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Jianyu Wei, J.-F. Halet, Samia Kahlal, Jean-Yves Saillard, Alvaro Munoz-Castro. Toward the Formation of N-Heterocyclic-Carbene-Protected Gold Clusters of Various Nuclearities. A Comparison with Their Phosphine-Protected Analogues from Density Functional Theory Calculations. Inorganic Chemistry, 2020, 59 (20), pp.15240-15249. 10.1021/acs.inorgchem.0c02219. hal-02998918

HAL Id: hal-02998918 https://hal.science/hal-02998918

Submitted on 18 Nov 2020 $\,$

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Towards the Formation of N-Heterocyclic Carbene-Protected Gold Clusters of Various Nuclearities. A Comparison with their Phosphine-Protected Analogs from DFT Calculations

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KEYWORDS: Gold, superatoms, NHC, phosphines

ABSTRACT: The structure and bonding of a series of selected phosphine-protected gold clusters (Au_n -P) of nuclearity varying from n = 6 to 13 were investigated by DFT calculations and compared to that of the hypothetical homologues in which phosphines were replaced by NHC analogs (Au_n -C). Both Au_n -P and Au_n -C series exhibit similar stabilities and structural features, except for n = 6 where some differences are noted. The NHC ligands are found even slightly more strongly bonded to the gold core (by a few kcal/mol per ligand) than phosphines. Investigation of the optical properties of both series using TD-DFT calculations indicates similarities in the nature and energies of the UV-Vis optical transitions and consequently relatively similar shapes of the simulated spectra, with a general blue-shift tendency when going from Au_n -P to Au_n -C. The fluorescence behavior observed experimentally for some of the Au_n -P species is expected to occur also for their Au_n -C analogs, which can be extended to other carbene ligand-protected nanoclusters. Our results show that it should be possible to stabilize gold clusters with NHC ligands, in relation to the seminal Au_{13} ligand-protected core, offering novel building blocks for the design of nanostructured materials with various properties.

1. Introduction

Ligated atom-precise gold nanoclusters (AuNCs) are currently the subject of considerable interest.¹⁻⁷ On one side, they represent the lowest size limit of gold nanoparticles (AuNPs), with, in addition, ideal mono-dispersity. They constitute thus interesting models for fundamentally understanding the numerous properties of potential technological interest of larger AuNPs.¹⁻¹⁶ On the other side, AuNCs have also their own intrinsic interest, due to their specific properties associated with their delocalized 6s electrons. The field of their various chemical, biochemical, physicochemical and physical properties is as large as their extremely rich structural chemistry.¹⁻⁷ Numerous theoretical and experimental research efforts have contributed to the rationalization of their structure and stability towards the design of novel noble-metal nanostructures.¹⁷⁻³¹ It appears obvious that the role played by the AuNC ligand shell is decisive in the stabilization of a given structure for a given electron count. Ligands do not only play the role of passivating the metal core surface, but can also have significant influence on the AuNC structure and properties. Thus, introducing new ligands in the synthetic chemistry of AuNCs is of prime interest, in particular for tuning their optical properties.

From this view point, it is worth noting that N-heterocyclic carbenes (NHC) have been very recently introduced as new protecting ligands of gold clusters.^{6,32-37} In particular, Crudden and coworkers synthezised NHC-protected Au₁₃ *superatoms* that exhibit large photoluminescent quantum yields.^{33,34} It turns out that one of us recently published a Density Functional Theory (DFT) investigation on the effect of substituting the diphosphine ligands by NHCs in the well-known $[Au_{13}(dppe)_5Cl_2]^{3+}$ cluster (dppe = diphenylphosphinethane).³⁸ It was found that the substitution does not substantially modify the AuNC stability, but significantly affects the optical

properties. Thus, NHCs appear to be an interesting alternative to their phosphine *isolobal* analogs, allowing increasing cluster versatility, owing to the electronic variability of NHCs, which range from strong to weak donor ligands.^{39–43}

As a continuation of our first work,³⁸ we report here a comprehensive DFT investigation on the substitution of phosphines by NHCs in a series of small and medium size phosphine-protected AuNCs. The analysis is mainly focused on the substitution-induced changes on the structural arrangement, electronic structure and optical (including emissive) properties. The chosen AuNCs phosphine reference series (see Table 1) is composed of the experimentally characterized $[\operatorname{Au}_{6}(\operatorname{dppp})_{4}]^{2+44,45}$ (Au₆-P), $[\operatorname{Au}_{8}(\operatorname{dppp})_{4}]^{2+46}$ (Au₈-P), $[\operatorname{Au}_{8}(\operatorname{dppp})_{4}\operatorname{Cl}_{2}]^{2+46}$ (Au₈Cl₂-P), $[Au_{9}(PPh_{3})_{8}]^{3+47,48}(Au_{9}-P), [Au_{11}(dppe)_{6}]^{3+49}(Au_{11}-P), [Au_{11}(PPh_{3})_{8}Cl_{2}]^{+50,51}(Au_{11}Cl_{2}-P), and$ $[Au_{13}(dppe)_5Cl_2]^{3+52}$ (Au₁₃Cl₂-P) (dppp = diphenylphosphinepropane). These compounds were chosen because their offer a reasonable range of nuclearity (from 6 to 13), structure types and superatom electron counts (from 4 to 8 – 5d electrons are not considered). Some of them have diphosphines, whereas others have simple phosphines. Some bear chloride ligands whereas the others are homoleptic. Moreover, photoluminescence data are available for most of them.^{46,47,52,53} The hypothetical $[Au_{13}(PPh_3)_9Cl_3]^{2+}$ (Au_{13}Cl_3-P) compound, which is the phosphine counterpart of several recently characterized NHC derivatives $[Au_{13}(NHC)_9Cl_3]^{2+}$ was added to this series.³³ Thus, we believe that the variety of these compounds makes this series a good reference sampling for investigating the changes occurring upon substituting the phosphine ligands by NHC homologs. These homologs were designed by substituting the mono-phosphines by the mono-carbene N,N'-diisopropylimidazolidene ligands (noted NHC' in the followings, see Scheme 1), taken from the litterature.³² The dppe and dppp diphosphine ligands were substituted by their NHC analogs, namely 1,3-bis{N-isopropylimidazolidenyl}ethane (di-NHC'e) and 1,3bis{N-isopropylimidazolidenyl}propane (di-NHC'p), respectively (Scheme 1). These carbenes are representative of standard NHCs and exhibit realistic steric volume. Thus, the computed NHC clusters are: $[Au_6(di-NHC'p)_4]^{2+}$ (Au_6-C), $[Au_8(di-NHC'p)_4]^{2+}$ (Au_8-C), $[Au_8(di-NHC'p)_4Cl_2]^{2+}$ (Au_8Cl_2-C), $[Au_9(NHC')_8]^{3+}$ (Au_9-C), $[Au_{11}(di-NHC'e)_6]^{3+}$ (Au_{11-C}), $[Au_{11}(NHC')_8Cl_2]^+$ (Au_{11}Cl_2-C), $[Au_{13}(di-NHC'e)_5Cl_2]^{3+}$ (Au_{13}Cl_2-C), and $[Au_{13}(NHC')_9Cl_3]^{2+}$ (Au_{13}Cl_3-C).



