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Ad aurum: tunable transfer of N-heterocyclic carbene complexes to gold surfaces[†]

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The exceptional stability of N-heterocyclic carbene (NHC) monolayers on gold surfaces and nanoparticles (AuNPs) is enabling new and diverse applications from catalysis to biomedicine. Our understanding of NHC reactivity at surfaces; however, is quite nascent when compared to the long and rich history of NHC ligands in organometallic chemistry. In this work, well-established transmetalation reactions, previously developed for NHC transfer in homogeneous organometallic systems, are explored to determine how they can be used to create carbene functionalized gold surfaces. Two classes of NHCs, based on imidazole and benzimidazole scaffolds, were tested. The resulting AuNP surfaces were analyzed using X-ray photoelectron spectroscopy (XPS), laser desorption ionization mass spectrometry (LDI-MS), and surface-enhanced Raman spectroscopy (SERS). Reaction of either a Au(i) or Ag(i) isopropyl benzimidazole NHC complex with citrate-capped AuNPs yields, in both cases, a chemisorbed NHC that is bound through a Au adatom. Theoretical calculations additionally illustrate that binding through the Au adatom is favored by more than 10 kcal mol⁻¹, in good agreement with experiments. Surprisingly, reaction of Au(i), Ag(i), and Cu(i) diisopropylphenyl imidazole NHCs do not follow the same pattern. The Cu complex undergoes transmetalation with very little deposition of Cu; whereas, unexpectedly, the Ag complex foregoes transmetalation and instead adducts to the AuNP with retention of the Ag–C bond. Theoretical calculations illustrate that the imidazole ligand affords significant dispersion interactions with the gold surface, which may stabilize binding through the Ag adatom motif, despite its less favorable bonding energies. Taken together these results suggest a unique ability to tune the reactivity by changing the carbene structure and raise critical questions about how established transmetalation reactions in organometallic chemistry can be applied to form NHC functionalized surfaces.

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Introduction

Gold nanoparticles (AuNPs) facilitate wide-ranging applications in biological sensing,¹ biomedicine,^{2–6} and catalysis^{7–10} and these applications rely almost exclusively on chemisorbed molecules to tune the nanoparticle surface chemistry.¹¹ N-heterocyclic carbene (NHC) ligands recently emerged as an alternate ligand for gold surface passivation^{12–17} with proven stability in conditions where state-of-the-art thiol

monolayers fail.^{18–24} Despite their promise, our understanding of NHC monolayers is still nascent when compared to organometallic chemistry of NHCs. Indeed, NHC ligands have a remarkable history in organometallics with decades of research establishing their reactivity and applications, most notably in chemical catalysis.^{25–29} Given the rich history of NHCs in organometallic chemistry, borrowing their well-established reactions may usher in new directions for NHC monolayers on AuNPs.

Transmetalation reactions in homogeneous organometallic chemistry provide a facile route to transfer NHC ligands to metal atom centers. In particular, silver^{30–33} and copper^{34,35} carbene complexes are routinely used to access gold carbene complexes, which then find frequent use as designer catalysts (Fig. 1, top).³⁶ In contrast to the gold complexes, these silver and copper complexes are often air stable and easily prepared *via* a base-free, one-step synthesis involving Ag₂O^{37–39} or Cu₂O,^{34,35} respectively. Despite the widespread use of transmetalation reactions in organometallic chemistry,⁴⁰ only one

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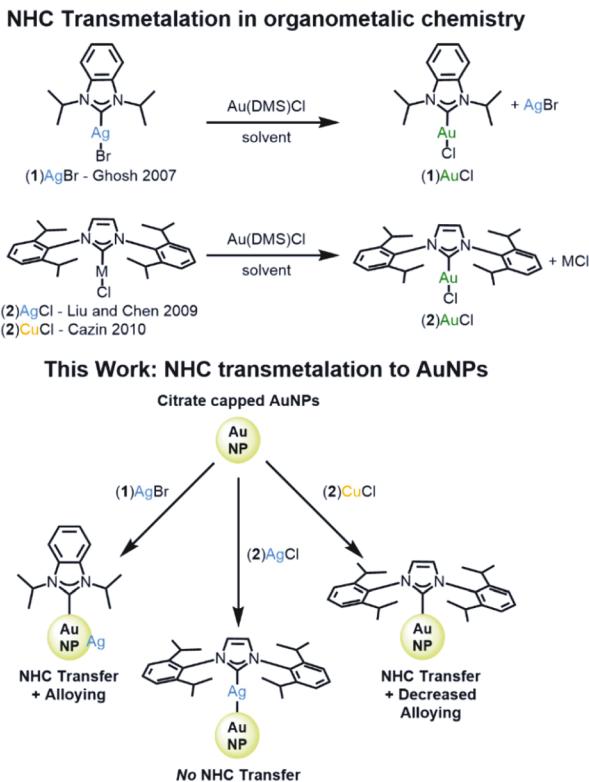


