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Small Gold(I) and Gold(I)-Silver(I) Clusters via C-Si Auration

*Xiao-Li Pei, Ana Pereira, Ekaterina S. Smirnova, and Antonio M. Echavarren**

Abstract: Auration of o-trimethylsilyl arylphosphines leads to the formation of gold and gold-silver clusters with ortho-metalated phosphines displaying 3c-2e Au-C-M bonds (M = Au/Ag). Hexagold clusters $[Au_6L_4](X)_2$ are obtained by reaction of (L-TMS)AuCl with AgX, whereas reaction with AgX and Ag_2O leads to gold-silver clusters $[Au_4Ag_2L_4](X)_2$. Oxo-trigold(I) species $[Au_3O]^+$ were identified as the intermediates in the formation of the silver-doped clusters. Other $[Au_5]$, $[Au_4Ag]$, and $[Au_{12}Ag_4]$ clusters were also obtained. Clusters containing PAu-Au-AuP structural motif display good catalytic activity in the activation of alkynes under homogeneous conditions.

Introduction

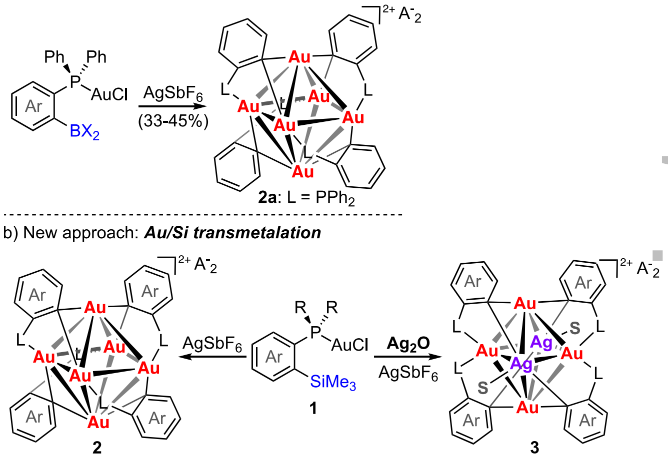
Aurophilicity has a fundamental importance on the wide structural diversity of gold complexes and clusters,[1] as well as on their photophysical properties[2] and their catalytic transformations.[3] Small gold Au_n clusters (n = 3-10) can catalyze different reactions[4] and it has been proposed that small gold clusters can activate of the C–H bond of methane.[5] However, polynuclear cationic Au(I) entities remain nearly unexplored in gold catalysis. To date, only a few catalytically active $Au(I)_n$ clusters (n ≥ 3) have been reported. Thus, the group of Toste found that trinuclear oxonium gold cluster $[(Ph_3PAu)_3O](BF_4)$ is a catalyst for the cycloisomerization of 1,5-allenyenes[6] and our group reported that tetranuclear and pentanuclear gold-silver clusters are active in the catalytic carbonylation of amines under homogeneous conditions.[7]

Ligands play a crucial role in the engineering of gold architectures and the tuning of their properties.[8] The strategy of combining neutral phosphines and anionic ligands such as thiolate/alkynyl ligands[9] has been gaining considerable attention for the construction of hetero-ligated gold clusters, because the higher affinity between gold and anionic fragments allows accessing gold systems of high nuclearity.[10] However, phosphines with both multi-coordination ability and anionic property have been less explored as ligands for the preparation of gold clusters.