Scheme 1. NHC Ligands Considered in the Calculations

Table 1. Structurally Characterize	d Phosphine-protected	d AuNCs from whic	ch Models Were
Considered in our Calculations			

Compound	Abbreviation	Number of 6s (Au) electrons	Structure of the Au _n core	Ref.
$\left[\operatorname{Au}_6(\operatorname{dppp})_4\right]^{2+}$	Au ₆ -P	4	edge-bridged tetrahedron	44, 45
$\left[\operatorname{Au}_8(\operatorname{dppp})_4\right]^{2+}$	Au ₈ -P	6	edge-sharing tri-tetrahedron	46
$\left[Au_8(dppp)_4Cl_2\right]^{2+}$	$[Au_8(dppp)_4Cl_2]^{2+} Au_8Cl_2-P$		bicapped edge-sharing bi- tetrahedron	46
$[Au_9(PPh_3)_8]^{3+}$	Au ₉ -P	6	bicapped centered chair	47, 48
$[Au_{11}(dppe)_6]^{3+}$	$[Au_{11}(dppe)_6]^{3+}$ Au ₁₁ -P		doubly-bridged bicapped centered chair	49
$\left[\mathrm{Au}_{11}(\mathrm{PPh}_3)_8\mathrm{Cl}_2\right]^+$	Au ₁₁ Cl ₂ -P	8 incomplete centered icosahedro		50,51
$[Au_{13}(dppe)_5Cl_2]^{3+}$	Au ₁₃ Cl ₂ -P	8	centered icosahedron	52
$[Au_{13}(PPh_3)_9Cl_3]^{2+}$	Au ₁₃ Cl ₃ -P ^a	8	centered icosahedron	33

^(a) Structure modelized from that of Crudden's NHC derivative [Au₁₃(NHC)₉Cl₃]^{2+.33}

2. Computational Details

Geometry optimizations were carried out at the Density Functional Theory (DFT) level⁵⁴ with the addition of Grimme's D3 empirical corrections⁵⁵ in order to take into account dispersion effects. The Amsterdam Density Functional code⁵⁶ (ADF2017), incorporating the relativistic scalar corrections via the ZORA Hamiltonian was used.⁵⁷ The all-electron triple- ξ Slater basis set plus a polarization function (STO-TZP),⁵⁸ were used, together with the Becke-Perdew (BP86)^{59,60} exchange-correlation functional. This functional was chosen for its good performance in reproducing cluster ground state geometries and its reasonable CPU time demand.¹⁹ An energy convergence criterion of 5×10^{-5} Hartree and a radial convergence criterion of 5×10^{-3} Å were employed. All the optimized structures were confirmed as true minima on their potential energy surface by analytical vibration frequency calculations. All the computed species have a closedshell ground state. The Gaussian16 package⁶¹ was used to calculate natural atomic orbital (NAO) populations and Wiberg bond indices (WBI) using the ADF-optimized geometries with its NBO6.0 module,⁶² with the Def2-SVP⁶³ basis set and the BP86 functional. In order to reduce computational efforts, the Gaussian16 package was also used for calculating the UV-Vis optical transitions by time-dependent density functional theory⁶⁴ (TD-DFT) calculations, using the Def2-SVP⁶³ basis set (which includes effective core potentials accounting for scalar relativistic effects) and the B3LYP functional.⁶⁵ The choice of this functional was made after having tested several of them, namely B3LYP,⁶⁵ BP86,^{59,60} and LB94,⁶⁶ with respect to the experimental spectra of the phosphine-protected AuNCs listed in Table 1. Similar trends were found for the three functionals, but the B3LYP-computed optical transitions were found to be in the closest quantitative agreement with experiment. The UV-Vis spectra were simulated from the computed

TD-DFT transition energies and their oscillator strength by using the SWizard program,⁶⁷ each transition being associated with a Gaussian function of half-height width equal to 3000 cm⁻¹, a value that best reproduces experimental spectra. To calculate the fluorescence emission wavelengths, the geometry of the excited singlet states was optimized at the TD-DFT/B3LYP level with the Gaussian16 program. To compute the phosphorescence emission wavelengths, the geometry of the triplet state was calculated at the DFT/BP86 level with ADF2017 and its energy and that of the ground state were recalculated for this geometry as single points at the B3LYP level with Gaussian16. To compute the energy differences between the singlet and triplet exited states, the ADF optimized triplet exited geometries were re-calculated via single point calculations using Gaussian 16.

3. Results and Discussion

3.1 Structures and Bonding Modes

The geometries of the phosphine-protected AuNCs (Au_n -P) and their NHC homologs (Au_n -C) were optimized and compared. The former are found to be in good agreement with their corresponding X-ray structures.^{33,44,46,47,49,51,52} Together with those of their NHC homologs (Au_n -C), they are shown in Figure 1. Their corresponding MO diagrams are represented in the form of density-of-states (DOS) plots in Figures S1-S6 (see also Figures S9-S16). They all exhibit similar features, with the 5d(Au) states contributing mainly to the large band below the HOMO and the 6s/6p(Au) to the lowest unoccupied states. As examples, those of the smallest Au_6 -X and the largest $Au_{13}Cl_2$ -X species (X = P, C) are shown in Figure 2. The HOMOs and LUMOs of the computed Au_n -P and Au_n -C species are pictured in Figures S7 and S8, respectively.



