

Addition of *N*-nucleophiles to gold(III)-bound isocyanides leading to short-lived gold(III) acyclic diaminocarbene complexes

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Reaction of [AuCl₃(CNR¹)] (R¹ = Xyl, Cy, (S)-CHMePh) with amines unexpectedly proceeds via the redox pathway giving gold(I)-isocyanide and imines, while the addition of benzophenone hydrazone to the isocyanide ligand in [AuCl₃(CNR¹)] at RT leads to short-lived gold(III) acyclic diaminocarbene complexes [AuCl₃{C(NHNCPh₂)NHR¹}].

In the recent years, complexes with *N*-heterocyclic carbenes (NHCs) and acyclic diaminocarbenes (ADCs) have emerged as valuable alternatives to other traditional catalysts in a number of organic transformations.¹ Most common routes to their preparation include (i) a coordination of the pre-formed carbenes (generated *in situ* from appropriate precursors and a base, or obtained via transmetalation from M-NHC) to a metal center,^{1b, 1e, 2} (ii) an oxidative addition of appropriate carbene precursors to electron-rich metal centers,^{1d, 1e, 2} and (iii) a metal-mediated nucleophilic addition or a dipolar cycloaddition to isocyanides.^{1a, 2-3}

A few reported Au(III)-NHC complexes were generated via (i) oxidation of the corresponding Au(I)-NHC species using X₂ (X = Cl,⁴ Br,^{4b, 5} I^{4b, 5a, 6}), PhICl₂,^{4a, 5, 6b, 7} ICl,^{5b, 6b} ICF₃,^{5b} or CsBr₃;⁸ (ii) upon reaction of *N*-alkyltriazolium salts with H[AuCl₄]⁹ or Na[AuCl₄]¹⁰ followed by addition of a base, or through interaction of lithiated triazole with [AuCl₃(THT)] (THT = tetrahydrothiophene) followed by addition of an acid;¹¹ (iii) treatment of Na[AuCl₄] with C≡N(CH₂)_nOH leading to a substitution of chloride with the isocyanide with consecutive intramolecular attack of the OH group on the carbon of the coordinated isocyanide;¹² (iv) transmetalation of the carbene

ligand from Ag(I), W(I), or Cr(I) to Au(III) center;¹³ and (v) disproportionation of Au(I)-NHC in the presence of [AuCl(SMe₂)] furnishing Au(III)-NHC complexes and metallic gold.¹⁴

As far as open-chain acyclic diaminocarbenes bound to gold(III) center are concerned, data available are even more scarce than for gold(III)-NHC congeners and only a few gold(III)-ADCs were reported. Known gold(III)-ADCs are mostly derived from the oxidative addition of bromine and iodine to corresponding gold(I)-ADCs.¹⁵ Single examples of other approaches include (i) intramolecular attack of the cycloaurated 2-(2-pyridylamino)phenyl ligand on an isocyanide;¹⁶ carbene transmetalation from chromium(I) to gold(III) center;¹⁷ and (ii) amine addition to gold(III)-bound CNR.¹⁸

Although complexes of gold(I) with ADC ligands^{1a, 15b, 19} are commonly assembled via the addition of *sp*³-*N* and *sp*³-*O* nucleophiles to gold(I)-isocyanides, only two examples of nucleophilic addition to gold(III)-CNRs were reported. Thus, Bartel and Fehlhammer studied¹² the reaction of Na[AuCl₄] with C≡N(CH₂)_nOH leading to substitution of a chloride with the isocyanide followed by an intramolecular attack of the OH group on the C-atom of the coordinated isocyanide¹² giving NHC-Au(III) complex; the intermediate ADC species were not isolated but postulated as reaction intermediates. In the other study, addition of amines to the isocyanide in [Au(C₆F₅)₃(*p*-CNC₆H₄Me)] gave corresponding gold(III)-ADC species;¹⁸ no spectroscopic properties of these complexes were provided.¹⁸ Intrigued by a limited number of known gold(III)-ADCs, we aimed to expand their family via the reaction of other gold(III)-isocyanide precursor, viz. [AuCl₃(CNR¹)] with different NH-nucleophiles. Considering limited spectroscopic data reported for a few known gold(III)-ADCs, we also aimed to extensively characterize new gold(III)-ADC species.