We have described the synthesis of a single example of a hexagold cluster via a Au^I/B transmetalation (Scheme 1a), which showed catalytic activity in some cycloisomerization of enynes.[11] Now we have developed a more general method by auration-assisted C-Si bond cleavage[12] from *ortho*-silylphosphines **1**, which leads to hexanuclear gold(I) clusters $[Au_6L_4](SbF_6)_2$ (**2**) bearing different phosphine L ligands (Scheme 1b). Interestingly, when the transmetalation was carried out in the presence of Ag_2O, heteronuclear clusters $[Au_4Ag_2L_4](SbF_6)_2$ (**3**) were obtained. All these hexanuclear clusters show 3c-2e Au-C-M bonds (M = Au/Ag)[13]. Under slightly different reaction conditions, other polynuclear gold clusters have been also obtained by C-Si auration.

a) Previous work from our group: ***Au/B transmetalation***11

b) New approach: ***Au/Si transmetalation***



Scheme 1. a) C-B Auration to form hexanuclear gold clusters **2a**.[11] b) C-Si Auration of *o*-sylylphosphine gold(I) complexes **1** to form hexanuclear gold clusters **2** of gold(I)-silver(I) clusters **3**. L = PR_2, A = SbF_6.

Oxonium trigold cluster $[Au_3O]^+$ was found to be the key intermediates in the formation of gold-silver clusters **3**. Furthermore, our studies reveal that clusters containing the PAu-Au-AuP structural motif activate alkynes under homogeneous conditions, presumably as a consequence of the presence of coordinatively labile gold(I), similar to gold cavities (pocket-like sites) that exist in the well-studied $[Au_{25}]$ cluster.[3b,14]

Results and Discussion

The *o*-trimethylsilylaryl phosphine gold(I) complexes **1a-e** were prepared in 89-95% yields from the corresponding *o*-trimethylsilylaryl phosphines and $[Me_2SAuCl]$ in CH_2Cl_2 at 23 °C. Complexes **1a-d** react with 1 equiv $AgSbF_6$ in MeOH-CH_2Cl_2 to form known **2a**[11] as well as new hexanuclear gold clusters **2b-e**, which were isolated as yellow or pale-yellow crystalline solids in 52-81% yields (Scheme 2).[15] The reaction of complex **1a** with different silver salts AgX (X = BF_4, OTf, NTf_2, NO_3) led to the corresponding $[Au_6(L)_4](X)_2$ clusters. However, other chloride scavengers such as $Cu(OTf)_2$, $Zn(OTf)_2$, $In(OTf)_3$, TMSOTf, or $Sc(OTf)_3$ were not effective. When using $NaBAr^F{}_4$, the corresponding hexanuclear gold species can be observed by ^{31}P NMR.

Complexes **1a-d** derived from triaryl phosphines show singlets in their $^{31}P\{^1H\}$ NMR spectra at 32.3-37.8 ppm in CD_2Cl_2, whereas the corresponding signals for dialkylarylphosphine and di(2-furyl)arylphosphine gold(I) complexes **1e** and **1d** were observed at 47.10 and -5.12 ppm, respectively. The resulting hexanuclear clusters showed their ^{31}P signals shfted downfield by 8-24 ppm: **2a-c** (44.6-48.2), **2d** (71.50), and **2e** (3.15).

New clusters **2b-e** were characterized by X-ray diffraction, showing a pseudo-octahedral geometry with six gold atoms

