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Air-Stable, Dinuclear and Tetranuclear σ , π -Acetylide Gold(I) Complexes and Their Catalytic Implications

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The possibility that σ,π -digold alkynide complexes play а key role as active species in the cycloadddition of alkynes^[1-9] has recently been put forward.^[10] Although precedents for the formation of digold-acetylide complexes^[11-17] and gemdiaurated species^[18-20] can be found in the literature, we were among the first to isolate fluxional complexes with two Au^I atoms of bulky biphenylphosphines connected to the C=C triple bond of phenylacetylene through the σ and π bonds.^[21] supporting their involvement in the catalytic intermolecular [2+2] alkyne-alkene cycloaddition reaction (Scheme 1).^[21]



Scheme 1. Intermolecular [2+2] cycloaddition of the alkyne–alkene reaction catalyzed by bulky Au¹ phosphines.

Simultaneously, Widenhoefer and co-workers succeeded in isolating dinuclear gold(I) σ , π -

arylacetylide complexes with bulky, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene as the co-ligand (Scheme 1).^[22] Herein, we will show the general tendency of phosphine Au^I precatalysts to form digold σ,π -acetylide complexes under the conditions in which Au^I catalysis is carried out.^[23] The

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301623. It contains details of the preparation, isolation, and characterization in full of new gold compounds 4, 5, 8, 9, 13, and 14, together with the experimental procedures, additional spectroscopic data, TEM images, and kinetic data of compounds 10, 15, 16, 17, 18, and 19 and CIF files for compounds 4, 5, 8, 9, 13, and 14.

influence of the nature of the terminal alkyne and the bulkiness of the Au^I ligand on the stability of the digold–alkyne complexes and the potential implications for catalysis of these digold–alkynide complexes will also be presented. To address this point and due to the interest in imines in organic synthesis and industrial chemistry,^[24-27] we have selected the Au^I-catalyzed coupling of amines with terminal alkynes with the goal of isolating the real active species formed during the catalytic process.^[28-42]

The reaction of hepta-1,6-diyne (1) with gold complexes $2^{[43]}$ or $3^{[44]}$ was initially studied (see Scheme 2). Slow addition of *n*-hexane to solutions containing 1 and complexes 2 or 3 gave, after 12 h at -30 °C, colorless crystals of the air-stable dicationic tetragold complexes 4 and 5, respectively, in good yields with respect to the initial Au^I complexes 2 and 3 (76 and 62%; see the Experimental Section in the Supporting Information). The structures of the stable dicationic tetragold complexes 4 and 5 could be resolved by X-ray crystal structure analysis (see Scheme 2 and atom coordinates in Tables S1 and S2 and Figures S7 and S11 in the Supporting Information). The solid-state structures of complexes 4 and 5 correspond to the space groups $P2_1/n$ and

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- 12239



Scheme 2. Synthesis and structures of dicationic tetragold complexes 4 and 5. Ellipsoids are drawn at the 30% probability level (X-ray singlecrystal data and ORTEP diagrams for 4 and 5 are given in Tables S1 and S2 and Figures S7 and S11 in the Supporting Information). The structures of L^1 and L^2 are given in Scheme 1. Note that formation of two σ LAu complexes releases two molecules of acid.

C2/c, respectively. Dicationic tetranuclear complexes **4** and **5** consist of an $\eta^1, \eta^2, \eta^1, \eta^2$ -propanediacetylide ligand acting as a bridge between four fluxional (phosphine)Au¹ moieties. The distance between the two proximal Au atoms of each [Au1(σ)C=CAu2(π)] fragment in complexes **4** and **5** is significantly longer than the 2.88 Å value for bulk Au metal. Nonetheless the Au–Au distance in our complexes (**4** and **5**) is still in the range in which weak "aurophilic" interactions occur.^[45] We propose that the Au1–Au2 contact [3.2983 (**4**) and 3.652 Å (**5**)], the short distance between each cationic Au¹ and each distal phenyl ring of the biphenyl ligand,^[21] and the interaction with the triple bond in acetylene all contribute to the stability of these unprecedented organometal-lic compounds, **4** and **5**.

