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Coordination Polymers

Main-Chain Organometallic Microporous Polymers Bearing Triphenylene–Tris(N-Heterocyclic Carbene)–Gold Species: Catalytic Properties

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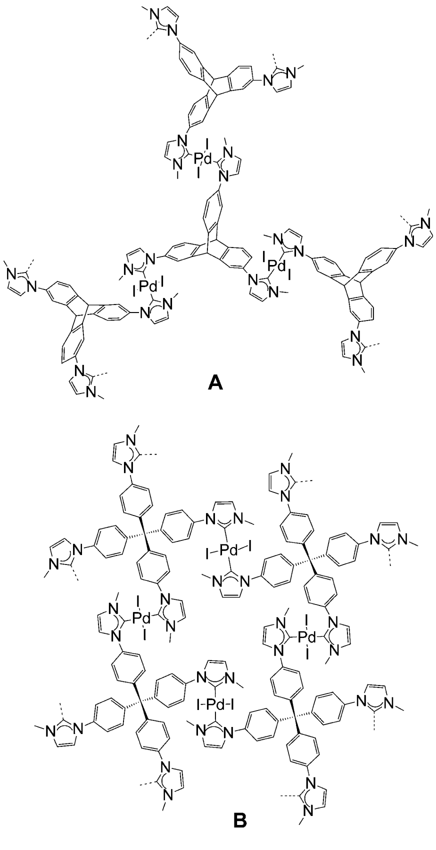
Abstract: Two triphenylene-based tris(N-heterocyclic carbene)–gold–acetylide main-chain organometallic microporous polymers (MOMPs) were obtained and fully characterized. Both materials show spherical shapes, and their size is highly dependent on the type of acetylene used in the synthetic protocol. The new solids were tested in the catalytic reduction of nitroarenes with $NaBH_4$ and in the three-component Strecker reaction for the synthesis of α-aminonitriles, and showed high activity in both processes. Whereas the activity of the solids in the reduction of nitroarenes may be attributed to the formation of Au nanoparticles due to the use of $NaBH_4$ as reducing agent, the activity in the Strecker reaction may originate from the Lewis acidic activation of the ketone or imine on coordination to Au.

Introduction

Since the first use of the term "coordination polymers" in the early 1960s,[1] the preparation of infinite one-, two-, and three dimensional metal–organic frameworks (MOFs)[2] has provided materials with a large number of applications, ranging from catalysis to the fabrication of chemical sensors and advanced materials with interesting optoelectronic properties.[3] While the term "coordination polymer" may refer to any kind of extended structure based on metals and organic bridging ligands, MOFs are mostly defined as coordination compounds exhibiting porosity.[2b] One of the major challenges in the design of hybrid polymeric materials is the ability to predict the network geometry while avoiding interpenetration of a second polymer into the first,[2g,4] which may result in filling of the potential cavities. This implies that the key to successful MOF design is the choice of both adequate linkers (ligands) and connectors (metal fragments).[5]

For the preparation of electronically active organometallic polymers, N-heterocyclic carbenes (NHCs) have been proposed as excellent scaffolds, because they combine high stability, great coordination versatility, and the possibility to enable communication between the metal d_π orbitals and the empty π orbitals of the ligand through metal-to-ligand π backdonation.[6] However, whereas NHC-based organometallic polymers are well-known materials due to the availability of convenient linearly opposed bis-NHC ligands,[7] those affording microporous materials, which are also called main-chain organometallic microporous polymers (MOMPs), are limited to two examples that recently appeared in the literature and were obtained by using a triptycene-based tris-imidazolylidene[8] and a tetraphenylmethane tetrakis-imidazolylidene[9] (Scheme 1).

We recently described the preparation of a planar triphenylene-based tris-NHC,[10] which we used for the preparation of



Scheme 1. NHC-based organometallic microporous polymers.