Fig. 1 General transmetalation route to access Au(i) carbene complexes as commonly found in organometallic chemistry (top). In this work, we explore transmetalation reactions between (1) benzimidazole and (2) imidazole complexes with citrate-capped gold nanoparticles (AuNPs) revealing unexpected reactivity dependence on carbene structure and the precursor metal ion (bottom). DMS stands for dimethylsulfide.

report employs a copper NHC complex for AuNP functionalization;⁴¹ however, they were unable to confirm transmetalation occurred and could not rule out the possibility of a carbene binding motif through a copper adatom.⁴²

In this manuscript, we present a comprehensive experimental and theoretical study of transmetalation reactions from silver and copper NHC complexes to create NHC functionalized AuNPs. The nanoparticle surface chemistry is probed with a suite of techniques including X-ray photoelectron spectroscopy (XPS), laser-desorption ionization mass spectrometry (LDI-MS) and surface-enhanced Raman spectroscopy (SERS), all of which were further augmented by theoretical calculations. By tracking these reactions, we elucidate surprising differences in how the NHC complex and ligand structure lead to dramatically different reactivity with the citrate-capped AuNP surfaces. While these results indicate that transmetalation could be an excellent strategy for NHC transfer to Au surfaces, the surface reactions depend on multiple variables when compared to their homogeneous organometallic chemistry counterparts.

Experimental

We investigated two classes of NHC: (1) benzimidazole-based with isopropyl side groups and (2) imidazole-based with diisopropylphenyl (Dipp) side groups, since these are the two general classes of NHCs previously reported on AuNPs (Fig. 1, bottom).^{19,22} All the AuNPs in this study were 23 ± 5 nm in diameter and were prepared *via* citrate reduction of gold aurate salt yielding citrate-capped AuNPs.⁴³ Complexes (1)AuCl, (2)AuCl, (2)AgCl, and (2)CuCl were purchased from commercial vendors while (1)AgBr was synthesized by the method of Ghosh.⁴⁴ (1)AgBr was synthesized in lieu of (1)AgCl because there are no published syntheses for (1)AgCl in the literature. 1-AuNPs were formed *via* the addition of (1)AuCl in acetonitrile to citrate-capped gold colloids to produce a final ligand concentration of $14.9 \mu\text{M}$ by the method of Camden and Jenkins.⁴⁵ While the detailed mechanism of 1-AuNP formation remains unexplored, we hypothesize that the carbene is deposited *via* the citrate reduction of the Au(i) complex with release of the halide into solution. Reactions with the other four complexes proceeded in the same manner with final ligand concentrations of $14.9 \mu\text{M}$ for (1)AgBr and $10 \mu\text{M}$ for the other three complexes.

All resulting AuNPs were characterized by XPS, inductively coupled plasma optical emission spectroscopy (ICP-OES), LDI-MS, and SERS and augmented with theoretical calculations. XPS characterization is a standard technique to distinguish between chemisorption and physisorption of the NHC to the metal surface. The presence of a Au-C bond is revealed primarily by the shifting of the N 1s peak^{46–48} to a lower binding energy (~ 400 eV) when compared to the unbound, positively charged, NHC ligand (~ 402 eV).⁴⁹ Additionally, XPS may elucidate the deposition of Ag or Cu onto the surface during the transfer process. ICP-OES characterization is routinely used to quantify alloys of Ag⁵⁰ and Cu⁵¹ with Au; therefore, we employ ICP-OES to quantify the nanoparticle composition after treatment with Ag and Cu NHC complexes. LDI-MS characterization is a powerful tool to probe the chemical composition of NHC monolayers and reveal reactions at the surface.⁵² Here, we use LDI-MS to probe the ligand transfer process. SERS is a highly surface sensitive technique capable of measuring the vibrational spectroscopy of ligands on AuNP surfaces.^{53,54} Our groups previously established SERS techniques as a probe of NHC monolayers on gold surfaces²¹ and AuNPs⁴⁵ with the added capability of determining the ligand orientation.⁵⁵ Here, we use SERS to elucidate whether AuNPs treated with Ag or Cu NHC complexes are distinguishable from AuNPs treated with Au complexes. Any differences in SERS spectra would show that monolayers with different surface orientation or binding motifs form on the surface.