¹H, ¹³C, ³¹P, and ¹⁹F NMR spectroscopy of solutions in CD_2Cl_2 provide evidence showing that under the reaction conditions the starting complexes **2** and **3** are completely converted into the corresponding dicationic tetragold complexes **4** and **5** (see Figures S1–S3 and S8–S10 in the Sup-



porting Information,). Thus, upon addition of complexes 2 or 3 to hepta-1,6-diyne 1, ³¹P NMR spectroscopy shows the appearance of a new peak at 61.84 or 38.83 ppm, corresponding to compounds 4 and 5, respectively. These peaks are different from those recorded for the original complexes 2 (57.49 ppm) and 3 (33.29 ppm) in CD_2Cl_2 and indicate that the transformation of 2 and 3 into 4 and 5 takes place spontaneously in the presence of diyne 1 (Scheme 2). It is interesting to note that dicationic tetragold complexes 4 and 5 were obtained even in the presence of a large excess of 1 (8 equiv with respect to 2 or 3), for which possible mono- or di-adducts of hepta-1,6-diyne with the Au¹ complexes would be favored versus the isolated tetragold complexes.

Similarly to the ³¹P NMR studies, ¹H NMR spectroscopy also shows new signals for methyl groups of complex **4** at 1.369 and 1.315 instead of those corresponding to the initial complex **2** (1.38 and 1.33 ppm) and for complex **5** at 0.90, 1.21, and 1.38 instead of those corresponding to the initial complex **3** (0.87, 1.19, and 1.27 ppm). Further evidence for the transformation of monogold(I) complexes **2** and **3** into **4** and **5** was obtained from liquid-phase ¹³C and ¹⁹F NMR spectroscopy (see Figures S3 and S10 in the Supporting Information) and solid-state ³¹P and ¹⁹F NMR spectroscopy (see Figures S4 and S5 in the Supporting Information).

Compared to isolation of tetragold complexes **4** and **5** by starting from Au¹ complexes with bulky biphenyl phosphine ligands L¹ and L² and aliphatic hepta-1,6-diyne, the behavior of the triphenylphosphine Au¹ complex with phenylacetylene **6** is significantly different. It should be noted that biphenylphosphine Au¹ complexes **2** and **3** have been previously reported^[21] to react with phenylacetylene (**6**) to form cationic σ and π digold complexes with the C=C bond in **6** (see Scheme 1). Therefore, complexes **2** and **3** behave similarly with phenylacetylene (**6**) and aliphatic hepta-1,6-diyne (**1**), leading to the corresponding σ , π -digold complexes. We were interested in determining whether a triphenylphosphine Au¹ complex (**7**)^[46] behaves similarly to Au¹ complexes **2** and **3** with phenylacetylene (**6**).

For this propose, we mixed triphenylphosphine Au^I complex 7 and phenylacetylene 6 (see Scheme 3). Interestingly, in this case, no evidence for the formation of a digold complex between 6 and 7 was obtained. Moreover, the data collected indicates completely different behavior of triphenylphosphine Au^I complex 7 than the bulky biphenylphosphine Au^I complexes 2 and 3. Thus, slow addition of *n*-hexane to the mixture of 6 and 7 in dichloromethane allowed collection, after 4 or 12 h at -30 °C, of two kinds of air-stable crystal, the structures of which could be determined by X-ray crystal structure analysis (Scheme 3). As can be seen in Scheme 3, the solid was formed from a mixture of neutral dicoordinate Au^I complex 8, with triphenylphosphine and phenylacetylide ligands coordinated through a σ bond, and complex 9, which corresponds to a cationic Au^I complex with two triphenylphosphine ligands with a bistrifluromethylsulphonylamide counteranion. Both Au^I intermediates were isolated as pure crystals suitable for X-ray crystal structure analysis (see Figures S12 and S13 and Tables S3

