

Hot Paper

First Evidence of Au-CH₃ Bonding in Superatomic Au₁₃ ClustersMatteo Bevilacqua,^[a] Marco Roverso,^[a] Sara Bogialli,^[a] Claudia Graiff,^[b] and Andrea Biffis^{*[a]}

Chemical reduction of a dinuclear [(di-NHC)Au₂Cl₂(di-NHC)] complex (NHC = imidazol-2-ylidene), using excess NaBH₄ as reducing agent in presence of dichloromethane (DCM) as solvent, provides a molecular cluster with formula [Au₁₃(di-NHC)₅(CH₃)₂]Cl₃, exhibiting covalent bonds between gold atoms of the cluster core and methyl groups. The presence of Au-CH₃ bonds, which is unprecedented in gold cluster chemistry, is confirmed by high resolution mass spectrometry (HRMS), NMR

and the reactivity of the reported cluster in solid state. The cluster has been further characterized with single crystal X-ray diffractometry, UV-Vis and emission spectroscopies. The cluster displays remarkable stability in solution, which is indicative of the possible role played by Au-CH₃ bond formation in the conventional preparation of molecular gold nanoclusters by reduction with excess borohydride in DCM.

Introduction

Molecular metal clusters have been for long the subject of intensive investigations, since they ideally represent the “missing link” between mononuclear metal complexes and metal nanoparticles. In this intermediate state, the metal presents peculiar, technologically relevant properties that can still be conveniently investigated through solution characterization techniques. Gold is arguably the metal forming molecular clusters with the greatest ease, and the stability of the resulting gold nanoclusters (AuNCs) can be further enhanced by using suitable stabilizing ligands. Beside thiolates, which are the most commonly employed ligands to date, neutral ligands are increasingly investigated, since they allow much greater variations in stereoelectronic properties, which in turn influence the cluster properties.

In recent times, traditional phosphane ligands have been supplemented by N-heterocyclic carbene (NHC) ligands, providing increased stability due to the strength of the gold-carbene bond. During 2019, Crudden et al. presented the synthesis of the first AuNCs stabilized by mono-NHCs.^[1] In the following years, several other groups, including ourselves,^[2] have focused their efforts towards the synthesis of NHC-stabilized AuNCs,^[3–13] exploiting also di-NHCs,^[5,6,8,10] thus combining the chelating

properties of these ligands with their ability to form strong Au–C bonds.^[7] The synthesis of NHC-stabilized AuNCs generally involves a chemical reduction, starting from the corresponding [(mono-NHC)AuX] or [(di-NHC)Au₂X₂] complex, where X is a halide, and using a boron hydride, most commonly NaBH₄, as reducing agent. The NHC-stabilized clusters obtained via this reduction usually present a “superatomic” (SA) configuration,^[13] in which the electronic configuration of the clusters is complete, leading to an additional stabilization of the core.

Therefore, [Au₁₁]³⁺, [Au₁₃]⁵⁺ and [Au₂₅]⁹⁺ are the most common SA-cores presenting NHC ligands.^[14,15] Only during 2022, the synthesis of non-SA AuNCs protected by NHCs has been achieved, with the isolation of two [Au₁₀]⁴⁺ clusters.^[4,6] This result has been pursued by Crudden et al., exploiting the complexes reported in Scheme 1, entries i and ii, and demonstrates that rigidity (case i) and steric hindrance (case ii) associated to NHCs are fundamental properties to favor these uncommon configurations. Moreover, such non-SA clusters can be obtained also using reduction of Au(I) in the presence of Pd(0) complexes, as reported by Zheng et al.^[16]

