Nanoscale

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Journal:	*Nanoscale*
Manuscript ID	NR-COM-01-2020-000869.R1
Article Type:	Communication
Date Submitted by the Author:	26-Feb-2020
Complete List of Authors:	Hosier, Chris; Colorado State University, Chemistry Anderson, Ian; Colorado State University, Chemistry Ackerson, Chris; Colorado State University, Chemistry

COMMUNICATION

Acetylide-for-Thiolate and Thiolate-for-Acetylide Exchange on Gold Nanoclusters

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Christopher A. Hosier, Ian D. Anderson and Christopher J. Ackerson*

Acetylide-protected gold nanoclusters represent a recently described class of nanocluster compounds that are computationally predicted to be more stable than well-studied thiolate-protected clusters. Ligand exchange of thiolates-for-acetylides on these clusters as well as the reverse reaction are so-far unknown. Such reactions can inform a practical understanding of stability and other differences between thiolate- and acetylide-protected gold clusters. Here it is shown that acetylide-for-thiolate ligand exchange is facile when using either a lithium phenylacetylide or a gold(I)-phenylacetylide complex as incoming ligand to thiolate-protected gold clusters, whereas the reaction fails when using phenylacetylene. Both partial and full exchange are possible, as is the reverse reaction. While the overall reaction resembles ligand exchange, it may be better described as a metathesis reaction. Notably, while the simple thiolate-for-acetylide exchange reaction is enthalpically unfavorable, metathesis reactions between these ligands are enthalpically favorable. Intercluster exchange is also observed between thiolate-protected and acetylide-protected clusters.

Soluble inorganic nanoclusters and nanoparticles are typically stabilized or protected by a passivating ligand shell. Ligand exchange is a fundamental reaction of such systems, and the interaction strength of ligand with metal can underlie and/or define kinetics, thermodynamics, and regiochemistry of ligand exchange. Because the ligand shell determines nanocluster or nanoparticle solubility, stability and reactivity, ligand exchange reactions can enable functionalization of metal clusters/nanoparticles for their use in bioimaging, catalysis, theranostics, and sensing applications.[1-4] Thiolate-protected gold nanoclusters have received substantial interest over the past two decades due to their ease of synthesis and overall stability.[5-7] Recent work has highlighted the propensity for rapid exchange of metal atoms and/or ligands between dissolved thiolate-protected coinage metal clusters.[8] Furthermore, thiolate-protected clusters are unstable to oxidative conditions.[9]

Whereas thiolate-protected gold clusters represent a now very well-defined class of atomically precise inorganic nanoparticles, gold nanoclusters ligated with organometallic ligands such as acetylides and N-heterocyclic carbenes have emerged only recently as alternatives that may present improved stability and/or catalytic properties.[10-12] Acetylides in particular attract interest as robust ligands for protecting gold nanoclusters. Such clusters are suggested as more stable than the widely studied thiolate-protected clusters, with calculations suggesting that acetylide-gold bonds are stronger by 6 to 52 kcal/mol than thiolate-gold bonds.[13-15] Acetylide-coated gold surfaces show more consistent conductance measurements, are less susceptible to oxidation, and maintain similar packing densities compared to thiolate-coated surfaces.[16] Furthermore, higher catalytic conversion efficiencies have been reported when using acetylide ligands on a gold nanocluster, and the ability for acetylides to adopt different binding motifs on cluster surfaces can potentially produce new properties in previously studied clusters.[10,17]

Synthesis of acetylide-protected clusters proceeds most often by reduction of Au(I)-acetylide complexes.[18-20] Only two examples of post-synthetic acetylide exchange on gold nanoparticles are so-far reported: Tsukuda and co-workers demonstrated that N-vinylpyrrolidone-protected clusters undergo exchange with free phenylacetylene to afford a series of homoleptic phenylacetylide-protected clusters, and Konishi later showed acetylide-for-chloride exchange by using free phenylacetylene in the presence of a base.[21,22] Examples of acetylide-for-thiolate exchange reactions and/or the reverse reaction are so-far unreported.

Herein, we reveal acetylide-for-thiolate and thiolate-for-acetylide exchange on gold nanoclusters for the first time. We provide insight into the nature of exchange by observing success or failure of exchange with different acetylide derivatives and/or reaction conditions (Fig. 1). Overall, we find that forward exchange, reverse exchange, and interparticle ligand exchange are all facile reactions provided incoming ligands are suitable.