Figure 1. Optimized geometries of the computed Au_n -X clusters (X = P, C).



Figure 2. Density of states of Au_6 -X (top) and $Au_{13}Cl_2$ -X (bottom) (X = P, C). Gaussian full width at half maximum: 0.05 eV. The dotted line corresponds to the energy of the HOMO.

The core structure of Au_6 -P consists of an edge-bridged tetrahedron (Figure 1). Whereas its Xray structure is of S_4 symmetry, its DFT-optimized geometry was found to be slightly distorted into D_2 symmetry. In a first approximation, the computed data given in Table 2 are consistent with a view of Au_6 -P made of two R₃P-Au(0)-Au(0)-PR₃ sub-systems (each containing a 2 electron/2-center bond) and two R₃P-Au(I)-PR₃ units. In both fragment types, the 14-electron gold centers adopt the (approximately) linear 'ML₂' coordination mode expected to favor its stability for this particular electron count.⁶⁸ This is confirmed by the nature of the HOMO (b_1) and HOMO-1 (a) of Au_6 -P, which can be described as the out-of-phase and in-phase combinations, respectively, of the σ (Au-Au) bonding orbitals of the two R₃P-Au(0)-Au(0)-PR₃ moieties (Figure S7). These orbitals, of large 6s/6p character, are moderately delocalized on the R₃P-Au(I)-PR₃ fragments, suggesting that the 4 electrons remain principally located on the two short Au-Au bonds of the Au₄ tetrahedron, as also confirmed by the much smaller Wiberg bond indices of the other Au-Au contacts (Table 2). It thus can be concluded that these longer Au-Au contacts are largely the result of metallophilic interactions. The LUMO (*a*) is also of important 6s/6p character and has significant localization on the two bridging Au atoms. **Au₆-C** differs from **Au₆-P** in the fact that each of its two L-Au(0)-Au(0)-L and two L-Au(I)-L fragments are even less interacting with the others (see data in Table 2), so that they can be considered as almost independent from each other. Nevertheless, the HOMO (*b₁*) and HOMO-1 (*a*) of **Au₆-C** are similar to their **Au₆-P** counterparts (Figure S8). The LUMO and LUMO+1 are ligand-based levels. Although localized in part on the bridging Au atoms, the LUMO is different from the LUMO of **Au₆-P**. The LUMO+2 (*a*), mainly localized on the outer Au atoms, is the counterpart of the **Au₆-P** LUMO.

Table 2. Relevant Computed Data for the $[Au_6L_4]^{2+}$ Clusters (L = dppp (Au₆-P) and L = di-NHC'p (Au₆-C)). Au_t and Au_b Designate the Atoms of the Central Tetrahedron and the Bridging Atoms, Respectively. Experimental Interatomic Distances of Au₆-P Are Provided for Comparison

		$\mathbf{Au_6} \cdot \mathbf{P} \exp^{44}(S_4)$	$\mathbf{Au_6}\text{-}\mathbf{P}\left(D_2\right)$	$\mathbf{Au_6}\text{-}\mathbf{C}\ (D_2)$
		2.630 × 2	2.630 [0.302] × 2	2.561 [0.462] × 2
	A., A.,	2.923×2	2.861 [0.032] × 2	3.178 [0.019] × 2
Distance (Å)	Au _t -Au _t	2.923 × 2	2.972 [0.023] × 2	3.390 [0.011] × 2
$[WBI]^a$		av. 2.825	av. 2.821 [0.119]	av. 3.043 [0.164]
	Au _b -Au _t	2.798 × 4	2.790 [0.090] × 4	3.601 [0.013] × 4
	Au-L	av. 2.378	av. 2.332 [0.391]	av. 2.069 [0.441]
HOMO-LUMC) gap (eV)		1.58	1.53
	Au _t		-0.02 × 4	-0.04 × 4
NAO ^b charge	Au _b		+0.27 × 2	$+0.42 \times 2$
	L		+0.39 × 4	+0.33 × 4

^aWiberg bond index. ^bNatural atomic orbital.

The core structure of Au_8-P consists of three edge-sharing linearly arranged tetrahedra (Figure 1). Its ideal symmetry is S_4 , whereas after relaxation its symmetry is lowered to C_2 . It can be described as made of four quasi-linear L-Au-Au-L units packed perpendicularly along a common pseudo- S_4 axis in a staggered fashion. The shortest Au-Au distances are those within these L-Au-Au-L fragments. The favored electron count for an Au₄ tetrahedron is 2,⁶⁹ so it is expected that the 6 electrons of Au_8-P are delocalized over the three tetrahedra. This is supported by the Au-Au WBIs given in Table 3 that are all significant, contrarily to the case of Au_6-P (Table 2). A more detailed analysis of their disparity and examination of the NAO charges tend to favor the view of a 2-electron central tetrahedron [$Au_4(PR_3)_4$]²⁺ interacting in a moderate but significant

covalent way with two linear R_3P -Au(0)-Au(0)-PR₃ units. The HOMO (*a*) and HOMO-1 (*b*), of large 6s/6p character, can be associated with the two outer Au(0)-Au(0) bonding pairs, partly delocalized on the central tetrahedron (Figure S7). It was not possible to identify a unique orbital associated with the third bonding pair, because of orbital mixing, but several 5d-type levels present some non-negligible 6s/6p bonding character within the central tetrahedron. The LUMO and LUMO+1, both of *b* symmetry, are 6s/6p Au-Au antibonding orbitals.

As for the Au_6 systems described above, substituting the phosphines in Au_8 -P by NHC ligands tends to reinforce the Au-Au bonding in the four R₃P-Au-Au-PR₃ units and weakens somewhat the other Au-Au contacts, but the effect is not as strong as in the Au₆ systems. The HOMO and HOMO-1 of Au₈-C are the counterparts of those of Au₈-P. The LUMO+2 and LUMO of Au₈-C are the counterparts of the LUMO and LUMO+1 of Au₈-P (Figure S8). As for the Au₆ systems, a slightly smaller HOMO-LUMO gap is computed when phosphines are substituted by NHC ligands.