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a series of Pd and Au complexes with improved catalytic properties.[10a] Due to the threefold symmetry of the ligand, we envisaged that this π-connected tris-NHC might be useful for the preparation of extended structures with interesting physicochemical properties. In principle, compared to the ligands used in **A** and **B**, our triphenylene-based tris-NHC has the advantage of having the three carbenes connected by a π-delocalized polyaromatic system, and therefore it has the potential to serve as a building block for constructing electronically active materials.[6c,d,f] Moreover, whereas NHC-based one-dimensional organometallic polymers with π-extended systems are known,[7] the related π-extended two- or three-dimensional materials have not been reported so far. We herein report the convenient synthesis of triphenylene-based tris-NHC–gold–acetylide MOMPs and their applications in the reduction of nitroarenes to anilines and in the three-component Strecker reaction for the synthesis of α-aminonitriles.

Results and Discussion

Acetylides can be easily incorporated on N-heterocyclic carbene gold chlorides by direct reaction between the gold complexes and the corresponding terminal acetylenes.[11] We carried out the reaction between triphenylene-tris-NHC gold complex **1**[10a] and 1,4-diethynylbenzene or 1,3,5-triethynylbenzene in the presence of NaOH in refluxing methanol to afford the MOMPs **2** (68% yield) and **3** (90% yield), respectively (Scheme 2), as highly insoluble, brownish solids.

The chemical compositions of the materials were determined through elemental analysis by combustion. The observed contents of carbon (**2**: 48.95; **3**: 47.75%), nitrogen (**2**: 5.39; **3**: 5.56%), and hydrogen (**2**: 4.60; **3**: 4.56%) matched well with the calculated values for **2** [$(C_{57}H_{63}N_6Au_3)_n$: C 49.29, H 4.55, N 5.75] and **3** [$(C_{57}H_{63}N_6Au_3)_n$: C 48.11, H 4.46, N 5.91]. The infrared spectra of **2** and **3** displayed bands at 2102 and 2103 cm^{-1}, respectively, which are characteristic of the presence of C≡C bonds. The presence of the $Au{-}C_{carbene}$ bond was confirmed by means of ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy, by comparison with the ^{13}C NMR spectrum of the related molecular triphenylene-tris-NHC gold acetylide complex **4** (Figure 1). The ^{13}C CP/MAS NMR spectra of **2** and **3** displayed characteristic signals due to $C_{carbene}$ at 200 ppm, very close to the region in which the related signal in **4** appears (199.61 ppm). The signals due to the remaining aliphatic and aromatic C atoms in **2** and **3** all perfectly match with those exhibited by **4**.

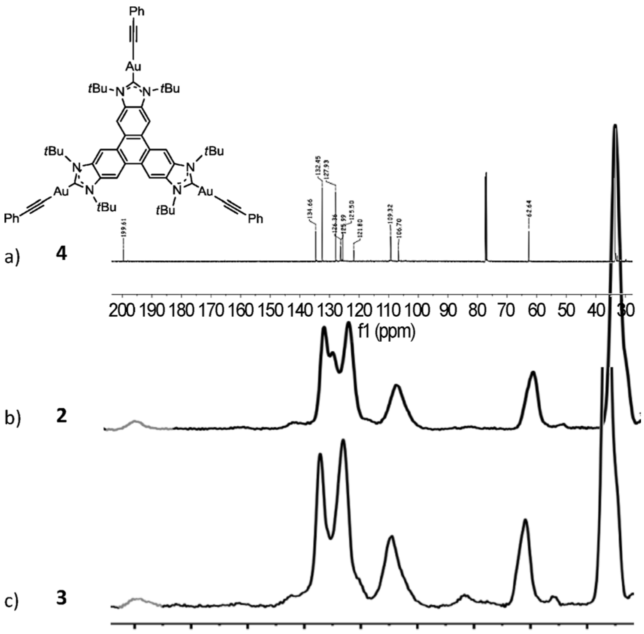


Figure 1. a) ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4**. b) ^{13}C CP/MAS NMR spectrum of **2**. c) ^{13}C CP/MAS NMR spectrum of **3**.