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States. Email: ackerson@colostate.edu

†Electronic Supplementary Information (ESI) available: Synthetic Details and Supplemental Figures. See DOI: 10.1039/x0xx00000x

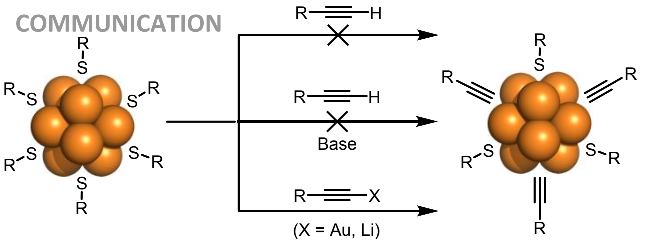


Fig. 1 Current reaction scheme.

The most straightforward reaction attempted—exchange between thiolate-protected clusters (e.g. $Au_{25}(SR)_{18}$ in our studies) and soluble phenylacetylene—resulted in no reaction. The reaction failed in all tested incoming ligand concentrations (up to a 100-fold molar excess of phenylacetylene), temperatures (up to 60 °C attempted), and in the presence of an exogenous base (Fig. S2-S5). However, when phenylacetylene is introduced as a gold(I) or lithium phenylacetylide complex, exchange is successful in mild conditions. Fig. 2 shows MALDI-MS spectra of phenylacetylide (PA) for phenylethanethiolate (PET) exchange after 30 minutes when gold(I)-phenylacetylide is added in 1 or 10 equivalents to solutions containing $Au_{25}(PET)_{18}$. The distribution of exchange products increases with time and eventually results in a Gaussian-like distribution commonly observed in partial exchange reactions (Fig. S6).[8] To determine the extent of exchange that can be obtained, we reacted 100 equivalents of gold(I)-acetylide with $Au_{25}(PET)_{18}$ for 18 hours. While MALDI-MS shows a large distribution of products, we observe a peak at m/z 6744.34, corresponding closely to the calculated mass of 6744.47 for $Au_{25}(PA)_{18}$ (Fig. S7).

This suggests an exchange-based synthetic route to a recently reported homoleptic acetylide-protected gold cluster, $Au_{25}(CCAr)_{18}$, which was synthesized by reduction of gold(I)-acetylide precursors.[17] We have not attempted isolation of this specific compound at this time due to the apparent large number of competing exchange products.

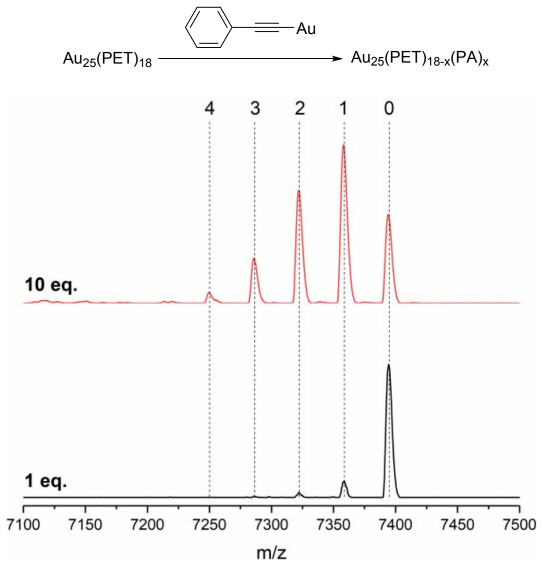


Fig. 2 Positive ion MALDI mass spectra of the resulting $Au_{25}(PET)_{18\text{-}x}(PA)_x$ from reacting $Au_{25}(PET)_{18}$ with 1 and 10 equivalents of gold(I)-phenylacetylide.

Our results differ somewhat from a recent report by Wang where addition of a gold(I)-phenylacetylide derivative to bis-phosphine-protected $Au_9(BINAP)_4$ resulted not in exchange but in addition of the gold(I)-phenylacetylide complex to the cluster.[23] Differences in the nature of the initial ligand layer (i.e.-monodentate ligands v. bidentate ligands, phosphines v. thiolates) between the clusters in the current reaction and the cluster in the reported reaction may account for this difference in reactivity. We observe that lithium phenylacetylide, like gold(I)-phenylacetylide, can ligand-exchange onto $Au_{25}(PET)_{18}$. Exchange of lithium phenylacetylide onto $Au_{25}(PET)_{18}$ in mild conditions is shown in Fig. S8. Notably, only the acetylide and thiolate ligands exchange in this case as no masses corresponding to lithium-for-gold exchange were observed. Since gold(I)-acetylide and lithium(I)-acetylide bond strengths are expected to be similar (and small), the success of lithium(I)-acetylide exchange suggests that both Li^+ and Au^+ may be spectators in the exchange reaction and not active participants. Overall, this implies an important mechanistic insight – that the overall exchange is a metathesis reaction – which we describe below.

