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Full Paper

Mesoionic Carbene Complexes

Synthesis and Catalytic Activity of Coumarin- and Chrysin-Tethered Triazolylidene Gold(I) Complexes

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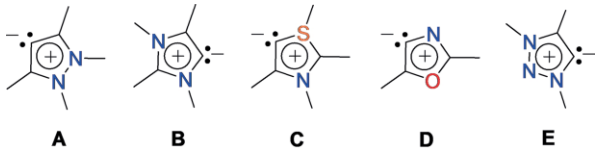
Abstract: A series sterically-encumbered coumarin- (**1**) and chrysin-functionalized triazolium salts (**2**,**3**) have been synthesized stepwise via copper catalyzed alkyne–azide cycloaddition and *N*-alkylation procedures. Their one-pot deprotonation with KHMDS in presence of AuCl(SMe_2) allowed for the preparation of the corresponding triazolylidene gold(I) complexes (**4–6**) in high yields (75–92 %). All new compounds were fully characterized by means of ^{1}H and ^{13}C NMR spectroscopy, FT-IR, elemental analyses and in the case of triazole **F**, triazolium **1** and the gold complex **4**, by single-crystal X-ray diffraction. The new triazolylidene gold complexes (**4–6**) were tested as precatalysts in the synthesis of indole derivatives via an intramolecular hydroamination reaction of several readily available anilines.

Introduction

Ever since their discovery in 2001 by Crabtree,[1] the field of stable mesoionic carbenes (MICs) has become a burgeoning area.[2] These type of ligands where the carbene center is not flanked by heteroatoms in both sides of their structures, have attracted a great deal of attention as they have demonstrated enhanced σ-donor properties compared to classical N-heterocyclic carbenes (NHCs).[3] Among the several types of mesoionic carbenes available in the literature (Scheme 1) including pyrazol-4-ylidenes (**A**),[4] imidazol-5-ylidenes (**B**),[5] thiazol-5-ylidenes (**C**)[6] and oxazol-4-ylidenes (**D**),[7] the coordination chemistry of 1,2,3-triazolylidenes (**E**) have found a wide range of applications as ligands for transition metals, typically employed in a variety of homogeneous catalysis processes.[8]



Scheme 1. Mesoionic carbene ligands reported in the literature.

The success of the triazolylidene coordination chemistry is related to the facile preparation of the triazole precursors by means of the regioselective copper(I) catalyzed "click" cycloaddition of alkynes and azides[9] and the subsequent N-alkylation which readily delivers the desired 1,2,3-triazolylidene precursors. Because of the ease in structural modification in triazolylidene scaffolds, great structural diversity is achieved by tuning the substituent appended at the N3- and C4-positions of the central triazole core. This structural diversity has significantly affected the electronic and steric properties of the MICs, which in turn accounts for the variation in the stability, reactivity lipophilicity, and biocompatibility of the resulting complexes. For several years, our group has been interested in the preparation of ligands featuring chrysin and coumarin derivatives as they have shown a wide variety of applications. For instance, coumarin derivatives have shown a broad spectrum of biological activity including anti-HIV, anticancer, and enzyme inhibition.[10] Moreover, coumarin-supported complexes have found application as catalysts for cross coupling reactions,[11] polymerization,[12] and olefin metathesis.[13] In the other hand, chrysin derivatives have demonstrated high activity as antiviral, antibacterial, antioxidant, and anxiolytic agents,[14] although surprisingly, their catalytic potential have not been broadly studied.

With this interesting background and with a single example of triazolylidene ligands featuring natural product derivatives (i.e. steroid derivatives),[15] we present in here the preparation of the first examples of coumarin- and chrysin-functionalized mono-triazolium salts (**1**,**2**) and the chrysin-derived bis-triazolium salt (**3**). Their subsequent one-pot deprotonation with KHMDS in presence of AuCl(SMe_2) permits the isolation of the corresponding triazolylidene mono- and bis-gold(I) complexes **4**–**6** in high yields. All new compounds have been fully characterized by means of ^{1}H and ^{13}C NMR spectroscopy, FT-IR, elemental analyses, and single-crystal X-ray diffraction. The application of the triazolylidene gold complexes (**4–6**) as precatalysts in the synthesis of indole derivatives via an intramolecular hydroamination reaction of several readily available anilines will be discussed.

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Results and Discussion

The preparation of the coumarin-functionalized triazolium salt **1** was performed according to Scheme 2. The first step involves the copper catalyzed cycloaddition of the propargylated coumarin in a mixture of DMF/water to provide the triazole **F** in 71 % yield after column chromatography purification. The subsequent treatment of the latter precursor with excess methyl iodide in acetonitrile, delivers the desired triazolium salt **1** obtained in 74 % yield after recrystallization of the crude material with acetonitrile/diethyl ether.

Formation of the triazolium salt **1** was easily monitored by the appearance of a new signal in the ^{1}H NMR spectrum at ca. δ = 4.78 ppm, indicating methylation of the triazolyl moiety (at *N*-3). Most of the other resonances in the ^{1}H NMR spectrum shifted only slightly, with the exception of the now acidic triazolium proton, which moves to higher frequency (from δ = 7.87 in triazole **A** to 9.27 ppm in **1**). A prototypical signal for the identification of the coumarin fragment is the presence of olefinic proton of the lactonic ring, which is displayed as a singlet at δ = 6.25 ppm. Unambiguous characterization of the triazole **F** and triazolium salt **1** was also achieved by X-ray crystallography with the molecular structures displayed in Figure 1.

In the case of the chrysin scaffold, the presence of two different phenolic positions provided the possibility of generating mono- and bis-triazolium derivatives if a stepwise propargylation was achieved. With this in mind, we attempted the monopropargylation of the chrysin at position O7- by its treatment with a slight excess of potassium carbonate and equimolar amounts of propargyl bromide. However, after several attempts using different solvents and base ratios, we found in all cases a mixture of the mono- and bis-propargylated species which proved very difficult to separate. With this issue, we then decided to use an O7-(5-bromopropyl) substituted chrysine[16] which after treatment with K_2CO_3 and propargyl bromide yields the expected mono-propargylated chrysin derivative. Following the standard catalysed click cycloaddition[17] and *N*-methylation procedures, we obtained the mono-triazolium salt **2** in 69 % yield (Scheme 3).