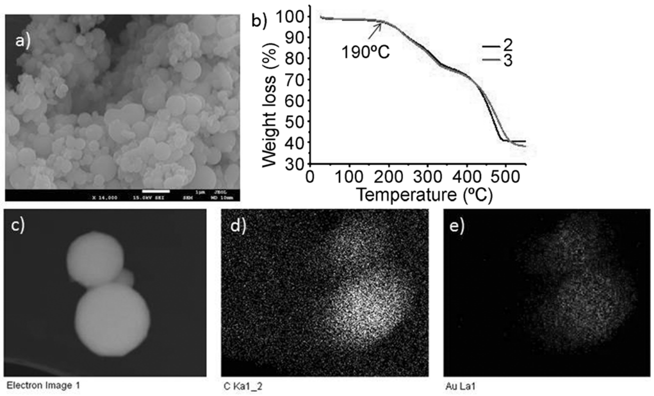
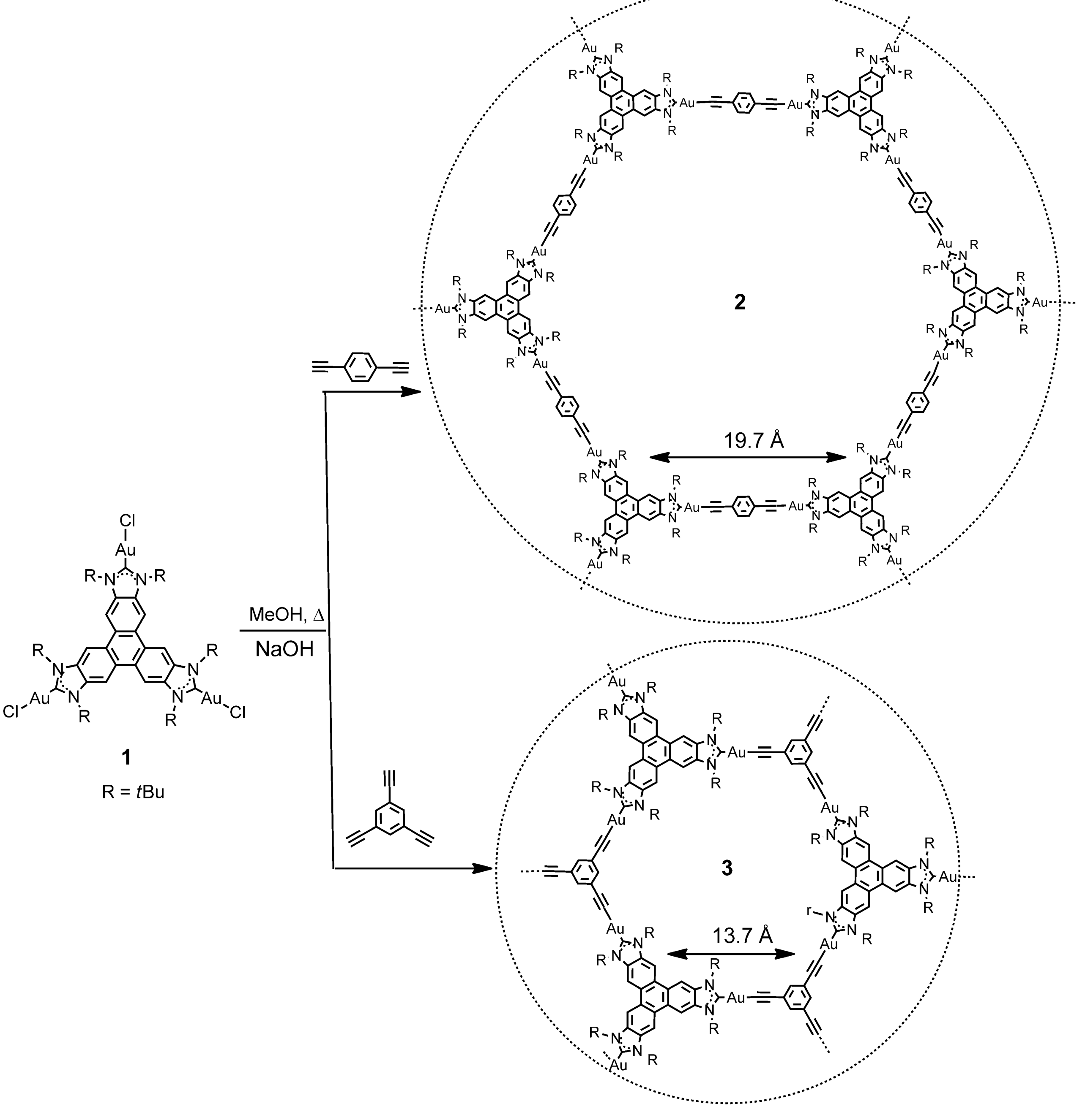


