1,3-Dipolar Cycloaddition of Nitrones to Gold(III)-bound Isocyanides

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ABSTRACT: Treatment of gold(III)-isocyanides [AuCl3(CNR1)] (R1 = Xyl **1**, Cy **2**, Bu*t* **3**) with an equimolar amount of 5,5-dimethyl-1-pyrroline-*N*-oxide (**4**) in CH2Cl2 at −74 °C leads to the generation of the heterocyclic aminocarbene species [AuCl3{C(ON*a*CMe2CH2CH2C*b*H)=N*e*R1}(N*a*−C*b*)(C*b*−N*e*)] **8** (for R1 = Bu*t*) or the gold(III) complexes *cis*-[AuCl2{N*a*(CMe2CH2CH2C*b*N*e*R1)C*d*=O}(N*a*=C*b*)(N*e*−C*d*)] **9** and **10** (for R1 = Xyl and Cy) in good isolated yields (75–87%). DFT calculations show that deprotonation of the endocyclic CH group in the carbene ligand leads to the spontaneous N–O bond cleavage, and acidity of this group is a factor controlling the different chemical behavior of **1**–**3** depending on the nature of substituent R1. The reaction of equimolar amounts of the *aldonitrone* *p*-TolCH=N+(Me)O– (**5**) or the *ketonitrones* Ph2C=N+(R2)O– (R2 = Ph **6**, CH2Ph **7**) with **1**−**3** in CD2Cl2 at −70 ºC in air (or under N2) revealed the formation of the carbene complexes [AuCl3{C(ONMeC*a*H-*p*-Tol)=N*b*R1}(C*a*−N*b*)] (R1 = Cy **11**, Xyl **12**, Bu*t* **13**), [AuCl3{C(ONPhC*a*Ph2)=N*b*R1}(C*a*−N*b*)] (R1 = Cy **14**, Bu*t* **15**) or [AuCl3{C(ON(CH2Ph)C*a*Ph2)=N*b*R1}(C*a*−N*b*)] (R1 = Cy **16**, Xyl **17**), as studied by 1H NMR. The reaction of **6** with **1**, and of **7** with **3** did not furnish carbene products. Compounds **8–10** were characterized by ESI-MS, IR, 1D (1H, 13C{H}) and 2D (1H,1H-COSY, 1H,13C-HSQC, 1H,13C-HMBC) NMR spectroscopic techniques and, only for **8**, by elemental analyses (C, H, N), while compounds **11**‒**17** were characterized by 1D (1H, 13C{H}) and 2D (1H,13C-HSQC) NMR. Structure of compounds **8**, **9** and **13** were additionally established by single-crystal X-ray diffraction.

INTRODUCTION

*N*-Heterocyclic carbenes (NHCs) have become one of the most important classes of ligands in modern organometallic chemistry and catalysis owing to their high chemical and thermal stability and superior catalytic activity of their metal species.1 Complexes of nearly all transition metals with NHC ligands have been prepared, including gold(I)-NHCs, which have been evaluated as catalysts,1a,2 potential drugs,3 or luminescent devices.4 Insofar as most efforts were focused on gold(I) species, the application of gold(III)-NHCs is rarely described, presumably due to the limited thermodynamic stability of the gold(III) oxidation state.5 Nevertheless, some reported examples point out to their promising catalytic,1a,6 biomedical (e.g. antitumor,7 antifungal,8 and antimalarial8) and luminescent9 properties.

General approaches for the preparation of metal-NHCs are based on either coordination of the pre-formed carbenes (generated *in situ* from appropriate precursors and a base, or obtained via transmetallation from M-NHC) to a metal center10 or a metal-mediated transformation of isocyanides via diverse intramolecular cyclizations including dipolar cycloaddition.11 Noteworthy that metal-isocyanide synthons can also lead to complexes with acyclic diaminocarbenes via the metal-mediated nucleophilic addition.12

When the generation of gold-NHCs is considered, cyclization strategies of gold-bound isocyanides are represented by three reported synthetic routes. The first approach involves a nucleophilic addition of β-functionalized nucleophiles to metal-bound isocyanides, and it was successfully used for the synthesis of gold(I)-NHC complexes by Hashmi et al. (addition of NHR1CH(R2)CO2Me13 or NHR1CH2CH(R2)Cl•HCl14, **Scheme 1**, **Route A**) and Beck et al. (addition of epoxides)15. The second route is based on cyclization of coordinated β- or γ-functionalized isocyanides and it was applied for the synthesis of gold(III)-NHC complexes by Fehlhammer et al. (metal-mediated cyclization of CN(CH2)nOH, **Scheme 1**, **Route B**).16 The third strategy includes a formal metal-mediated 1,3-dipolar cycloaddition of dipoles to metal-bound isocyanides, which allows the generation of both gold(I)-NHCs and also gold(I)/(III) complexes featuring NHC-like species. Herein, Hashmi et al.17 reported on cycloaddition of azometine ylides (allyl anion type dipoles) to AuI-coordinated isocyanides furnishing complexes with the so-called abnormal *N*-heterocyclic carbenes (**Scheme 1**, **Route C**). Inspection of the early literature also revealed two more examples of the metal-mediated interaction between azides and isocyanides leading to the formal cycloaddition products.18 Thus, the coupling of the azide gold(I) complex [Au(N3)(PPh3)] with methyl isocyanide or the gold(I/III)-azide complexes [AsPh4][Au(N3)n] (n = 2, 4) with

Scheme 1. Approaches to Au-NHC and NHC-like species via metal-mediated cyclization of isocyanides.