12240 -

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Scheme 3. Synthesis and molecular structure of monogold neutral and cationic complexes 8 and 9 from decomposition of digold complex 10. Complexes 8 and 9 could be resolved by X-ray single-crystal analysis; ellipsoids are shown at the 30% probability level. The plot shows the UV/ Vis absorption spectra recorded in CH_2Cl_2 at room temperature of a) complex 7 and b) the reaction mixture of phenylacetylene 6 and 7 after 1 h. The absorption band peaking at 560 nm corresponds to the formation of Au NPs. The TEM image of the reaction mixture of phenylacetylene 6 and gold complex 7 is shown.

and S4 in the Supporting Information for atom coordinates). Crystals of neutral $[Au(PPh_3)(phenylethynyl)]$ (8) have already been obtained^[47,48] by a different synthetic method and the crystal structure has been determined previously. However, our analysis of the new X-ray diffraction data for the gold compound (8; crystallized from toluene) resulted in significantly different unit-cell parameters.

Liquid-phase ³¹P NMR spectra recorded for complexes **8** and **9** show the presence of two characteristic peaks at 36.23 and 45.02 ppm, instead of at 30.47 ppm (starting complex **7**; see Figures S14 and S15 in the Supporting Information). At short contact times (15 min) between **6** and **7**, complex **8** is the main complex formed, accompanied by residual complex **7** (see Figure S16 in the Supporting Information). Over time (1 h), complex **7** completely disappears, giving complexes **8** and **9** (see Figure S17 in the Supporting Information). If the reaction mixture is allowed to evolve for longer (3 h), the transformation of complex **8** into **9** was observed, and cationic Au^I complex **9** becomes the predominant species (see Scheme 3 and Figure S14 in the Supporting Information).

The formation of monoaurate complex **8** from Au^I complex **7** and the conversion of complex **8** into **9** (see Scheme 3) can be followed easily by ESI-MS (see Figures S18–S20 in the Supporting Information). ESI-MS of a solution recorded immediately after dissolving compounds **6** and **7** in CH₂Cl₂/methanol (1:1) shows two positive MS

peaks at 599.4 and 721.5 amu that correspond to the expected mass of the neutral gold complex PhC=CAuPPh₃ (8) ionized with a potassium atom and the cationic $[Au(PPh_3)_2]^+$ fragment of gold complex 9 (see Figure S18 in the Supporting Information). For pure complex 9, we succeeded in recording the positive 721.5 amu signal for $[Au(PPh_3)_2]^+$ and the negative 279.7 amu signal for $[N(SO_2CF_3)_2]^-$ (see Figure S19 in the Supporting Information). It is interesting to note that, as well as the previously mentioned peaks corresponding to complex 9, we were able to detect, in positivemode MS, an extra, weak peak, the value (1019.6 amu) of which matches that expected for the cationic digold complex $[PhC \equiv C(AuPPh_3)_2]^+$ (10), formed very early in the reaction, but never isolated due its low stability (see Figures S20 and S52 in the Supporting Information for the MALDI-TOF-MS experiment), providing support for the formation of unstable digold σ and π complexes with the C=C bond in 6 that quickly decompose to form 8, 9, and Au nanoparticles (NPs; see Scheme 3).