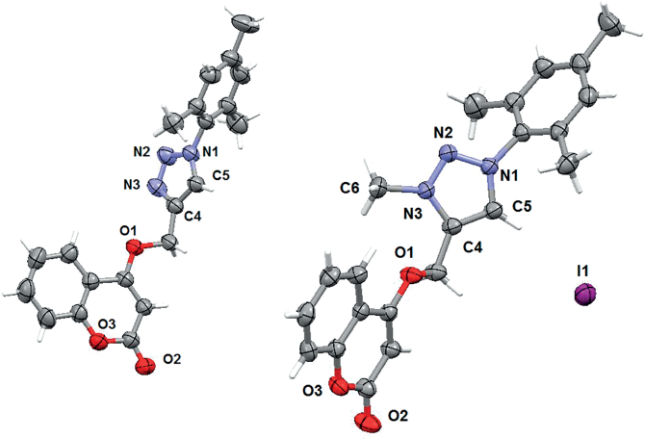


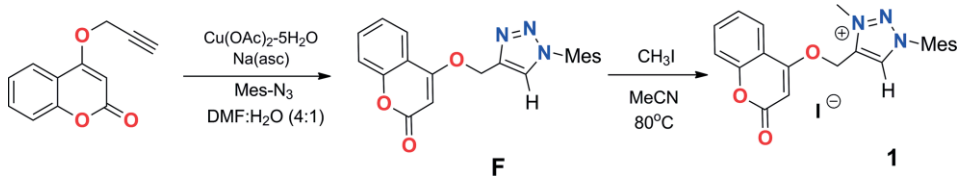
Figure 1. Molecular structures of triazole **F** (left) and triazolium **1** (right). Ellipsoids are shown at 50 % probability.

To favour the deprotonation of both phenolic positions on the chrysin scaffold we proceeded to its treatment with a large excess of potassium carbonate (fivefold) and 3 equivalents of propargyl bromide yielding the desired bis-propargylated derivative in 81 % after column chromatography separation. The subsequent double click process followed by *N*-methylation renders the bis-triazolium salt **3** in 81 % yield (Scheme 4).

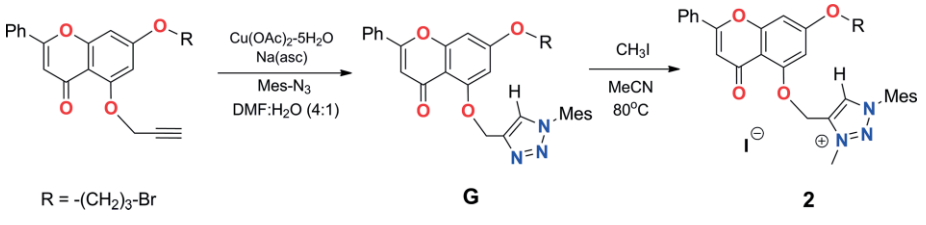
Both chrysin-functionalized triazolium salts **2** and **3** were characterized by means of ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. The expected CH(+) triazolium proton for the mono-salt **2** display a shift at δ = 9.23 ppm, while the two acidic protons for bis-triazolium **3** are located at δ = 9.07 and 9.61 ppm, respectively.

To explore the coordination capabilities of the new monotriazolium salts **1** and **2**, we initially tested their reactivity with hexamethyldisilazane (KHMDS) in the presence of $AuCl(SMe_2)$ under strict light absence (Scheme 5). After work up and purification, the respective products **4** and **5** were obtained as crystalline powders in 92 and 84 % yield, respectively.

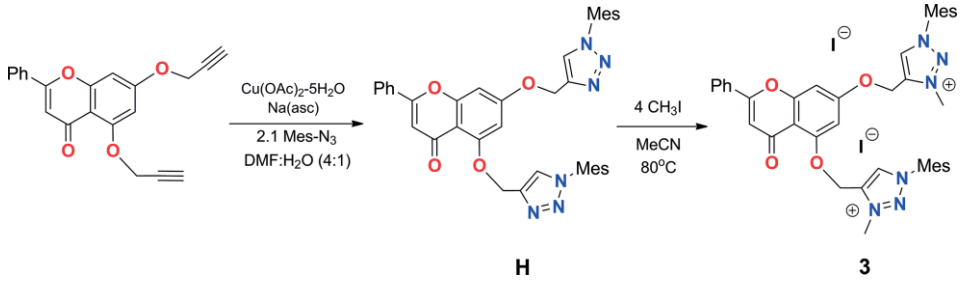
NMR spectroscopy studies and elemental analyses confirmed the formation of the expected Au^I-MIC complexes **4** and **5** by



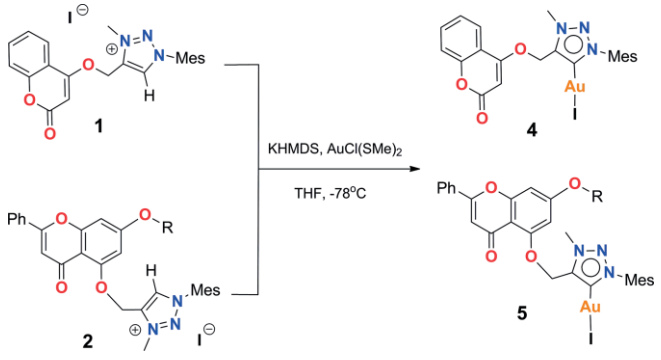
Scheme 2. Synthesis of coumarin-functionalized salt **1**.



Scheme 3. Synthesis of chrysin-functionalized mono-triazolium **2**.