The experimental measurements were further augmented with theoretical calculations of carbene molecules bound to a gold cluster, which is known to well model the NHC-surface interactions.^{45,55} Briefly, density functional theory employing the BP86 functional^{56,57} with dispersion correction⁵⁸ in the Amsterdam density functional program (ADF)^{59,60} was used to perform geometry optimizations, normal mode calculations, and bonding analysis.

Additional experimental and theoretical details are contained in the ESL.†



Results and discussion

Citrate-capped AuNPs treated with (1)AuCl form 1-AuNP.⁴⁵ High resolution XPS spectra of this system illustrate the presence of an N 1s peak at 400.5 eV, in excellent agreement with previous studies for ligand **1** immobilized onto Au surfaces (Fig. 2, top).^{19,45} We then compared these results to AuNPs treated with (1)AgBr, revealing not only the N 1s peak at 400.4 eV, but also a characteristic signal for Ag 3d_{5/2} in the XPS spectra (Fig. 2, bottom). The Ag 3d_{5/2} peak appears at 367.8 eV, within the range observed for Ag⁰ in Ag/Au nanoparticle alloys.^{61,62} ICP-OES measurements illustrate that, within experimental uncertainty, all ($102 \pm 14\%$) of the silver added to the sample is incorporated into the AuNPs after treatment with (1)AgCl (Table S5†). While these data illustrate that chemisorbed carbenes form on AuNPs treated with (1)AgBr, XPS cannot distinguish between carbenes bound to different coinage metals.⁶³ Moreover, STM studies indicate that carbenes may bind through Ag, Cu, or Au adatoms.⁴²

LDI-MS characterization of a control sample of gold nanoparticles with acetonitrile and no NHCs contains predominately Au₂⁺ and Au₃⁺ clusters at 394 *m/z* and 590 *m/z*, respectively (Fig. 3, top). Treatment of citrate-capped AuNPs with (1) AuCl gives predominantly [(1)₂Au]⁺ at 601 *m/z* (Fig. 3, middle).⁵² Most notably, treatment of AuNPs with (1)AgBr gives predominantly [(1)₂Au]⁺ at 601 *m/z* (Fig. 3, bottom). Notably, no NHC-silver clusters appear in the mass spectra,

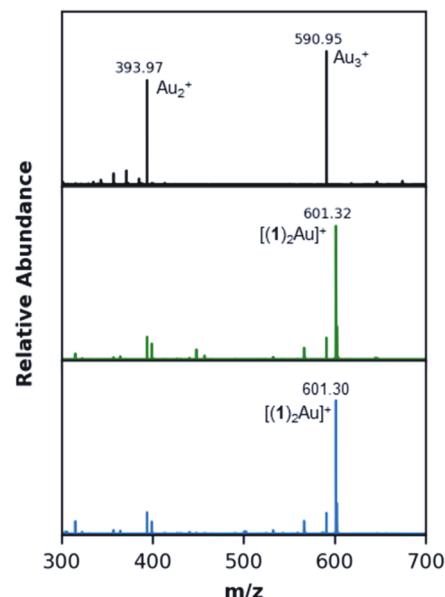


Fig. 3 LDI-MS spectra of AuNPs deposited on an LDI target plate from a water/acetonitrile solution. Citrate-capped AuNPs before exposure to NHC complexes (top, black). NHC-AuNPs after exposure to (1)AuCl (middle, green) or (1)AgBr (bottom, blue). In both spectra the predominant ion is [(1)₂Au]⁺ at 601 *m/z*, indicating both reactions yield the same surface structure, *i.e.* the ligand attaches to the surface via the Au–C bond.