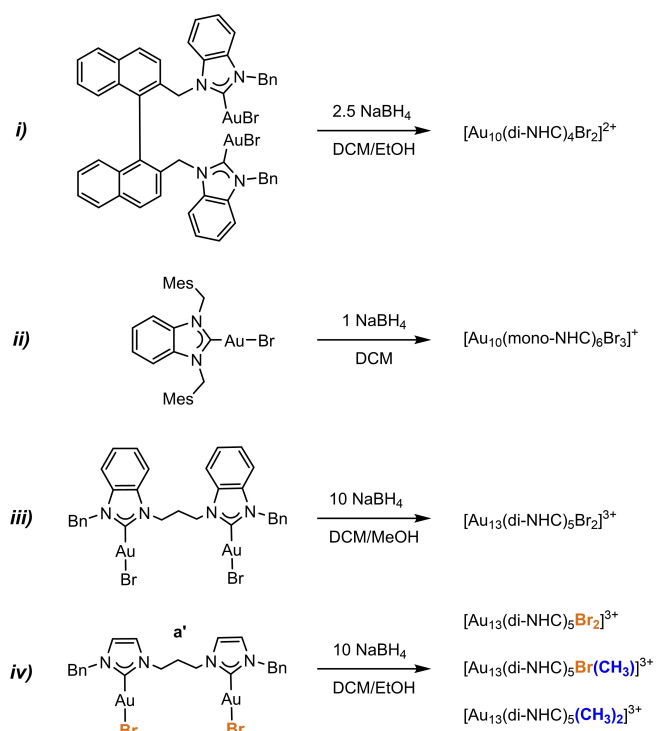
However, no study has been yet reported in the literature, in which the effect of the electronic properties of the employed NHC ligands on cluster formation, stability and properties is analyzed. So far, benzimidazole-2-ylidenes have been invariably exploited as NHC scaffolds, likely due to their electron-accepting properties,^[17] which enable π -retrodonation from the cluster core and enhance cluster stabilization. Consequently, when our group decided to embark in such a study, we started by using an alternative kind of di-NHC complex, called hereafter a', similar to the one employed by Zheng et al.^[8] and reported in Scheme 1, entry iii, but with a significant variation in the electronic properties of the ligand, since the benzimidazol-2-ylidene moieties are substituted by imidazol-2-ylidene ones (Scheme 1/iv). As it will be apparent in the following, this variation has no consequences on the nuclearity and structure of the resulting cluster, whereas it has notable consequences on its selectivity for peculiar coordinated anionic ligands.

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/ejic.202400351>

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Scheme 1. From top, syntheses reported by Crudden et al. using i) rigid^[4] and ii) bulky^[6] NHCs, iii) synthesis reported by Zheng et al.^[8] and iv) this work.

Results and Discussion

As illustrated in Scheme 1, entry iv, reduction of **a'** with excess NaBH_4 provides three clusters, presenting $[\text{Au}_{13}(\text{di-NHC})_5\text{Br}_2]^{3+}$, $[\text{Au}_{13}(\text{di-NHC})_5\text{Br}(\text{CH}_3)]^{3+}$ and $[\text{Au}_{13}(\text{di-NHC})_5(\text{CH}_3)_2]^{3+}$ stoichiometry, renamed here as **[Br₂]**, **[(CH₃)Br]** and **[(CH₃)₂]**, respectively. The first cluster (1500.81 m/z) presents two bromide anions coordinated to the metallic core, in agreement with most common SA clusters presenting the same stoichiometry.^[5,7,8,10,18–20] The other two AuNCs (1479.18 and 1457.68 m/z), appear to be stabilized by one and two CH_3^- anionic fragments, respectively, substituting the bromido ligands in **[Br₂]**. The resulting stoichiometries fully match the recorded m/z values in the HRMS analysis as well as the isotopic distribution (Table S1 and Figures S38, S39 and S41 in the SI). This result is truly interesting, since whereas it is known that AuNCs can be protected by hydrides, in particular when phosphane ligands are involved in cluster stabilization,^[21] a cluster exhibiting methyl groups or more generally alkyl groups bonded to the core is unprecedented in cluster chemistry. In the following, we will provide experimental evidence that allows us to claim that **[(CH₃)Br]** and **[(CH₃)₂]** are indeed the first reported gold clusters featuring Au-alkyl bonds.