We initiated this study from preparation of gold(III)-isocyanides via the oxidative addition of chlorine to [AuCl(CNR¹)] (Scheme 1). Thus, vigorous bubbling of dry gaseous chlorine through a solution of [AuCl(CNR¹)] (R¹ = Xyl **1**; Cy **2**, Bu^t **3**, (S)-CHMePh **4**) in dry CH₂Cl₂ led to the corresponding complexes [AuCl₃(CNR¹)] (R¹ = Xyl **5**; Cy **6**, Bu^t **7**, (S)-CHMePh **8**).

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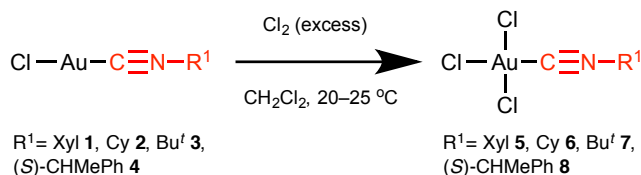
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At 20–25 °C, all reactions were completed almost immediately furnishing gold(III)-isocyanide species that were isolated as either yellow crystalline solids (**5–7**) or yellow oily residue (**8**) in 96–99% yield. Preparation of the related $[\text{AuBr}_3(\text{CNR}^1)]$ species via the oxidative addition of bromide to $[\text{AuBr}(\text{CNR}^1)]$ was previously described.²⁰

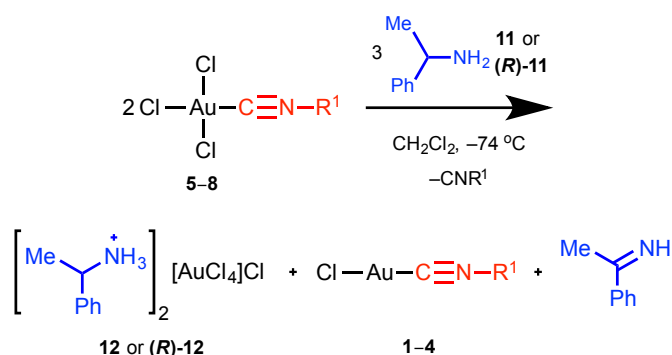


Scheme 1. Chlorination of **1–4** leading to gold(III)-isocyanides.

Prepared isocyanide complexes **5–8** were characterized by ESI^{+/–}-MS, FT-IR, ¹H and ¹³C{¹H} NMR spectroscopy, while complexes **6** and **7** additionally by CHN elemental analyses, and **5** by single-crystal X-ray diffraction (Figure 1S and 2S in the Electronic Supplementary Information, ESI).

Amines are *sp*³-N nucleophiles conventionally used for coupling with coordinated isocyanides, including gold(I)-CNRs,^{1a} therefore, we have selected representative primary and secondary amines as our first choice in the reaction with gold(III)-isocyanides.

Reaction of $[\text{AuCl}_3(\text{CNR}^1)]$ with amines. Reaction of complexes **5–8** with one or two equivs of primary (benzylamine **9**) or secondary (morpholine **10**) amine in CH₂Cl₂ led to the corresponding amine hydrochloride and product of reduction of the starting complex in solution (to **1–4**, respectively) along with some yet unidentified species. With the more sterically hindered α -methylbenzylamine (**11**) as a nucleophile, reaction proceed via an unusual reduction pathway (Scheme 2).

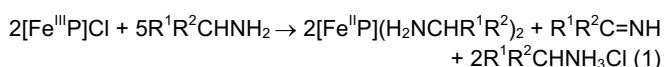


Scheme 2. Interplay between α -methylbenzylamine and Au^{III}-isocyanide complexes.

Thus, the reaction of equimolar amounts of any one of **5–8** with **11** in CH₂Cl₂ at –74 °C led to the precipitation of complex salt **12** as a bright yellow crystalline solid (ca. 20% yield). Maximum yield of **12** (40–42%) was achieved with 2:3 ratio of **5–8** to **11**. In the solution, the presence of **12**•HCl, respective gold(I)-isocyanide complexes **1–4**, alongside with 1-

phenylethan-1-imine and trace amounts of some yet unidentified species, were established using ESI-MS, FT-IR, and ¹H NMR spectroscopy. No carbene complexes were detected in this mixture. Similar results were obtained for optically pure α -(R)-methylbenzylamine (**R**)-**11**. Complex salts **12** and (**R**)-**12** were isolated and characterized by elemental analyses, ESI-MS, FT-IR and NMR and by X-ray diffraction for (**R**)-**12** (see ESI).