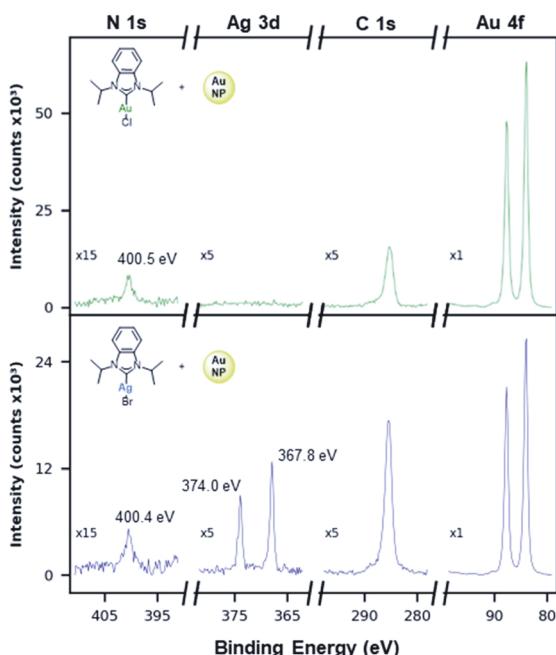


Fig. 2 XPS characterization of citrate-capped AuNPs treated with (1) AuCl (green) or (1)AgBr (blue) in the N 1s, Ag 3d, C 1s, and Au 4f regions. The N 1s peak is in excellent agreement with previous studies indicating a chemisorbed carbene at \sim 400.5 eV. When citrate-capped AuNPs are mixed with (1)AgBr, a strong peak corresponding to Ag 3d_{5/2} is observed at 367.8 eV illustrating the presence of silver at the AuNP surface.

which suggests that the Au-bound NHC is the dominant surface species, as opposed to the Ag-bound NHC. These LDI-MS results, in concert with XPS data, demonstrates that exposure of citrate-capped AuNPs to (1)AgBr results in a transmetalation reaction.

Performing SERS on the AuNPs after treatment with (1)AuCl or (1)AgBr furthermore reveals spectra that are quantitatively the same (Fig. 4 and S3†). If transmetalation provides monolayers of different surface orientation, the SERS spectra would reflect these changes. Therefore, the similarity of the SERS spectra suggests that treatment with Ag or Au NHC complexes produces surface bound ligands with indistinguishable surface orientation. These data are in excellent agreement with previous SERS studies of ligand **1** chemisorbed to AuNPs and bound in an upright configuration, showing that each metal complex leads to the same SAM.^{45,55}

We employed density-functional theory (DFT) simulations to compare the bonding energy (BE) and dispersion energy (DE) of carbenes bound through either a gold or silver adatom (Fig. 5). BE calculations were computed using an Au₅₇ cluster with an Ag or Au adatom to illustrate the two possible binding motifs. Ligand **1** has two conformations of the isopropyl side groups: the methyl groups of the isopropyl substituent can point toward or away from the surface.⁵⁵ Only the “away from” conformation is discussed here as both conformations lead to similar relative energies (Table S3†). The BEs illustrate that the gold adatom binding motif is >10 kcal mol⁻¹ lower energy than the silver adatom binding motif (Fig. 5), in agreement

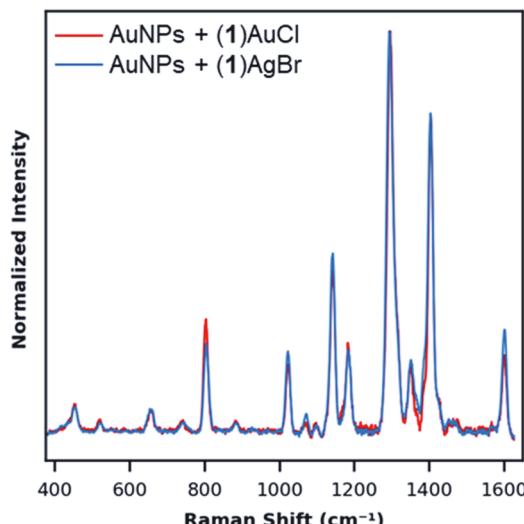


Fig. 4 SERS spectra of citrate-capped AuNPs exposed to either (1)AuCl (red) or (1)AgBr (blue). The spectra are indistinguishable within their uncertainties (confidence intervals provided in ESI†) suggesting that the chemisorbed ligands adopt the same orientation regardless of the starting material employed. Spectra are normalized to the band maximum at 1296 cm^{-1} .