Figure 2. a) SEM image of **2**, scale bar = 1 μm. b) TGA of **2** and **3**. c) STEM image of **2**. EDS elemental mapping images performed by means of TEM of **2** showing the homogeneous distribution of d) carbon and e) gold.

The morphologies of **2** and **3** were investigated by SEM and TEM (Figure 2a and c; see also Supporting Information), which revealed that both materials have spherical shapes. The sizes of the spheres in **2** range from 100 to 600 nm, and those of **3** from 50 to 100 nm. Elemental mapping by energy-dispersive X-ray spectroscopic (EDS) analysis performed by means of TEM on **2** (Figure 2d and e) and **3** (Supporting Information) confirmed the homogeneous distribution of carbon and gold. The powder X-ray diffraction patterns of **2** and **3** showed amorphous character. Thermogravimetric analysis (TGA) revealed similar thermal stabilities of **2** and **3**, which were both stable up to 190 °C (Figure 2b). Nitrogen-sorption analysis at 77 K gave BET surface areas for **2** and **3** of 43 and 222 m^2g^{-1}, respectively, which correlate well with the smaller size of the spheres of **3**.

Heterogeneous catalysts often display size-dependent activities, because the catalytic efficiency depends on the surface area and substrate transport. Because **2** and **3** have similar chemical compositions but different morphological properties, we assumed that any differences in their catalytic properties should be attributable merely to their different surface areas. We tested the catalytic activities of **2** and **3** in the reduction of nitroarenes with sodium borohydride in aqueous medium. Among reactions catalyzed by gold nanoparticles, the reduction of nitroarenes to anilines is one of the most widely stud-

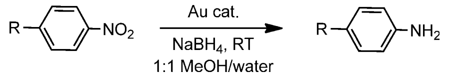


Scheme 2. Synthetic route to MOMPs **2** and **3**.

ied,[12] due to the applications of functionalized anilines in the synthesis of pharmaceuticals and fine chemicals. The reactions were carried out in water/methanol (1/1) at room temperature with $NaBH_4$ as reducing agent. Both catalysts showed high activity in the reduction of 4-methoxynitrobenzene and moderate activity for the reduction of *p*-nitrotoluene and 4-bromonitrobenzene (Table 1). In general, the activity of **2** was higher than that of **3**, an observation that is opposite to our expectation that the material with the larger surface area should have higher activity in the reaction. During the course of the reaction, the solid catalyst turned into a dark gray material that contained Au nanoparticles, as confirmed by images recorded by using the backscattered SEM signal (see Figure S6.3 in the Supporting Information), and therefore we cannot rule out that the activity of the solids is mainly due to the gold nanoparticles formed in the course of the reaction, rather than to the organometallic polymer.