Scheme 4. Synthesis of chrysin-functionalized bis-triazolium **3**.



Scheme 5. Synthesis of mono-triazolylidene gold complexes **4** and **5**.

the disappearance of the acidic CH^+ proton in the ^1H NMR (above 9 ppm), and the observation of a low field ^{13}C NMR signal at δ = 171.1 ppm for complex **4** and 173.2 for complex **5**, both similar to previously reported mononuclear MIC-gold(I) complexes.[18] Complex **4** was crystallized from a mixture of dichloromethane/pentane at room temperature and the crystal structure is depicted in Figure 2.

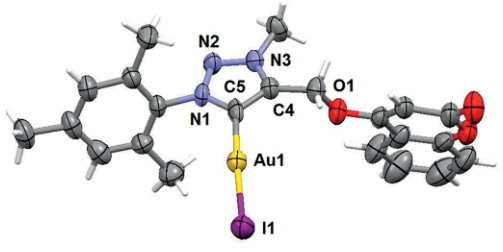
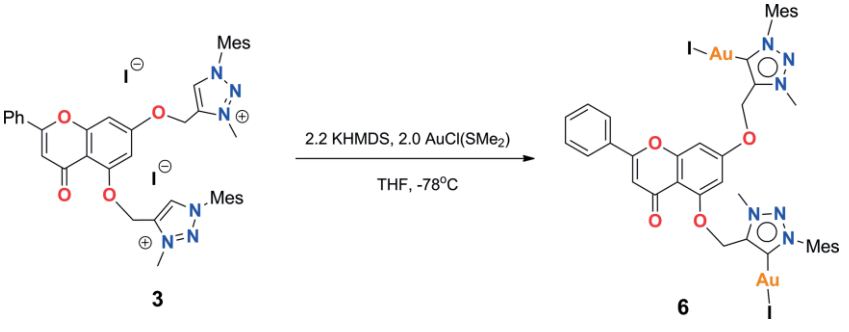


Figure 2. Molecular structure of coumarin-functionalized MIC-gold complex **4**. Ellipsoids are shown at 50 % probability.

Complex **4** crystallizes in the monoclinic system with the $P2_n/1$ space group, and the monomeric structure display a carbene–gold bond length of 2.022(10) Å, which is in the range of recently reported MIC-Au^I complexes.[19] As usually observed in Au^I carbene complexes, the metal center features an almost linear environment with a C(5)–Au^I–I(1) bond angle of 175.89(19)°. The carbene bond angle in **4** [104.61(9)°] is slightly more acute than the corresponding triazolium salt **1** [105.96(10)°]. This feature is consistent with the increased s-character of the σ lone pair orbital in the carbene atom in **4** as compared with the C(H+) bond orbital in **1**. Both the mesityl and coumarin fragments are tilted almost orthogonal to the triazolylidene plane.

With the successful metalation of the mono-triazolylidene precursors, we followed a similar methodology for the preparation of the chrysine-functionalized dinuclear complex **6**. Hence, the one-pot treatment of the bis-triazolium **3** with excess of KHDMS and two equivalents of $AuCl(SMe)_2$ delivers after purification the expected gold complex in 75 % yield (Scheme 6). The formation of complex **6** was easily observed by the disappearance of the two acidic protons of the dicationic precursor **3** and the emergence of two new signals located at δ = 173.3 and 173.6 ppm in the ^{13}C NMR spectra.

Recent studies have demonstrated unquestionably that gold is an excellent Lewis acid for the selective activation of unsaturated carbon–carbon bonds under mild conditions.[20] In particular, NHC-based gold(I) complexes have shown applicability as precatalysts in various processes such as C–H bond functionalizations, cyclization of enynes, hydroaminations, among others.[21] However, to the best of our knowledge there are only few reports dedicated to gold-catalyzed synthesis of functionalized indoles. For instance, Nakamura and co-workers have re-

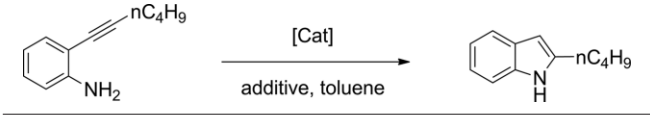


Scheme 6. Synthesis of the chrysin-derived dinuclear complex **6**.

ported the gold-catalyzed synthesis of a variety of 3-sulfonylindoles in good yields although with the drawback of a high catalyst loading (10 mol-% of $AuBr_3$).[22] Arcadi and co-workers have found that heterocyclization of anilines takes place in the presence of gold(I) or gold(III) species.[23] Recently Nolan has reported the application of cationic NHC-gold complexes in the high yield synthesis of azepinindoles starting from available propargylic alcohols.[24] In line with our ongoing research on new applications of MIC-Au^I complexes, we decided to test our new coumarin- and chrysin-tethered triazolylidene complexes in the catalytic synthesis of indole derivatives starting from readily available anilines.

We began our investigation by testing precatalysts **4**–**6** in the intramolecular hydroamination of 2-(hexyl-1-yn-1-yl)aniline as model reaction. Initial conditions included loading of 3 mol-% of the appropriate precatalyst, excess of $AgBF_4$ as halogen scavenger, toluene as solvent, and 2 h of reaction. As observed in Table 1, complexes **4** and **5** display similar activities with yields over 91 %, while the dinuclear complex **6** display the best conversion of the series reaching quantitative conversion. Optimization of the reaction conditions including variation of the catalyst loading and several additives, demonstrate that loading of complex **6** can be reduced to 0.5 mol-% (based in metal), without significant loss on the conversions. In case of the mononuclear complexes **4** and **5** a noticeable yield decrease (below 75 %) is observed when gradually decreasing the catalyst loading.

Table 1. Intramolecular hydroamination of 2-(hexyl-1-yn-1-yl)aniline using precatalysts **4**–**6**.