The first problem to be tackled was the separation and purification of these AuNCs. Whereas all three AuNCs appeared reasonably stable, they presented similar chemical and physical properties, making common separation methods useless for this purpose. Preferential formation of **[Br₂]** could be achieved using only an equimolar amount of NaBH_4 , 3 h reaction time

and LiBr as a bromide source, together with **[(CH₃)Br]** as minor co-product which proved impossible to convert to **[Br₂]** even by reaction with excess HBr (Figure S13); incidentally, this result suggests a particularly strong, nonpolar $\text{Au}_{13}\text{-CH}_3$ interaction. Furthermore, **[Br₂]** proved to be not particularly stable and to slowly degrade with time in CD_3CN solution, providing after a few days at 4 °C the starting gold complex as degradation product (Figure S9). These findings indicate that a CH_3^- ligand provides higher stabilization to the cluster core compared to bromido.

In order to direct the synthesis towards the preferential formation of **[(CH₃)₂]**, we supposed that a more easily exchangeable X ligand, for instance chlorido instead of bromido, could enhance the selectivity of the synthetic process towards the formation of methylated clusters. Furthermore, it was evident from the previous experiment that an excess of NaBH_4 favors the formation of **[(CH₃)₂]**. For these reasons, we carried out the synthesis of starting complex **a**, analogous to **a'** but presenting chlorides instead of bromides as anionic ligands. The reduction of **a** has been performed using 72 h reaction time and 30 moles of NaBH_4 , divided in three portions of 10 moles each and added every 24 h. As solvent we used DCM:EtOH (4:1 v:v), i.e. we replaced MeOH used in previous synthesis with EtOH, in order to determine whether the observed methyl groups on the cluster derive from DCM or from MeOH (the only two possible C1 sources present in the system).

The reaction was followed by HRMS, as reported in Figure 1. After 24 h and 10 moles of NaBH_4 , it is possible to detect three clusters: **[(CH₃)₂]** ($[\text{Au}_{13}(\text{di-NHC})_5(\text{CH}_3)_2]^{3+}$, 1457.68 m/z), **[(CH₃)Cl]** ($[\text{Au}_{13}(\text{di-NHC})_5(\text{CH}_3)\text{Cl}]^{3+}$, 1464.33 m/z) and **[Cl₂]** ($[\text{Au}_{13}(\text{di-NHC})_5\text{Cl}_2]^{3+}$, 1471.31 m/z) (for peak identification, see also Table S1 and Figures S40 and S42 in the SI). After addition of 20 more moles of NaBH_4 and 72 h reaction time, only **[(CH₃)₂]** is present and can be isolated, albeit with a reaction yield of only 5% after work-up. In order to improve the yield, we

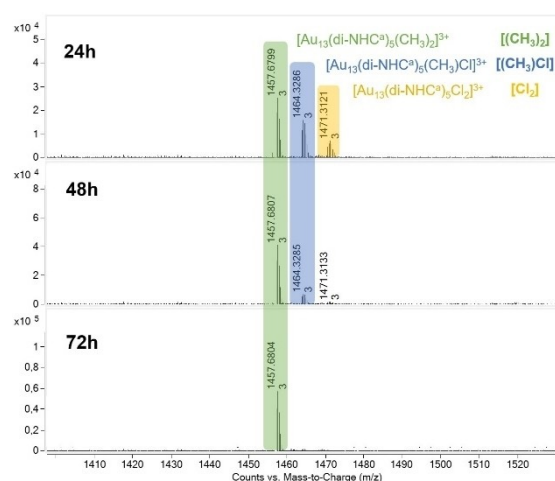
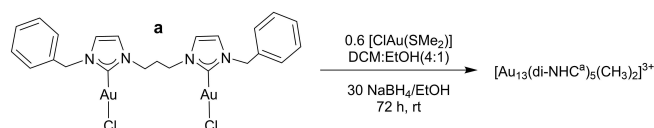