Importantly, ESI-MS and ³¹P NMR spectroscopy show no peaks or signals besides those corresponding to complexes 8, 9, and 10, suggesting that they were the only species present. Transformation of 8 into 9 requires a PPh₃/Au stoichiometry of 2:1, which is double than that of the starting complex 7 and indicates that up to one half on the total number of gold atoms must be forming a different species. Since Au NPs and clusters are frequently observed in gold catalysis,^[49–52] we speculated that the gold atoms that have lost PPh₃ ligands and are not present in the form of complex 9 could have evolved into Au NPs. To support this hypothesis, we recorded the optical spectra of the solution upon reacting 6 and 7 in CH₂Cl₂; this mixture was also characterized by transmission electron microscopy (TEM). As can be seen in Scheme 3, an absorption band appears for this solution at 520-650 nm, which is characteristic of the surface plasmon band of Au NPs;^[53] the TEM image shows the presence of two kinds of crystal, squares and needles, corresponding to complexes 8 and 9, respectively, together with a homogenous distribution of Au NPs with diameters of 8-25 nm (see Figure S61 in the Supporting Information). This lends support to the theory of the spontaneous generation of Au NPs concomitant with the formation of the cationic complex $\{[Au^{I}(PPh_{3})_{2}]^{+}[N(SO_{2}CF_{3})_{2}]^{-}\}$ (9) from $Au^{I}PPh_{3}$ (7) in the presence of PhC=CH (6).

To gain an understanding of the implications of digold(I)– alkynide complexes in catalysis, we selected the hydroamination of terminal alkynes by using complex **2** as a precatalyst and followed the reaction by ¹H and ³¹P NMR spectroscopy. In the first step, gold complex **2** (3 mol%) was added to 1-octyne (**11**). ³¹P NMR spectroscopy of this mixture shows a new peak at 62.64 ppm, which is different from the original complex **2** (57.49 ppm) in CD₂Cl₂, that disappeared completely over time (30 min), indicating the spontaneous transformation of **2** into a new compound when alkyne **11** is present (see Figure S21 in the Supporting Information). In view of the previous isolation of digold complexes, we anticipated the formation of a digold–1-octyne adduct and this

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- 12241

assumption was firmly supported by an independent experiment (see below). In a second step, aniline **12** was added to the mixture and changes were followed by ¹H and ³¹P NMR spectroscopy. ³¹P NMR spectroscopy after 1 h shows a new peak at 57.95 ppm, along with the peak at 62.64 ppm formed in the first step (see Figure S22 in the Supporting Information). The peak at 62.64 ppm was gradually consumed over time (48 h; see Figure S23 in the Supporting Information). The variations in the ³¹P NMR spectra are compatible with the generation of a new species, **13**, by reaction of catalyst **2** with an alkyne; species **13** then reacts with aniline.

To elucidate the nature of the intermediates, we performed two independent experiments mixing Au^{I} complex 2 with either 1-octyne (11) or aniline (12; see Scheme 4 and



Scheme 4. Synthesis and molecular structure obtained by X-ray singlecrystal analysis of diaurated–alkynide complex 13 and cationic amine gold complex 14 (see Scheme 1 for L¹; ellipsoids are drawn at the 30% probability level) and their subsequent reactivity with 12 and 11, respectively, to obtain 15. Complex 15 can also be obtained in a single step upon mixing gold complex 2 with 11, and 12. Gold imine complex 15 can be hydrolysed to 14 and the corresponding ketone. Dashed lines propose the catalytic reaction mechanism of the formation of imine 16 in the presence of 11 and 12, with complex 2 used as the catalyst. See the Supporting Information for reaction times, yields of products, and reaction conditions.