Entry	Cat	[cat] [mol-%][b]	Additive [mol-%]	Yield [%][c]
1	**4**	3	$AgBF_4$-[3]	92
2	**5**	3	$AgBF_4$-[3]	91
3	**6**	3	$AgBF_4$-[6]	99
4	**4**	1	$AgBF_4$-[1]	87
5	**5**	1	$AgBF_4$-[1]	89
6	**6**	1	$AgBF_4$-[2]	98
7	**4**	0.5	$AgBF_4$-[1]	73
8	**5**	0.5	$AgBF_4$-[1]	70
9	**6**	0.5	$AgBF_4$-[1]	97
10	**6**	0.5	AgOTf-[1]	93
11	**6**	0.5	$KBAr^F$-[1]	89
12	**6**	0.1	$AgBF_4$-[0.2]	91

[a] Reaction conditions: 2-(hexyl-1-yn-1-yl)aniline (1.0 mmol), toluene 2 mL, 2 h, room temperature. [b] Based in the metal. [c] Isolated yields as the average of two runs.

In order to get more insight into the catalytic behavior of complexes **4**–**6**, the catalytic profiles for the intramolecular hydroamination of 2-(hexyl-1-yn-1-yl)aniline using precatalysts **4**–**6** were performed with the reaction conditions presented in Table 1 (Entries 7–9). As illustrated in Figure 3, catalysts **6** reach conversions higher than 75 % after only 45 min of reaction and their maximum conversions are observed in 105 min. In the case of monometallic **4** and **5**, the generation of products is slower reaching their maximum conversion after 120 min, and remaining unchanged after that time. The overall profile results suggest that the local concentration of active sites provided by the multinuclear complex **6** have an effect of the efficiency and stability of the catalytic species.[25]

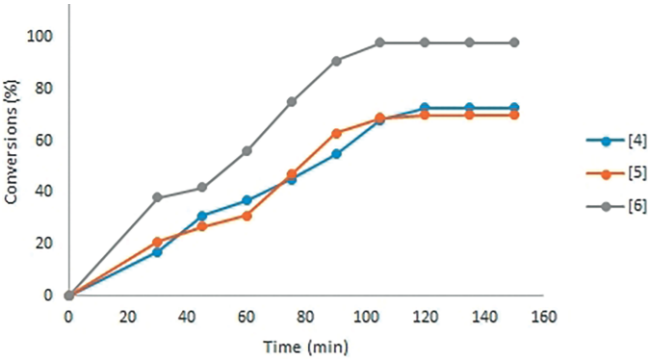
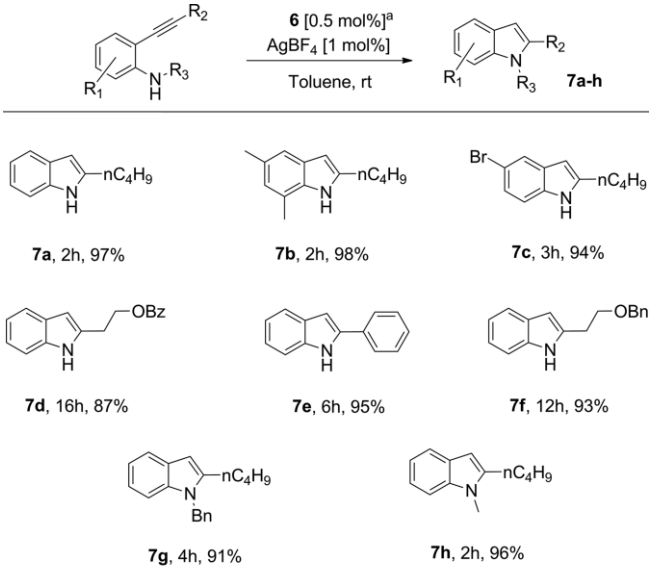


Figure 3. Intramolecular hydroamination of 2-(hexyl-1-yn-1-yl)aniline using precatalysts **4**–**6**. Reactions carried out with $[D_8]$toluene at room temperature. Conversions determined by ^1H NMR spectroscopy based on the amount of aniline remaining in solution.

With the optimal catalytic conditions for the model system, we decided next to investigate the reaction scope. As observed in Table 2, a series of aniline derivatives possessing different substituents in the aryl ring can be employed in the hydroamination reaction (**7a–c**) with the bromo derivative requiring longer time for optimal conversion.

Table 2. Scope of the intramolecular hydroamination of various substituted anilines using precatalyst **6**.



[a] Reaction conditions: 0.5 mol-% based in the metal. 2-(hexyl-1-yn-1-yl)-aniline (1.0 mmol), toluene 2 mL, room temperature. [b] Isolated yields as the average of three runs.

The present methodology can be also extended to substrates bearing various substituents at the triple bond (**7d–f**) although the reaction times for reaching maximum conversions increase considerably. Additionally, it was observed that substi-

tution at the *N*-position was tolerated, delivering products **7g–h** in good yields.

Conclusions

In summary, we have reported the convenient synthesis of a series of coumarin- (**1**) and chrysin-tethered triazolium salts (**2**,**3**) and used them as ligand precursors for the high yield preparation of the respective mono- and dinuclear triazolylidene gold(I) complexes (**4–6**). All new compounds have been properly characterized by NMR spectroscopy and elemental analysis, and in case of **F**, **1** and **4** by X-ray diffraction. The new air and moisture stable triazolylidene gold complexes (**4–6**) were tested as precatalysts in the synthesis of indole derivatives via an intramolecular hydroamination reaction of several anilines. The catalytic trials established the enhanced performance of complex **6** compared with the mononuclear complexes **4**–**5** efficiency be related to the effect of the higher concentration of active catalytic sites in multinuclear species. The reaction scope described in the present study demonstrate the broad applicability of the bis-triazolylidene complex **6** in the catalysed synthesis of a variety of substituted indoles opening a new alternative for this important organic transformation. Further exploration of the catalytic potential of complexes **4**–**6** is currently being explored in our laboratory.