various aliphatic and aromatic RNCs led to the corresponding gold(I)/(III) species featuring NHC-like ligands, *viz*. *C*-coordinated tetrazolates (**Scheme 1**, **Route D**).18

Within the scope of our ongoing project on reactivity of metal-bound isocyanides,11,12b,19 we undertook a theoretical study on 1,3-dipolar cycloaddition of nitrones (allyl anion type dipoles) to transition metal-isocyanides and found that the gold(III) metal center is an efficient promoter (along with AuI, PdII, PtII, PtIV, and ReV centers) of the dipolar cycloaddition.19b,d In the only experimental report,19b palladium(II)-mediated cycloaddition of nitrones to isocyanides led to corresponding cycloadducts. Taking into account these result and the fact that the addition of allyl anion type dipoles to AuIII-coordinated isocyanides has never been reported, we decided to explore the reaction of allyl anion type dipoles (namely, nitrones) toward gold(III)-isocyanide complexes [AuCl3(CNR1)]. Results described in the sections that follow show that the reactions promoted by gold(III) center proceed far differently from those at palladium(II).

Results and discussion

For our study we addressed, on the one hand, the known AuIII-isocyanide complexes of the general formula [AuCl3(CNR1)] (R1 = Xyl **1**, Cy **2**, Bu*t* **3**).20 On the other hand, we employed allyl anion type dipoles, viz., 5,5-dimethyl-1-pyrroline-*N*-oxide (**4**), aldonitrone *p*-TolCH=N+(Me)O– (**5**), and the ketonitrones Ph2C=N+(R2)O– (R2 = Ph **6**, CH2Ph **7**)21 as reaction partners.

*Metal-Mediated Cycloaddition of Nitrones* ***4****−****7*** *to Gold(III)-Bound Isocyanides.* Treatment of any of the AuIII-isocyanide complexes **1**−**3** with an equimolar amount of 5,5-dimethyl-1-pyrroline-*N*-oxide (**4**) in CH2Cl2 at −74 °C leads to the generation of the carbene complex **8** (**Scheme 2**, **Reaction A**) or the AuIII-metallacycles **9** or **10** (**Reaction B**) in good isolated yields (75–87%).

We believe that complexes **9** and **10** are formed via a multi-step process that includes (*i*) generation of the respective carbene complexes via the cycloaddition, (*ii*) subsequent N−O bond cleavage, and (*iii*) substitution of chloride with the *N*-atom of the heterocycle that results in generation of a thermodynamically stable five-membered metallacycles **9** and **10**. Complexes **8**−**10** were recrystallized from a CH2Cl2-Pr*i*2O solution. All **8**−**10** are stable in the solid state or in solution (CH2Cl2 or CHCl3) for at least 4 d (for **8** and **9**) or 2 d (for **10**) and then start to gradually decompose producing a mixture of yet unidentified species.

Complex **9** represents the first structurally characterized (see below) example of gold complexes bearing a *N*,*C*-coordinated bidentate ligand of the type N=C−N−C=O. In the literature, only four examples of complexes containing bidentate ligands of this type have been described, including species generated via the (*i*) intramolecular reaction of coordinated CO with a carbene ligand promoted by a MnI metal core,22 (*ii*) intermolecular reaction of uncoordinated CO with amidinate-amine FeII complexes,23 or (*iii*) reaction of uncomplexed CO with guadiniato or diketimidinate dimeric CoI species.22b

The formation of compounds **9** and **10** from the isocyanide ligands and the *N*-oxide represents a novel reactivity type for the cyclic nitrone **4**. Indeed, although the cycloaddition of **4** to metal-bound isocyanides followed by the N−O bond cleavage leading to metal-bound imines via deoxygenation reaction is known,5,19b in our work we observed the formation of stable metallacyclic species, whereas imine species were not detected. Nevertheless, we believe that the key step of formation of **9** and **10** is also the N−O bond cleavage, whose instability could be explained by the electronic repulsion of the two atoms.19d As a hypothesis (see Mechanistic aspects section in **Supporting Information**) we suggest that deprotonation of the endocyclic CH group in the carbene cycloadducts is the first step of a transformation into the metallacyclic gold(III) species, and it results in spontaneous N–O bond cleavage. The substituent depending chemical behavior of the isocyanide complexes is controlled by the acidity of the corresponding endocyclic CH group. Although, quantum chemistry calculations are in agreement with these ideas, more detailed theoretical studies are required to support the hypotesis.

Numerous attempts were undertaken to convert **8** to the corresponding metallacyclic species analogous to **9** and **10** and also to generate carbene analogues of **9** and **10** that are similar to **8**. Reactions were monitored either in solution (CD2Cl2 or toluene-*d*8, from −74 °C to RT) using 1H and 13C{1H} NMR, or in the solid state (at 40 °C), but they did not lead to the expected transformations. For **8**, only gradual decomposition in solution (ca. 4 h at RT, ca. 2 d at −74 °C), or solid state (1 d solid state) giving a broad mixture of decomposition products, including metallic gold, was observed. Although in the ESI–-MS spectrum of **8**, the signal of the fragmented ion [M – HCl – H]– appeared, we believe it corresponds to either fragmentation of **8** or deprotonation of the corresponding metallacyclic gold complex; we were unable to detect the latter complex by IR or 1H NMR spectroscopy. For reaction of **1** and **2** with **4**, only the gradual accumulation of **9** and **10** was undoubtedly detected at −74 °C.