Table 3. Relevant Computed Data for $[Au_8L_4]^{2+}$ Clusters (L = dppp (Au_8-P) and L = di-NHC'p (Au_8-C)). Experimental Interatomic Distances of Au_8-P Are Provided for Comparison

		$\mathbf{Au_8} \cdot \mathbf{P} \exp^{46}(S_4)$	$\mathbf{Au_{8}}\textbf{-}\mathbf{P}\left(C_{2}\right)$	$\mathbf{Au_8-C} (C_2)$
	Au _t -Au _t	min. 2.630	min. 2.687 [0.213]	min. 2.649 [0.268]
	(center)	max. 2.896	max. 2.887 [0.086]	max. 3.083 [0.074]
Distance (Å)	()	av. 2.785	av. 2.790 [0.135]	av. 2.842 [0.151]
[WBI]	Au _t -Au _t	min. 2.607	min. 2.646 [0.302]	min. 2.640 [0.331]
[יי טו	(outer)	max. 2.854	max. 2.866 [0.064]	max. 3.096 [0.038]
	× ,	av. 2.795	av. 2.812 [0.108]	av. 2.864 [0.115]
	Au-L	av. 2.304	av. 2.314 [0.381]	av. 2.067 [0.399]
HOMO-LUN	IO gap (eV)		1.79	1.67
NAO charge	Au (center)		+0.10 x 4	+0.17 x 4
(av.)	Au (outer)		-0.01 x 4	+0.06 x 4
()	L		+0.41 x 4	+0.27 x 4

The structural arrangement of the Au_8Cl_2 -P cluster differs from that of Au_8 -P (Figure 1). It exhibits a core made of two edge-sharing tetrahedra capped on both sides by two nearly linear R₃P-Au_b-Cl units. Its ideal symmetry is D_{2h} , but DFT computations found it slightly distorted into C_1 after relaxation. This is a 4-electron species, and the NAO charge distribution (Table 4) indicates that the two bridging atoms can be considered as Au_b(I) centers. The 4 electrons can thus be associated with the bi-tetrahedron, where they are predominantly located on the R₃P-Au_m-Au_m-PR₃ and R₃P-Au_s-Au_s-PR₃ bonds, as shown by the corresponding WBIs. This is in line with the composition and shape of the HOMO and HOMO-1 (Figure S7) orbitals of Au₈Cl₂-P, which are associated with these 4 electrons. The LUMO and LUMO+1 are 6s/6p in composition associated with the bridging Au_b atoms and the bi-tetrahedron, respectively (Figure S7). Compound Au_8Cl_2 -C has similar arrangement and electronic structure as its phosphine homolog (Figure S8). When going from Au_8Cl_2 -P to Au_8Cl_2 -C, a strengthening of the R₃PAu-AuPR₃ bond and some weakening of the other Au-Au bonds is observed, a tendency already noted in the previous clusters, but less pronounced in the present systems. In contrast with the previous Au₆ and Au₈ systems, a larger HOMO-LUMO gap is computed when phosphine ligands are substituted by NHC ligands.

Table 4. Relevant Computed Data for $[Au_8Cl_2L_4]^{2+}$ Clusters (L = dppp (Au_8Cl_2-P) and L = di-NHC'p (Au_8Cl_2-C)). Experimental Interatomic Distances of Au_8Cl_2-P Are Provided for Comparison. Au_m and Au_s Designate the Middle and Side Atoms of the Bi-tetrahedron, Respectively, and Au_b the Bridging Atoms

		$\mathbf{Au_8Cl_2} \cdot \mathbf{P} \exp^{46}(D_{2h})$	$\mathbf{Au_8Cl_2}\text{-}\mathbf{P}\left(C_1\right)$	$\mathbf{Au_8Cl_2-C} (C_1)$
	Au _m -Au _m	2.648	av. 2.676 [0.196]	av. 2.667 [0.230]
	Au _s -Au _s	av. 2.654	av. 2.692 [0.244]	av. 2.691 [0.273]
Distance (Å)	Au _m -Au _s	av. 2.821	av. 2.849 [0.089]	av. 2.878 [0.093]
[WBI]	Au _s -Au _b	av. 3.026	av. 2.960 [0.042]	av. 3.034 [0.032]
	Au-L	av. 2.302	av. 2.311 [0.441]	av. 2.062 [0.449]
	Au-Cl	av. 2.289	av. 2.348 [0.394]	av. 2.346 [0.423]
HOMO-LUM	O gap (eV)		1.87	2.03
	Au _m)	+0.14 x 2	+0.22 x 2
NAO charge	Au _s		+0.05 x 4	+0.12 x 4
(av.)	Au _b		+0.30 x 2	+0.37 x 2
	L		+0.49 x 4	+0.35 x 4
	Cl		-0.52 x 2	-0.54 x 2

The 6-electron Au₉-P cluster that we investigated (Figure 1) is generally described as a bicapped centered chair,^{47,48} that is, a centered Au₆ chair-like ring with two opposite vertices

capped by two supplementary gold atoms. It has an isomer exhibiting a centered crown,⁷⁰ which is not discussed here. The whole structure of **Au₉-P** is of ideal D_2 symmetry. Analysis of the data in Table 5 and its Kohn-Sham orbitals allows us to describe **Au₉-P** as an oblate-distorted *superatom*, with corresponding $1S^2 1P^4$ closed-shell electron configuration. The HOMO (b_2) and the HOMO-1 (b_1) are the P_x and P_y orbitals, whereas the LUMO+1 is the P_z counterpart (Figure S7). The LUMO is the D_{x2-y2} orbital. The electronic structure of **Au₉-C** is the same as that of **Au₉-P**, except the LUMO and LUMO+1, which are inverted in energy (Figure S8). Again, a small strengthening of the Au-Au bonding is noted when going from **Au₉-P** to **Au₉-C**. Comparable HOMO-LUMO gaps are computed for both species.