Experimental Section

Commercially available reagents and solvents were used as received. The series of 2-alkyl anilines,[26] mesityl azide,[27] 4-(propargyloxy)coumarin,[28] 5-(bromopropane)-7-(propargyloxy)chrysin[16] and 5,7-(bis-propargyloxy)chrysin[29] were synthesized as reported in the literature. Synthesis of all metal complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. IR spectra were recorded on a Bruker Alpha FT-IR/ATR spectrometer. Melting points were determined on a Fisher–Johns apparatus and are uncorrected. NMR spectra were obtained with a Bruker Ascend (400 MHz) spectrometer. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin–Elmer Series II CHNS/O 2400 instruments. X-ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved by direct methods, using SHELX 2014 and refined by full-matrix least-squares against F^2.[30] All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters.

Synthesis of Coumarin-functionalized Triazole F: To a 20 mL round-bottomed flask equipped with a magnetic stirrer, were charged 0.05 mmol (5 mol-%) of $Cu(OAc)_2{\cdot}H_2O$, 0.05 mmol (5 mol-%) of 1,10-phenanthroline monohydrate, and 1.0 mmol of sodium L-ascorbate. After addition of 5 mL of a mixture DMF/H_2O (4:1 v/v), the resulting suspension was stirred for five minutes at room temperature. Subsequently, 1.0 mmol of 4-(propargyloxy)coumarin, and 1.2 mmol of mesityl azide were added to the reaction mixture, which was stirred during 16 h at room temperature. The organic phase was extracted with 30 mL of dichloromethane (DCM), washed with brine and dried with magnesium sulfate. After evaporation under vacuum, the crude product was purified by column chromatography (CH_2Cl_2) yielding the title product in 71 % yield (257 mg, 0.71 mmol) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.99 (s, 6 H, CH_3), 2.36 (s, 3 H, CH_3), 5.45 (s, 2 H, CH_2), 5.91 (s, 1 H, CH), 7.01 (s, 2 H, CH_{ar}), 7.24–7.32 (m, 2 H, CH_{ar}), 7.53–7.55 (m, 1 H, CH_{ar}), 7.80–7.82 (m, 1 H, CH_{ar}), 7.83 (s, 1 H, $CH_{triazole}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.3 (CH_3), 21.1 (CH_3), 62.8 (CH_2), 91.2 (CH), 115.5 (CH_{ar}), 116.8 (C_q), 123.2 (CH_{ar}), 124.0 (CH_{ar}), 125.4, 129.2, 132.6 (CH_{ar}), 133.1 (C_q), 135.0 ($CH_{triazole}$), 140.4 (C_q), 141.3 (CH_{ar}), 153.4 (C_q), 162.6 (C_q), 165.1 (CO) ppm. $C_{21}H_{19}N_3O_3$ (361.40): calcd. C 69.79, H 5.30, N 11.63; found C 66.47, H 5.23, N 11.28.

Synthesis of Chrysin-functionalized Mono-triazole G: To a 20 mL round-bottomed flask equipped with a magnetic stirrer, were charged 0.05 mmol (5 mol-%) of $Cu(OAc)_2{\cdot}H_2O$, 0.05 mmol (5 mol-%) of 1,10-phenanthroline monohydrate, and 1.0 mmol of sodium L-ascorbate. After addition of 5 mL of a mixture DMF/H_2O (4:1 v/v), the resulting suspension was stirred for five minutes at room temperature. Subsequently, 1.0 mmol of 5-(bromopropane)-7-(propargyloxy)chrysin, and 1.2 mmol of mesityl azide were added to the reaction mixture, which was stirred during 16 h at room temperature. The organic phase was extracted with 30 mL of dichloromethane (DCM), washed with brine and dried with magnesium sulfate. After evaporation under vacuum, the crude product was purified by column chromatography (CH_2Cl_2/MeOH, 95:5 v/v) yielding the title product in 77 % yield (442 mg, 0.77 mmol) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.99 (s, 6 H, CH_3), 2.26 (pent, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 4.21 (t, J = 4.8 Hz, 2 H, CH_2), 4.43 (t, J = 4.8 Hz, 2 H, CH_2), 5.49 (s, 2 H, CH_2), 6.99 (s, 2 H, CH_{ar}), 7.51–7.53 (m, 4 H, CH_{ar}), 7.87–7.89 (m, 2 H, CH_{ar}), 8.03 (s, 1 H, CH), 8.12 (s, 1 H, CH_{ar}), 8.15 (s, 1 H, $CH_{triazole}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.3 (CH_3), 21.2 (CH_3), 28.3 (CH_2), 36.5 (CH_2), 60.4 (CH_2), 64.9 (CH_2), 94.5 (CH), 109.0 (C_q), 109.8 (C_q), 125.2 (CH_{ar}), 125.6 (CH_{ar}), 128.9 (CH_{ar}), 129.0 (CH_{ar}), 131.3 (CH_{ar}), 133.5 ($CH_{triazole}$), 135.1 (C_q), 139.9 (CH_{ar}), 144.3 (C_q), 159.4 (CH_{ar}), 159.7 (CH_{ar}), 160.9 (C_q), 161.0 (C_q), 162.5 (C_q), 163.1 (CO), 177.4 ppm. $C_{30}H_{28}BrN_3O_4$ (574.47): calcd. C 62.72, H 4.91, N 7.31; found C 62.61, H 5.00, N 7.29.

