Simple and Efficient: Ethylene Glycol Isonitrile Gold(I) Chlorides for the Formation and Stabilization of Gold Nanoparticles

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Ethylene glycol isonitriles $C\equiv N(CH_2CH_2O)_nCH_3$ (**5a**, $n = 1$; **5b**, $n = 3$; **5c**, $n = 4$) with different chain lengths were prepared by using straightforward synthesis methodologies including the Gabriel synthesis and an Appel-type reaction protocol. Upon treatment with $[AuCl(SMe)_2]$, compounds **5a–c** gave the corresponding isocyanide gold(I) chlorides $[AuCl\{C\equiv N(CH_2CH_2O)_nCH_3\}]$ (**7a**, $n = 1$; **7b**, $n = 3$; **7c**, $n = 4$). Single-crystal X-ray diffraction studies reveal a polymeric (**7a**) or dimeric (**7c**) structure with aurophilic interactions. Gold(I) complexes **7a–c** were applied in the formation and stabilization of gold nanoparticles (AuNPs). The isonitriles with their ethylene glycol functionalities, which provide multiple donating capabilities, are able to stabilize the encapsulated gold colloids. The reduction of **7a–c** by the addition of $Na[BH_4]$ in tetrahydrofuran or methanol produces AuNPs without the further addition of any stabilizer, since metal-organic **7a–c** combine the stabilizing component and gold source in one molecule. The dependency of different solvents, concentrations, and varying ethylene glycol chain lengths on the NP size and size distribution is reported. Characterization by TEM, UV/Vis spectroscopy, and XRPD revealed that AuNPs are formed with a size between $6.4(\pm1.4)$ to $9.5(\pm2.3)$ nm in methanol and $18.2(\pm2.3)$ to $27.2(\pm3.5)$ nm in tetrahydrofuran.

Introduction

In recent decades, considerable efforts have been made to synthesize and stabilize defined transition-metal nanoparticles (NP). As these materials have discrete particle sizes between 1 and 100 nm diameter, their unique physicochemical properties are affected by the particle size, shape, size distribution, and particle-to-particle interaction.[1] In particular, group 11 metal NPs allow the design of new generations of nanodevices and smart materials[2] due to their unique optic,[3] electric,[4] magnetic,[5] catalytic,[6] or biological[7] properties. Bottom-up and top-down methodologies are widely applied in NP formation. The bottom-up method allows their selective synthesis (e.g., defined structures through chemical reduction of a gold source),[8] decomposition of metal-organic compounds,[9] or electrochemical[10] and photochemical[11] methods. For the first time, Turkevich et al. synthesized gold colloids in aqueous media by reducing chloroauric acid with sodium citrate.[12] Another synthesis methodology is the so-called Brust–

Schiffrin method, in which chloroauric acid is reduced by sodium borohydride in presence of an alkanethiol.[13] Möller and co-workers generated AuNPs by using sodium borohydride or hydrazine as reducing agent in micelles that behave like "nanoreaction vessels".[14] These procedures require the addition of stabilizing agents and the use of hygroscopic chloroauric acid, which is also light-sensitive. For the synthesis of high-quality AuNPs, stabilizing agents that feature donating functionalities or atoms like N, O, P, and S are required, which will attach to the particle surface and hence prevent aggregation. (Poly)ethylene glycols,[15] polymers/block copolymers,[16] dendrimers,[17] phosphanes,[18] amines,[19] thioethers,[20] and surfactants[21] are typically used as stabilizing components.

We report here on the synthesis of $[AuCl\{C\equiv N-(CH_2CH_2O)_nCH_3\}]$ ($n = 1, 3, 4$) and its use in the formation of gold NPs by a bottom-up methodology. The addition of any further stabilizing agent is not necessary because the appropriate gold(I) complex combines the gold source and the stabilizing component in one molecule. The influence of the ethylene glycol chain length, the use of different organic solvents, and the ethylene glycol isocyanide gold(I) chloride concentration on the NP size and the size distribution is discussed.

Results and Discussion

Synthesis and Characterization

Starting from ethylene glycol monomethyl ether, the appropriate gold(I) complexes $[AuCl\{C\equiv N(CH_2CH_2O)_n$-

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CH$_3$}] (**7a**, n = 1; **7b**, n = 3; **7c**, n = 4) were available through a five-step synthesis procedure using Gabriel synthesis and an Appel analogue reaction procedure (Scheme 1). Subsequent treatment of ethylene glycol monomethyl ethers **1a** (n = 1), **1b** (n = 3), or **1c** (n = 4) with phthalimide, PPh$_3$, and diisopropyl azodicarboxylate (DIAD) gave the corresponding ethylene glycol monomethyl ether substituted phthalimides **2a–c** in yields between 85 and 96% (see Exp. Sect.). Treatment of **2a–c** with hydrazine hydrate followed by addition of concentrated aqueous HCl produced amines **3a–c** (59–70%). Further reaction with methyl formate and p-toluenesulfonic acid monohydrate resulted in the formation of formamides **4a–c** (93–99%) (Scheme 1). The latter molecules gave isonitriles **5a–c** along with PPh$_3$, NEt$_3$, and CCl$_4$. Isonitrile gold(I) chlorides **7a–c** were accessible by treating **5a–c** with [AuCl(SMe$_2$)] (**6**) in virtually quantitative yield.
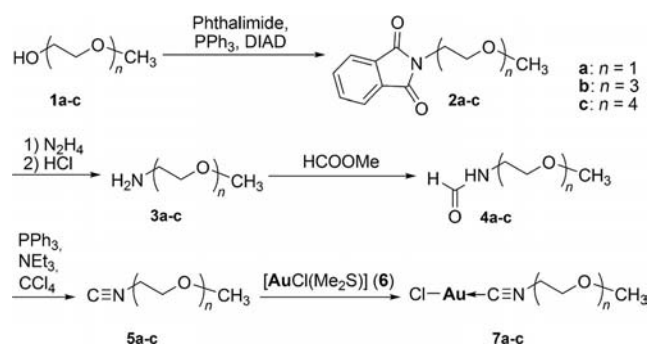
Scheme 1. Synthesis of isocyanide gold(I) complexes **7a–c** from **1a–c**.