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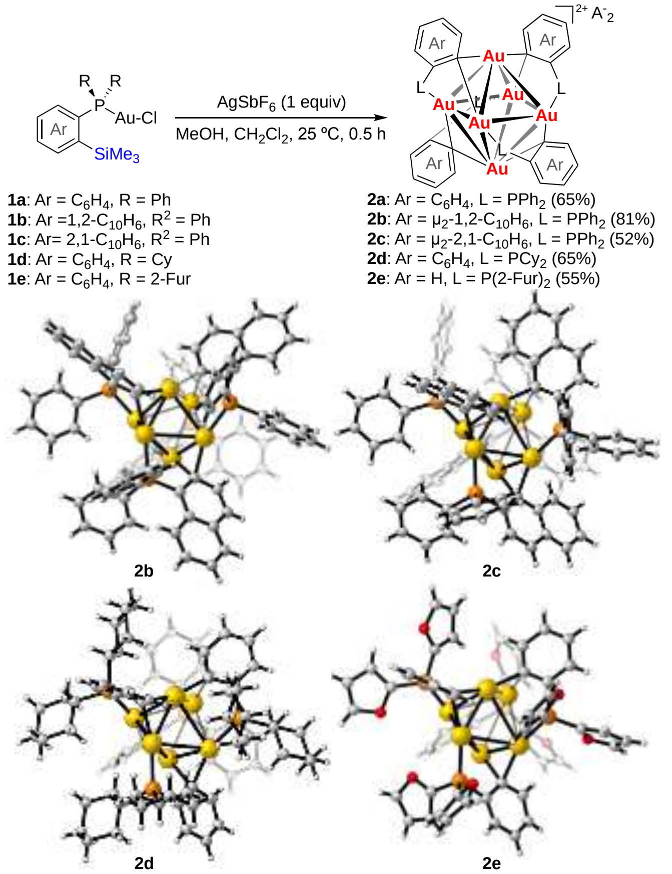
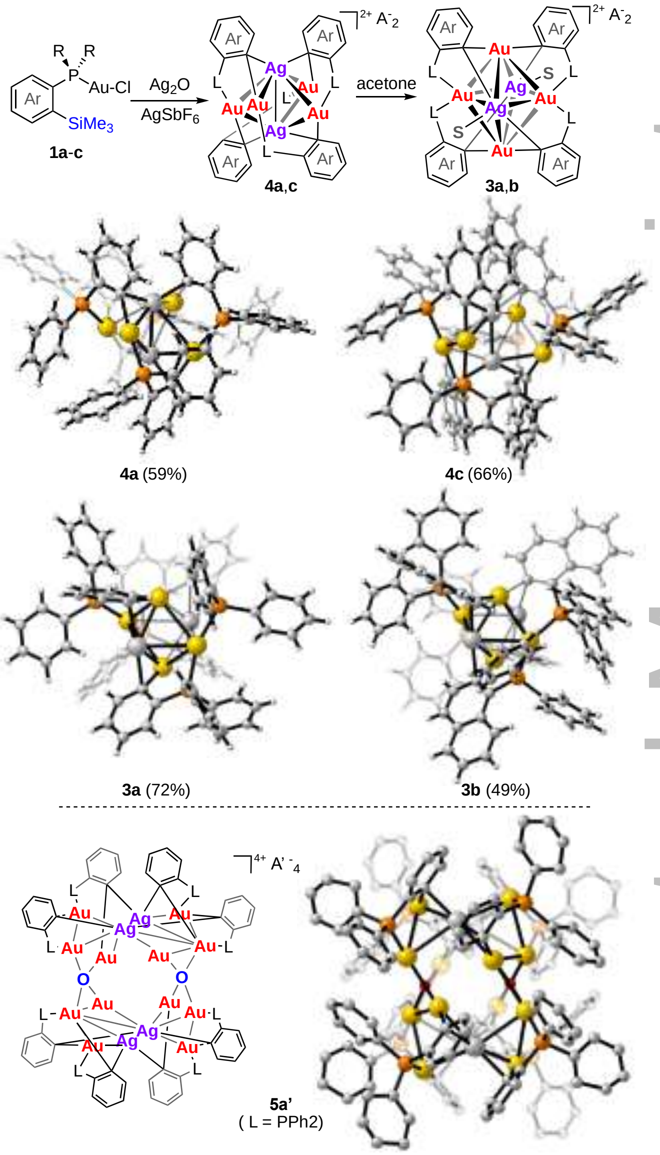
stabilized by only four formally anionic-phosphine ligands, different from the hexanuclear gold clusters.[16,17] Compared to aurophilic interactions of 2.706(4)–3.351(4) Å found in **2a**,[11] the Au–Au bonds lie in the range of 2.689(7)–3.162(8) Å in **2b**, 2.718(6)–3.352(6) Å in **2c**, 2.726(4)–3.325(4) Å in **2d**, and 2.709(2)–3.341(2) Å in **2e**, respectively. In clusters **2b**-**c**, two naphthyl groups stabilize the gold atoms in the 3c–2e Au–C–Au bonds, while two phenyl groups are involved in the 3c–2e bonds in clusters **2d**-**e**. The average C–Au–C angles in **2b (**159.6(6)°) and **2c** (162.1(4)°) are slightly bigger than those of **2a (**159.1(3)°). In clusters **2d** and **2e**, the average C–Au–C angles are 157.8(3)° and 162.2°, respectively.[15]