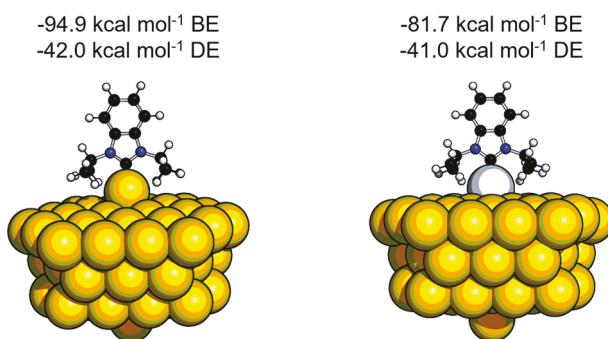


Fig. 5 Bonding energies (BE) and dispersion energies (DE) of ligand 1 bound to Au_{58} (left) or AgAu_{57} (right) clusters calculated with DFT illustrates the significantly lower BE of the gold adatom binding motif $>10 \text{ kcal mol}^{-1}$ and comparable DE.

with trends observed for transmetalation reactions in homogeneous organometallic chemistry ($\text{Au} > \text{Ag}$).³⁰ Although the DE is a significant part of the BE (40–50%), it is similar for both Au and Ag adatom systems as it is largely determined by the interactions with the underlying Au surface. The significantly lower BE of the Au adatom system is in excellent agreement with the observed transmetalation starting from (1)AgBr complex onto AuNPs.

To explore how different carbene structures react with the gold surface, we repeat the above procedures with an imidazole-based NHC (2) and its respective Au, Ag and Cu complexes. XPS spectra of AuNP surfaces after treatment with the NHC complexes (Fig. 6) reveals the N 1s peak in each spectra is at the energy expected for a chemisorbed carbene ($\sim 400 \text{ eV}$),¹⁹

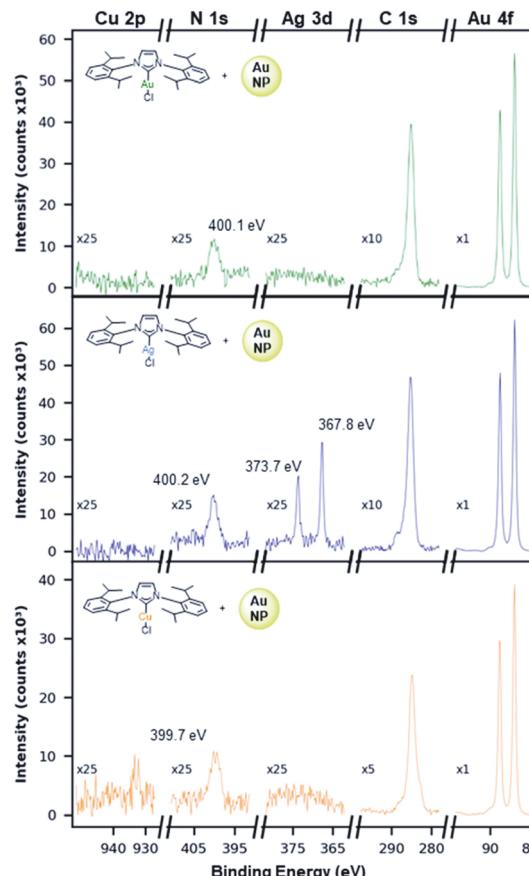


Fig. 6 XPS spectra of citrate-capped AuNPs after treatment with (2)AuCl (green, top), (2)AgCl (blue, middle), and (2)CuCl (orange, bottom). In all cases the N 1s peak is consistent with ligand 2 chemisorbed to the metal surface. The strength of the Ag 3d peaks observed for AuNPs reacted with (2)AgCl contrasts with the significantly weaker Cu 2p signal observed for AuNPs reacted with (2)CuCl.

indicating that 2 is chemically bound to the gold surface in all three cases (Fig. 6). As observed for ligand 1, the $\text{Ag 3d}_{5/2}$ peak appears at 367.8 eV (ref. 61 and 62) for AuNPs reacted with (2)AgCl. However, in the case of the reaction with (2)CuCl we observe a small $\text{Cu 2p}_{3/2}$ peak was detected. Using ICP-OES we find that $31 \pm 5\%$ of the Ag atoms from (2)AgCl alloy with the AuNPs whereas only $10 \pm 1\%$ of the Cu atoms from (2)CuCl alloy with the AuNPs (Table S7†). These measurements illustrate that Cu does not alloy significantly with the AuNP upon transfer. Instead, the reaction of (2)CuCl with AuNPs yields a soluble copper salt which is removed during centrifugation. In summary, all three reactions yield a chemisorbed carbene on the AuNP surface, but they exhibit different degrees of alloying depending on the identity of the metal precursor and ligand.

