h at RT and then filtered through a glass frit. The solid was washed with CH₂Cl₂ (3×80.0 mL) and dried under vacuum. The wash solution was analyzed by FTIR to detect unreacted metal isocyanide complex.

Au@PS6_NTf₂: The polymer Au@PS6_AC (100 mg) was suspended in CH₂Cl₂ (2.00 mL), and the suspension was magnetically stirred at 150 rpm. HNTf₂ (36.0 mg, 128 µmol) dissolved in CH₂Cl₂ (2.00 mL) was added. The mixture was stirred for 25 min at RT. Finally, the solid was filtered through a glass frit. The solid was washed with CH₂Cl₂ (3×20.0 mL) and dried under vacuum.

General methods

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. Unless otherwise declared, all chemicals were purchased from SigmaAldrich, Acros Organics, or AlfaAesar and were used without further purification. Piperazinemodified polystyrene supports were ordered from SigmaAldrich and AlfaAesar. All solvents were dried on a column by using activated alumina and stored in the presence of activated molecular sieves (4 Å). Synthesis procedures for all compounds are provided in the Supporting Information. NMR spectra of liquid solutions were recorded with a Bruker Avance 500 spectrometer (500.13 MHz for 1 H) at 30 °C. ¹H NMR spectra are referenced to the residual solvent signals. Transmission electron microscopy (TEM) was performed with FEI Tecnai F30 ST (FEG, 300 kV) and Hitachi HD2700CS (aberration-corrected dedicated STEM, cold FEG, 200 kV) microscopes. SEM was performed with a field-emission Zeiss Ultra 55 microscope. The RIXS experiments were performed at the SuperXAS beamline of the Swiss Light Source. The $L_{\alpha 1}$ X-ray fluorescence from the sample was recorded by means of a von Hamostype spectrometer operated with a cylindrically bent Ge(660) crystal^[45,46] by using a position sensitive detector, the Mythenll.^[47] The incident beam energy was tuned around the Au L_3 absorption edge by a double crystal monochromater equipped with a Si(111) crystal. The use of the von Hamos geometry enabled the XES in an energy-dispersive manner to be detected, which allowed recording of the XES on a shot-by-shot basis. The Au¹–carbene on polystyrene samples were freshly dispersed in CH₂Cl₂ and sealed in a vial, which was positioned in the beam.

Batch reactions were performed in sealed tube vials with magnetic stirring. Under ambient conditions, *N*-(prop-2-yn-1-yl)benzamide (159 mg, 1.00 mmol) was dissolved in CH₂Cl₂ (4.00 mL). Au@PS6_ NTf₂ (5.00 mol%, 100 mg) and dodecane (226 μ L, 1.00 mmol) were added. Samples were taken from the reaction mixture at fixed time intervals.

Continuous flow experiments were performed in a glass tube reactor with inner diameter of 6 mm and a length of 250 mm. The reactor was closed by septa penetrated by capillaries at both ends. The reactor was filled with the defined amount of Au@PS6_NTf₂, and CH₂Cl₂ was used as eluent. The amount of catalyst was 10 mol% relative to the whole amount of substrate used in a single run. The oxazole substrate (0.1 \times in CH₂Cl₂) was pumped through the reactor by a syringe pump with a flow rate of 1.5 mLh⁻¹. Samples were taken regularly for GC analysis, and the syringe was refilled four times after flushing with CH₂Cl₂ (20 mL).

In both batch and continuous flow modes, the yield was determined by integration of the GC signals. GC analyses were performed with an Agilent 7693/6890 GC equipped with an HP-5 column (50 m×0.32 mm×1.05 μ m, 5% phenyl methylsiloxane), flame ionization detector, and helium as the carrier gas.

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