Scheme 2. Hexanuclear gold clusters **2a**-**e**, obtained by C-Si auration from **1a**-**e**. A = SbF_6. Fur: furyl. 1,2-$C_{10}H_4$ and 2,1-$C_{10}H_4$ derived from 1-diphenylphosphino-2-trimethylsilylnaphthalene and 2-diphenylphosphino-1-trimethylsilylnaphthalene, respectively. Counteranions and solvent molecules and omitted for clarity.

Reaction of **1a** with excess of silver(I) salts did not result in the formation of gold-silver clusters. However, addition of excess $AgSbF_6$ to a suspension of **1a** and 1 equiv of Ag_2O in CH_2Cl_2 led to the formation of heterometallic cluster **4a** (Scheme 3). Notably, cluster **4a** rearranges in the presence of acetone to form cluster **3a**, in which each of the silver atoms coordinates with a molecule of acetone. Similar behaviour was observed in acetonitrile or methanol. Upon removal of the coordinating solvent under vacuum, **3a** was slowly converted into **4a**. Two related gold-silver clusters **3b** and **4c** were also obtained and structurally characterized. In the silver-doped hexanuclear gold-silver clusters **4a** and **4c**, silver atoms substitute the two axial positions, forming 3c-2e Au-C-Ag bonds.[15] Due to the argentophilic interactions in **4a** and **4c** (*ca.* 2.9 Å), the hexanuclear heterometallic cores are distributed as a distorted octahedrons with edge-sharing bi-tetrahedral geometry, similar to the structure of hexanuclear nanogold cluster $[(p\text{-}C_6H_4MeP)_6Au_6](NO_3)_2$.[17] The ligand coordination in **3a** and **3b** is very different. In cluster **3a**, four gold atoms are linked together by the R_2P group and the aryl rings, displaying the same coordinating mode as in hexagold(I) analogues **2a**-**e**. The structure of **3b** is more distorted and can be viewed as the fusion of two binuclear gold complexes bridged by two silver atoms by Au-Ag interactions.

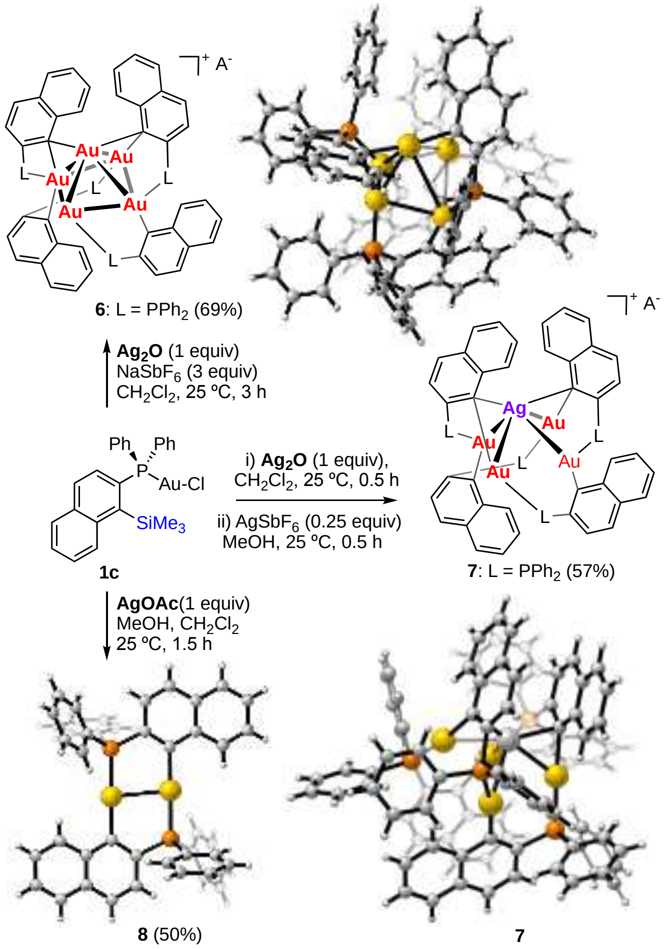
Clusters **4a** and **4c** display doublets at 46.5 and 40.3 ppm, respectively in the $^{31}P\{^1H\}$ NMR spectra, whereas **3a** and **3b** show triplets at 52.2 and 55.8 ppm, respectively.