Synthesis of Chrysin-functionalized (Bis)triazole H: To a 20 mL round-bottomed flask equipped with a magnetic stirrer, were charged 0.1 mmol (10 mol-%) of $Cu(OAc)_2{\cdot}H_2O$, 0.1 mmol (10 mol-%) of 1,10-phenanthroline monohydrate, and 2.0 mmol of sodium L-ascorbate. After addition of 10 mL of a mixture DMF/H_2O (4:1 v/v), the resulting suspension was stirred for five minutes at room temperature. Subsequently, 1.0 mmol of 5,7-(bis-propargyloxy)chrysin, and 2.4 mmol of mesityl azide were added to the reaction mixture, which was stirred during 16 h at room temperature. The organic phase was extracted with 30 mL of dichloromethane (DCM), washed with brine and dried with magnesium sulfate. After evaporation under vacuum, the crude product was purified by column chromatography (CH_2Cl_2/MeOH, 95:5 v/v) yielding the title product in 81 % yield (528 mg, 0.81 mmol) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.98 (s, 6 H, CH_3), 1.99 (s, 6 H, CH_3), 2.36 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 5.46 (s, 2 H, CH_2), 5.48 (s, 2 H, CH_2), 6.64 (s, 1 H, CH), 6.74 (d, J = 2.2 Hz, 1 H, CH), 6.85 (d, J = 2.2 Hz, 1 H, CH_{ar}), 7.01 (s, 2 H, CH), 7.52–7.53 (m, 3 H, CH_{ar}), 7.78 (s, 1 H, $CH_{triazole}$), 7.88–7.90 (m, 2 H, CH_{ar}), 8.16 (s, 1 H, $CH_{triazole}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.33 (CH_3), 17.35 (CH_3), 21.1 (CH_3), 62.6 (CH_2), 64.5 (CH_2), 94.9 (CH), 98.7 (CH_{ar}), 109.0 (C_q), 110.0 (C_q), 125.0 (CH_{ar}), 125.3 (CH_{ar}), 126.0 (CH_{ar}), 129.0 (CH_{ar}), 129.02 (CH_{ar}), 129.2 (CH_{ar}), 131.4 (C_q), 133.3 (C_q), 113.5 (CH_{ar}), 135.0 ($CH_{triazole}$), 135.06 (CH_{ar}), 139.9 (CH_{ar}), 140.3 (CH_{ar}), 142.8 (CH_{ar}), 144.3 (C_q), 159.4 (C_q), 159.8 (C_q), 161.1 (C_q), 162.7 (C_q), 177.5 (CO) ppm. $C_{39}H_{36}N_6O_4$ (652.75): calcd. C 71.76, H 5.56, N 12.87; found C 71.51, H 5.89, N 12.49.

Synthesis of Coumarin-functionalized Triazolium Salt 1: Methyl iodide (0.98 g, 6.92 mmol) was added to a 10 mL of acetonitrile solution of triazole **F** (500 mg, 1.38 mmol) and the resulting clear solution was refluxed for 24 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume and diethyl ether was added until a precipitate was formed. The solid was collected by filtration and washed thoroughly with cold diethyl ether. Pure product as colorless crystals is obtained in 74 % yield (514 mg, 1.02 mmol) after recrystallization with acetonitrile/diethyl ether (1:3). m.p. 178–180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 6 H, CH_3), 2.38 (s, 3 H, CH_3), 4.78 (s, 3 H, NCH_3), 6.25 (s, 1 H, CH), 6.30 (s, 2 H, CH_2), 7.02 (s, 2 H, CH_{ar}), 7.17–7.19 (d, J = 7.6 Hz, 1 H, CH_{ar}), 7.25–7.29 (m, 1 H, CH_{ar}), 7.49–7.51 (m, 1 H, CH_{ar}), 7.81–7.83 (m, 1 H, CH_{ar}), 9.27 (s, 1 H, $CH_{triazolium}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.2 (CH_3), 21.2 (CH_3), 41.6 (NCH_3), 61.3 (CH_2), 93.0 (CH), 114.7 (C_q), 116.7 (C_q), 123.0 (CH_{ar}), 124.4 (CH_{ar}), 130.0 (CH_{ar}), 131.0 (CH_{ar}), 132.9, 133.1 (CH_{ar}), 134.5 (C_q), 139.5 ($CH_{triazolium}$), 142.8 (C_q), 153.1 (C_q), 162.0 (C_q), 163.9 (CO) ppm. $C_{22}H_{22}IN_3O_3$ (503.34): calcd. C 52.50, H 4.41, N 8.35; found C 52.31, H 4.27, N 8.51.

Synthesis of Chrysin-functionalized Mono-triazolium Salt 2: Methyl iodide (0.64 g, 4.46 mmol) was added to a 10 mL of acetonitrile solution of triazole **G** (500 mg, 0.89 mmol) and the resulting clear solution was refluxed for 24 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume and diethyl ether was added until a precipitate was formed. The solid was collected by filtration and washed thoroughly with cold diethyl ether. Pure product as colorless crystals is obtained in 69 % yield (431 mg, 0.61 mmol) after recrystallization with acetonitrile/diethyl ether (1:3). m.p. 195–197 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (s, 6 H, CH_3), 2.25 (pent, 2 H, CH_2), 2.41 (s, 3 H, CH_3), 4.36 (t, J = 4.8 Hz, 2 H, CH_2), 4.44 (t, J = 4.8 Hz, 2 H, CH_2), 4.90 (s, 3 H, NCH_3), 6.10 (s, 2 H, CH_2), 6.59 (s, 1 H, CH), 6.72 (s, 1 H, CH_{ar}), 7.08 (s, 2 H, CH_{ar}), 7.53–7.55 (m, 3 H, CH_{ar}), 7.87–7.89 (m, 2 H, CH_{ar}), 8.12 (s, 1 H, CH_{ar}), 9.23 (s, 1 H, $CH_{triazolium}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.9 (CH_3), 21.2 (CH_3), 28.3 (CH_2), 41.4 (NCH_3), 60.6 (CH_2), 62.7 (CH_2), 66.1 (CH_2), 97.3 (CH), 99.4 (CH_{ar}), 108.5 (C_q), 109.3 (C_q), 126.1 (CH_{ar}), 129.1 (CH_{ar}), 130.0 (CH_{ar}), 131.1 (CH_{ar}), 131.2 (CH_{ar}), 131.6 (CH_{ar}), 132.8, 134.4, 141.4 ($CH_{triazolium}$), 142.8 (C_q), 157.7 (CH_{ar}), 159.3 (CH_{ar}), 161.1 (C_q), 161.6 (C_q), 163.7 (C_q), 177.5 (CO) ppm. $C_{31}H_{31}BrIN_3O_4$ (716.41): calcd. C 51.97, H 4.36, N 5.87; found C 51.68, H 4.43, N 5.76.