We also examined the reverse reaction, specifically the exchange of thiolates onto $Au_{25}(CCAr)_{18}$, where CCAr = 3,5-bis(trifluoromethyl)phenylacetylide (Fig. 3). The crystal structure of $Au_{25}(CCAr)_{18}$ has been recently reported as the acetylide-protected analogue to $Au_{25}(SR)_{18}$.[27] Synthesis of this cluster is found in the supporting information. MALDI-MS reveals exchange after simple mixing of thiols at room temperature with the $Au_{25}(CCAr)_{18}$ cluster, even at a short time scale. This result contrasts a previous report by Zheng and co-workers where addition of free thiol to the $Au_{24}Ag_{20}(2\text{-}SPy)_4(PA)_{20}Cl_2$ cluster results only in thiolate-for-halide exchange and not in thiolate-for-acetylide exchange.[24] The difference between these results and the results reported herein may be attributed to differences in metal doping (single

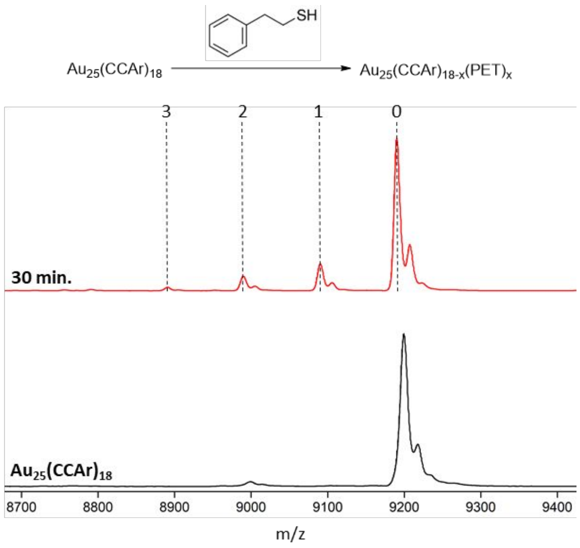


Fig. 3 Negative ion MALDI mass spectra of the reaction between $Au_{25}(CCAr)_{18}$ and 1 equivalent of PET. The peak labelled 0 corresponds to the parent peak of $Au_{25}(CCAr)_{18}$, while those labelled 1-3 correspond to the value x in the formula $Au_{25}(CCAr)_{18\text{-}x}(PET)_x$. The average distance between said peaks is m/z 100.03 (calc. CCAr-PET = 99.9). Smaller peaks correspond to fluorine adducts of the adjacent peak.

metal versus mixed), ligand identities (homoleptic versus mixed ligand layers, aliphatic thiolate versus aromatic thiolate), or acetylide binding motifs (μ_2 versus μ_3).

Recent works by Pradeep and Bürgi have demonstrated that thiolate-protected gold clusters readily undergo intercluster exchange of ligands.[8,25] As such, we attempted to determine if intercluster exchange occurs between thiolate- and acetylide-protected clusters. Multiple intercluster ligand exchange products derived from $Au_{25}(PET)_{18}$ and $Au_{44}(PA)_{28}$ are observed within five minutes of mixing, indicating that thiolate-for-acetylide intercluster exchange is a similarly facile process like thiolate-for-thiolate intercluster exchange (Fig. 4).