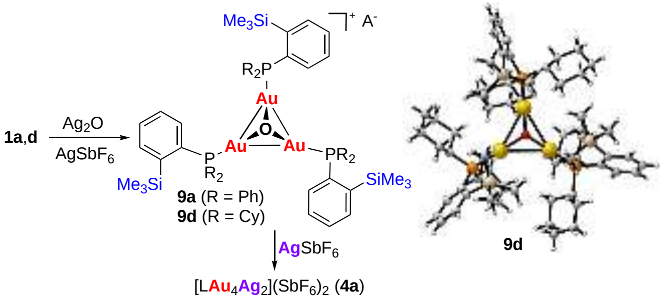
Scheme 3. Hexanuclear gold-silver clusters **3a**,**b**, **4a**,**c**, and **5a'** by C-Si auration in the presence of Ag_2O. A = SbF_6, A' = NTf_2. Counteranions and solvent molecules and omitted for clarity.

Hexadecanuclear heterometallic cluster **5a** was obtained as a byproduct in the preparation of **4a** (Scheme 3). This cluster was better obtained from a complex $[(L)Au(NEt_3)](SbF_6)$ **1a'**, prepared by reaction of **1a** with $AgSbF_6$ in the presence of excess NEt_3. Treatment of **1a'** in CH_2Cl_2 containing excess water with $AgSbF_6$ (2 equiv) led to **5a** in 47% yield. Cluster **5a'** was prepared similarly using $AgNTf_2$ instead of $AgSbF_6$. The structure of **5a´** shows 3c-2e Au-C-Au and Au-C-Ag bonds, as well as an interesting μ^4-O^{2-} coordinating mode, which to the best of our knowledge, corresponds to the highest-nuclei oxo-bridged gold-silver assembly among the known oxo-gold clusters.[15,18]

Interestingly, treatment of **1c** with $NaSbF_6$ and Ag_2O led to pentanuclear gold(I) cluster **6** in 69% yield,[19] along with pentanuclear gold(I)-silver(I) **7** as a minor product (*ca.* 5%) (Scheme 4). Cluster **7** could be obtained from **1c** in 57% yield using 0.25 equiv $AgSbF_6$.[15] Moreover, digold complex[15, 20] **8** was obtained by reaction of **1c** with AgOAc through the initial formation of neutral [LAu(OAc)]. The addition of excess $AgSbF_6$ to a solution of **8** in CH_2Cl_2 led quantitatively to the formation of cluster **4c**.



Scheme 4. Clusters **6**-**8** obtained from gold(I) complex **2c**. A = SbF_6. Counteranions and solvent molecules and omitted for clarity.



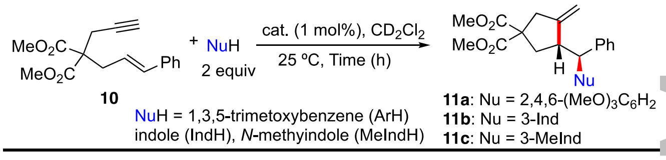
Scheme 5. Oxonium gold intermediates **9a**,**b** from **1a**,**d**. A = SbF_6. Counteranions and solvent molecules and omitted for clarity.