		$\mathbf{Au}_{9}\mathbf{-P}\exp^{47}\left(D_{2}\right)$	$\mathbf{Au}_{9}\mathbf{-P}\left(D_{2}\right)$	Au ₉ -C (D_2)
Distance (Å)	Au _c -Au _p	av. 2.692	av. 2.717 [0.132]	av. 2.729 [0.144]
[WBI]	Au _p -Au _p	av. 2.834	av. 2.842 [0.096]	av. 2.888 [0.099]
	Au-L	av. 2.281	av. 2.294 [0.441]	av. 2.043 [0.460]
HOMO-LUM	O gap (eV)		1.54	1.50
NAO charge	Au _c		-0.05	-0.05
(av.)	Aup		+0.08	+0.16
	L		+0.30	+0.22

Table 5. Relevant Computed Data for $[Au_9L_8]^{3+}$ Clusters (L = PPh₃ (Au₉-P) and L = NHC' (Au₉-C)). Experimental Interatomic Distances of Au₉-P Are Provided for Comparison. Au_c and Au_p Designate the Unique Central and the Eight Peripheral Atoms, Respectively

The 8-electron Au_{11} -P cluster (Figure 1) can be viewed as resulting from the bridging of the Au_9 -P metal core on two opposite sides (along the *y* axis) by two supplementary $Au(PPh_3)_2$ units. It has two more electrons than Au_9 -P that are located in a kind of $1D_y^2$ HOMO, resulting in the prolate $1S^2 1P^4 1D^2$ closed-shell configuration. Its LUMO can be tentatively described as a

 $2P_y$ level (Figure S7). Au₁₁-C has comparable geometry (Table 6) and electronic structure (Figure S8).

Table 6. Relevant Computed Data for $[Au_{11}L_6]^{3+}$ Clusters (L = dppe (Au_{11}-P) and L = di-NHC'e (Au_{11}-C)). Experimental Interatomic Distances of Au_{11}-P Are Provided for Comparison. Au_c, Au_p and Au_b Designate the Unique Central, the Eight Peripheral Atoms and the Two Bridging Atoms, Respectively

		Au₁₁-P exp ⁴⁹ (C_2)	$\mathbf{Au_{11}}\textbf{-}\mathbf{P}\left(C_{2}\right)$	$\mathbf{Au}_{11}\mathbf{-C}(C_2)$
Distance (Å)	Au _c -Au _p	av. 2.746	av. 2.745 [0.101]	av. 2.828 [0.110]
[WBI]	Au _p -Au _p	av. 2.859	av. 2.878 [0.104]	av. 2.973 [0.109]
	Au _b -Au _p	av. 2.801	av. 2.773 [0.126]	av. 2.814 [0.158]
	Au-L	av. 2.319	av. 2.317 [0.420]	av. 2.087 [0.388]
HOMO-LUM	O gap (eV)		1.40	1.49
NAO charge	Au _c		-0.16	-0.18
(av.)	Au _p		+0.03	+0.12
	Au _b		+0.29	+0.48
	L		+0.39	+0.21

Finally, the last three phosphine clusters of the series (Table 1), namely $Au_{11}Cl_2$ -P, $Au_{13}Cl_2$ -P (already theoretically studied previously)⁷¹ and $Au_{13}Cl_3$ -P (Figure 1), are more compact, exhibiting a centered icosahedral core (incomplete in the case of $Au_{11}Cl_2$ -P). The somewhat distorted icosahedra display rather homogeneous Au_c - Au_p distances (Table 7). They are all regular 8-electron pseudo-spherical *superatoms* with $1S^2$ 1P⁶ configuration. The HOMOs and LUMOs are of 1P and 1D nature, respectively (Figure S7). Their NHC counterparts, $Au_{11}Cl_2$ -C, $Au_{13}Cl_2$ -C, and $Au_{13}Cl_3$ -C exhibit quite similar features (Table 7 and Figure S8).

Hence, besides the already characterized NHC-protected as protecting ligands for Au_6 and Au_{13} clusters,^{32,33} carbene ligands appear to be able to stabilize gold clusters of any size. Thus, size-dependent properties related to cluster core nuclearity can be explored, in addition to the versatility shown by NHC's characteristics ranging from strong to weak donor ligands.⁴⁰

Table 7. Relevant Computed Data for $[Au_{11}Cl_2L_8]^+$ Clusters (L = PPh₃ (Au_{11}Cl_2-P) and L = NHC' (Au_{11}Cl_2-C)); $[Au_{13}Cl_2L_5]^{3+}$ Clusters (L = dppe (Au_{13}Cl_2-P) and L = di-NHC'e (Au_{13}Cl_2-C)); $[Au_{13}Cl_3L_9]^{2+}$ Clusters (L = PPh₃ (Au_{13}Cl_3-P) and L = NHC' (Au_{13}Cl_3-C)). Experimental Interatomic Distances Are Provided for Comparison. Au_c and Au_p Designate the Central and Peripheral Atoms, Respectively

		$\mathbf{Au_{11}Cl_2}\text{-}\mathbf{X}(C_1)$			$\mathbf{Au_{13}Cl_2}\text{-}\mathbf{X}\left(C_1\right)$			$\mathbf{Au_{13}Cl_{3}}\text{-}\mathbf{X}\left(C_{1}\right)$		
		$\begin{array}{c} \mathbf{Au_{11}Cl_2}\text{-}\mathbf{P}\\ exp^{51} \end{array}$	Au ₁₁ Cl ₂ -P	Au ₁₁ Cl ₂ -C	$\begin{array}{c} \mathbf{Au_{13}Cl_2-P}\\ \exp^{52} \end{array}$	Au ₁₃ Cl ₂ -P	Au ₁₃ Cl ₂ -C	$\begin{array}{c} \mathbf{Au_{13}Cl_{3}-C}\\ exp^{33} \end{array}$	Au ₁₃ Cl ₃ -P	Au ₁₃ Cl ₃ -C
	Au _c -Au _p	av. 2.687	av. 2.702 [0.140]	av. 2.718 [0.155]	av. 2.764	av. 2.773 [0.121]	av. 2.787 [0.135]	av. 2.768	av. 2.801 [0.119]	av. 2.800 [0.131]
Distance (Å)	Au _p -Au _p	av. 2.954	av. 2.877 [0.072]	av. 3.019 [0.069]	av. 2.906	av. 2.916 [0.063]	av. 2.930 [0.063]	av. 2.911	av. 2.946 [0.065]	av. 2.945 [0.066]
[WBI]	Au _p -Cl	av. 2.357	av. 2.388 [0.322]	av. 2.422 [0.285]	av. 2.351	av. 2.348 [0.381]	av. 2.355 [0.384]	av. 2.352	av. 2.381 [0.324]	av. 2.394 [0.316]
	Au-L	av. 2.289	av. 2.288 [0.411]	av. 2.042 [0.429]	av. 2.289	av. 2.289 [0.664]	av. 2.036 [0.448]	av. 2.051	av. 2.313 [0.440]	av. 2.047 [0.442]
HOMO-LUMO gap (eV)			1.89	1.91		1.74	2.02		1.90	2.13
	Au _c		-0.22	-0.24		-0.32	-0.33		-0.27	-0.27
NAO charge	Au _p		+0.10	+0.16		+0.15	+0.21		+0.15	+0.21
(av.)	Cl		-0.60	-0.63		-0.55	-0.57		-0.57	-0.61
	L		+0.17	+0.12		+0.54	+0.39		+0.24	+0.17