Addition of equimolar amounts of the *aldonitrone* *p*-tolyl-CH=N+(Me)O– (**5**) or the ketonitrone Ph2C=N+(CH2Ph)O– (**7**) to any one of **1**−**3** in CH2Cl2 or toluene at −74 ºC in air (or under N2) resulted in a change of the reaction color from bright yellow to pale yellowish green. When the system was gradually warmed to RT, monitoring of the formed yellow (**5**), green (upon addition of **7** to **1**), or orange (upon addition of **7** to **2** or **3**) solutions using 1H NMR and ESI+/−-MS revealed the presence of a broad mixture of species, including *p*-tolyl-aldehyde (for reaction with **5**) or diphenylketone (for reaction with **7**) among other compounds; no carbene species were detected.

Scheme 2. 1,3-Dipolar cycloaddition of 4–7 to complexes 1–3.



Addition of equimolar amounts of the *ketonitrone* Ph2C=N+(Ph)O– (**6**) to **1**−**3** in CH2Cl2 or toluene at −74 ºC in air (or under N2) resulted in the change of the reaction colour from bright yellow to pale yellowish green (**1**) or maroon (**2** and **3**). When the system was warmed to RT, monitoring of the formed yellow (**1**) or red (**2** and **3**) solutions indicated the presence of metallic gold, isocyanide, diphenylketone, protonated **4**24 along with other yet unidentified decomposition products.

To prove the formation of the cyclic carbene species, we studied the addition of **5**−**7** to **1**−**3** in CD2Cl2 at low temperature in air (see Experimental section for the detailed experimental description) using 1H NMR spectroscopy. Thus, immediately after addition of 1.0 equiv of any one of **5**−**7** to **1**−**3** at −70 ºC, the 1H NMR spectrum of the reaction mixture was recorded. Inspection of the spectra revealed the presence of signals due to the pure carbene complexes [AuCl3{C(ONMeC*a*H-*p*-Tol)=N*b*R1}(C*a*−N*b*)] (R1 = Cy **11**, Xyl **12**, Bu*t* **13**), [AuCl3{C(ONPhC*a*Ph2)=N*b*R1}(C*a*−N*b*)] (R1 = Cy **14**, Bu*t* **15**) or [AuCl3{C(ON(CH2Ph)C*a*Ph2)=N*b*R1}(C*a*−N*b*)] (R1 = Cy **16**, Xyl **17**) (**Scheme 2**, **Reactions C** and **D**) accompanied with the resonances from the slight excess of the corresponding dipoles. Insofar as complexes **11**–**17** due to their instability could only be analyzed in solution by NMR spectroscopy, we believe that they should be treated as only *suggested* structures. Resonances of the starting complexes **1**−**3** were not observed suggesting nearly quantitative conversion leading to **11**–**16**. For **17**, conversion was of ca. 80% and signals of remaining starting complex **1** were present. In the 13C{1H} NMR, signals of newly formed carbene species in the 169.7–176.0 range, were detected. The reaction of **6** with **1** and **7** with **3** did not furnish carbene products (no carbene signals were detected by both 1H and 13C{1H} NMR), but the nature of the products formed was not established.

Upon gradual warming of the reaction mixture to RT we found that complexes **11**−**17** are stable up to −20 ºC and at this temperature they gradually decompose (5 d for **11** and **12**; 1 d for **13**−**17**) giving, in particular, *p*-tolyl-aldehyde (**11**−**13**) or a broad mixture of yet unidentified products (**14**–**17**). In the solid state, all complexes **11**−**17** were unstable at temperatures higher than −10 ºC. However, slow evaporation of a CH2Cl2 solution of **13** at ca. −14 ºC brought about the formation of crystals suitable for X-rays (see later for X-ray diffraction of **13**).

For comparative purposes we studied the reaction of the dipoles **4**‒**7** with the gold(I) isocyanide complex [AuCl(CNXyl)]. Mixing equimolar amounts of the reagents in CH2Cl2 or toluene at RT in air (or under N2) did not lead to the generation of carbene products even after 1 d (in accord with IR and 1H NMR), but results in a decomposition of the starting material giving uncomplexed isocyanide and metallic gold. Similar results were observed at 40 ºС, albeit the reaction proceeded faster and it was essentially complete within 1 h. In the blank experiment, no reaction between the equimolar amounts of the uncomplexed XylNC and **4**−**7** was observed even upon reflux in CH2Cl2 for 1 d. Furthermore, attempts to reduce cycloadducts **8** and **11**–**17** with the carbonyl-stabilized phosphorous ylides Ph3P=CHCO2R (R = Me, Et), that are known as mild reducing agents for organometallics,25 led to a broad mixture of decomposition species, where no carbene derivatives were detected. These experiments indicate that the observed 1,3-dipolar cycloaddition is mediated by a AuIII-center, but not by a AuI one.

*Characterization of* ***8****,* ***11****‒****17****.* Detailed characterization of **8** and **11**‒**17** is given in the **Supporting Information**. Herein, we provide most significant features and the crystallographic description of the most important species.

Complex **8** was characterized by elemental analyses (C, H, N), ESI‒-MS, IR, 1D (1H, 13C{H}) and 2D (1H,1H-COSY, 1H,13C-HSQC, 1H,13C-HMBC) NMR spectroscopic techniques, and by single-crystal X-ray diffraction. Satisfactory elemental analyses were achieved for **8**. In the ESI–-MS spectrum, the set of signals of the ions [M – H]– and [M – HCl – H]– with specific isotopic distribution was observed, while in the IR spectrum of **8**, one strong band corresponding to *ν*(Ccarbene=N) was detected at 1637 cm–1. Both 1H  and 13C{1H} NMR spectra (**Figures** **S1**–**S3**) support the proposed formulation of **8**. For instance, in the 1H NMR spectrum of **8**, the CH2 groups of the pyrroline ring emerged as three multiplets with intensities of 1*H*, 1*H*, and 2*H* in the ranges 2.51−2.39, 2.23−2.15, and 2.05−1.89 ppm, respectively, whereas the CH proton was detected as a doublet of doublets at 5.57 ppm (3*J*HH 7.2 and 2.3 Hz). In the 13C{1H} NMR spectrum, the carbene carbon resonance emerged as a singlet at 172.0 ppm.