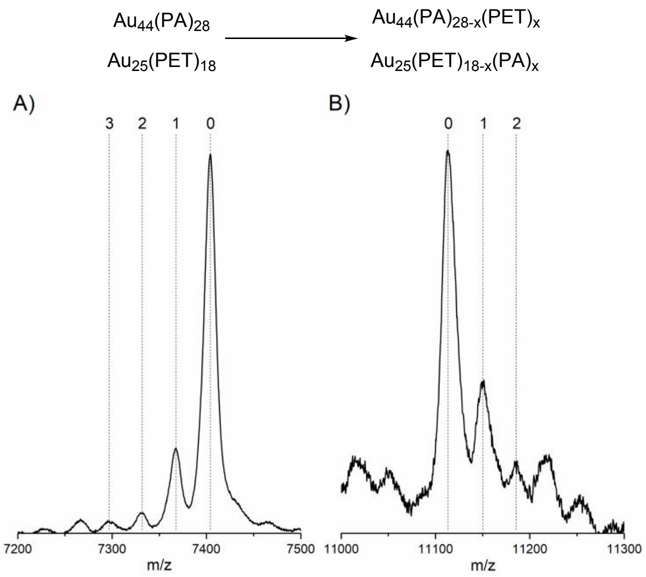


Fig. 4 Positive ion MALDI mass spectra of the product clusters A) $Au_{25}(PET)_{18\text{-}x}(PA)_x$ and B) $Au_{44}(PA)_{28\text{-}x}(PET)_x$ after mixing $Au_{25}(PET)_{18}$ with $Au_{44}(PA)_{28}$ for 5 minutes, where x is equal to the number of ligands exchanged.

Combined, the failure of phenylacetylene-for-thiolate exchange with the success of thiolate-for-acetylide, lithium phenylacetylide-for-thiolate and gold(I)-phenylacetylide-for-thiolate exchanges suggest that the net exchange reaction may be described as a metathesis reaction involving cluster, thiolate, acetylide, and hydrogen when present. Three versions of this metathesis reaction are shown in Fig. 5. Net bond enthalpies for each metathesis reaction can help rationalize observed reaction successes and failures. Given that reported bond energies suggest that the carbon-hydrogen bond in an alkyne is 46 kcal/mol stronger than the sulfur-hydrogen bond and that previous computational results suggest the gold cluster-alkynyl bond is 6–20 kcal/mol stronger than the gold-thiolate bond, the enthalpic favorability of the overall metathesis reaction accounting for thiol-for-acetylide exchange is between -26 and -40 kcal/mol.[15,16,26] The reverse reaction of phenylacetylene exchanging onto thiolate-protected clusters would be enthalpically unfavorable by the same value (i.e. between +26 and +40 kcal/mol) and thus should not occur. The predicted favorability for these reactions matches with our experimental results.

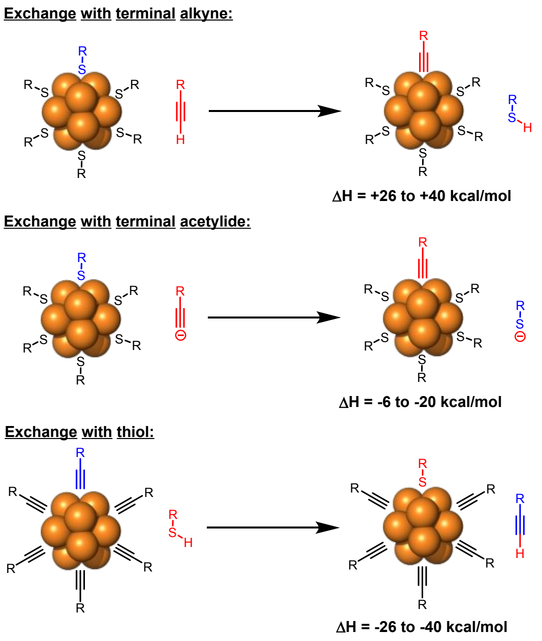


Fig. 5 Balanced reactions and net change in bond energies for exchange reactions with terminal alkynes, terminal acetylides, and thiols.

The bond enthalpies of lithium-acetylide and gold(I)-acetylide are presently unknown. As such, we are unable to estimate the enthalpies of the overall metathesis reactions involving gold(I)-phenylacetylide and lithium phenylacetylide. However, the success of the metathesis reaction with thiolate-protected clusters when these are used as incoming ligands suggests that the differences between lithium-acetylide/lithium-sulfur and gold(I)-acetylide/gold(I)-sulfur bonds are much smaller than the enthalpy difference between hydrogen-alkyne/hydrogen-sulfur bonds.

Conclusions

We report herein the apparent criteria for successful incorporation of acetylides into thiolate-protected clusters. The present work suggests that acetylide-protected clusters are more susceptible to exchange with thiolates than previously assumed and/or computationally predicted, and that intercluster exchange of thiolate-for-acetylide ligands is also spontaneous at room temperature. These results may be rationalized by considering reactions as metathesis reactions rather than traditional cluster ligand exchange reactions.