3.2 Bonding Energies

A more quantitative comparison of the thermodynamic stability of the investigated phosphine and NHC species can be performed from the comparison of the energies of interaction between the ligands and the metal core, but also from the evaluation of the energy cost associated with the distortion afforded by the metal core upon complexation. To this end, we optimized the geometries of the bare $[Au_n]^{x+}$ core of the investigated species, obtained after removal of the neutral phosphine (or NHC) and anionic chloride (if any) ligands. Interestingly, these optimized bare ionic metal cores maintain the structure that they adopt in the Aun-P, AunClm-P experimental structures (see Figure S17). Apart from the icosahedral $[Au_{13}]^{5+}$ core,⁷² there is no certainty that such configurations are global minima,⁷³ but at least they are local minima, as ascertained by vibrational frequency analyses. Consistently, they all present a significant HOMO-LUMO gap (> 1 eV), except that of $[Au_8]^{2+}$ (0.39 eV), perhaps due to its low compacity. Interestingly, the two optimized $[Au_{11}]^{3+}$ structures differ by a substantial energy difference of 1.07 eV at the expense of the less compact one. The energy cost afforded by the bare metal cores to prepare their structure to bonding with ligands (E_{Prep}) is given in Table 8. It is computed as the difference between the energy of the $[Au_n]^{x+}$ core as it is in the optimized Au_n-X or Au_nCl_x-X species and that of the free $[Au_n]^{x+}$. Most of these values are small, consistently with the moderate change of the metal configuration upon complexation. The exception of Au₆-C can be explained by its structural difference with its Au₆-P counterpart (see above). That of the two $[Au_{11}]^{3+}$ cores constitute also an exception, but they show similar E_{Prep} values for both phosphine and NHC clusters. Thus, except for the Au₆-X (X = P, C) clusters, the $E_{Prep.}$ values of the phosphine and NHC couples are very similar.

Table 8. Energetic Data Associated with Cluster Bonding (all Values in eV). $E_{Prep.}$ = Energy Cost Afforded by the Bare $[Au_n]^{x+}$ Metal Core to Go From its Equilibrium Structure to That It Adopts in the Au_n-X or Au_nCl_m-X Cluster. $E_{bond.} = E(Au_n-X) - E([Au_n]^{x+}) - E(neutral ligand sphere)$ or $E_{bond.} = E(Au_nCl_m-X) - E([Au_nCl_m]^{(x-m)+}) - E(Neutral Ligand Sphere)$.

Compound	Corresponding	$\mathbf{X} = \mathbf{P}$	$\mathbf{X} = \mathbf{C}$	$\mathbf{X} = \mathbf{P}$	$\mathbf{X} = \mathbf{C}$
Compound	optimized metal core ^a	$E_{Prep.}$ (metal core)	$E_{Prep.}$ (metal core)	E _{Bond.}	E _{Bond.}
Au ₆ -X	$[\mathrm{Au}_6]^{2+}(D_2)$	0.19	2.85	-24.97	-29.25
Au ₈ -X	$[\mathrm{Au}_8]^{2+}(C_2)$	0.38	0.32	-26.88	-28.70
Au ₈ Cl ₂ -X	$\left[\operatorname{Au}_{8}\right]^{4+}(D_{2h})$	0.21	0.23	-29.59	-31.36
Au ₉ -X	$\left[\operatorname{Au}_{9}\right]^{3+}(D_{2h})$	0.09	0.15	-33.78	-35.86
Au ₁₁ -X	$[\operatorname{Au}_{11}]^{3+}(C_2, \Delta \mathrm{E} = 1.07^{\mathrm{b}})$	1.09	1.24	-39.68	-41.53
Au ₁₁ Cl ₂ -X	$[\mathrm{Au}_{11}]^{3+}(C_2,\Delta\mathrm{E}=0.00^{\mathrm{b}})$	1.02	1.00	-25.01	-27.23
Au ₁₃ Cl ₂ -X	$[Au_{12}]^{5+}(I_k)$	0.49	0.40	-40.04	-42.58
Au ₁₃ Cl ₃ -X		0.38	0.33	-33.67	-37.32

Neutral Ligands = Phosphines or NHCs. All Fragment Structures Taken From the Au_n-X or Au_nCl_m-X Optimized Geometries

^a See Figure S17.

^b Relative energies between [Au₁₁]³⁺ isomers.

The bonding energy (E_{Bond}) of the neutral phosphine or NHC ligand sphere to the $[Au_n]^{x+}$ or $[Au_nCl_m]^{(x-m)+}$ fragments in the Au_n-X or Au_nCl_m-X , respectively, was computed according to $E_{bond.} = E(Au_n-X) - E([Au_n]^{x+}) - E(neutral ligand sphere)$ or $E_{bond.} = E(Au_nCl_m-X) - E([Au_nCl_m]^{(x-m)+}) - E(neutral ligand sphere)$, respectively. In these equations, all the considered (frozen) fragment structures were taken from the Au_n-X or Au_nCl_m-X optimized geometries. It is clear from Table 8 that the NHCs are more strongly bonded than their phosphine analogues in all the investigated systems. The difference is not very large, but significant (a few eVs). Even taking into account the $E_{Prep.}$ destabilizing component, the difference remains in favor of stronger NHC bonding. When this difference is normalized to one phosphine/carbene function, it is found

to lie within a range of 4-7 kcal/mol ($E_{Prep.}$ -corrected in the case of Au₆-X couple), except for the Au₁₃Cl₃-X system where it is a bit higher (10 kcal/mol).