Figure 1. HRMS analyses of withdrawals of reaction mixture after (from above) 24 h, 48 h and 72 h related to not-optimized synthesis of **[(CH₃)₂]** performed using starting complex **a** and DCM:EtOH (4:1 v:v) as solvent. **[Cl₂]** is highlighted in yellow, **[(CH₃)Cl]** in blue and **[(CH₃)₂]** in green.

decided to use a molar amount of an external gold complex in order to reproduce in the reaction mixture the same gold:ligand ratio present in the final cluster product. Indeed, the starting complex presents Au:di-NHC molar ratio of 2:1, but in $[(\text{CH}_3)_2]$ the molar ratio is 13:5. Therefore, 0.6 moles of $[\text{AuCl}(\text{SMe}_2)]$ were added to the reaction mixture to balance the amount of gold. Thanks to this, a significant increase in the reaction yield was achieved, obtaining a value of 22% after purification. The optimized conditions for the synthesis of $[(\text{CH}_3)_2]$ are reported in Scheme 2.

After the optimization of the synthesis, we focused our efforts on the rationalization of the Au-CH₃ interaction. First of all, we verified that the imidazole-2-ylidene moieties present in our di-NHC ligand indeed favor the formation of AuNCs capped by methyl ligands. To confirm this, we run our optimized synthesis using complex **b** (Figure 2/a) bearing more usual benzimidazol-2-ylidene moieties. After addition of 30 total moles of NaBH₄ and 72 h reaction time, it is possible to detect the formation of three stable SA clusters, with formula $[\text{Au}_{11}(\text{di-NHC}^b)_5]^{3+}$ (1483.01 m/z), $[\text{Au}_{13}(\text{di-NHC}^b)_5\text{Cl}(\text{CH}_3)]^{3+}$ (1631.33 m/z) and $[\text{Au}_{13}(\text{di-NHC}^b)_5\text{Cl}_2]^{3+}$ (1637.97 m/z), with cluster $[\text{Au}_{13}(\text{di-NHC}^b)_5(\text{CH}_3)_2]^{3+}$ (1624.34 m/z) barely present in the mass spectra, reported in Figure 2/b. This result confirms that imidazol-2-ylidene ligands have a key role in the stabilization of AuNCs exhibiting Au-CH₃ interactions.

Additional investigations have been conducted to shed light on the origin of the methyl groups. As it has been outlined above, initial experiments in DCM:EtOH indicate that the methyl groups derive from reduction of DCM by excess borohydride, possibly promoted by gold species in the reaction mixture. For



Scheme 2. optimized synthesis of $[(\text{CH}_3)_2]$ cluster.

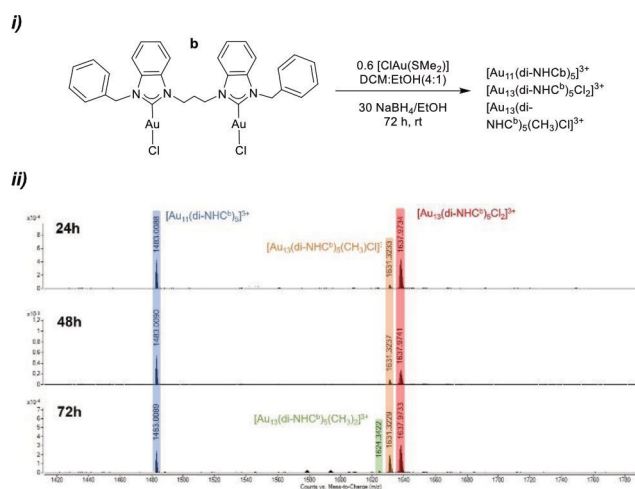


Figure 2. i) reduction of complex **b**; ii) mass spectra at 24 h, 48 h and 72 h reduction.

this reason, we conducted the same experiment to prepare $[(\text{CH}_3)_2]$ but replacing DCM with 1,2-dichloroethane (DCE) in a DCE:EtOH (4:1 v:v) solvent mixture. This reaction has been monitored with HRMS. In the mass spectra (Figure S30); it is possible to observe the presence of appreciable amount of $[\text{Cl}_2]$ after 1 h from NaBH₄ addition, although mass spectra at 24 h, 48 h and 72 h do not provide similar signals. No peaks related to methylated clusters were recorded at all times.