Metal-organic complexes **7a–c** are stable to air and moisture both in the solid state and in solution. All newly prepared compounds have been identified by elemental analysis, IR, and NMR (^{1}H, ^{13}C{^{1}H}) spectroscopy. Additionally, high-resolution-ESI TOF mass spectrometry and single-crystal X-ray structure analysis (**7a** and **7c**) were carried out. Advantages of the reaction of **3a–c** with methyl formate to give **4a–c** is that it can easily be monitored by IR spectroscopy, since the NH-deformation (δ_{NH} = 1597–1600 cm^{-1}) and -valence vibrations (ν_{NH} = 3360–3368 cm^{-1}) are shifted bathochromically (δ_{NH} = 1530–1536 cm^{-1}, ν_{NH} = 3297–3318 cm^{-1}) when going from **3a–c** to **4a–c**. Additionally, the typical formamide C=O valence vibration occurs at approximately 1680 cm^{-1}. Further conversion of **4a–c** to isonitriles **5a–c** can also be monitored by IR spectroscopy due to the disappearance of the N-amide and C=O vibrations accompanied by the appearance of the isocyanide C≡N absorption between 2151 and 2155 cm^{-1} (see Exp. Sect.). Coordination of isonitriles **5a–c** to [AuCl] causes a hypsochromic shift of the C≡N bonds (2259–2268 cm^{-1}), which is typical in gold(I) isocyanide chemistry.[22]

Characteristic for formamides **4a–c** in the ^{1}H NMR spectra is the appearance of a broad signal at $\delta \approx 6.6$ ppm for the N-amide functionality. The CHO moiety gives rise to a signal at $\delta \approx 8.1$ ppm. Very characteristic in the ^{13}C{^{1}H} NMR spectra of **4a–c** is the appearance of the carbonyl carbon atom at $\delta \approx 161.2$ ppm, whereas transformation to isonitriles **5a–c** causes a high-field-shifted isocyanide carbon atom, which could be detected at $\delta \approx 157.5$ ppm with typical coupling constants (see Exp. Sect.). These signals
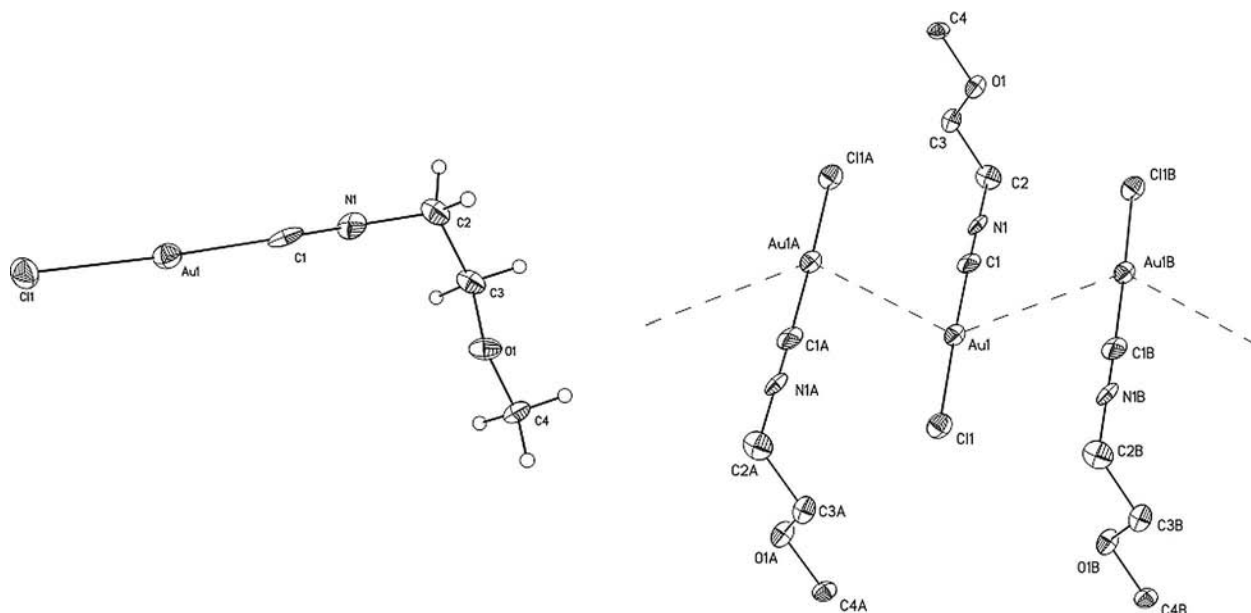

Figure 1. Left: ORTEP diagram (50% probability level) of **7a** with the atom-numbering scheme of selected bond lengths [Å] and angles [°]: Au1–Cl1 2.262(3), C1–Au1 1.949(11), N1–C1 1.119(12), C2–N1 1.429(13), C2–C3 1.508(13), C3–O1 1.425(11), O1–C4 1.433(10); Cl1–Au1–C1 1177.7(2), Au1–C1–N1 178.9(9), C1–N1–C2 179.7(9), C3–O1–C4 109.8(7). Right: 1D chain of **7a** setup by aurophilic interactions [Au1–Au1A 3.4557(6), Au1–Au1B 3.7320(5) Å] (symmetry-generated atoms are indicated by the suffix A and B; symmetry codes: –x, 1 – y, 1 – z and –x, 2 – y, 1 – z.).
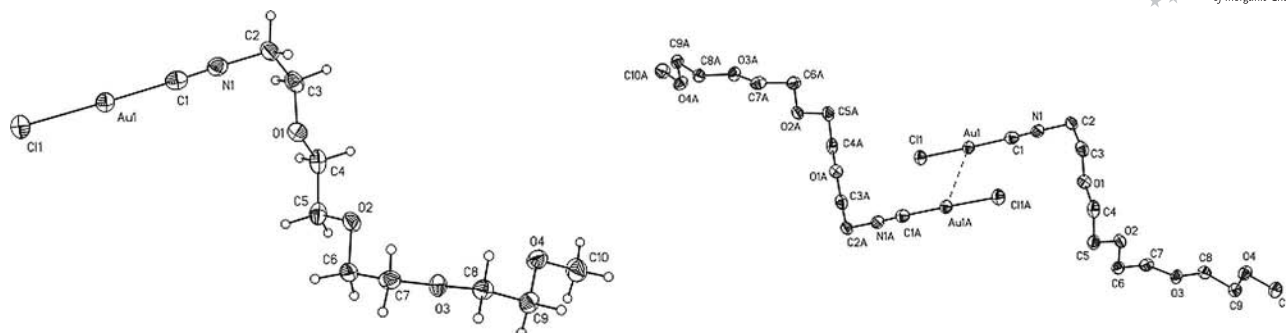
Figure 2. Left: ORTEP diagram (50% probability level) of **7c** with the atom-numbering scheme of selected bond lengths [Å] and angles [°]: Au1–Cl1 2.2603(10), C1–Au1 1.943(4), N1–C1 1.135(5), N1–C2 1.447(5), C2–C3 1.493(7), C3–O1 1.422(5), O1–C4 1.423(5); Cl1–Au1–C1 178.27(14), Au1–C1–N1 177.6(4), C1–N1–C2 176.8(5), C3–O1–C4 112.3(3). Right: aurophilic interaction between two *anti*-periplanar-oriented molecules of **7c** in the solid state with Au1–Au1A contacts [3.5317(2) Å] (symmetry-generated atoms are indicated by the suffix A; symmetry code: 1 – *x*, –1 – *y*, 1 – *z*.).