LDI-MS analysis of the Dipp-NHC nanoparticle systems reveals more complex mass spectra than AuNPs with ligand 1 (Fig. 3), due to the presence of sodium chloride adducts and cyanide adducts (Fig. S7†). The LDI-MS of a citrate-capped AuNP control sample (Fig. 7) revealed predominately Au_3^+ ions at 590 m/z and a very low background in the region of interest

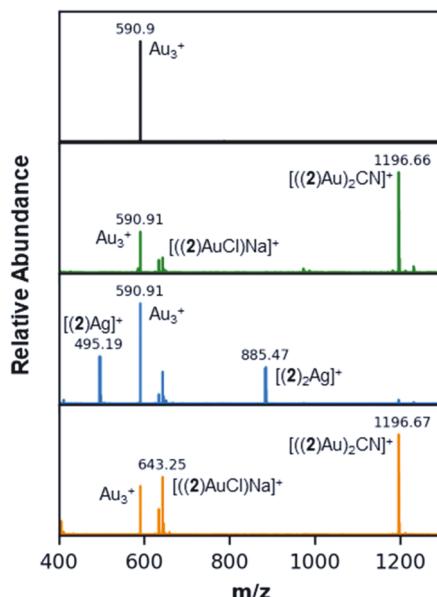


Fig. 7 LDI-MS spectra of AuNPs deposited on an LDI target plate from a water/acetonitrile solution. Citrate-capped AuNPs before exposure to NHC complexes (black). AuNPs treated with (2)AuCl (green), (2)AgCl (blue) or (2)CuCl (orange). AuNPs treated with Au or Cu complexes yield similar spectra. Conversely, AuNPs treated with Ag complexes predominantly form $[(2)Ag]^\pm$ and $[(2)_2Ag]^\pm$ ions indicating retention of Ag–C bond at the surface.

(400–1250 m/z). The mass spectra from AuNPs reacted with (2) AuCl displays ions at 643 m/z and 1196 m/z corresponding to $[(2)AuCl]Na^+$ and $[(2)Au]_2CN^+$, respectively. In contrast, AuNPs reacted with (2)AgCl yields ions at 495 m/z and 885 m/z arising from $[(2)Ag]^\pm$ and $[(2)_2Ag]^\pm$, respectively. In contrast to AuNPs treated with (1)AgBr, AuNPs treated with (2)AgCl adopt a distinctly different binding motif: (2)AgCl does not transmetalate and ligand 2 binds to the gold surface through the Ag adatom. Conversely, AuNPs reacted with (2)CuCl give exactly the same spectra as AuNPs reacted with (2)AuCl, suggesting that treatment of AuNPs with either (2)AuCl or (2)CuCl forms the same surface species (Fig. 7). Therefore, reaction with (2) CuCl can be viewed as a partial transmetalation reaction, whereas, (2)AgCl does not transmetalate and Ag is retained at the surface.

SERS spectra obtained from AuNPs treated with Au, Ag or Cu complexes of 2 were also acquired. Similar to the ligand 1 systems, the spectra are indistinguishable within their uncertainties, suggesting that the ligand surface orientation is consistent regardless of whether the NHC source is an Au, Ag or Cu complex (Fig. S4 and S5†). This conclusion is further corroborated by theoretical calculations showing the upright configuration as the most favorable regardless of the adatom (*vide infra*).