We confirmed that the reaction of [Ph_3PAuCl] with Ag_2O and $AgSbF_6$ gives oxonium gold cluster [$O(AuPPh_3)_3$](SbF_6),[21] which suggests that similar oxonium gold complexes might be involved as intermediates in the formation of the gold-silver clusters. Indeed, upon addition of $AgSbF_6$ to a mixture of **1a** and Ag_2O in CD_2Cl_2, a new species corresponding to **9a** was formed, which reacted further to finally form **4a** (Scheme 5). Oxonium gold cluster **9a** was isolated as white solid and its structure was confirmed by mass spectrometry (*m/z* 1609.2049). Starting from **1d**, a similar oxonium trigold(I) complex **9d** was obtained, whose structure was determined by X-ray diffraction.[15,22]

Presumably, reaction of **1a**-**d** complexes with AgX salts leads to complexes [$(L\text{-}TMS)Au(S)]^+X^-$, which immediately evolve to form hexanuclear gold(I) clusters **2a**-**d**. On the other hand, when the reactions are performed in the presence of Ag_2O, oxonium trigold complexes **9** are formed as intermediates, which are less reactive in the C-Si auration and, as a result, can incorporate silver(I) leading to the formation of gold(I)-silver(I) clusters.

Hexagold clusters **2a**-**d** are stable in solution. Thus, cluster **2a** was recovered unchanged upon recrystallization in acetonitrile as well as after being heated at 80 °C in 1,2-dichloroethane for 24 h. Thermogravimetric analysis shows that clusters **2a**, **2e**, **3a**, and **4a** only undergo decomposition in the solid state at high temperatures (230-270 °C).[23] However, treatment of **2a** with PPh_3 in CH_2Cl_2 led to the formation of a known digold complex similar to **8**.[19] In the case of pentagold cluster **6**, the ^{31}P NMR signals became broad in acetonitrile solution, although **6** was recovered unchanged after crystallization in this solvent.

Table 1. Addition of aromatic and heteroaromatic nucleophiles to 1,6-enyne **19** to form **20a**-**c** catalyzed by gold or gold-solver clusters.



Entry	NuH	Catalyst	Time (h)	**11a**-**c** (yield, %)[a]
1	ArH	**2a**	20	**11a** (76)
2	IndH	**2a**	20	**11b** (40)
3	MeIndH	**2a**	16	**11c** (76)
4	ArH	**2b**	12	**11a** (71)
5	ArH	**2c**	12	**11a** (87)
6	ArH	**2d**	12	**11a** (3)
7	ArH	**2e**	3.3	**11a** (98, 95[b])
8	IndH	**2e**	8	**11b** (79)
9	MeIndH	**2e**	8	**11c** (67)
10	ArH	**4a**	4	**11a** (98)
11	ArH	**3a**	4.5	**11a** (97)
12	ArH	**3b**	9	**11a** (99)
13	ArH	**4c**	6.5	**11a** (96)
14	ArH	**6**	12	**11a** (< 1)
15[c]	ArH	**6** + $NaBAr^F_4$	12	**11a** (99)
16	ArH	**7**	12	-[d]
17[c]	ArH	**7** + $NaBAr^F_4$	12	-[d]
18	ArH	**8**	24	-[d]
19	ArH	**5a**[e]	3.5	**11a** (93)

[a] Yield and product rations determined by ^1H NMR using 1,3,5-tris(trifluoromethyl)benzene as internal standard. [b] Isolated yield. [c] Reaction in the presence of $NaBAr^F_4$ (10 mol%). [d] < 1% yield. [e] catalyst loading 0.05%.