are shifted to higher field in Au^I complexes **7a**–**c** ($\delta \approx$ 135.3 ppm), which indicates the coordination of **5a**–**c** to a transition-metal atom.[22]

The structures of **7a** (Figure 1) and **7c** (Figure 2) in the solid state were determined by single-crystal X-ray diffraction analysis. Relevant crystallographic and structure refinement data are summarized in the Exp. Sect. Selected bond lengths [Å] and bond angles [°] are given in the captions of Figures 1 and 2.

Metal-organic **7a** crystallized in the triclinic space group $P\bar{1}$ and **7c** in the monoclinic space group $P2_1/n$. As expected, the Cl–Au–C≡N–CH$_2$ building blocks are linear with bond angles between 177 and 180° and a maximum deviation of 0.115(4) (**7a**, for Cl1) or 0.100(2) Å (**7c**, for Cl1). Weak aurophilic interactions are observed, thereby resulting in the formation of a 1D chain with Au–Au separations of 3.4557(6) and 3.7320(5) Å (Figure 1, right).[23] Complex **7c** forms an *anti*-periplanar-oriented dimer with an Au–Au distance of 3.5317(2) Å in the solid state (Figure 2, right). Similar species have recently been published {i.e., [AuX(C≡NR)] (X = Cl, NO$_3$; R = C$_3$H$_7$, C$_6$H$_{11}$)} by Schmidbaur and co-workers. The bond angles of the X–Au–C moiety are almost in the same range; however, the Au–C bond lengths are enlarged in **7a** and **7c**, respectively.[24]

Nanoparticle Formation and Characterization

For generation of gold nanoparticles, isocyanide gold(I) chlorides **7a**–**c** were dissolved in tetrahydrofuran or methanol (1×10^{-2} to 8×10^{-4} M) and reduced by the addition of Na[BH]$_4$ to the appropriated gold(I) solutions. A change from colorless to intensive purple was observed, thus indicating the formation of zero-valent AuNPs stabilized by the isocyanide ethylene glycol chains. For completion of the reducing process, stirring for 5 min was required (see Exp. Sect.). Further addition of any stabilizing agents was not necessary. The formation of gold NPs was proven by electron diffraction pattern and X-ray powder diffraction studies (XRPD) (see the Supporting Information). Electron dif-

fraction analysis of the AuNPs showed the presence of a face-centered cubic (fcc) lattice structure. The ring pattern can be indexed as derived from (111), (200), (220), (222), and (311) lattice planes of gold. In addition, XRPD analyses of the synthesized Au colloids were carried out in methanol solutions and show four characteristic reflexes at 38.19, 44.37, 64.59, and 77.57° (ICDD C03–068–2870), which correspond to Miller indices (111), (200), (220), and (311), thereby confirm an fcc lattice structure.[25]

Optical characterization of the AuNP solutions was done by UV/Vis spectroscopy (Figure 3). All UV/Vis spectra show a strong absorption in the range of 450–650 nm due to the plasmon resonance caused by the interaction of electromagnetic radiation with the electron fluctuation of colloidal gold (see the Supporting Information). The plasmon maximum of the AuNP was observed between 513 and 518 nm in methanol (Table 1).[26] When tetrahydrofuran was used as solvent, the absorption maximum was bathochromic shifted (527–538 nm) (Figure 3, Table 1). This indicates that larger AuNPs are formed in tetrahydrofuran than in methanol. Most probably the coordinating (stabilizing) behavior of tetrahydrofuran is lower than methanol, thus leading to larger particles, which corresponds with observations described in the literature.[27] The different ethylene glycol chain lengths show only a little effect on the AuNP

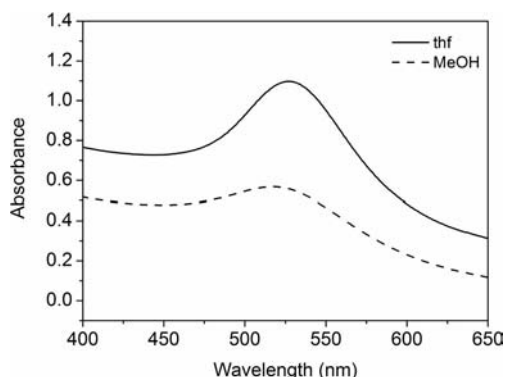Figure 3. UV/Vis spectrum of **7c** in methanol (dashed line) and tetrahydrofuran (solid line) ($T = 25$ °C; $c = 6.3 \times 10^{-3}$ M).

size formation, as can be concluded from almost identical UV/Vis spectra in tetrahydrofuran and methanol, respectively.

Table 1. Comparison of the plasmon maxima and the AuNP size depending on ethylene glycol chain lengths and solvent (see the Supporting Information).