DFT calculations are employed to probe the binding of ligand 2 with a Au_{57} cluster *via* an Au, Ag or Cu adatom. The BE comparison indicates that transmetalation reactions should be favorable for both the Ag and Cu complexes (Fig. 8);

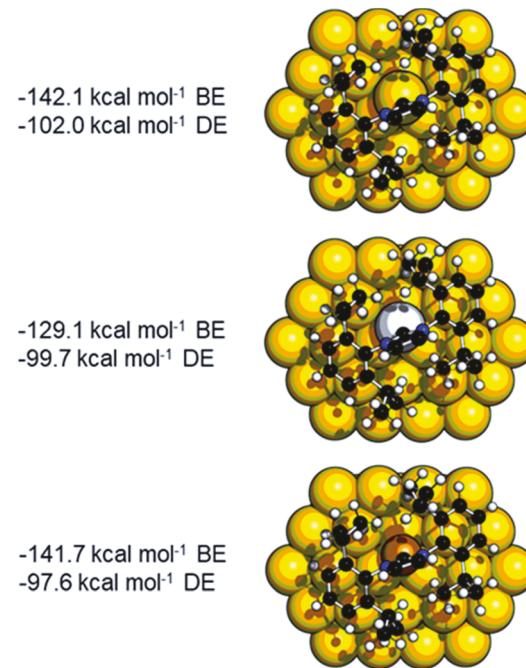


Fig. 8 Bonding energy (BE) and dispersion energy (DE) of ligand 2 bound to Au_{58} (top), $Au_{57}Ag$ (middle) or $Au_{57}Cu$ (bottom) clusters calculated with DFT. Despite the lower BE of the Au adatom configuration relative to the Ag and Cu configurations, the Dipp ligand systems are dominated by dispersion forces.

however, transmetalation was only observed starting from (2) CuCl. To explore this apparent disagreement and gain insight into reactivity differences between silver complexes of ligand 1 and 2, we computed the DE of the carbene–metal interactions. These calculations show that for ligand 2 the dispersion contribution to the BE is around 70–80%, compared to the 40–50% for ligand 1. These large differences in DE arise from the sterically bulky Dipp side groups of 2 which likely enables more significant dispersion interaction with the Au surface than the isopropyl groups of ligand 1. Therefore, the strong bonding through dispersion interactions might enable the kinetic product Ag–adatom system to form rather than the thermodynamically favorable Au–adatom system.

Glorius and Fuchs recently explored the influence of side groups on the surface mobility of carbenes in an STM study,⁶⁴ where they demonstrate that the surface mobility of ligand 2 is dramatically lower than imidazole ligands with less sterically bulky side groups.⁶⁴ These results, in concert with our DFT calculations and experiments, illustrate the differences between reactions at NHC surfaces and their analogous homogeneous organometallic reactions. For example, ligand transfer of 1⁴⁴ or 2³² from an Ag atom to an Au atom is routine in organometallic chemistry; however, here we find that only Ag complexes of ligand 1 perform ligand transfer to gold, likely due to surface specific variables (DE and surface mobility) favoring an Ag adatom motif for ligand 2. Therefore, we must conclude that the reactivity of carbene complexes with citrate-capped

gold nanoparticles relies heavily on the carbene side groups and choice of metal complex.

Conclusions

We evaluated how a common reaction in organometallic chemistry, transmetalation, provides a facile route to transfer NHC ligands to citrate-capped AuNPs *via* Ag and Cu complexes, but discovered an unexpected reaction dependence on the NHC structure and the precursor metal ion. For both Dipp-imidazole and isopropyl-benzimidazole Ag complexes, the silver metal alloyed to the AuNP during the transmetalation reaction. However, by switching from the isopropyl-benzimidazole Ag complex to the Dipp-imidazole Ag complex, the NHC does not transmetalate to the nanoparticle. Instead, an exotic NHC-Ag adatom structure is formed on the AuNP surface, which may provide an alternate route to thiol based methods for doping Ag atoms onto the AuNP surface.⁶⁵ In the case of the Dipp-NHC-Cu complex the NHC transfer process retains significant transmetalation character, but a small amount of copper is still retained at the nanoparticle surface. Our results demonstrate that detailed surface measurements must be combined with ligand design to achieve the desired reactivity and NHC surface functionality.

This work demonstrates that transmetalation is a viable route towards the creation of NHC surfaces and raises critical questions of how the rich history of homogeneous organometallic NHC chemistry may influence the burgeoning field of NHC surface chemistry. By transferring homogeneous organometallic chemistry reactions to metal surfaces, old reactions may find renewed significance.

Author contributions

N. L. D., S. L. S., T. R., C. Q. K. and W. C. B. carried out experiments and data analysis; R. C. and A. V. B. S. carried out theoretical calculations; L. J., D. M. J. and J. P. C. conceptualized the project; and N. L. D., D. M. J. and J. P. C. prepared the manuscript.

Conflicts of interest

There are no conflicts to declare.

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