These data suggest that DCM is indeed the methyl source in this reaction. Furthermore, they indicate that the first cluster obtained in the reduction process is $[\text{Cl}_2]$, which is subsequently transformed into $[(\text{CH}_3)_2]$ (Figure 1). This observation leads to the hypothesis that Au₁₃ cores might act as catalyst of DCM reduction, ultimately producing the methyl groups necessary for $[(\text{CH}_3)_2]$ formation; investigations aimed at providing support for this hypothesis are currently underway.

To further confirm the origin of the methyl groups, we performed the same experiment to obtain $[(\text{CH}_3)_2]$ but using NaBD₄ as reagent, aiming at observing formation of mixed CD₃-_nH_n groups bonded to cluster cores. The reaction product exhibits again a singlet in the methyl region in the ¹H NMR spectrum (Figure S27), but with a reduced integral value of ca. 5H and slightly upfield shifted to 0.26 ppm, therefore pointing towards partial formation of CH₂D groups; another small peak appears in the same region, centered at 0.28 ppm. The HRMS analysis confirms this result, highlighting a peak centered at 1458.19 m/z (Figure S28), for which it was initially difficult to provide an unambiguous interpretation. The difference in mass between $[(\text{CH}_3)_2]$ and this new cluster is 1.5 Da, suggesting indeed a cluster stoichiometry close to $[\text{Au}_{13}(\text{di-NHC}^b)_5(\text{CH}_2\text{D})_2]^{3+}$, with a calculated value of 1458.21 m/z, supporting the ¹H NMR analysis. Despite this, the isotopic pattern of the experimental signal does not match with the calculated one (Figure S28), which leads to the hypothesis that a mixture of clusters bearing methyl groups with different degrees of deuteration has formed during the reduction, producing overlapping peaks in the mass spectrum. These data partially confirm our hypothesis, since deuteride placed on the final clusters can derive only from NaBD₄.

The AuNCs were characterized using different techniques beside HRMS. The ¹H NMR spectra of $[\text{Br}_2]$ and $[(\text{CH}_3)_2]$ are similar but differ for: 1) the position of the peaks and 2) the absence in the $[\text{Br}_2]$ spectrum of methyl signals. Both spectra are reported in Figure 3. In the $[(\text{CH}_3)_2]$ spectrum in CD₃CN it is possible to note a singlet centered at 0.29 ppm, with an integral value equal to 6H, attributable to two magnetically equivalent -CH₃ groups. The same signals and integrals can be found in the spectrum of $[(\text{CH}_3)_2]$ recorded in CD₂Cl₂, reported in Figure 4. As mentioned before, there are no examples in the literature regarding AuNCs exhibiting Au-CH₃ bonds; however it is possible to compare the $[(\text{CH}_3)_2]$ spectrum with complexes having $[(\text{di-NHC})\text{Au}_2(\text{CH}_3)_2]$ stoichiometry. These present methyl signals centered around 0.32–0.19 ppm in their proton spectra, matching perfectly with the signal attributed to methyl groups observed in the spectrum of $[(\text{CH}_3)_2]$.^[22,23]

We subsequently performed a TOCSY experiment on the $[(\text{CH}_3)_2]$ sample (Figure S17), to shed light on the other proton

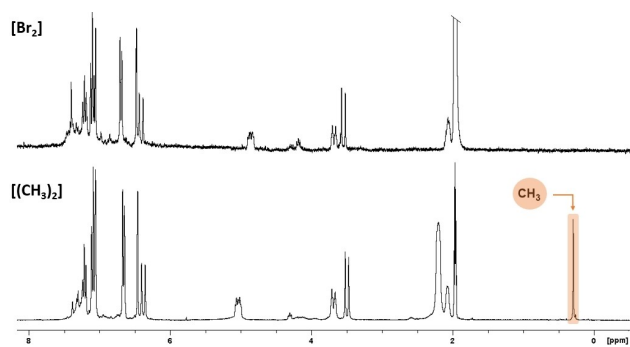


Figure 3. ^1H NMR spectra of $[\text{Br}_2]$ (above) and $[(\text{CH}_3)_2]$ (below) in CD_3CN . The CH_3 peak is highlighted in orange.