We attempted to shed light on the nature of this process. In the early works by Castro et al.,²¹ oxidation of the amines by iron(III)-porphyrins led to the formation of appropriate imines as oxidation products, corresponding iron(II)-porphyrine complexes as reduction product as well as amine hydrochlorides (eq. 1). Reduction of gold(III)-NHCs to corresponding gold(I)-derivatives in the presence of free isocyanide is also known from the studies of Bartel and Fehlhhammer.¹²



Taking these data into consideration and on basis of our experimental evidence (gold(I)-isocyanides **1–4**, free isocyanide and 1-phenylethan-1-imine were identified in the reaction mixture) as well as observed stoichiometry, we assume that overall reaction of **5–8** with **11** proceeds via the redox pathway depicted on Scheme 2. Herein, one equiv of methylbenzylamine (**11**) is oxidized to 1-phenylethan-1-imine by one equiv of gold(III)-isocyanide (**5–8**), that are simultaneously reduced to corresponding gold(I) species (**1–4**). Two equivalents of protons that are released during this oxidation are accepted by two additional equivs of free amine furnishing corresponding quaternary ammonium salt $[\text{Ph}(\text{Me})\text{CHNH}_3^+]\text{Cl}$. This further reacts with the second equiv of $[\text{AuCl}_3(\text{CNR}^1)]$ to give rise of a complex salt **12** and free isocyanide.

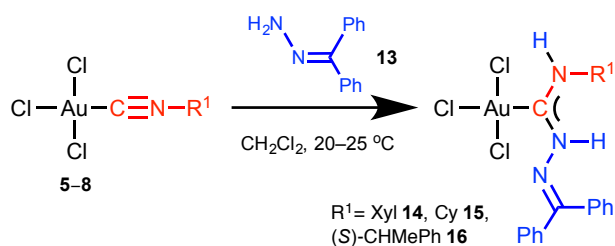
To the best of our knowledge, this gold(III)-mediated oxidation of amines was not previously reported. In the earlier study, addition of amines to $[\text{Au}(\text{C}_6\text{F}_5)_3(p\text{-CNC}_6\text{H}_4\text{Me})]$ gave corresponding gold(III)-ADC species, and no oxidation of amine by gold(III) was observed.¹⁸ We believe that this can be rationalized by a stronger *sigma* donation from the coordinated C₆F₅ in $[\text{Au}(\text{C}_6\text{F}_5)_3(p\text{-CNC}_6\text{H}_4\text{Me})]$ (when compared to that from chlorides in **5–8**) resulting in decrease of the oxidation potential of gold(III) below required threshold.

Insofar as our attempts to prepare gold(III)-ADCs via coupling of gold(III)-CNRs with amines led to oxidation of the latter, we focused our attention on hydrazines, that are stronger nucleophiles than relevant amines due to the α -effect.²² Among hydrazine derivatives, aldo- and ketohydrazones are recognized as the most stable toward oxidation²³ and were selected for further studies.

Reaction of $[\text{AuCl}_3(\text{CNR}^1)]$ with hydrazones. Recently we reported the addition of aldo- and ketohydrazones to an isocyanide ligand in *cis*- $[\text{MCl}_2(\text{CNR})_2]$ (M = Pd(II), Pt(II)) that result in the corresponding aminocarbene species.²⁴ Extensive experimental and theoretical studies on properties of hydrazones²⁵ revealed that the hybridization of the NH₂ center is intermediate between *sp*³-N and *sp*²-N, and it depends

strongly on the nature of substituents, approaching sometimes the pure sp^2 -N state.

To our knowledge, nucleophilic attack of $H_2N-N=CPh_2$ on gold-bound isocyanides has never been described, presumably because Au(I) does not provide sufficient electrophilic activation to coordinated isocyanide moiety toward nucleophilic attack. To compare the susceptibility of gold(III)- and gold(I)-isocyanides toward nucleophilic attack, we carried out theoretical DFT calculations [viz., geometry optimization procedure in gas phase, calculation of vibrational frequencies, and natural bond orbital (NBO) analysis] using $[AuCl_3(CNMe)]$ and $[AuCl(CNMe)]$ as model compounds (see full details in ESI). The energy level of first unoccupied MO bearing $\pi^*(C\equiv N)$ orbitals (viz., LUMO-1, **Figure S3**) in $[AuCl_3(CNMe)]$ (-2.07 eV) is significantly lower than that in $[AuCl(CNMe)]$ (-1.47 eV), suggesting that the Au(III) center is stronger activator of the isocyanide ligands toward the addition of nucleophiles. Computed NBO charges on isocyanide carbon atoms in $[AuCl_3(CNMe)]$ and $[AuCl(CNMe)]$ are 0.44 and 0.30, respectively. Finally, the calculated value of the unscaled normal mode frequency $\nu(C\equiv N)$ in $[AuCl_3(CNMe)]$ (2389 cm^{-1}) is greater than that in $[AuCl(CNMe)]$ (2321 cm^{-1}), and this reflects higher electrophilic activation of CNR bound to gold(III) center.^{3a} Note, these calculated values of the normal mode frequencies $\nu(C\equiv N)$ are unscaled, and are expectedly overestimated.²⁶ Recommended multiplication of the calculated $\nu(C\equiv N)$ values on the scaling factor 0.96 gives 2293 cm^{-1} and 2228 cm^{-1} , respectively, and it is in perfect agreement with the experimental data.²⁶ Thus, orbital, charge, and frequency arguments reveal that Au(III) center is better activator of CNR ligand toward nucleophilic addition when compared to Au(I). Taking these results into consideration, we studied the reactivity of Au(III)-isocyanide complexes in the coupling with hydrazones.