	Solvent	UV/Vis [nm]	NP size [nm]
7a	methanol	515	8.2 ($\pm$2.0)
7b	methanol	513	8.1 ($\pm$1.0)
7c	methanol	518	8.3 ($\pm$1.5)
7a	tetrahydrofuran	538	27.2 ($\pm$4.1)
7b	tetrahydrofuran	533	23.0 ($\pm$2.9)
7c	tetrahydrofuran	527	24.3 ($\pm$3.5)

The particle size, size distribution, and shape of the AuNPs were determined by tranmission electron microscopy (TEM) measurements to reveal an average size diameter between 8.1($\pm$1.1) and 8.3($\pm$1.5) nm in methanol (Figure 4). It can be seen that the ethylene glycol chain length in methanol has no effect on the particle size. In tetrahydrofuran, the AuNP size diameters are significant larger 23.0($\pm$3.3) to 27.2($\pm$4.1) nm. An increase of the gold particle size, effected by the shortest ethylene glycol chain, occurs due to the lower number of donating functionalities and hence the smaller organic matrix. Contrary to our expectations is that the obtained particle sizes of **7b** and **7c** are nearly identical. This is most probably caused by the small difference of only one additional CH_2CH_2O repeating unit between **7a** and **7b**. The higher polarity of methanol compared with tetrahydrofuran influences the formation of smaller NPs. In addition to UV/Vis measurements (vide supra), TEM studies were carried out to verify that different chain lengths of appropriate isonitriles have only a small influence on the NP size formation in both solvents (Figure 5; see also the Supporting Information).
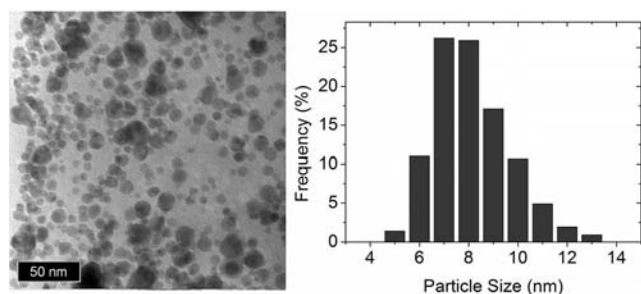

Figure 4. TEM images and size distribution of AuNPs (8.3 $\pm$ 1.5 nm) generated from **7c** upon addition of Na[BH$_4$] in methanol (ϑ = 25 °C; c = 6.3 $\times$ 10^{-3} M).

It is well known that the stabilizing effect depends on the number of donating functionalities of the stabilizer as well as the solvent.[28] The narrowest NP size distributions were found for **7b** and **7c**, which feature the longest ethylene glycol chain length (n = 4) independent of the solvent used (vide supra).

Typical NP preparation was carried out in a concentration of 6.3 $\times$ 10^{-3} M. To study the influence of the concentration on particle size and shape concentrations of
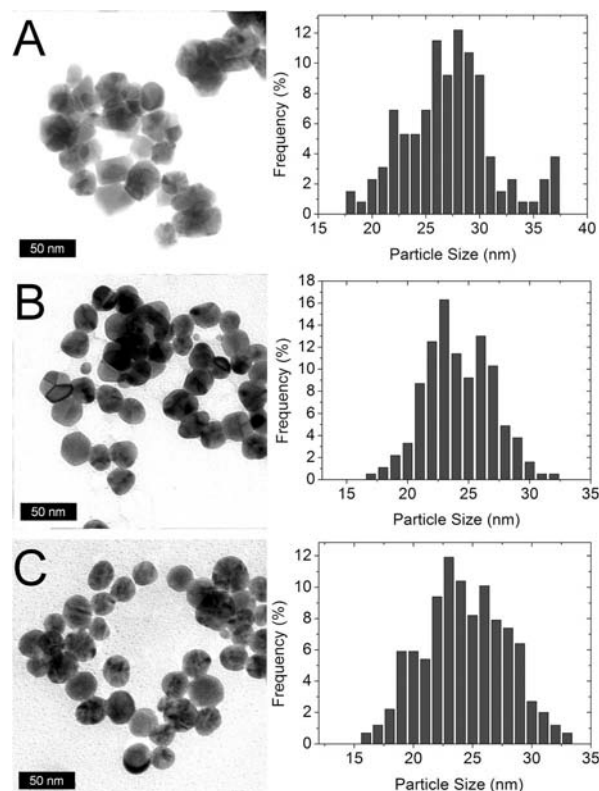

Figure 5. TEM images and size distributions of AuNPs received from **7a–c** in tetrahydrofuran [T = 25 °C; c = 6.3 $\times$ 10^{-3} M; (A) **7a**, (B) **7b**, (C) **7c**].

1.6 $\times$ 10^{-2} M and 7.8 $\times$ 10^{-4} M, respectively, were used. For these studies, complex **7c** was chosen, due to its highest donation capacity and hence the largest organic stabilizing framework.

To determine the nature of the plasmon band, the plasmon full width at half-maximum (FWHM) was determined by deconvolution of the absorption spectra using four Gaussian-shaped overlapping absorptions.[29] The fits are good enough to allow an almost exact overlay of the sum of the spectral components with the experimental data. The increase of FWHM is caused by an increase in the concentration (Table 2), which indicates a broader size distribution of the AuNPs. This indicates an increase of the particle size. TEM analyses are in agreement with the results of FWHM and show a growth of the NP size from 18.2($\pm$2.3) to 23.6($\pm$3.5) nm for tetrahydrofuran and 6.4($\pm$1.4) to 9.5($\pm$2.3) nm for methanol solutions by increasing concentration. In addition, the NP size distribution became broader. The sharpest size distributions in tetrahydrofuran were obtained at low concentrations (7.8 $\times$ 10^{-4} M) for **7c**. In methanol, the sharpest size distribution is obtained by reducing **7c** at concentrations of 6.3 $\times$ 10^{-3} and 7.8 $\times$ 10^{-4} M, respectively. Higher concentrations lead to agglomeration due to the higher probability of colliding (Table 2; see also the Supporting Information). The determination of the polydispersity for NPs generated in methanol is between 12.4 and 24.4 %, whereas for particles formed in tetrahydrofuran a polydispersity of 10.7–24.2 % was found.

Table 2. Comparison of the AuNP size, plasmon maxima, and plasmon FWHM at different concentrations and solvents for **7c** (see the Supporting Information).