To test the catalytic activity of the two solids in a reaction that does not need a strong reductant such as $NaBH_4$, we chose the three-component Strecker reaction for the synthesis of α-aminonitriles from an amine, an aldehyde (or ketone), and trimethylsilyl cyanide (TMSCN).[13] Although this reaction has at-

Table 1. Reduction of nitroarenes catalyzed by **2** and **3**.[a]

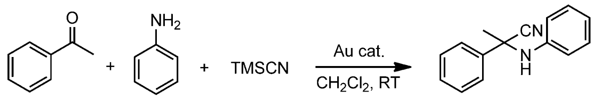


Entry	R	Catalyst	Yield [%][b]
1	Me	**2**	65
2	Me	**3**	45
3	OMe	**2**	>95 (92)
4	OMe	**3**	>95 (90)
5	Br	**2**	84
6	Br	**3**	65

[a] Reaction conditions: 1.078 mmol of nitroarene and 50 mmol of $NaBH_4$ were stirred in 10 mL of Milli-Q water/MeOH (1/1) under a nitrogen steam for 15 min. Then 2.5 mg of **2** or **3** was added and the resulting mixture stirred for 5 h. [b] Yields determined by ^1H NMR spectroscopy. Yields of isolated products in parentheses.

tracted much attention, we are unaware of any catalyst based on gold, and there is only one example of the use of an NHC-based heterogeneous catalyst to promote this reaction.[9] We thought that the gold centers in **2** and **3** could provide the Lewis acidic function of the catalyst to promote this reaction. The reactions were carried out in CH_2Cl_2 at room temperature with 4 mol% of catalyst (based on Au content). The reaction between acetophenone and aniline with **2** or **3** as catalyst afforded almost quantitative yields of the α-aminonitrile product, although **3** seemed to show slightly higher activity (Table 2). After the reaction finished, the catalyst could be easily separated from the reaction mixture by centrifugation, and be reused for subsequent runs, although a considerable loss of activity was observed. SEM analysis of **2** and **3** after catalysis showed significant changes in the morphologies of the solids, although the composition seemed not to have been altered, and no trace of Au nanoparticles could be found. The BET surface areas of **2** and **3** after being used as catalysts showed large decreases compared to the pristine materials. The BET surface areas of **2** and **3** after the catalytic reaction were 18 and 26 m^2g^{-1}, respectively. This major modification of the morphology of the solids is in contrast to the slight changes found in the composition of the two catalysts. The IR spectra of the two solids showed bands due to the presence of C≡C bonds. TGA measurements on the two catalysts after the catalytic reaction revealed similar behavior to the pristine catalysts, with decomposition temperatures above 190 °C. Finally, the elemental analyses of the two solids after being used in the Strecker reaction showed little variation compared to the pristine materials. All these observations indicate the loss of activity of the catalysts after the first run is mainly due to morphological changes of the solid.

Table 2. Recycle test of **2** and **3** in the three-component Strecker reaction.[a]



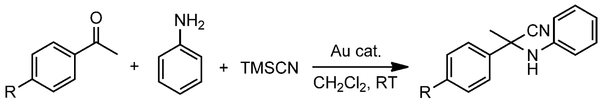
Run	Catalyst	Yield [%][b]	Run	Catalyst	Yield [%][b]
1	**2**	95	1	**3**	98
2	**2**	59	2	**3**	70
3	**2**	29	3	**3**	61

[a] Reaction conditions: 0.5 mmol acetophenone, 0.55 mmol aniline, 1 mmol TMSCN, 4 mol% catalyst loading (based on Au), 2 mL of CH_2Cl_2, 12 h at room temperature. [b] Yields determined by GC with anisole (0.5 mmol) as internal standard.

We also wondered whether the gold nanoparticles formed in the reduction of nitroarenes could also be active in catalyzing the Strecker reaction. To this end, we used the gold nanoparticles generated from **2** and **3** after being used as catalysts in the reduction of nitroarenes and observed that they were completely inactive in the Strecker reaction. This experiment verifies that the original polymeric materials **2** and **3** are responsible for the catalytic activity, rather than any possible traces of gold nanoparticles formed during the process.