Scheme 3. Nucleophilic addition of benzophenone hydrazone to Au^{III}-bound isocyanide.

Reaction of **5**, **6**, or **8** with benzophenone hydrazone (**13**, 1 equiv) in dry CH_2Cl_2 proceeds at RT for ca. 15 min giving the short-lived complexes $[AuCl_3\{C(NHNCPh_2)NHR^1\}]$ ($R^1 = \text{Xyl } \mathbf{14}$; $\text{Cy } \mathbf{15}$, $(S)\text{-CHMePh } \mathbf{16}$; Scheme 3). No such reaction was observed between **7** and **13**, that is apparently because of the low reactivity Bu^tNC .²⁷ Reaction of **5-8** with 9-fluorenone hydrazone (**17**) and salicylaldehyde hydrazone (**18**) in dry CH_2Cl_2 or toluene at RT led to the formation of unstable species that almost immediately decompose giving metallic gold and a solution of yet unidentified species.

Compound **14** and **16** possess low stability in solution and in the solid state, but we could characterize them by FT-IR, ESI-MS, and 1H and $^{13}C\{^1H\}$ (only for **14**) NMR spectroscopy. In addition, the structure of **14**, that was stable enough at 150 K when compared to **15** and **16**, was elucidated by single-crystal X-ray diffraction. Compound **15** rapidly (ca. 10 min) decomposes both in solution and in the solid state, and was characterized solely by solution 1H NMR spectroscopy immediately after its formation. Detailed characterization of **14-16** is provided in the Electronic Supplementary Information, and herein we discuss the most important details of the solid-state X-ray structure of complex **14** (Table S1, ESI contains crystallographic data and processing parameters for **14**).

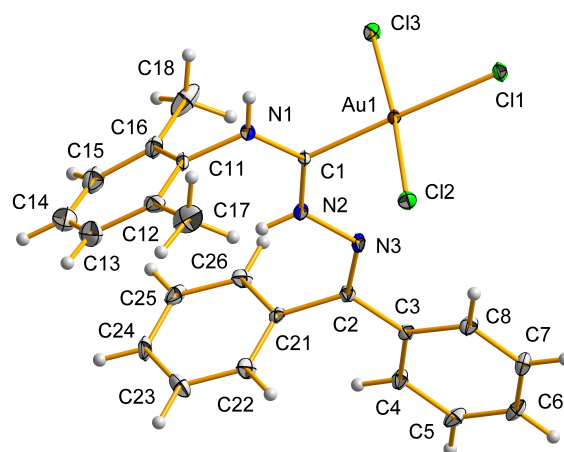


Figure 1. Crystal structure of **14** with the atomic numbering scheme (hydrogen labels and chloroform molecule were omitted for simplicity). Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles ($^\circ$): Au1-Cl1 2.3255(12), Au1-Cl2 2.2687(14), Au1-Cl3 2.3001(14), Au1-C1 2.005(5), C1-N1 1.312(6), C1-N2 1.318(5), C2-N3 1.293(6), N2-N3 1.387(5), C1-Au1-Cl1 178.55(12), C1-Au1-Cl2 87.21(16), C1-Au1-Cl3 89.29(16), Cl1-Au1-Cl2 92.63(5), Cl2-Au1-Cl3 175.16(5), N1-C1-Au1 121.9(3), N1-C1-N2 118.4(4), N2-C1-Au1 119.7(3).