The catalytic activity of the new clusters was studied in the addition of 1,3,5-trimethoxybenzene, indole, and *N*-methylindole to 1,6-enyne **10** to give cycloadducts **11a**-**b** regio- and stereoselectively (Table 1).[24] Clusters **2a**-**e** showed activities in the order **2e** > **2c** > **2a** ≈ **2b** > **2d** (Table 1, entries 1-9). These results correlate with the electronic and steric properties of the ligands, since 2-furyl group in **1e** is the most electron-withdrawing and less bulky phosphine substituent. Remarkably, 1 mol% of cluster **2e** led to **11a** in 95% yield in *ca.* 3 h (Table 1, entry 7), showing a catalytic activity comparable to that displayed by a bulky phosphite gold(I) complex (5 mol%, 2 h, 66% yield),[24] which is one of the most reactive gold(I) complexes used routinely in the activation of alkynes. The catalyst loading with **2a** and **2d** could be decreased to 0.05 mol% maintaining good conversions.[23] Cluster **2e** was also found to be the most reactive[23] for the formation of indenes from 7-phenylethynyl cycloheptatriene,[25] and for the formal [4+2] intramolecular cycloaddition of arylalkynes with alkenes.[26]

Clusters **3a**,**b** and **4a**,**c** display higher catalytic activity than the corresponding hexagold congeners probably due to the structure effect by silver doping[27] (Table 1, entries 10-11). In contrast, the reaction with cluster **6** led only to traces of **11a** (Table 1, entry 14), although the reactivity could be restored in the presence of $NaBAr^F_4$ (Table 1, entry 15), while $NaBAr^F_4$ by itself does not promote this transformation. However, cluster **7** was unreactive even in the presence of $NaBAr^F_4$ (Table 1, entries 16 and 17). Digold complex **8** showed no reactivity (Table 1, entry 18). Hexadecanuclear cluster **5a** [$Au_{12}Ag_4$] also displays good activity (0.05 mol%, 3.5 h, 93% yield of **20a**) (Table 1, entry 19). Similar catalytic activity was found with enynes bearing internal alkynes.[23]

Homometallic gold clusters **2a**-**c**, **2d,** and **6** did not undergo decomposition when the corresponding reactions in Table 1 were monitored by ^{31}P NMR spectroscopy.[23] On the other hand, the gold(I)-silver(I) clusters underwent slow decomposition, which might explain why heteronuclear clusters **4a** and **4c**, which present only PAu-Ag-AuP motifs, are also catalytically active (Table 1, entries 10 and 13). In these cases, as suggested by ^{31}P NMR, decomposition or structural rearrangement of **4a** and **4c** to generate an active gold(I) species probably takes place in solution.

To probe our hypothesis that the catalytically active site is the central gold atom in the PAu-Au-AuP structural motifs, we also examined the reactivity of known full-phosphine-protected gold and gold-silver clusters [Au_6C],[16a] [Au_6Ag_4C],[16b] nanogold clusters nano-[Au_6][19] and [Au_{13}].[28] However, none of these species displayed catalytic activity in the addition of 1,3,5-trimethoxybenzene to 1,6-enyne **10** at 25 °C.[23]

Conclusions

In summary, we have found that the auration of trimethylsilyl phosphines leads to the formation of well-defined small gold and gold-silver containing 3c-2e Au-C-M (M = Au/Ag) bonds. On the other hand, when the chloride abstraction of complexes [(L-TMS)AuCl] was performed with $AgSbF_6$ in the presence of Ag_2O, hexanuclear gold-silver clusters [Au_4Ag_2]$^{2+}$ were obtained. Trinuclear oxonium gold species [Au_3O]$^+$ acts as the intermediate in this silver-doping process, which takes place due to a slower C-Si auration process. Other clusters [Au_5], [Au_4Ag], [Au_2] and [$Au_{12}Ag_4$] have also been obtained. The activity of these small gold clusters has been studied in typical Au(I)-catalyzed reactions of enynes. Remarkably, hexanuclear gold cluster **2e** with difurylphosphine ligand displays a reactivity similar or even higher than other commonly used mononuclear gold catalysts.

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Keywords: Gold clusters · Silver clusters · Gold catalysis · C(sp^2)-Si auration • Metalophilic interactions

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