Synthesis of Chrysin-functionalized (Bis)triazolium Salt 3: Methyl iodide (1.14 g, 8.00 mmol) was added to a 10 mL of acetonitrile solution of (bis)triazole **H** (500 mg, 0.80 mmol) and the resulting clear solution was refluxed for 24 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume and diethyl ether was added until a precipitate was formed. The solid was collected by filtration and washed thoroughly with cold diethyl ether. Pure product as colorless crystals is obtained in 81 % yield (589 mg, 0.648 mmol) after recrystallization with acetonitrile/diethyl ether (1:3). m.p. 201–203 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (s, 6 H, CH_3), 2.19 (s, 6 H, CH_3), 2.39 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 4.85 (s, 3 H, NCH_3), 4.89 (s, 3 H, NCH_3), 6.22 (s, 2 H, CH_2), 6.28 (s, 2 H, CH_2), 6.34 (s, 1 H, CH), 7.04 (s, 2 H, CH_{ar}), 7.08 (s, 2 H, CH_{ar}), 7.45–7.52 (m, 4 H, CH_{ar}), 7.53 (s, 1 H, CH_{ar}), 7.86–7.88 (m, 2 H, CH_{ar}), 9.07 (s, 1 H, $CH_{triazolium}$), 9.61 (s, 1 H, $CH_{triazolium}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.2 (CH_3), 18.4 (CH_3), 21.23 (CH_3), 21.24 (CH_3), 41.9 (NCH_3), 42.4 (NCH_3), 62.7 (CH_2), 63.2 (CH_2), 98.2 (CH), 99.6 (CH_{ar}), 108.1 (C_q), 109.7 (C_q), 126.3 (CH_{ar}), 128.9 (CH_{ar}), 129.9 (CH_{ar}), 129.91 (CH_{ar}), 131.3 (CH_{ar}), 132.1 (C_q), 134.4 (CH_{ar}), 134.5 (CH_{ar}), 141.3 ($CH_{triazolium}$), 142.0 (CH_{ar}), 142.3 (CH_{ar}), 142.5 (CH_{ar}), 157.4 (C_q), 159.1 (CH_{ar}), 161.4 (C_q), 161.5 (C_q), 176.9 (CO) ppm. $C_{41}H_{42}I_2N_6O_4$ (936.63): calcd. C 52.58, H 4.52, N 8.97; found C 52.79, H 4.91, N 8.65.

Synthesis of Complexes 4–6: Complex **4**. In strict absence of light, choloro(dimethylsulfide)gold (62 mg, 0.21 mmol), potassium hexamethyl disylazide (48 mg, 0.24 mmol) and coumarin-functionalized triazolium salt **1** (101 mg, 0.20 mmol) were combined in a Schlenk flask and dissolved in THF (7 mL) at –78 °C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was washed with hexane (3 mL) and diethyl ether (3 mL) and further extracted with benzene. After cannula filtration and removal of the solvent the crude product is dissolved in 1 mL of DCM and precipitated by addition of 10 mL of petroleum ether. The solid is filtered and dried under vacuum yielding the title product in 92 % yield (129 mg, 0.184 mmol) as white solid. m.p. 115–117 °C. ^{1}H NMR ([D_6]DMSO, 400 MHz): δ = 2.02 (s, 6 H, CH_3), 2.35 (s, 3 H, CH_3), 4.37 (s, 3 H, NCH_3), 5.65 (s, 2 H, CH_2), 6.30 (s, 1 H, CH), 7.14 (s, 2 H, CH_{ar}), 7.37 (t, J = 7.6 Hz, 1 H, CH_{ar}), 7.42 (d, J = 7.8 Hz, 1 H, CH_{ar}), 7.68 (t, J = 7.6 Hz, 1 H, CH_{ar}), 8.05 (dd, J = 7.8 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR ([D_6]DMSO, 100.6 MHz): δ = 17.5 (CH_3), 21.2 (CH_3), 38.6 (NCH_3), 61.5 (CH_2), 92.6 (CH), 115.3 (C_q), 116.9 (C_q), 124.0 (CH_{ar}), 124.7 (CH_{ar}), 129.6 (CH_{ar}), 133.4 (CH_{ar}), 134.5 (CH_{ar}), 135.6 (CH_{ar}), 140.9 (C_q), 153.2 (C_q), 161.8 (C_q), 164.5 (CO), 171.1 (Au=C) ppm. $C_{22}H_{21}AuIN_3O_3$ (699.30): calcd. C 37.79, H 3.03, N 6.01; found C 38.04, H 3.18, N 6.27.