Compounds **11**‒**17** were characterized by 1D (1H, 13C{H}) and 2D (1H,13C-HSQC) NMR at −50 ºC (for **11**, **12**, **14**‒**17**) or at −15 ºC (for **13** in order to increase its solubility), and by single-crystal X-ray diffraction (for **13**). Due to low stability of **11**–**17** at RT, elemental analyses (C, H, N), ESI‒-MS, and IR could not be performed. All 1H and 13C{1H} NMR spectra are given in Supporting Information (**Figures** **S4**–**S17**). In the 1H NMR spectra of **11**‒**13**, the characteristic signal of the proton of CH group of dipole was detected as a sharp singlet in the 5.86–5.52 ppm range. Addition of the nitrones to the coordinated isocyanides is accompanied by a pronounced *δ* 13C shift to a lower field. Thus, in **11**–**17**, the Ccarbene=N 13C resonances were found in the range 176.0−169.7 ppm, *i*.*e*. shifted by *ca*. 60 ppm to the lower field in comparison with the starting (isocyanide)AuIII complexes (*e*.*g*. 111.8 ppm for C≡N in **1**). These values for the Ccarbene=N 13C signals are comparable to those observed for **7** (172.0 ppm) and are slightly shifted to lower field compared to the peaks exhibited by [PdCl2{C(ONR2C*c*H(*p*-Tol))=N*d*R1}(C≡NR1)(C*c*–N*d*)] (157–159 ppm).19b Additional NMR details for **11**–**17** are discussed in the **Supporting Information**.



**Figure 1**. Crystal structure of **8** with the atomic numbering schemes (hydrogen labels are omitted for simplicity). Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles (°): Au1‒Cl1 2.3098(11), Au1‒Cl2 2.2826(12), Au1‒Cl3 2.2793(12), Au1‒C1 1.999(4), C1‒N1 1.292(5), C1‒O1 1.307(4), O1‒N2 1.519(4), Au1‒C1‒N1 132.8(3), O1‒C1‒N1 114.6(3), Au1‒C1‒O1 112.5(2).

The crystal data collection and refinement details and selected bond lengths and angles for complexes **8** and **13** are summarized in **Table S1** and plots are provided on **Figures 1** and **2**. The asymmetric unit of **8** contains one molecule of the complex, whereas in the structure of **13** it contains one molecule of the complex along with one molecule of CH2Cl2. The coordination polyhedron of both complexes is built up by one carbene ligand and three Cl– ligands furnishing a typical slightly distorted square-planar coordination geometry (*τ*4 = 0.04 in both cases).26 All the corresponding bond lengths and angles of the aminooxycarbene cycles and the polyhedra of **8** and **13** are equal within 3*σ*. All bond angles around the AuIII cores are close to 90° varying from 87.17(14)° to 92.22(4)° (**Table S1**). The Au‒Cl1 (2.3098(11) and 2.3056(12) Å) distances opposite to the carbon atom are slightly longer than the other two Au‒Cl distances (2.2793(12) and 2.2826(12) or 2.2846(12) and 2.2842(12) Å for **8** and **13**, correspondingly) reflecting substantial ground-state *trans*-influence of the carbene ligand.



**Figure 2**. Crystal structure of **13** with the atomic numbering schemes (hydrogen labels are omitted for simplicity). Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles (°): Au1‒Cl1 2.3056(12), Au1‒Cl2 2.2846(12), Au1‒Cl3 2.2842(12), Au1‒C1 2.015(5), C1‒N1 1.288(6), C1‒O1 1.313(6), O1‒N2 1.509(5), Au1‒C1‒N1 132.4(4), O1‒C1‒N1 115.5(4), Au1‒C1‒O1 112.0(3).

The Au‒C bond lengths (1.999(4) and 2.015(5) Å) are comparable to those observed in the related gold(I) aminooxycarbene complex [Au(CN){C(OCH2C*a*HPh)N*b*H(C*a*−N*b*)}] (2.019 Å)15 and the gold(III) complex containing *N*-heterocyclic diaminocarbenes [AuCl3(IMes)] (2.016(7) Å; IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazolium).27 The carbene moieties in **8** and **13** are almost planar, with the C1 atoms deviating from the Au‒N‒O planes by ca. 0.012 and 0.025 Å for **8** and **13**, respectively. In both structures, the Au1‒C1‒N1 angles (132.8(3) and 132.4(4)° for **8** and **13**, respectively) are larger than the other two angles (114.6(3) and 112.5(3)º or 115.5(4) and 112.0(3)° for O1‒C1‒N1 and Au1‒C1‒O1 in **8** and **13**, correspondingly) probably due to the tension from both the bulky Bu*t* substituents and the five-membered ring. This steric effect was also observed for the related complex *trans*-[PdCl2{C(ON*a*CMe2CH2CH2C*b*H)=N*e*Bu*t*}{N*f*CMe2CH2CH2C*g*H)}(N*a*−C*b*)(C*b*−N*e*)(N*f*−C*g*)] derived from the reaction of **4** with *cis*-[PdCl2(CNBu*t*)2] (ca. 132.9, 115.4 and 111.8° for Pd‒C‒N, Pd‒C‒O and O‒C‒N angles, respectively).19b