Given the high activities shown by **2** and **3**, we extended their use to the coupling of other substituted acetophenones (Table 3). Both materials were highly active for acetophenones with a bromo or methoxy group at the *para* position, and **3** showed higher activity. Interestingly, the catalysts tolerate well the presence of a halo substituent (Table 3, entries 1 and 2), and this is a clear advantage over palladium-based catalysts, for which dehalogenation of halo-substituted acetophenones may constitute a serious side reaction. The presence of a *p*-NO_2 group resulted in a clear deactivation of the process, although the final compound could be obtained in 20% yield when **2** was used. Although this yield may be considered to be low, it is among the highest yields described for the coupling of *p*-nitroacetophenone with aniline (a 17% yield was described for a homogeneous palladium–NHC catalyst).[13a] The activity of **2** and **3** is expected to originate in the Lewis acidic activation of the ketone or imine on coordination to Au.

Table 3. Three-component Strecker reaction of ketones.[a]



Entry	R	Catalyst	Yield [%][b]
1	Br	**2**	85
2	Br	**3**	88
3	NO_2	**2**	20
4	NO_2	**3**	13
5	MeO	**2**	76
6	MeO	**3**	92

[a] Reaction conditions: 0.5 mmol ketone, 0.55 mmol aniline, 1 mmol TMSCN, 4 mol% catalyst loading (based on Au), 2 mL of CH_2Cl_2, 12 h at room temperature. [b] Yields determined by GC with anisole (0.5 mmol) as internal standard.

Conclusion

We have obtained and fully characterized two NHC–gold–acetylide MOMPs based on our recently described triphenylene-tris-NHC ligand. The new solids were tested in the catalytic reduction of nitroarenes with $NaBH_4$ and in the three-component Strecker reaction for the synthesis of α-aminonitriles, and showed high activity in both processes. Whereas their activity in the reduction of nitroarenes can be attributed to the formation of Au nanoparticles due to the use of $NaBH_4$ as reducing agent, the activity in the Strecker reaction may originate from Lewis acidic activation of the ketone or imine on coordination to Au. We believe that this is the first time that a gold catalyst has been used in the Strecker reaction, and therefore the results described here represent a new application of gold in a heterogeneously catalyzed reaction.

Experimental Section

Synthesis of 2

NaOH (40.6 mg, 0.51 mmol) and 1,4-diethynylbenzene (7.13 mg, 0.054 mmol) were dissolved in 20 mL of methanol. This mixture was heated to reflux for 15 min and then compound **1** (50 mg, 0.036 mmol) was added as a solid. The resulting suspension was heated to reflux for 4 h. The resulting brown solid was collected by filtration and washed with water, methanol, acetonitrile, dichloromethane, toluene, hexane, and diethyl ether. Yield: 35 mg (68 %); IR (ATR): $\tilde{\nu}(C\equiv C) = 2102\ \mathrm{cm^{-1}}$; elemental analysis calcd (%) for $(C_{60}H_{66}N_6Au_3)_n$: C 49.29, H, 4.55, N 5.75; found: C 48.95, H, 4.60, N 5.39.

Synthesis of 3

NaOH (31.7 mg, 0.76 mmol) and 1,3,5-triethynylbenzene (5.43 mg, 0.036 mmol) were dissolved in 20 mL of methanol. This mixture was heated to reflux for 15 min and then compound **1** (50 mg, 0.036 mmol) was added as a solid. The resulting suspension was heated to reflux for 4 h. The resulting yellow solid was collected by filtration and washed with water, methanol, acetonitrile, dichloromethane, toluene, hexane, and diethyl ether. Yield: 46.6 mg (90 %); IR (ATR): $\tilde{\nu}(C\equiv C)$: $2103\ \mathrm{cm^{-1}}$; elemental analysis calcd (%) for $(C_{57}H_{63}N_6Au_3)_n$: C 48.11, H 4.46, N 5.91; found: C 47.75, H 4.56, N 5.56.