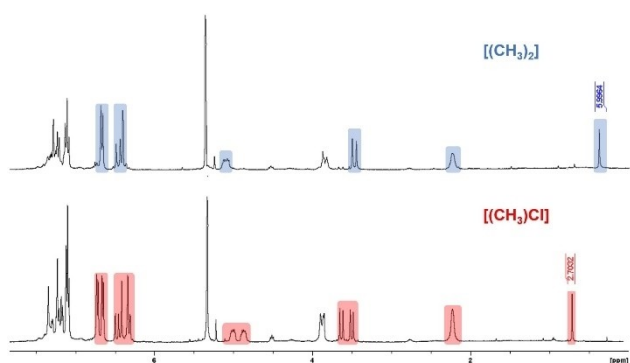


Figure 4. ^1H NMR spectra of $[(\text{CH}_3)_2]$ (above) and $[(\text{CH}_3)\text{Cl}]$ (below) dissolved in CD_2Cl_2 . The splitting of signals is highlighted in the two spectra.

signals belonging to di-NHCs. The experiment established that ^1H NMR signals of the 1,3-propylenic bridge (centered at 5.04, 3.69 and 2.07 ppm, respectively) present an anisotropy due to chelate coordination, providing increased rigidity to the system. The methylene groups belonging to the benzylic wingtips undergo a similar fate; indeed, they appear in the spectrum as two doublets centered at 6.66 and 3.50 ppm, therefore presenting a diastereotopic behavior, again due to the rigidity of the ligand. The methyl signal presents only a diagonal cross peak, as expected from its singlet nature. Finally, an HMQC experiment (Figure S18) confirms the presence of CH_3 groups, thanks to the cross peak between carbon and hydrogen spectra.

A particular chemical behavior of the $[(\text{CH}_3)_2]$ cluster was apparent when the cluster was isolated and stored in the solid state. Indeed, cluster $[(\text{CH}_3)_2]$ is tricationic and is isolated with chlorides as counteranions, which is confirmed also by the X-ray structure (see below). In the solid state a partial inner-external sphere exchange of anionic ligands appears to slowly take place. Indeed, thanks to the proximity between the cluster core and chloride anions, after about 20 days in solid state at -16°C , cluster $[(\text{CH}_3)\text{Cl}]$ is obtained from the total conversion of $[(\text{CH}_3)_2]$. HRMS confirms the result, detecting the peaks $[\text{Au}_{13}(\text{di-NHC})_5(\text{CH}_3)\text{Cl}]^{3+}$ and $[\text{Au}_{13}(\text{di-NHC})_5(\text{CH}_3)\text{Cl}]\text{Cl}^{2+}$ centered respectively at 1464.19 m/z and 2214.28 m/z (Figure S34). In the ^1H NMR spectrum of $[(\text{CH}_3)\text{Cl}]$, obtained in CD_2Cl_2 (Figure 4), almost all signals are split in two new sets of signals, indicating

a break of symmetry compared to $[(\text{CH}_3)_2]$ (in Figure 4, the $[(\text{CH}_3)_2]$ and $[(\text{CH}_3)\text{Cl}]$ proton spectra are reported for comparison). Furthermore, the singlet belonging to CH_3 is downfield-shifted to 0.66 ppm, with an integral value of 3H, in accordance with the stoichiometry detected with HRMS. The chemical shift is consistent with a more electron-poor character of the cluster, which is expected upon substitution of a methyl group with a chlorido ligand; incidentally, the same chemical shift has been recorded in cationic $\text{Au}(\text{III})$ complexes bearing methyl ligands.^[24]