In the carbene moieties, the C1‒N and C1‒O distances are equal within 3*σ* (**Table S1**) and their values are typical for the delocalized one-and-a-half C‒N or C‒O bonds (e.g. 1.337(12) Å for Car‒N in pyridine and 1.308(19) Å for C‒O in carboxylic acids28). The angles between the least-square planes defined by the carbene-containing heterocycles in **8** and **13** are almost perpendicular to the ones defined by the three halide ligands (83.37 and 79.23º, in this order), which is typical for square-planar carbene complexes, e.g. of PdII.19b In both structures there are intermolecular interactions involving the butyl groups (as donors) and the O- (in **13**) and one of the N-atoms (in **8** and **13**) as acceptors (**Figure S23** of **Supporting Information**), thus leading to infinite 1D chains which further expand to a 3D network by means of CH⋅⋅⋅Cl contacts.

*Characterization of* ***9*** *and* ***10***. Complexes **9** and **10** were characterized by ESI‒-MS, IR, 1D (1H, 13C{H}) and 2D (1H,1H-COSY, 1H,13C-HSQC, 1H,13C-HMBC) NMR and by single-crystal X-ray diffraction (for **9**). Compound **9** gave satisfactory results of CNH elemental analyses, while for **10** those were not undertaken due to its fast decomposition even in the dark under N2. Although the full characterization of **10** could not be performed, comparison of ESI‒-MS, IR and 1D (1H, 13C{H}) NMR data of **8**−**10** allows the assumption that **10** has a gold(III)-metallacycle structure similar to **9** rather than the carbene structure similar to **8**. The ESI−-MS spectrum of **9** displayed signals that were attributed to the [M + Cl]− and [M − H]− ions. In each of the IR spectra of **9** or **10**, two bands corresponding to *ν*(C=O) and *ν*(C=N) stretching vibrations appeared at 1771 and 1607 or at 1764 and 1606 cm–1 for **9** and **10**, respectively. 1H and 13C{1H} NMR spectra are given in Supporting Information (**Figures** **S18**–**S22**). Both 1H and 13C{1H} NMR spectra support the proposed formulation of **9** and **10**. Thus, in the 1H NMR spectra of **9** and **10**, the resonances of the CH2 groups of the pyrroline ring were found as two triplets of matching intensity at 3.06 and 2.31 ppm for **9** or at 2.59 and 2.31 ppm for **10**, correspondingly. In the 1H NMR spectrum of **9**, the CH proton of the cyclohexyl ring was detected as a broad multiplet in the range 3.59–3.48 ppm, whereas in the 1H NMR spectrum of **10**, the characteristic signal of the Me group from the xylyl fragment emerged as a singlet at 2.21 ppm. In the 13C{1H} NMR spectra of **9** and **10**, the carbonyl carbon resonances emerged as singlets at 155.1 and 156.2 ppm, correspondingly. Additional details on characterization of **9** and **10** are given in the **Supporting Information**.



**Figure 3**. Crystal structure of **9** with the atomic numbering scheme (hydrogen labels are removed for simplicity). Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles (°): Au1‒Cl1 2.382(3), Au1‒Cl2 2.280(3), Au1‒C1 2.085(11), Au1‒N2 2.024(9), C1‒O1 1.169(13), C1‒N1 1.389(14), N2‒C2 1.246(13), C2‒N1 1.353(13), C1‒Au1‒N2 78.9(4), C1‒Au1‒Cl2 92.5(4), Cl1‒Au1‒Cl2 89.56(12), Cl1‒Au1‒N2 99.2(3), Cl2‒Au1‒N2 171.3(3), Au1‒C1‒O1 123.8(9), O1‒C1‒N1 126.6(11), Au1‒C1‒N1 109.6(8), C1‒N1‒C2 115.8(9), N1‒C2‒N2 121.2(10), Au1‒N2‒C2 114.4(8), Au1‒N2‒C5 131.1(7), C2‒N2‒C5 114.3(9).

The crystal data collection and refinement details and selected bond lengths and angles for complex **9** are summarized in **Table S1** and plot is provided on **Figure 3**. The coordination environment of the complex **9** is built up by two Cl– ligands and *N*,*C*-coordinated bidentate ligand and give rise to the typical slightly distorted square-planar geometry (*τ*4 = 0.10, **Figure S23**).26 Two bond angles around the AuIII core are close to 90° (89.56(12)° and 92.5(4)°, while two others have different values (78.9(4) and 99.2(3)°) due to the steric reasons, namely the presence of the strained five-membered metallacycle and the bulky CMe2 group. The values of the Au‒Cl distances are typical for Au‒Cl bonds29 with the bond opposite to the nitrogen atom being shorter than the other one (2.280(3) and 2.382(3) Å, respectively). The structure of **9** represents an example of an *N*,*C*-coordinated five-membered gold metallacycle, which is rare and includes complexes of gold(III) with dmamp (dmamp = 2-(*N*,*N*-dimethylaminomethyl)phenyl)) ligand and its derivatives30 and hybrid complexes of hexaphyrin(1.1.1.1.1.1).31

The Au‒C distance (2.085(11) Å) is longer than that observed in **8** (1.999(4) Å) and in the range of the Au‒C distances of the related [(Ph3P)Au{C(=O)NHMe}] (2.056(13) Å),32 [(Ph3P)AuMe2{C(=O)OMe}](2.02(3) Å)33 and [(Ph3P)AuC(=O)Ph] (mean value 2.063(20) Å)34 complexes. The Au‒N bond length (2.024(9) Å) is comparable to that observed for the related five-membered imino complex of gold(III) [AuCl2(dmamp)], where dmamp = 2-(*N*,*N*-dimethylaminomethyl)phenyl) (2.051(8) Å).30 The Au−C1(O1)−N1−C2−N2−C5 is strictly planar. In **9**, the complex is also involved in CH⋅⋅⋅Cl contacts, which extends the structure to a 3D framework (**Figure S24**).