Complex 5: In strict absence of light, choloro(dimethylsulfide)gold (62 mg, 0.21 mmol), potassium hexamethyl disylazide (48 mg, 0.24 mmol) and chrysin-functionalized mono-triazolium salt 2 (143 mg, 0.20 mmol) were combined in a Schlenk flask and dissolved in THF (10 mL) at –78 °C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was washed with hexane (3 mL) and diethyl ether (3 mL) and further extracted with benzene. After cannula filtration and removal of the solvent the crude product is dissolved in 1 mL of DCM and precipitated by addition of 10 mL of petroleum ether. The solid is filtered and dried under vacuum yielding the title product in 84 % yield (153 mg, 0.168 mmol) as pale yellow solid. m.p. 143–145 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (s, 6 H, CH_3), 2.27 (pent, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 4.29 (t, J = 4.8 Hz, 2 H, CH_2), 4.44 (t, J = 4.8 Hz, 2 H, CH_2), 4.61 (s, 3 H, NCH_3), 5.59 (s, 2 H, CH_2), 6.62 (s, 1 H, CH), 6.73 (s, 1 H, CH_{ar}), 6.97 (s, 2 H, CH_{ar}), 7.53–7.55 (m, 3 H, CH_{ar}), 7.87–7.89 (m, 2 H, CH_{ar}), 8.10 (s, 1 H, CH_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.6 (CH_3), 21.2 (CH_3), 28.1 (CH_3), 38.5 (NH_3), 60.6 (CH_2), 61.2 (CH_2), 65.7 (CH_2), 97.0 (CH), 99.5 (CH_{ar}), 108.7 (C_q), 126.1 (CH_{ar}), 129.1 (CH_{ar}), 129.4 (CH_{ar}), 131.3 (CH_{ar}), 131.5 (CH_{ar}), 134.1 (C_q), 135.0 (CH_{ar}), 140.8 (CH_{ar}), 140.9 (CH_{ar}), 157.6 (C_q), 159.5 (C_q), 161.0 (C_q), 161.4 (C_q), 163.3 (CO), 173.2 (Au=C), 177.4 ppm. $C_{31}H_{30}AuBrIN_3O_4$ (912.37): calcd. C 40.81, H 3.31, N 4.61; found C 41.07, H 3.18, N 4.74.

Complex 6: In strict absence of light, choloro(dimethylsulfide)gold (62 mg, 0.21 mmol), potassium hexamethyl disylazide (48 mg, 0.24 mmol) and chrysin-functionalized (bis)triazolium salt **3** (187 mg, 0.20 mmol) were combined in a Schlenk flask and dissolved in THF (10 mL) at –78 °C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was washed with hexane (3 mL) and diethyl ether (3 mL) and further extracted with benzene. After cannula filtration and removal of the solvent the crude product is dissolved in 1 mL of DCM and precipitated by addition of 10 mL of petroleum ether. The solid is filtered and dried under vacuum yielding the title product in 75 % yield (199 mg, 0.150 mmol) as beige solid. m.p. 156–159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.95 (s, 6 H, CH_3), 2.01 (s, 6 H, CH_3), 2.34 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 4.45 (s, 3 H, NCH_3), 4.58 (s, 3 H, NCH_3), 5.60 (s, 2 H, CH_2), 5.65 (s, 2 H, CH_2), 6.98 (s, 2 H, CH_{ar}), 7.13 (s, 2 H, CH_{ar}), 7.24 (s, 1 H, CH), 7.54–7.56 (m, 3 H, CH_{ar}), 7.53 (s, 1 H, CH_{ar}), 7.94–7.97 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR ($CDCl_3$,

100.6 MHz): δ = 17.6 (CH_3), 17.9 (CH_3), 21.23 (CH_3), 21.24 (CH_3), 38.4 (NCH_3), 39.0 (NCH_3), 60.5 (CH_2), 61.0 (CH_2), 97.1 (CH), 100.4 (CH_{ar}), 108.5 (C_q), 110.9 (C_q), 126.3 (CH_{ar}), 129.4 (CH_{ar}), 130.8 (CH_{ar}), 131.7 (CH_{ar}), 134.1 (CH_{ar}), 134.2 (CH_{ar}), 134.9 (CH_{ar}), 135.0 (CH_{ar}), 140.6 (C_q), 140.80 (CH_{ar}), 140.82 (CH_{ar}), 157.5 (C_q), 159.5 (C_q), 161.3 (C_q), 161.7 (C_q), 173.3 (Au=C), 173.6 (Au=C), 177.3 (CO) ppm. $C_{41}H_{40}Au_2I_2N_6O_4$ (1328.55): calcd. C 37.07, H 3.03, N 6.33; found C 37.43, H 3.21, N 6.59.

General Procedure for the MIC-Au^I Catalyzed Indole Formation: The appropriate gold complex (0.5 mol-%, based on the metal) and $AgBF_4$ (1 mol-% for complexes **4**–**5** and 2 mol-% for complex **6**) were charged in a Schlenk flask and dry toluene (3 mL) was added. After 5 min of stirring, a solution of the aniline derivative (1.0 mmol) in 1 mL of toluene was added to the reaction mixture and stirred at room temperature. At the end of the reaction (followed by ^{1}H NMR or TLC monitoring), the solvent was removed under pressure. The crude product was directly purified by column chromatography on silica gel using hexane/ethyl acetate as mobile phase.

CCDC 1857941 (for **1**), 1857942 (for **5**), and 1857943 (for **F**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Chrysin · Coumarin · Gold · Mesoionic carbenes · Triazolium salts

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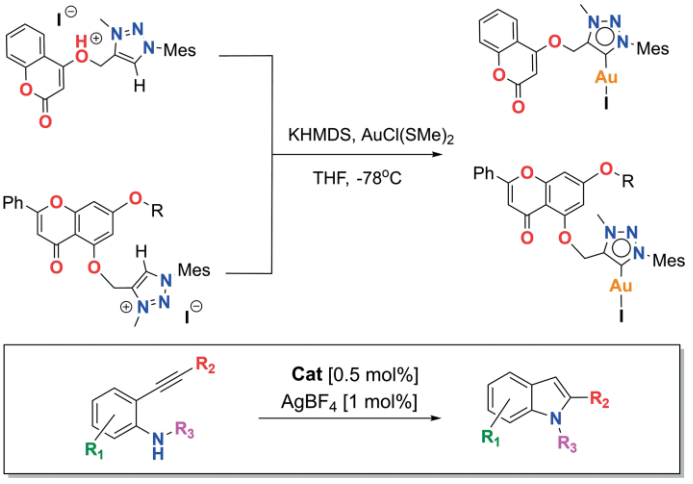
Mesoionic Carbene Complexes



We report the synthesis and characterization a series of coumarin- and chrysin-functionalized triazolylidene gold(I) complexes. Their catalytic performance in the synthesis of indoles via an intramolecular hydroamination reaction of several anilines is discussed.

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