To get further confirmation of this behavior, we attempted to carry out the same reaction in solution, exploiting different deuterated solvent (CD_3OD , CD_2Cl_2 and CD_3CN) and following the evolution of the cluster by ^1H NMR spectroscopy (Figures S35–S37). The experiments have been performed at 40°C , to speed up the exchange. However, despite the presence of free chlorides, counter anions of $[(\text{CH}_3)_2]$, in all solution the exchange does not take place even after eight days of warming. In all three experiments the $[(\text{CH}_3)_2]$ cluster remains stable in solution, highlighting that the proximity between Au_{13} core and chloride anions in the solid state is fundamental to achieve an extensive substitution of the anionic ligands.

We have been able to obtain crystals from a solution of $[(\text{CH}_3)_2]$ in $\text{DCM}:\text{acetone}$ and layering *n*-hexane on it. After one week, it is possible to observe the formation of crystals. The structure is reported in Figure 5, whereas crystal data are listed in Table S2. The crystallized cluster exhibited the expected icosahedral core with five di-NHCs each bridging two external gold atoms, in agreement with similar AuNCs already reported in the literature.^[5,6,8,10] However, the apical positions were found to be occupied by chlorido ligands rather than by the expected methyl groups. Apparently, the reaction leading to substitution of the anionic ligands is faster in the crystal under the employed conditions and leads to complete removal of the methyl groups instead of stopping after substitution of only one methyl, as in the case of the amorphous solid. Assuming that the chlorido ligands in the structure occupy the positions of the methyl groups in the parent $[(\text{CH}_3)_2]$ cluster, it can be appreciated that these positions lie on the symmetry axis of the cluster, and therefore justify the perfect magnetic equivalence observed for the methyl groups in $[(\text{CH}_3)_2]$.

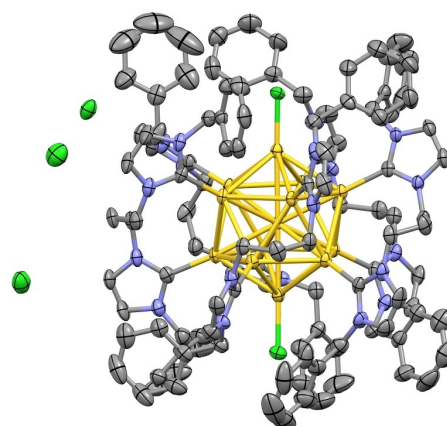
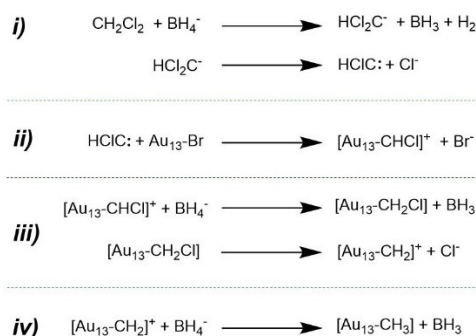


Figure 5. X-ray structure of $[\text{Cl}_2]$ cluster obtained upon crystallizing $[(\text{CH}_3)_2]$ cluster.

Finally, to evaluate the optical proprieties of $[(\text{CH}_3)_2]$, UV-Vis and emission spectra have been recorded. The analyses have been performed on $[(\text{CH}_3)_2]$ presenting PF_6^- as counteranions, which was easily prepared by anion exchange with AgPF_6 , in the hope of producing more stable crystals of the methylated cluster. Unfortunately, with the new counteranion the cluster invariably separated from solution as an amorphous solid. In the UV-Vis spectrum of the cluster, three weak absorption bands are present, centered respectively at 401 nm, 420 nm and 499 nm, plus another one, more intense, centered at 320 nm (Figure S24). The emission proprieties of this cluster are obtained exciting it with radiation at 320 nm. The obtained emission spectrum presents one broad band at 722 nm (Figure S25). The emission quantum yield has been evaluated, leading to a value equal to 6.28%, lower than similar clusters reported in literature.^[5,6,8,10]