the Experimental Section). Interestingly, in the first experiment, evidence for the formation of a digold complex 13 between 2 and 11 was obtained. The data collected in the second experiment indicates that the initial biphenylphosphine Au^I complex 2 is transformed into a new amine–Au^I complex (14) by replacement of acetonitrile with aniline (12). Complexes 13 and 14 were successfully isolated in good yields with respect to the initial Au^I complex 2 (ca. 74 and 89% for 13 and 14, respectively), and fully characterized (see the Experimental Section and Figures S24-S29 for 13 and S30–S34 for 14 in the Supporting Information,). Scheme 4 summarizes the isolation of complexes 13 and 14, which were characterized by X-ray crystal structure analysis (see Figure S29 for 13 and S34 for 14 and Tables S5 and S6 in the Supporting Information for atom coordinates), and their subsequent reactivity with 12 and 11, respectively, to obtain 15, which was characterized in situ by ¹H, ³¹P, and ¹³C NMR spectroscopy (see Figures S35–S37 in the Supporting Information) and MALDI-TOF-MS, showing its ability to lose imine ligand 16 due the weakness of the gold(I)-nitrogen interactions^[54] (see Figure S38 in the Supporting Information). When intermediate complex 15 was submitted to hydrolysis, it decomposed to amine-Au^I complex 14 and the corresponding ketone (see Scheme 4). Although this intermediate (15) could not be characterized by single-crystal XRD, its presence with very high purity upon addition of 2, 11, and 12 was supported by MALDI-TOF-MS and ³¹P, ¹³C, and ¹H NMR spectroscopy. Furthermore, ³¹P, ¹³C, and ¹H NMR spectroscopic data for **15** agree with the peaks observed under the reaction conditions of 11 and 12 promoted by 2.

Besides X-ray crystal structure analysis, cationic digold(I) complex **13** and cationic gold(I) amine complex **14** were also characterized by NMR spectroscopy, ESI-MS, and combustion analysis (see the Experimental Section and Supporting Information). ESI-MS of a solution obtained after dissolving complex **13** in CH₂Cl₂/CH₃CN (1:1) shows mainly a positive MS peak at 1099.5 amu, attributable to the cationic digold complex $[C_{48}H_{67}Au_2P_2]^+$ (see Figure S28 in the Supporting Information). Complex **14** dissolved in CH₂Cl₂/MeOH (0.01:1) exhibits a positive MS peak at 588.2 amu, as expected for the cationic gold complex $[C_{26}H_{34}AuNP]^+$ (see Figure S33 in the Supporting Information).

Similarly, ¹H, ¹³C, and ³¹P NMR spectroscopy in CD₂Cl₂ provide evidence that under the reaction conditions the starting complex 2 is completely converted to the corresponding cationic digold and cationic monogold complexes 13 and 14, depending on the reagent added (see Figures S24-S27 and S30-S32 in the Supporting Information). ³¹P NMR spectroscopy shows new peaks at 62.63 and 59.25 ppm for complexes 13 and 14, respectively, upon addition of complex 2 (57.49 ppm) to 1-octyne (11) and aniline (12), indicating that the transformation of 2 into 13 and 14 takes place spontaneously in the presence of 11 and 12, respectively (Scheme 4). It is interesting to note that cationic digold complex 13 is obtained even in the presence of a large excess of 11 (4 equiv with respect to 2), for which possible monoadducts of 1-octyne (11) with the Au^{I} complex 2 should be favored with respect to the isolated digold complex 13. Similarly to ³¹P NMR spectroscopy, ¹H NMR spectroscopy shows new signals of methyl groups for complex 14 at 1.337 and 1.283 ppm instead of the peaks at 1.38 and 1.33 ppm, which correspond to the initial complex 2 (see Figure S30 in the Supporting Information). Further evidence showing the transformation of monogold(I) complex 2 into 13 and 14 was obtained in liquid-phase ¹³C NMR spectrosco-

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py (see Figures S26, S27, and S32 in the Supporting Information).

When the intermolecular hydroamination reaction of 1octyne with aniline was carried out by using complex 2 as the catalyst under typical reaction conditions, ³¹P NMR spectroscopy initially shows the peak at 62.64 ppm, characteristic of 13, and gradual growth of a new peak at 57.93 ppm, attributable to complex 15, in which the imine is coordinated to a Au^I complex (see Scheme 4). Evidence of the intermediacy of 15 was obtained by ¹H, ³¹P, and ¹³C NMR spectroscopy (see Figures S35–S37 in the Supporting Information) and by MALDI-TOF-MS (see Figure S38 in the Supporting Information) of the reaction mixture. Release of N-(2-octylidene)aniline (16)^[30] as the final product by ligand exchange with 1-octyne or aniline would lead to gold complexes 13 or 14, respectively, ready for the next catalytic cycle. Only the Markovnikov product is formed (> 99%). Imine 16 was isolated and characterized by ¹H NMR spectroscopy and GC-MS (see Figures S39 and S40 in the Supporting Information).