Final Remarks

The results of this work may be considered from several perspectives. *Firstly*, we observed the coupling of 5,5-dimethyl-1-pyrroline-*N*-oxide (**4**) with gold(III)-coordinated isocyanide in the complexes [AuCl3(CNR1)] which represents the first example of addition of any one of allyl anion type dipoles to gold(III)-isocyanide complexes. *Secondly*, we observed that this reaction depends on the substituent in the isocyanide moiety and leads to either gold(III) aminooxycarbene complex (R1 = Bu*t*) or metallacyclic gold(III) species (R1 = Cy, Xyl) (**Scheme 2**). To our knowledge, the generation of the metallacyclic gold(III) species **9** and **10** represents a novel type of reactivity of the nitrone **4**. Mechanism of this process was also proposed (see **Supporting Information**). The substituent depending chemical behavior of the isocyanide complexes is controlled by the acidity of the corresponding endocyclic CH group. The vast majority of reactions involving **4** includes radical spin trapping,35 dipolar cycloaddition with5,36 or without19b,37 subsequent deoxygenation, *C*- or *O*-functionalization,38 and oxidation-reduction35b,39 reactions. *Finally*, we observed that the 1,3-dipolar cycloaddition of keto- and aldonitrones **5**−**7** to isocyanides in [AuCl3(CNR1)] in CD2Cl2 at −70 ºC led to the corresponding NHC complexes exhibiting a low stability under normal conditions. Generated cycloadducts **8** and **11**–**17** can be considered as oxadiazolidine analogous of Enders’s triazol-5-ylidene carbenes.40 One can expect comparable electronic and steric properties from these species, although additional studies on a wider range of examples to attest this are required. Such a versatile reactivity of gold(III)-isocyanide complexes compared to respective gold(I) species deserves to be further explored toward a wide variety of 1,3-dipole reagents and nucleophiles.

EXPERIMENTAL SECTION

*Materials and Instrumentation*. Dipole **4** was obtained from Aldrich and used as received without further purification. All the solvents were ordered from Fisher Scientific and were used without further purification if not noted otherwise. Dichloromethane and toluene were dried over CaCl2 or P2O5, distilled and used without further purification. Gold complexes [AuCl3(CNR1)] (**1**–**3**),20 aldonitrone **5**,21 and ketonitrones **6** and **7**41 were synthesized according to the previously reported methods. C, H, N elemental analyses were carried out by the Microanalytical Service of the Instituto Supérior Técnico. ESI mass spectra were measured on a Bruker HCT quadrupole ion trap equipped with an electrospray ion source, operated in the negative ion mode; MeOH was used as the solvent. HRESI-MS were acquired on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source; MeOH was used as the solvent. Infrared spectra (4000−400 cm–1) were recorded on a Bruker Vertex 70 instrument in KBr pellets. 1H (400.13 MHz), 13C{1H} (100.61 MHz) and all the 2D NMR spectra were recorded on Bruker Avance II+ 400 MHz (UltraShieldTM Magnet) spectrometers at ambient temperature if not stated otherwise (see Experimental for details).

*X-ray structure determination.* Crystals were mounted in Nylon loops with small amount of cryo-oil and measured at 150 K, (**8**), ambient temperature (**9**) or at 100 K (for **13**). Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer (for **8** and **9**) or Agilent Technologies Xcalibur diffractometer (for **13**) with graphite monochromatic Mo-Kα (λ 0.71073) radiation. Data were collected using omega scans of 0.5º per frame and full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT42 (for **8** and **9**) and CrysAlisPro program complex (for **13**) on all the observed reflections. Absorption corrections were applied using SADABS43 (for **8** and **9**) and CrysAlisPro program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (for **13**). Structures were solved by direct methods by using the SHELXS-9744 package and refined with SHELXL-2014/7.44 Calculations were performed using the WinGX System-Version 2013.0342 (for **8** and **9**) and OLEX2 program package45 (for **13**). The hydrogen atoms were located from the difference Fourier synthesis, but inserted at geometrically calculated positions and included in the refinement using the riding-model approximation. There were disordered molecules present in the structure of **8** and **9**. Since no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/SQUEEZE46 was used to correct the data and potential volumes of 236 or 535 Å were found with 82 or 360 electrons per unit cell worth of scattering for **8** and **9**, respectively. The crystallographic data and some parameters of refinement are given in **Table S1** (**Supporting Information**). Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Center (CCDC 1469510 or 1469511 for **8** and **9**, and 1058628 for **13**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif.

*Generation of* ***8***–***10***. A solution of **4** (0.05 mmol) in CH2Cl2 (0.5 mL) was added to a solution of **1**–**3** (0.05 mmol) in CH2Cl2 (0.5 mL) at –74 °C (acetone-liquid nitrogen cooling bath) to form a pale yellow solution. The reaction mixture was warmed to RT and it was left to stand for ca. 15 min. The solvent was then removed under a stream of dinitrogen and the oily residue formed was washed with Et2O (two 1-mL portions) and dried in air at RT. Complexes **8**−**10** were recrystallized from CH2Cl2-Pr*i*2O solutions. Yields were 65–96%. Crystals of **8** and **9** were obtained by slow evaporation of CH2Cl2-Pr*i*2O solutions.