Conc. [M]	Solvent	UV/Vis [nm]	FWHM[a] [cm^{-1}]	NP size [nm]
1.6×10^{-2}	methanol	515	3257	9.5($\pm$2.3)
6.3×10^{-3}	methanol	518	3256	8.3($\pm$1.5)
7.8×10^{-4}	methanol	513	2815	6.4($\pm$1.4)
1.6×10^{-2}	tetrahydrofuran	531	3596	23.6($\pm$3.5)
6.3×10^{-3}	tetrahydrofuran	527	2767	24.3($\pm$2.6)
7.8×10^{-4}	tetrahydrofuran	525	2664	18.2($\pm$2.3)

[a] FWHM = plasmon full width at half-maximum.

Obtained TEM images and corresponding size distributions are given in Figure 6. It can be seen that a lower concentration causes smaller AuNPs and a sharper size distribution, which is in agreement with the results of the FWHM studies.
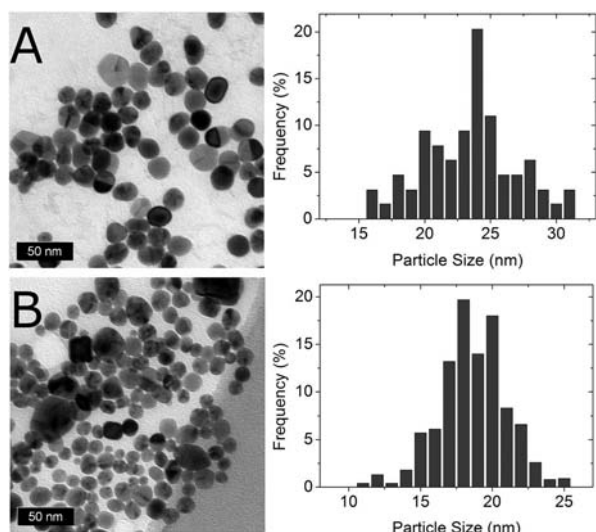

Figure 6. TEM images and size distribution of **7c** in tetrahydrofuran [ϑ = 25 °C; (A) $c = 1.6 \times 10^{-2}$ M; (B) $c = 7.8 \times 10^{-4}$ M].

Experiments on the long-term stability showed that NPs generated by precursor **7a** are only stable for several hours. In contrast, particles formed from **7b** and **7c** are stable for weeks. In general, the stability of particles in methanol is higher than in tetrahydrofuran due to the better stabilization (vide supra). In agreement with literature that deals with different low-molecular-mass colloid stabilizing agents (e.g., oligo-ethers, sodium citrate, or low-generation dendrimers), the obtained particle size and size distributions are in a similar range.[30] Particle sizes obtained in methanol as solvent correspond well with those obtained by the Brust–Schiffrin method. Particle sizes obtained in tetrahydrofuran are similar to the ones from the Turkevich methodology.[12,13,31] Please note that in our approach no additional stabilizing component has to be added.

Currently, the performance of the thus-obtained well-defined AuNPs as heterogeneous catalysts in hydrogenation reactions of α,β-unsaturated aldehydes is being tested.[32–34]

Conclusion

Ethylene glycol isonitriles with different chain lengths $C\equiv N(CH_2CH_2O)_nCH_3$ (n = 1, 3, 4) were prepared by using straightforward synthesis methodologies. Their coordination to gold(I) chloride gave the corresponding isocyanide gold(I) chloride complexes $[AuCl\{C\equiv N(CH_2CH_2O)_n-CH_3\}]$. These species show in relation to the chain length in the solid state weak aurophilic interactions to give 1D chains $[AuCl\{C\equiv N(CH_2CH_2O)CH_3\}]$ or *anti*-periplanar-oriented dimers ($[AuCl\{C\equiv N(CH_2CH_2O)_4CH_3\}]$) with Au–Au contacts between 3.4557(6) and 3.7320(5) Å. The gold(I) complexes were used for the generation and stabilization of gold NPs without any addition of a further stabilizing agent. The oligo(ethylene glycol) isonitriles provide multiple donating functionalities, which are essential for the stabilization of gold colloids. Gold NPs are accessible through an efficient reductive method, whereby the appropriate gold(I) precursor possesses stabilizer and gold source in one molecule. These metal-organic complexes are able to produce AuNPs that are reproducible through a reductive method (the addition of Na[BH$_4$]). The colloids were characterized by TEM, UV/Vis, and XRPD experiments. The relationship between different solvents, concentrations, and variable ethylene glycol chain lengths and the AuNP size and size distribution was studied. Gold NPs were formed with a size of 8.1($\pm$1.1) to 8.3($\pm$1.5) nm (methanol) and 24.1($\pm$2.9) to 27.2($\pm$4.1) nm (tetrahydrofuran), respectively, in relation to different ethylene glycol chain lengths. In methanol, no influence on the average particle size diameter was observed, whereas in tetrahydrofuran an increase in the particle diameter for $[AuCl\{C\equiv N(CH_2CH_2O)CH_3\}]$ due to the poor stabilizing effect of the isocyanide is characteristic. Increasing concentrations create an increase in the AuNP size [methanol 6.4($\pm$1.4) to 9.5($\pm$2.3) nm, tetrahydrofuran 18.2($\pm$2.3) to 24.3($\pm$3.6) nm] due to higher probability of colliding, which results in an agglomeration of the AuNPs. Within this strategy, different particle sizes with small size distribution could be obtained by changing the concentration or varying the chain length of the isocyanide. The low influence of the ethylene glycol is caused by a too small increase in the donating functionalities and hence the small organic matrix. Further experiments with significantly more repeating units (>30) should show a larger effect on the AuNP size and size distribution. However, our methodology to generate gold NPs at ambient temperature by using a "two-in-one" molecule (which contains the gold source and a stabilizer) results in the formation of small particles with small size distributions.

Experimental Section

Instruments and Materials: All synthetic procedures were performed under an argon atmosphere with the solvents and reagents degassed prior to use. 3,6,9-Trioxadecylamine[35] (**3b**), 1-isocyano-2-methoxyethane[36] (**5a**), and [AuCl(SMe$_2$)][37] (**6**) were prepared according to literature procedures. All other chemicals were obtained commercially and used without further purification.