3.3 Optical properties

The UV-Vis absorption spectra of the computed clusters were simulated (see Computational Details above). They are gathered in Figure 3 and the major computed electronic transition energies associated with are given in Table 9, together with corresponding experimental λ_{max} values taken from the literature where available.^{33,44-53} Although spin orbit corrections were not considered in our calculations, a good match was obtained between the computed excitation energies and the available experimental λ_{max} values, in particular for the low-energy transitions. This agreement provides confidence in the reliability of our results, retaining small deviations (0.07 to 0.32 eV) within the method error.¹⁹ Going from L = phosphine to L = NHC does not change importantly the nature and the energies of the optical transitions of a given cluster and consequently the shape of its simulated spectrum. A general blue-shift tendency is observed when going from L = phosphine to L = NHC, except for the low-energy absorption band of Au₉-X (Figure 3) in agreement with the smaller HOMO-LUMO gaps computed for the later over all. Indeed, in the Au_6-P to $Au_{11}-P$ series, the lowest energy band is associated with a HOMO→LUMO transition of metal-to-metal charge transfer (MMCT) nature (Table 9). A transition involving orbitals of the same nature is found for the homologous Au₆-C to Au₁₁-C series, although in the cases of Au_6 -C and Au_9 -C it is a HOMO \rightarrow LUMO+2 transition, which is mainly responsible. In the pseudo-spherical $Au_{11}Cl_2 X$ to $Au_{13}Cl_3 X$ (X = P, C) series, the lowenergy band is associated to MMCT $1P \rightarrow 1D$ transitions.

In the two Au_6-X and $Au_{11}-X$ (X = P, C) series the major transitions of higher energy are mainly of 5d(Au) \rightarrow ligand character, sometimes mixed with some 5d(Au) \rightarrow 6s/6p(Au) character. In the pseudo-spherical $Au_{11}Cl_2$ -X and $Au_{13}Cl_3$ -X (X = P, C) series, the high-energy transitions are mainly of 5d(Au) \rightarrow 1D character. Note that similar results were theoretically obtained for $Au_{13}Cl_2$ -P.⁷¹



Figure 3. Simulated UV-Vis absorption spectra for computed Au_n -P (solid line) and Au_n -C (dotted line) clusters.

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Table	9.	Major	TD-DFT-Computed	UV-Vis	Excitation	Energies.	Bold	Values	Are
Associ	ated	l With	the More Intense Abs	orption I	Bands in the	e Simulated	l Spect	ra Show	n in
Figure	3.	Availab	le Experimental λ _{max} V	alues Ar	e Reported f	or Compar	rison		

Compound	Ab	Absorption λ (nm)					
Compound	Exp. ^{<i>a</i>}	$\mathbf{X} = \mathbf{P}$	$\mathbf{X} = \mathbf{C}$	(X = P, C)			
Au ₆ -X	587, 432, 326 ⁴⁵	564 , 417, 299, 272	517 , 363, 321, 262	$Au_t \rightarrow Au_b$			
Au ₈ -X	590 (sh), 520, 308 ⁴⁶	516 , 390, 304	538 , 322, 277	$Au_{outer} \rightarrow Au_{center}$			
Au ₈ Cl ₂ -X	508, 390, 322 ⁴⁶	494, 327, 281	460, 298, 277	$Au_{m+s} \rightarrow Au_b$			
Au9-X	443, 375 (Sh), 352 (sh), 314 ⁴⁷	404, 332	488, 347, 262	$1P_x \rightarrow 1D_{x2-y2}$			
Au ₁₁ -X	663, 471 (sh), 390, 316 ⁴⁹	625 , 445, 370	573 , 472, 326	$1D_{y2} \rightarrow 2P_y$			
Au ₁₁ Cl ₂ -X	416, 312, 240 ⁵¹	426, 353	416, 298	1P→1D			
Au ₁₃ Cl ₂ -X	493, 359, 304 (sh) ⁵²	505, 390, 340	470, 408, 354, 307	1P→1D			
Au ₁₃ Cl ₃ -X	490, 420, 330 ³³	466, 391, 329	434, 376, 304	1P→1D			

 ${}^{a}X = P$ except for Au₁₃Cl₃-X, for which X = C.³³

In order to get an idea of the emission wavelength change when going from phosphine- to NHC-protected species, we have computed the corresponding transitions assuming both fluorescence and phosphorescence behavior. The emission energies were calculated by TD-DFT as vertical transitions between the optimized singlet excited state and the ground state (see Computational Details). They are given in Table 10, together with the experimental data available for the Au_n -P series^{46,47,52,53} and $Au_{13}Cl_3$ -C.³³ A reasonably good agreement is found between the experimental and TD-DFT values, giving us confidence in the computed data. When comparing the two Au_n -P and Au_n -C series, similar values are obtained, except for the Au_6 -X homologues for which the large difference in their emission wavelength can be related to the

significant difference in their structure (see below). In any case, no systematic tendency (blue- or red-shifting) is found when going from Au_n -P to Au_n -C, which is attributable to size-dependent and core-composition effects exhibited by the respective cluster core along the series.

Compound	$E_{ m emission}$	Compound	$E_{ m emission}$
Au ₆ -P	2.24 eV (552 nm)	Au ₆ -C	1.25 eV (992 nm)
Au ₈ -P	1.81 eV (683 nm) Non-luminescent ⁵³	Au ₈ -C	1.75 eV (707 nm)
Au ₈ Cl ₂ -P	2.08 eV (595 nm) Exp. 2.07 eV (597 nm) ⁴⁶	Au ₈ Cl ₂ -C	2.62 eV (473 nm)
Au ₉ -P	1.39 eV (891 nm) Exp. 2.14 eV, 1.45 eV (579 nm, 853 nm) ⁴⁷	Au ₉ -C	1.52 eV (814 nm)
Au ₁₁ -P	1.85 eV (670 nm)	Au ₁₁ -C	1.82 eV (683 nm)
Au ₁₁ Cl ₂ -P	1.62 eV (764 nm) Non-luminescent ⁵³	Au ₁₁ Cl ₂ -C	1.86 eV (667 nm)
Au ₁₃ Cl ₂ -P	1.75 eV (709 nm) Exp. 1.62 eV (766 nm) ⁵²	Au ₁₃ Cl ₂ -C	1.72 eV (720 nm)
			1.71 eV (723 nm)
Au ₁₃ Cl ₃ -P	1.76 eV (705 nm)	Au ₁₃ Cl ₃ -C	Exp. 1.59 – 1.70 eV
			$(730-780 \text{ nm})^{33}$

 Table 10. TD-DFT computed hypothetical fluorescence emission energies.