Synthesis of 4

NaOH (31.7 mg, 0.76 mmol) and phenylacetylene (17.6 µL, 0.108 mmol) were dissolved in 20 mL of methanol. This mixture was heated to reflux for 15 min and then compound **1** (50 mg, 0.036 mmol) was added as a solid. The resulting suspension was heated to reflux for 4 h. A white solid formed. The volatile materials were evaporated. The resulting solid was dissolved in dichloromethane, filtered through a pad of Celite, and the solvent removed under vacuum. Precipitation from CH_2Cl_2/hexane gave the desired product as a white solid. Yield: 77 mg (91 %); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.01$ (s, 6 H, CH_{arom}), 7.52 (d, $^3J_{HH} = 8.3$ Hz, 6 H, CH_{arom}), 7.23 (t, $^3J_{HH} = 7.4$ Hz, 6 H, CH_{arom}), 7.17 (d, $^3J_{H-H} = 7.4$ Hz, 3 H, CH_{arom}), 2.39 ppm (s, 54 H, $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 199.6$ ($AuC_{carbene}$), 134.7 ($C_{q\ arom}$), 132.4 ($CH_{arom\ acetylide}$), 127.9 ($CH_{arom\ acetylide}$), 126.4 ($CH_{arom\ acetylide}$), 126.0 ($C_{q\ acetylide}$), 125.5 ($C_{q\ arom}$), 121.8 ($C_{q\ acetylide}$), 109.3 (CH_{arom}), 106.7 ($C_{q\ acetylide}$), 62.6 ($C(CH_3)_3$, 33.5 ppm ($C(CH_3)_3$; MS (electrospray, 20 V): $m/z = 1281.6$ $[M-Au-C_8H_5+H]^+$, 492.5 $[M-2Au-2C_8H_5+2H]^{2+}$; elemental analysis calcd (%) for $C_{69}H_{75}N_6Au_3(H_2O)_2$: C 51.3, H 4.93, N 5.2; found: C 51.4, H 5.25, N 5.05.

General procedure for the reduction of nitroarenes in aqueous medium

Nitroarene (1.078 mmol) and sodium borohydride (50 mmol) were placed in a Schlenk tube, which was evacuated and filled with nitrogen three times. The solids were stirred in 10 mL of Mili-Q water/MeOH (1/1) under a nitrogen steam for 15 min. Then, solid **2** or **3** (2.5 mg containing 5.1×10^{-3} mmol of gold, 0.5 mmol %) was added. The resulting mixture was stirred at room temperature for 5 h. The solid residue was separated by filtration and washed with distilled water and acetone. The filtrate was extracted with ethyl acetate (3×10 mL) and the extract dried over $MgSO_4$. The solvent was evaporated under vacuum. Yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene (1.078 mmol) as internal standard.

General procedure for the synthesis of α-aminonitriles (Strecker reaction)

A capped vessel containing a stirrer was charged with the corresponding ketone (0.5 mmol), aniline (0.55 mmol), TMSCN (1 mmol), anisole as internal reference (0.5 mmol), the catalyst (0.02 mmol Au), and 2 mL of dichloromethane. The resulting mixture was stirred for 12 h at room temperature. For recycle tests, the catalyst was recovered by centrifugation and washed with dichloromethane. The evolution of the reactions and yields were determined by GC analysis.

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Keywords: carbene ligands · coordination polymers · gold · heterogeneous catalysis · Strecker reaction

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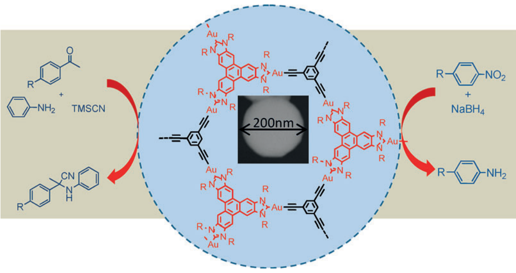

Catalytic MOMPs: Two triphenylene-based tris(N-heterocyclic carbene)–gold–acetylide main-chain organometallic microporous polymers (MOMPs) were prepared. The two solids proved to be effective catalysts in the reduction of nitroarenes and in the three-component Strecker reaction for the synthesis of α-aminonitriles (see figure, TMSCN = trimethylsilyl cyanide).

Coordination Polymers

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Main-Chain Organometallic Microporous Polymers Bearing Triphenylene–Tris(N-Heterocyclic Carbene)–Gold Species: Catalytic Properties