The ^{1}H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.303 MHz in the Fourier transform mode; the ^{13}C{^{1}H} NMR spectra were recorded at 125.800 MHz. Chemical shifts are reported in δ [ppm] downfield from tetramethylsilane with the solvent as reference (^{1}H NMR: CHCl$_3$, δ = 7.26 ppm; ^{13}C{^{1}H} NMR: CDCl$_3$, δ = 77.00 ppm). The melting points of analytically pure samples (sealed off in nitrogen-purged capillaries) were determined with a Gallenkamp MFB 595010M melting-point apparatus. Microanalyses were performed with a Thermo FLASHEA 1112 Series instrument. Infrared spectra were recorded with an FT-Nicolet IR 200 spectrometer. UV/Vis absorption spectra were recorded with a Thermo Genesys 6 spectrophotometer. High-resolution mass spectra were recorded with a micrO-TOF QII Bruker Daltonite workstation. Transmission electron microscopy (TEM) imaging was performed with a PHILIPS CM 20 instrument operating at 200 kV. X-ray powder diffraction (XRPD) was carried out with a STOE-STAD IP device with Cu-K_α (1.5404 Å) radiation.

General Preparation Procedure for Gold Nanoparticles: The generation of gold NPs was carried out in solution. Therefore, Au^I complexes **7a**–**c** were dissolved in tetrahydrofuran or methanol (c = 1.6×10^{-2} M, 6.3×10^{-3} M, 7.8×10^{-4} M). The reaction solution (20 mL) was stirred for 10 min at ambient temperature followed by the addition of an equimolar amount of Na[BH$_4$]. The color changed immediately from colorless to purple by the addition of Na[BH$_4$]. The mixture was further aged for 5 min for completeness. Colloidal gold solutions were used as obtained without further purification. Boric acid and sodium chloride that was formed by reduction of **7a**–**c** with Na[BH$_4$] did not influence the NP characterization due to their noncoordinating behavior.[38]

2-(2,5,8,11-Tetraoxatridecan-13-yl)isoindoline-1,3-dione (2c): Phthalimide (21.48 g, 0.15 mol) and triphenylphosphane (37.8 g, 0.15 mol) were dissolved in tetrahydrofuran (400 mL). 2,5,8,11-Tetraoxatridecan-13-ol (25.00 g, 0.12 mol) was added dropwise to this solution, and the mixture was stirred for an additional 15 min at ambient temperature. DIAD (28.38 mL, 0.15 mol) was added dropwise to this mixture over a period of 30 min, and stirring was continued for an additional 12 h at ambient temperature and ethanol (250 mL) was added. After evaporation of all volatiles in an oil-pump vacuum, the residue was treated with a mixture of n-hexane/ethyl acetate (100 mL, 1:1 v/v) and heated to 40 °C for 1 h. The formed solid was filtered off and washed twice with n-hexane/ethyl acetate (20 mL, 1:1 v/v). All volatiles were removed in an oil pump vacuum and the crude product was subjected to chromatography on silica (n-hexane/ethyl acetate, 1:4; column size 3 × 40 cm) to afford **2c** (37.3 g, 0.102 mol, 85% based on **1c**) as a colorless oil. C$_{17}$H$_{23}$NO$_6$ (337.37): calcd. C 60.52, H 6.87, N 4.15; found C 60.22, H 6.91, N 4.06. FTIR (NaCl): $\tilde{\nu}$ = 2873 (s), 1773 (s), 1711 (s), 1429 (m), 1394 (s), 1109 (s), 1026 (m), 722 (s) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.34 (s, 3 H, OCH$_3$), 3.50 (m, 2 H, CH$_2$), 3.55 (m, 8 H, CH$_2$), 3.62 (m, 2 H, CH$_2$), 3.71 (t, $^3J_{H,H}$ = 5.87 Hz, 2 H, NCH$_2$), 3.87 (t, $^3J_{H,H}$ = 5.87 Hz, 2 H, NCH$_2$CH$_2$), 7.68 (m, 2 H, CH), 7.82 (m, 2 H, CH) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 37.22 (s, NCH$_2$), 58.94 (s, OCH$_2$), 67.84 (s, CH$_2$), 67.87 (s, CH$_2$), 70.05 (s, CH$_2$), 70.42 (s, CH$_2$), 70.50 (s, CH$_2$), 70.55 (s, CH$_2$), 71.87 (s, CH$_2$), 123.15 (s, CH), 132.11 (s, CHCCO), 133.84 (s, CH), 168.19 (s, CON) ppm. HRMS: m/z: calcd. for C$_{17}$H$_{24}$NO$_6$: 338.1598; found 338.1601 [M + H]$^+$.

2,5,8,11-Tetraoxatridecan-13-amine (3c): 2-(2,5,8,11-Tetraoxatridecan-13-yl)isoindoline-1,3-dione (26.00 g, 0.077 mol) was dissolved in ethanol (250 mL) and treated with hydrazinemonohydrate (5.3 mL, 0.1 mol). The mixture was heated to reflux for 12 h and a

colorless precipitate formed. After cooling to 25 °C, the solid was filtered off and all volatiles were removed in an oil-pump vacuum. The residue was dissolved in water (50 mL) and basified with NaOH (100 mL, 1 N). The obtained solution was extracted with dichloromethane (12 × 20 mL). The combined organic phases were dried with MgSO$_4$. After evaporation of the solvent, the residue was distilled under vacuum (0.1 Torr, 85 °C) to afford **3c** as a colorless oil (10.3 g, 0.049 mol, 65%, based on **2c**). Analytical data agree with the literature.[39]

N-{2-[2-(2-Methoxyethoxy)ethoxy]ethyl}formamide (4b): 3,6,9-Trioxadecylamine (8.0 g, 0.05 mol) and p-toluenesulfonic acid monohydrate (13 mg, 0.07 mmol) were dissolved in methyl formate (50 mL) and heated at reflux for 24 h. After removing all volatiles in an oil-pump vacuum, the residue was distilled (9 Torr, 145 °C) to give colorless **4b** (8.9 g, 0.046 mol, 93% based on **2b**). Elemental analysis, FTIR, and ^{1}H NMR spectra are in agreement with the data given in the literature.[40] ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 37.76 (s, NHCH$_2$), 58.93 (s, OCH$_3$), 69.60 (s, CH$_2$), 70.13 (s, CH$_2$), 7.42 (s, CH$_2$), 70.46 (s, CH$_2$), 70.54 (s, CH$_2$), 71.86 (s, CH$_2$), 161.41 (s, HCO) ppm. HRMS: m/z: calcd. for C$_8$H$_{18}$NO$_4$: 192.1230; found 192.1298 [M + H]$^+$.