An alternative catalytic experiment was carried out, in which 15 mol% of gold complex 2 was added to aniline (12) at RT and, after 1 h, the mixture was analyzed by ³¹P NMR spectroscopy, showing the peak at 59.26 ppm characteristic of complex 14 instead of the peak at 57.53 ppm for complex 2 (see Figures S41 and S42 in the Supporting Information). At this time, an excess of 1-octyne (11, 2 equiv) with respect to the starting aniline (12) was added at RT and, after 1 h, the ³¹P NMR spectrum was recorded again. It was observed that complex 14 (59.26 ppm) was completely consumed and complex 13 was formed (62.64 ppm), together with an NMR peak at 57.98 ppm, attributable to complex 15 (see Scheme 4 and Figure S43 in the Supporting Information). Over time (12 h), the peak corresponding to 15 was consumed with the concomitant formation of N-(2-octylidene)aniline (16). The final gold species was 13 due to the conditions for this experiment, with an excess of alkyne versus amine (see Figure S44 in the Supporting Information); thus, ³¹P NMR spectroscopy conclusively shows that starting complex 2, added as a precatalyst, is completely and consecutively converted under the conditions of the hydroamination of a terminal alkyne into the corresponding complexes 14, 13, and 15 and finally 13 depending upon the composition of the reaction mixture and the relative concentrations of the potential Au^I ligands.

Similar catalytic studies of the hydroamination by aniline (12) of terminal alkynes 6 and 11 were carried out by using complexes 2, 3, 7, and 13 as catalysts (Table S7 in the Supporting Information). *N*-(1-Phenylethylidene)aniline (17)^[28] was also isolated and characterized by ¹H and ¹³C NMR spectroscopy and GC-MS (see Figures S45, S46, and S47 in the Supporting Information). The corresponding gold imine complexes, 18 or 19, were characterized in situ by ¹H, ³¹P, and ¹³C NMR spectroscopy (see Figures S48–S50 for 18 in the Supporting Information) and by MALDI-TOF-MS (see Figure S51 for 18 and S52 for 19 in the Supporting Information), whereas the imine, 17, formed by hydroamination of

phenylacetylene 6 by aniline 12, with 2, 3, or 7 as the catalyst, was obtained with high Markovnikov regioselectivity (see Figures S53–S60 in the Supporting Information for kinetic ¹H and ³¹P NMR study).

In summary, in this study, we have been able to isolate single crystals of a series of cationic digold and dicationic tetragold complexes involving terminal C=C groups as σ and π ligands, showing the general tendency of phosphine Au^I precatalysts to form this type of complex. When the phosphine ligand is not a sufficiently bulky and stabilizing agent, decomposition of the digold(I)-alkynide complex occurs with the formation of monogold complexes and Au NPs. ³¹P NMR spectroscopy and MALDI-TOF mass spectrometry of the catalytic hydroamination reaction of terminal alkynes shows that digold-alkynide complexes are formed under the reaction conditions and their distribution varies depending upon the reaction mixture. Overall, our study provides a detailed description of the structures of the Au¹ species during alkyne activation, showing the prevalence of cationic digold complexes as intermediates.

Experimental Section

X-Ray crystal structure analysis for 4, 5, 8, 9, 13, and 14: CCDC-921288 (4), CCDC-921289 (5), CCDC-921290 (8), CCDC-921291 (9), CCDC-921292 (13), and CCDC-921293 (14) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a-c.uk/data_request/cif.

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Keywords: gold • gold complexes • gold nanoparticles • homogeneous catalysis • hydroamination reactions

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12244 ·