(**8**), pale yellow solid, 87%. Anal. calcd for C11H20N2Cl3OAu: C, 26.44; H, 4.04; N, 5.61%. Found: C, 26.50; H, 3.88; N, 5.29%. ESI−-MS, *m/z*: 497 [M − H]− [calcd. 497], 461 [M − HCl − H]− [calcd. 461]. IR (KBr, selected bands, cm–1): 2980, 2938, and 2916 m *ν*(C−H), 1637 s *ν*(Ccarbene=N). 1H NMR in CDCl3, *δ*: 5.57 (dd, *J*HH 7.2 and *J*HH 2.3 Hz, 1*H*, NCH), 2.51−2.39 and 2.23−2.15 (2m, 1*H* and 1*H*, CH2 from CHCH2), 2.05−1.89 (m, 2*H*, CH2 from CCH2), 1.84 (s, 9*H*, Bu*t*), 1.58 and 1.21 (2s, 3*H* and 3*H*, CMe2). 13С NMR in CDCl3, *δ*: 172.0 (Ccarbene), 83.6 (NCH), 72.4 (NC), 61.8 (C from Bu*t*), 34.9 and 34.2 (CH2 groups), 30.6 (Me from Bu*t*), 25.8 and 23.6 (Me from CMe2).



(**9**), colourless crystalline solid, 82%. Anal. calcd for C13H21N2Cl2OAu: C, 31.92; H, 4.33; N, 5.73%. Found: C, 32.06; H, 4.06; N, 5.65%. ESI−-MS, *m/z*: 523 [M + Cl]− [calcd. 523], 487 [M − H]− [calcd. 487], 427 [M + Cl – NCCH2CH2CMe2]− [calcd. 427]. IR (KBr, selected bands, cm–1): 2956, 2940, and 2857 m *ν*(C−H), 1771 s *ν*(C=O), 1607 s *ν*(C=N). 1H NMR in CD2Cl2, *δ*: 3.59–3.48 (m, 1*H*, CH from Cy), 3.06 (t, 3*J*HH 8.0 Hz, 2*H*) and 2.31 (t, 3*J*HH 8.0 Hz, 2*H*, CH2 groups from the pyrroline ring), 2.20–2.02 (m, 2*H*) and 1.96–1.79 (m, 4*H*, α- and β-CH2 groups from Cy), 1.71 (s, 6*H*, Me), 1.40–1.15 (m, 4*H*, β-CH2 group from Cy). 13С{1H} NMR in CD2Cl2, *δ*: 174.1 (CN), 155.1 (CO), 74.4 (CMe2), 61.3 (CH from Cy), 37.9 and 29.0 (CH2 groups from the pyrroline ring), 29.8 (α-CH2 groups), 28.0 (Me), 25.8 (β-CH2 groups), 24.6 (γ-CH2 group).



(**10**), pale yellow solid, 75%. Elemental analyses were not undertaken due to insufficient stability of the complex. ESI−-MS, *m/z*: 509 [M − H]− [calcd. 509 for C15H18N2Cl2OAu]. IR (KBr, selected bands, cm–1): 2961 and 2922 m *ν*(C−H), 1764 s *ν*(C=O), 1606 m *ν*(C=N). 1H NMR in CDCl3, *δ*: 7.40 (t, 3*J*HH 7.6 Hz, 1*H*, *p*-CarH), 7.26 (d, 3*J*HH 7.6 Hz, 2*H*, *m*-CarH), 2.59 (t, 3*J*HH 8.1 Hz, 2*H*) and 2.31 (t, 3*J*HH 8.1 Hz, 2*H*, CH2 groups), 2.21 (s, 6*H*, Me groups from Xyl), 1.80 (s, 6*H*, Me groups from CMe2). 13С{1H} NMR in CDCl3, *δ*: 173.6 (CN), 156.2 (CO), 135.7 (*o*-CarH), 133.0 (NCar), 130.9 (*p*-CarH), 129.3 (*m*-CarH), 76.1 (C from CMe2), 38.9 and 27.8 (CH2), 28.1 and 17.9 (Me).

*Generation of* ***11***–***17***. A solution of **5**−**7** (0.017 mmol) in CD2Cl2 (0.1 mL) was added to a solution of **1**–**3** (0.015 mmol) in CD2Cl2 (0.4 mL) at −74 °C (acetone-liquid nitrogen cooling bath) to form a pale yellow (**11**–**13**), yellow (**14**, **16** and **17**), or maroon (**15**) solution. The reaction mixture was then placed into an NMR tube and was immediately frozen in liquid nitrogen to avoid warming. The NMR tube with the frozen reaction mixture was placed inside the spectrometer (Bruker Avance II+ 400 MHz) and gradually warmed to −50 (**11**, **12**, **14**–**17**), or −15 °C (**13**). Consequently, the 1H (400.13 MHz) and 13C{1H} (100.61 MHz) NMR spectra were recorded showing that the conversion of starting **1**–**3** into corresponding **11**−**14**, **15**, and **16** was nearly quantitative by NMR (ca. 99%) and good (80%) in case of **17**. Due to insufficient stability of **11**–**17** at RT, elemental analyses (C, H, N), ESI‒-MS, and IR could not be performed, therefore their structures can be treated as *suggested* structures.