Despite all characterization efforts, the main question that remains unanswered about these new clusters is the chemical origin of the methyl groups, since no obvious methyl source has been employed in the reaction. Considering the results of the experiments discussed above, it is reasonable that excess NaBH_4 reduces both the gold complex precursor and CH_2Cl_2 used as solvent. Reductions of halogenated solvents are known^[25,26] and these can be performed using strong bases, forming carbene molecules as product. For instance, starting from CHCl_3 it is possible to form Cl_2C : carbene exploiting deprotonation with a strong base, which affords CCl_3^- ; the latter forms Cl_2C : by losing a chloride anion.^[26,27] According to this chemistry, we can suppose the mechanism of formation of methyl-capped clusters reported in Scheme 3.

We suppose that first the formation of $[\text{X}_2]$ ($\text{X}=\text{Cl}, \text{Br}$) cluster takes place, since halide anions are already bonded to gold centers during the reduction of the starting gold(I) complex precursors. The formation of $[\text{X}_2]$ provides a scaffold where the reduction of CH_2Cl_2 can take place. The initial steps (Scheme 3/i) are formation of HClC : carbene from DCM, analogous to formation of Cl_2C : from CHCl_3 . The formed carbene substitutes a halido anion on the cluster core, sharing its lone pair and capping it (Scheme 3/ii). The resulting cluster might undergo a hydride transfer to the carbene carbon by NaBH_4 , forming a CH_2Cl^- anion bonded to the core. The latter can lose another Cl^- anion, forming coordinated H_2C : on the gold core.



Scheme 3. hypothetical mechanism of formation of coordinated methyl-capped $[\text{Au}_{13}]^{5+}$ cores.

(Scheme 3/iii). Finally, another hydride transfer from NaBH_4 provides the methyl group (Scheme 3/iv).

Conclusions

In conclusion, we have been able to synthesize the first methyl-substituted, di-NHC protected AuNCs. A reaction yield improvement can be achieved using a stoichiometric amount of $[\text{ClAu}(\text{SMe}_2)]$ complex as co-reagent, together with the $[(\text{di-NHC})\text{Au}_2\text{Cl}_2]$ substrate. Using different spectroscopic techniques, we can confirm the presence of CH_3 groups coordinated on the AuNCs. Furthermore, the formation in the solid state of another cluster, $[(\text{CH}_3)\text{Cl}]$, presenting different mass and NMR spectra, is another proof of the existence of Au- CH_3 interactions.

Acknowledgements

Partial financial support of this work by the University of Padova (Progetto P-DiSC 2023 "GOLDBULLET" no. BIFF_BIRD23_01) is gratefully acknowledged. Open Access publishing facilitated by Università degli Studi di Padova, as part of the Wiley - CRUI-CARE agreement.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Gold cluster · NHC · Gold-carbon bonds

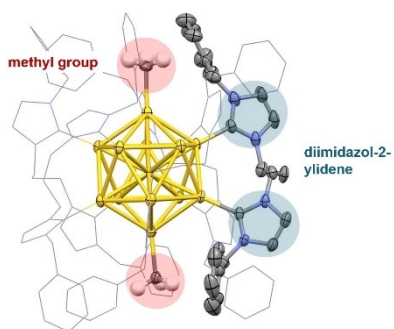
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Manuscript received: June 13, 2024
Revised manuscript received: October 19, 2024
Accepted manuscript online: November 5, 2024
Version of record online: ■■, ■■

RESEARCH ARTICLE

Molecular gold nanoclusters capped by methyl groups have been synthesized for the first time upon chemical reduction of dinuclear gold(I) complexes with di-imidazol-2-ylidene ligands using excess NaBH_4 as reducing agent.



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First Evidence of Au-CH₃ Bonding in Superatomic Au₁₃ Clusters