N-(2,5,8,11-Tetraoxatridecan-13-yl)formamide (4c): Compound **4c** was synthesized as described for **4b**. Thus, 2,5,8,11-tetraoxatridecan-13-amine (7.14 g, 0.034 mol) was treated with p-toluenesulfonic acid monohydrate (10 mg, 0.05 mmol). Vacuum distillation (0.1 Torr, 135 °C) gave **4c** as a colorless oil (7.8 g, 0.033 mol, 98% based on **2c**). C$_{10}$H$_{21}$NO$_5$ (235.28): calcd. C 51.05, H 9.00, N 5.95; found C 50.90, H 8.77, N 6.16. FTIR (NaCl): $\tilde{\nu}$ = 3317 (s), 3051 (m), 28.71 (s), 1697 (s), 1531 (s), 1456 (w), 1385 (w), 1245 (w), 1109 (m), 878 (m) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.31 (s, 3 H, OCH$_3$), 3.40 (m, 2 H, CH$_2$), 3.50 (m, 4 H, CH$_2$), 3.58 (m, 6 H, CH$_2$), 6.66 (br. s, 1 H, NH), 8.10 (s, 1 H, HCO) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 37.57 (s, NHCH$_2$), 58.76 (s, OCH$_3$), 69.40 (s, CH$_2$), 69.91 (s, CH$_2$), 70.20 (s, CH$_2$), 70.24 (s, CH$_2$), 71.71 (s, CH$_2$), 161.34 (s, HCO) ppm. HRMS: m/z: calcd. for C$_{10}$H$_{21}$KNO$_5$: 274.1051; found 274.1052 [M + K]$^+$.

1-Isocyano-2-[2-(2-methoxyethoxy)ethoxy]ethane (5b): N-{2-[2-(2-Methoxyethoxy)ethoxy]ethyl}formamide (4.0 g, 0.021 mol) was dissolved in dichloromethane (50 mL) and treated with triethylamine (2.12 g, 0.021 mol), triphenylphosphane (6.59 g, 0.025 mol), and carbon tetrachloride (3.22 g, 0.021 mol) in this order. The reaction mixture was heated at reflux for 3 h. After all volatiles had been removed in an oil-pump vacuum the residue was extracted with n-hexane (10 × 10 mL). The combined extracts were dried with MgSO$_4$, and after removing the solvent in an oil-pump vacuum the crude product was purified by distillation (9 Torr, 135 °C) to afford **5b** as a colorless oil (3.1 g, 0.018 mol, 85% based on **4b**). C$_8$H$_{15}$NO$_3$ (173.21): calcd. C 55.47, H 8.73, N 8.09; found C 55.73, H 8.98, N 8.28. FTIR (NaCl): $\tilde{\nu}$ = 2878 (s), 2151 (s), 1685 (w), 1458 (s), 1451 (s), 1351 (w) 1248 (w), 1109 (s) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.40 (s, 3 H, OCH$_3$), 3.57 (m, 4 H, CH$_2$) 3.68 (m, 4 H, CH$_2$), 3.71 (m, 4 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 41.71 (t, $^1J_{N,C,N}$ = 7.05 Hz, CNCCH$_2$), 59.00 (s, OCH$_3$), 68.85 (s, CH$_2$), 70.80 (s, CH$_2$), 70.85 (s, CH$_2$), 157.30 (t, $^1J_{C,N}$ = 4.5 Hz, CNCCH$_2$) ppm. HRMS: m/z: calcd. for C$_8$H$_{15}$KNO$_3$: 212.0684; found 212.0759 [M + K]$^+$.

13-Isocyano-2,5,8,11-tetraoxatridecane (5c): Colorless **5c** was isolated as described for **5b**. Thus N-(2,5,8,11-tetraoxatridecan-13-yl)formamide (6 g, 0.026 mol), triethylamine (2.5 g, 0.026 mol), triphenylphosphane (8 g, 0.03 mol), and carbon tetrachloride (3.91 g, 0.26 mol) were reacted. Vacuum distillation gave colorless **5c** as oil (4.9 g, 0.022 mol, 87% based on **4c**). C$_9$H$_{17}$NO$_4$ (203.27): calcd. C

55.28, H 8.81 N 6.41; found C 54.90, H 8.63, N 6.41. FTIR (NaCl): $\tilde{\nu}$ = 2875 (s), 2151 (s), 1734 (w), 1454 (s), 1350 (s), 1297 (w), 1247 (m), 1199 (m), 1110 (s), 944 (m) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.33 (s, 3 H, OCH_3), 3.51 (m, 4 H, CH2), 3.61 (m, 12 H, CH_2) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 41.60 (t, $^{1}J_{N,C}$ = 7.27 Hz, CNCCH_2), 58.83 (s, OCH_3, CN), 70.35 (s, CH_2), 70.43 (s, CH_2), 70.49 (s, CH_2), 70.69 (s, CH_2), 71.77 (s, CH_2), 157.09 (t, $^{1}J_{N,C}$ = 5.45 Hz, CNCCH$_2$) ppm. HRMS: m/z: calcd. for C$_9$H$_{22}$NO$_4$: 208.1543; found 208.1552 [M + H]$^{+}$.