The asymmetric unit of **14** contains one molecule of the complex and one of chloroform (Figure 1). The square-planar coordination environment of **14** ($\tau_4 = 0.05$)²⁸ is fulfilled by one carbene and three chloride ligands. All bond angles around the Au(III) center are close to 90° varying from $87.21(16)^\circ$ to $92.63(5)^\circ$. The Au-Cl1 (2.3255(12) Å) distance opposite to the carbene fragment is slightly longer than the other two Au-Cl distances (2.2687(14) and 2.3001(14) Å) and that in **5** (2.2687(19) Å) indicating significant ground-state *trans* influence of the carbene ligand when compared to parent isocyanide in **5**. The Au-C bond distance (2.005(6) Å) is comparable to that observed in **5** (1.954(7) Å) and in the related complexes containing *N*-heterocyclic carbenes $[AuCl_3(I\text{Mes})]$ (2.016(7) Å),⁹ $[AuCl_3(1,3\text{-dihydro-1-methyl-3-(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene})]$ (1.994(4) Å),⁷ and $[AuCl_3(I\text{Pr})]$ (2.013(9) Å).^{4a} The carbene moiety is almost planar (C1 deviates from Au1-N1-N2 plane by 0.017 Å) and the angles

around the carbene C1 atom are nearly equal to 120° varying from 118.4(4)° to 121.9(3)°, indicating its sp² hybridization. Both C_{carbene}-N distances are equal within 3σ (1.312(6) and 1.318(5) Å) and their values are typical for delocalized one-and-a-half C-N bond (e.g. 1.337(12) for C_{ar}-N in pyridine).²⁹ The carbene plane (built on N1, C1, and N2 atoms) is almost perpendicular to the plane defined by the chloride ligands (angle of 77.66°). The carbene C1-N1 and C1-N2 bonds adopt E- and Z-configurations, correspondingly. The solid-state structure of **12** exhibits intermolecular T-shaped C-H...π interactions involving both the C26-H8 and the C23-H10 bonds of every molecule and the C3-C8 phenyl rings of adjacent ones. Such interactions give rise to infinite chains along the crystallographic *a* axis (see ESI for more details).

Finally, evaluation of the bonding situation in the dimeric clusters of **5**, **14**, and (**R**)-**12** was carried out using theoretical DFT calculations and topological analysis of the electron density distribution within the formalism of Bader's theory (QTAIM analysis),³⁰ this approach has already been successfully used by us upon studies of non-covalent interactions and properties of coordination bonds in various transition metal complexes.³¹ QTAIM analysis (Table S2, ESI) indicates the presence of two bond critical points (3, -1) (BCPs) for covalent bonds Au-Cl and two BCPs for Au•••Cl non-covalent interactions, and no BCPs for Au•••Au contacts in all studied dimers. The magnitudes of the electron density, values of the Laplacian and energy density, the ratio -G(r)/V(r) in BCPs for Au-Cl and Au•••Cl contacts as well as appropriate Wiberg bond indices (WI) are typical for covalent bonds M-L in coordination complexes and for non-covalent electrostatic interactions, respectively. We have defined energies for these contacts according to the procedures proposed by Espinosa et al.³² and Vener et al.³³ (Table S2, ESI), and one can state that the relativistic and non-relativistic approaches give very similar estimates. Results of theoretical calculations led to the conclusion that weak Au•••Cl non-covalent electrostatic interactions are most likely responsible for the stabilization of dimeric associates **5**, **14**, and (**R**)-**12** in the solid state.

As a conclusion, direct oxidative addition of chlorine to [AuCl(CNR¹)] gives the corresponding Au^{III}-CNR species in nearly quantitative yields. Attempted nucleophilic addition of amines to gold(III)-isocyanides does not lead to carbene complexes but furnishes imines and gold(I)-isocyanides generated via the redox pathway. At the same time, addition of benzophenone hydrazone to the coordinated isocyanide in [AuCl₃(CNR¹)] furnishes new types of short-lived gold(III)-ADC species that gradually decompose to give metallic gold. Insofar as stability of gold(III)-ADCs is concerned, one should consider that although the instability of complexes has negative impact on their shelf-life, it might turn positive for their catalytic activity. It is argued that many modern organometallic catalytic processes, i.e. cross-coupling, are essentially catalysed by the nano-sized particles formed from the starting molecular compounds during the precatalyst activation step.³⁴ Herein, in situ prepared gold(III)-ADCs can promptly generate gold nanoparticles enabling subsequent catalytic transformations and further studies in this direction are currently underway in our group.

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