(**11**) 1H NMR in CD2Cl2, *δ*: 7.26 (s, 4*H*, CarH), 5.52 (s, 1*H*, newly formed CH group), 4.42 (t, 3*J*HH 12.2 Hz, 1*H*, CH from Cy), 3.06 (s, 3*H*, NMe), 2.35 (s, 3*H*, Me from *p*-Tol), 2.09 (d, 3*J*HH 12.0 Hz, 1*H*), 1.86 (d, 3*J*HH 12.9 Hz, 1*H*), 1.77−1.50 (m, 4*H*), 1.45−1.10 (m, 2*H*) and 1.00–0.71 (m, 2*H*) (CH2 from Cy). 13С{1H} NMR in CD2Cl2, *δ*: 172.8 (CcarbeneN), 141.9 and 130.5 (Car), 130.3 and 126.7 (CarH), 84.6 (newly formed CH group), 60.2 (CH from Cy), 48.4 (NMe), 31.6, 30.8, 24.7, and 24.2 (CH2), 21.3 (Me from *p*-Tol).



(**12**) 1H NMR in CD2Cl2, *δ*: 7.55–6.90 (m, 8*H*, CarH from Xyl, *p*-Tol and excess **5**), 5.86 (s, 1*H*, newly formed CH group), 3.41 (s, 3*H*, NMe), 2.57 (s, 3*H*, Me from *p*-Tol), 2.36, 2.31, and 1.48 (3s, 6*H*, Me from Xyl). 13С{1H} NMR in CD2Cl2, *δ*: 174.1 (CcarbeneN), 142.2, 137.2, 135.3, 131.2, 130.0, 129.8, 129.7, 129.4, 128.4, and 127.6 (10s, Car), 88.7 (newly formed CH group), 48.4 (NMe), 21.3, 19.6, and 17.9 (Me from Xyl and *p*-Tol).



(**13**) 1H NMR in CD2Cl2, *δ*: 7.26 (s, 4*H*, CarH), 5.65 (s, 1*H*, newly formed CH group), 3.00 (s, 3*H*, NMe), 2.34 (s, 3*H*, Me from *p*-Tol), 1.62 (s, 9*H*, Me from Bu*t*). 13С{1H} NMR in CD2Cl2, *δ*: 175.9 (CcarbeneN), 143.6 and 133.1 (Car), 132.3 and 128.3 (CarH), 88.3 (newly formed CH group), 64.7 (C from Bu*t*), 50.1 (NMe), 32.5 (Me from Bu*t*), 23.2 (Me from *p*-Tol).



(**14**) 1H NMR in CD2Cl2, *δ*: 8.07−6.85 (m, ca. 18*H*, CarH), 3.45–3.10 (m, br, 0.86*H*, CH from Cy), 2.29−1.08 (3m, 10*H*, CH2 from Cy). 13С{1H} NMR in CD2Cl2, *δ*: 169.7 (CcarbeneN), 141.5, 132.0, 131.0, 130.4, 129.9, 128.9, 128.6, 128.3, 124.4, and 121.5 (CarH), 98.1 (NCN), 61.2 (CH from Cy), 33.8, 26.0, and 24.5 (CH2).



(**15**) 1H NMR in CD2Cl2, *δ*: 8.05−6.60 (m, 15*H*, CarH), 1.68 and 1.35 (2s, 9*H*, Me). 13С{1H} NMR in CD2Cl2, *δ*: 170.1 (CcarbeneN), 142.9, 135.6, 133.7, 133.1, 132.7, 132.5, 131.8, 131.5, 129.9, 129.8, 129.6, 129.5, 129.0, 128.9, 128.8, 128.5, 128.2, 125.9, 123.9, and 121.1 (20s, Car), 63.9 and 56.0 (C from Bu*t*), 31.7 and 29.1 (Me), the NCN signal was not detected.



(**16**) 1H NMR in CD2Cl2, *δ*: 8.00−7.15 (m, ca. 15*H*, CarH), 3.81 (d, 2*J*HH 14.3 Hz, 1*H*) and 3.19 (d, 2*J*HH 14.3 Hz, 1*H*, CH2 from CH2Ph), 3.33 (t, 3*J*HH 10.7 Hz, 1*H*, CH from Cy), 2.63 and 2.52 (2s, br, ca. 1.7*H*), 1.95 and 1.39 (2d, *J*HH 10.0 Hz, 1+1*H*), 1.65−1.45 (m, 2*H*), 1.27−1.02 (m, 2*H*), 0.74 and 0.28 (2s, br, ca. 2*H*, CH2 from Cy). 13С{1H} NMR in CD2Cl2, *δ*: 170.0 (CcarbeneN), 132.0, 131.4, 131.1, 130.1, 129.2, 128.9, 128.8, and 128.5 (Car), 95.7 (NCN), 60.9 (CH from Cy), 58.5 (CH2 from CH2Ph), 35.2, 33.2, 26.9, 25.7, and 24.8 (CH2 from Cy).



(**17**) 1H NMR in CD2Cl2, *δ*: 8.05−6.40 (m, ca. 30*H*, CarH), 3.90 (d, 2*J*HH 15.5 Hz, 1*H*) and 3.66 (d, 2*J*HH 15.5 Hz, 1*H*, CH2 from CH2Ph), 2.25 and 1.55 (2s, ca. 6*H*, Me). 13С NMR in CD2Cl2, *δ*: 176.0 (CcarbeneN), 140.7, 136.6, 133.8, 132.8, 131.8, 131.5, 131.3, 130.9, 130.5, 130.3, 130.0, 129.7, 129.4, 129.3, 129.1, 128.9, 128.8, 128.5, 128.1, 127.9, and 127.5 (Car), 95.6 (NCN), 57.5 (CH2 from CH2Ph), 22.3 and 20.1 (Me).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed characterization and NMR spectra of complexes, crystal data and structure refinement details, **t**heoretical calculation data and Cartesian atomic coordinates (PDF)

X-ray diffraction data (CIF)

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Table of Contents artwork

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