The phosphorescence emission energies were computed as vertical transitions between the triplet state in its equilibrium geometry and the singlet state in the same geometry. The results are given in Table 11. To our knowledge, no experimental evidence of phosphorescence has been reported for the known compounds. As in the case of fluorescence, the results do not show any

general trend when going from phosphine- to NHC-protected clusters. Most of the computed transition energies are within the near-IR and IR range, which probably explains why phosphorescence is disfavored with respect to thermal relaxation, with perhaps the exception of $Au_{13}Cl_2$ -X, $Au_{13}Cl_3$ -X and Au_8Cl_2 -X (X = P, C).

Compound	$E_{ m emission}$	Compound	$E_{ m emission}$
Au ₆ -P	1.46 eV (849 nm)	Au ₆ -C	1.13 eV (1097 nm)
Au ₈ -P	0.68 eV (1823 nm)	Au ₈ -C	0.85 eV (1458 nm)
Au ₈ Cl ₂ -P	1.70 eV (729 nm)	Au ₈ Cl ₂ -C	1.82 eV (681 nm)
Au ₉ -P	1.09 eV (1137 nm)	Au ₉ -C	0.40 eV (3099 nm)
Au ₁₁ -P	1.37 eV (904 nm)	Au ₁₁ -C	1.02 eV (1215 nm)
Au ₁₁ Cl ₂ -P	1.01 eV (1227 nm)	Au ₁₁ Cl ₂ -C	0.81 eV (1530 nm)
Au ₁₃ Cl ₂ -P	1.40 eV (885 nm)	Au ₁₃ Cl ₂ -C	1.41 eV (879 nm)
Au ₁₃ Cl ₃ -P	1.45 eV (855 nm)	Au ₁₃ Cl ₃ -C	1.50 eV (826 nm)

Table 11. DFT-Computed Hypothetical Phosphorescence Emission

Going from Au₆-P to Au₆-C, a red shift in the fluorescence emission wavelength is found, which is also observed to a lesser extend in the Au₈-P/Au₈-C counterparts. Interestingly, a blue shift is found in the case of the chlorine-derivatives Au₈Cl₂-P/Au₈Cl₂-C, which is also observed for the Au₁₁-P/ Au₁₁-C and Au₁₁Cl₂-P/ Au₁₁Cl₂-C pairs. A blue shift in the emission is also calculated for the Au₉-P/Au₉-C pair, depicting strong differences with the Au₆, Au₈, and Au₁₁ cores. Hence, different cluster cores retain different behavior when NHC's ligands are included, increasing the versatility of the properties. Finally, we would like to make some comments about the energy difference between the first excited singlet and triplet states (Table S1). These gaps range 1.9-3.3 eV and 0.7-1.8 eV for the Au_n -P and Au_n -C series, respectively. Although these values are not accurate due to the way they were calculated (see Computational Details), two general trends can be noted. The first one is that within each series, this gap increases with the nuclearity. The second one is that it is much larger for Au_n -P than for their Au_n -C counterparts, whatever *n*. The particularly large gap computed for the Au_n -P derivatives disfavors the intersystem crossing, also in agreement with the non-observation of phosphorescence in this experimentally characterized series. From this point of view, the Au_n -C series appears more capable for enabling intersystem crossing and possible phosphorescence.

4. Conclusions

The hypothetical NHC-protected gold clusters we have calculated exhibit similar structural chemistry as their experimentally characterized phosphine-protected analogs. The similarities in bond distances and Wiberg bond indices are indicative of analogous thermodynamic stability. This is confirmed by the evaluation of the gold-P and gold-C bonding energies in these species, the latter being even slightly stronger than the former by a few kcal/mol. This is in phase with what is known from the few NHC-protected gold clusters known so far.^{32-34,36} The comparable HOMO-LUMO gaps are also indicative of comparable kinetic stability. Their optical properties are also likely to be quite similar, the NHC derivatives being however more prone to exhibit phosphorescence behavior. Our results show the feasibility to achieve variable-sized stable NHC-protected gold clusters with properties related to their parent phosphine-protected species. This allows further evaluation of size-dependent properties, which in addition, takes advantage

of the versatility in the electronic properties of the NHC's family, ranging from strong to weak donor ligands.

ASSOCIATED CONTENT

Supporting Information.

Details regarding the calculated density of states and MO diagrams for the cluster series investigated by the paper, the plotted frontier orbitals, the computed energy difference between the first excited singlet and triplet states and structures of the investigated $[Au_n]^{x+}$ bare systems. (PDF).

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Notes

The authors declare no conflict of interest.

DEDICATION

This paper is dedicated to our colleague and friend Dr. Jean-René Hamon on the occasion of his 65th birthday.

ACKNOWLEDGMENTS

The authors are grateful to the Chilean-French ECOS-CONYCYT program (project C18E04) and to the French-Chilean International Associated Laboratory for "Multifunctional Molecules and Materials" (LIA-CNRS N°1027). The GENCI (Grand Equipment National de Calcul Intensif) is acknowledged for HCP support (project a0010807367). J. W. thanks the China Scholarship Council for a Ph.D. grant. A.M.-C. acknowledges support from Fondecyt 1180683. Dr. R. Marchal is acknowledged for technical support.

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(73) Results obtained from a non-exhaustive search for low-energy isomers of the $[Au_n]^{x+}$ systems are provided in Figure S18.

Table of Contents Graphics and Synopsis



The structure and bonding of phosphine- and NHC-protected gold clusters are compared by means of DFT calculations