(1-Isocyano-2-methoxyethane)gold(I) Chloride (7a): [AuCl(SMe$_2$)] (0.5 g, 1.7 mmol) was suspended in dichloromethane (50 mL) and treated with **7a** (0.145 g, 1.7 mmol) dissolved in dichloromethane (5 mL). The suspension was stirred for 1 h at ambient temperature. Evaporation of the solvent from the clear reaction solution gave the title compound as a colorless solid (0.540 g, 1.7 mmol, 100% based on **6**). M.p. 60 °C. C$_4$H$_7$AuClNO (317.52): calcd. C 15.13, H 2.22, N 4.41; found C 15.25, H 2.17, N 4.12. FTIR (KBr): $\tilde{\nu}$ = 2922 (m), 2890 (m), 2830 (m), 2268 (s), 1462 (s), 1340 (s), 1196 (m), 1119 (s), 1083 (m), 1016 (m), 828 (m) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.44 (s, 3 H, OCH_3), 3.70 (m, 2 H, CH_2), 3.82 (m, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 44.51 (t, $^{1}J_{N,C}$ = 7.27 Hz, CNCCH_2), 59.16 (s, OCH_3), 68.04 (s, CH_2), 135.32 (t, $^{1}J_{N,C}$ = 25.43 Hz, CNCCH$_2$) ppm. HRMS: m/z: calcd. for C$_6$H$_{10}$AuN$_2$O: 323.0412; found 323.0453 [C$_4$H$_7$AuNO + CH$_3$CN]$^{+}$.

{1-Isocyano-2-[2-(2-methoxyethoxy)ethoxy]ethane}gold(I) Chloride (7b): The title complex was prepared as described for **7a**. Thus, [AuCl(SMe$_2$)] (0.25 g, 0.85 mmol) was treated with 1-isocyano-2-[2-(2-methoxyethoxy)ethoxy]ethane (0.147 g, 0.85 mmol). After appropriate workup, complex **7b** was obtained as a colorless oil (0.37 g, 0.85 mmol, 100% based on **6**). C$_{10}$H$_{21}$AuClNO$_3$ (435.70): calcd. C 27.57, H 4.86, N 3.21; found C 27.12, H 4.53, N 3.46. FTIR (NaCl): $\tilde{\nu}$ = 2875 (s), 2259 (s), 1679 (w), 1581 (m), 1453 (s), 1351 (s), 1271 (w), 1107 (s), 1028 (m), 931 (w), 850 (m), 734 (s) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.29 (s, 3 H, OCH_3), 3.47 (m, 2 H, CH_2), 3.60 (m, 4 H, CH_2), 3.62 (m, 2 H, CH_2), 3.75 (m, 2 H, CH_2), 3.61 (m, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 44.64 (t, $^{1}J_{N,C}$ = 6.36 Hz, CNCCH_2), 58.72 (s, OCH_3), 66.69 (s, CH_2), 70.17 (s, CH_2), 70.20 (s, CH_2), 70.49 (s, CH_2), 71.53 (s, CH_2), 134.37 (t, $^{1}J_{N,C}$ = 25.43 Hz, CNCCH$_2$) ppm. HRMS: m/z: calcd. for C$_{10}$H$_{22}$AuNO$_3$: 201.0666; found 201.0710 [M + H]$^{+}$.

(13-Isocyano-2,5,8,11-tetraoxatridecane)gold(I) Chloride (7c): Compound **7c** was prepared as described for **7a**. Thus, [AuCl(SMe$_2$)] (0.5 g, 1.70 mmol) was treated with 13-isocyano-2,5,8,11-tetraoxatridecane (0.37 g, 1.70 mmol). After appropriate workup, **7c** was isolated as a colorless solid (0.81 g, 1.70 mmol, 100% based on **6**). M.p. 45 °C. C$_{12}$H$_{25}$AuClNO$_4$ (479.75): calcd. C 30.04, H 5.25, N 2.92; found C 29.86, H 5.05 N 3.06. FTIR (KBr): $\tilde{\nu}$ = 2872 (s), 2266 (s), 1474 (m), 1343 (s), 1281 (m), 1245 (w), 1102 (s), 950 (m), 860 (m) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.37 (s, 3 H, OCH_3), 3.55 (m, 2 H, CH_2), 3.65 (m, 8 H, CH_2), 3.70 (m, 2 H, CH_2), 3.83 (m, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 44.66 (t, $^{1}J_{N,C}$ = 7.26 Hz, CNCCH_2), 58.92 (s, OCH_3), 70.39 (s, CH_2), 70.47 (s, CH_2), 70.53 (s, CH_2), 70.55 (s, CH_2), 70.87 (s, CH_2), 134.99 (t, $^{1}J_{N,C}$ = 26.34 Hz, CNCCH$_2$) ppm. HRMS: m/z: calcd. for C$_{10}$H$_{19}$AuNO$_4$: 414.0974; found 414.0957 [M]$^{+}$.

Single-Crystal X-ray Diffraction Analysis: Single crystals of **7a** and **7c** suitable for X-ray diffraction analysis were obtained by crystallization from diethyl ether at –30 °C. Data were collected with an Oxford Gemini S diffractometer at 110 K using Mo-K_a (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2.[41] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

CCDC-815758 (for **7a**) and -815757 (for **7c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 7a: C$_4$H$_7$AuClNO, M_r = 317.52 gmol^{-1}, crystal dimensions $0.18 \times 0.12 \times 0.10$ mm, T = 110 K, triclinic, $P\bar{1}$, a = 4.8467(4) Å, b = 6.3034(5) Å, c = 11.3673(9) Å, α = 96.738(7)°, β = 94.318(7)°, γ = 96.026(7)°, V = 341.62(5) Å^3, Z = 2, $\rho_{calcd.}$ = 3.087 gcm^{-3}, μ = 21.826 mm^{-1}, θ range = 3.28–26.03°, reflections collected: 2116, independent: 1329 (R_{int} = 0.0531), R_1 = 0.0345, wR_2 = 0.0693 [$I > 2\sigma(I)$].

Crystal Data for 7c: C$_{10}$H$_{19}$AuClNO$_4$, M_r = 449.68 gmol^{-1}, crystal dimensions $0.30 \times 0.30 \times 0.05$ mm, T = 110 K, monoclinic, $P2_1/n$, a = 9.6493(2) Å, b = 13.8603(3) Å, c = 11.1234(3) Å, β = 101.214(2)°, V = 1459.27(6) Å^3, Z = 4, $\rho_{calcd.}$ = 2.047 gcm^{-3}, μ = 10.267 mm^{-1}, θ range = 2.94–26.00°, reflections collected: 5693, independent: 2831 (R_{int} = 0.0235), R_1 = 0.0243, wR_2 = 0.0502 [$I > 2\sigma(I)$].

Supporting Information (see footnote on the first page of this article): Electron diffraction pattern, XRPD, TEM images with size distribution, UV/Vis and NMR (^{1}H, ^{13}C{^{1}H}) data.

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