Conflicts of interest

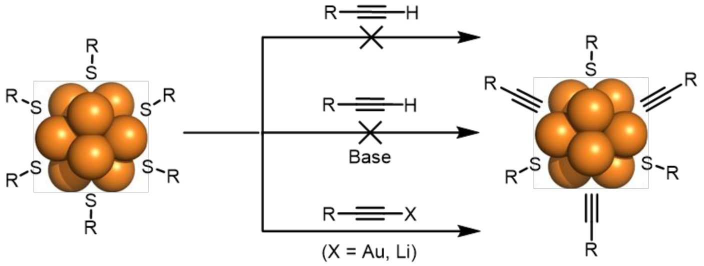
There are no conflicts to declare.

Acknowledgements

This work was supported by NSF career grant CHE-1455099.

Notes and references

1 P.R. Nimmala, S. Theivendran, G. Barcaro, L. Sementa, C. Kumara, V.R. Jupally, E. Apra, M. Stener, A. Fortunelli, A. Dass *J. Phys. Chem. Lett.* **2015**, *6*, 2134-2139.
2 A. Corma, H. Garcia *Chem. Soc. Rev.* **2008**, *37*, 2096-2126.
3 A.J. Mieszawska, ,W.J.M. Mulder, Z.A. Fayad, D.P. Cormode, *Mol. Pharmaceutics* **2013**, *10*, 831-847.
4 K. Saha, S.S. Agasti, C. Kim, X. Li, V.M. Rotello *Chem. Rev.* **2012**, *112*, 2739-2779.
5 R. Jin, B.Z. Chenjie, M. Zhou, Y. Chen *Chem. Rev.* **2016**, *18*, 10346-10413.
6 N. Goswami, Q. Yao, T. Chen, J. Xie *Coord. Chem. Rev.* **2016**, *329*, 1-15.
7 X. Kang, H. Chong, M. Zhu *Nanoscale* **2018**, *23*, 10758-10834.
8 K.R. Krishnadas, A. Baksi, A. Ghosh, G. Natarajan, A. Sorn, T. Pradeep *Acc. Chem. Res.* **2017**, *50*, 1988-1996.
9 C.B. Collins, M.A. Tofanelli, M.F. Crook, B.D. Phillips, C.J. Ackerson *RSC Adv.* **2017**, *7*, 45061-45065.
10 X.-K. Wan, J.-Q. Wang, Z.-A. Nan, Q.-M. Wang *Sci. Adv.* **2017**, *10*, e1701823.
11 M.R. Narouz, K.M. Osten, P.J. Unsworth, R.M.W. Man, K. Salorinne, S. Takano, R. Tomihara, S. Kaappa, S. Malola, C.-T. Dinh, J.D. Padmos, K. Ayoo, P.J. Garrett, M. Nambo, J.H. Horton, E.H. Sargent, H. Häkkinen, T. Tsukuda, C.M. Crudden *Nature Chemistry* **2019**, *11*, 419-425.
12 H. Shen, G. Deng, S. Kaappa, T. Tan, Y.-Z. Han, S. Malola, S.-C. Lin, B.K. Teo, H. Häkkinen, N. Zheng *Angew. Chem. Int Ed.* 10.1002/anie.201908983.
13 Q. Tang, D.-e. Jiang *J. Phys. Chem C* **2015**, *119*, 10804-10810.
14 Q. Tang, D.-e. Jiang *Chem. Mater.* **2017**, *29*, 6908-6915.
15 F. Bejarano, I.J. Olavarria-Contreras, A. Droghetti, I. Runnger, A. Rudnev, D. Gutiérrez, M. Mas-Torrent, J. Veciana, H.S.J. van der Zant, C. Rovira, E. Burzuri, N. Crivillers *J. Am. Chem. Soc.* **2018**, *140*, 1691-1696.
16 T. Zaba, A. Noworolska, C.M. Bowers, B. Breiten, G.M. Whitesides, P. Cyganik *J. Am. Chem. Soc.* **2014**, *136*, 11918-11921.
17 J.-J. Li, Z.-J. Guan, Q.-M. Wang *Angew. Chem. Int. Ed.* **2017**, *56*, 11494-11497.
18 X.-K. Wan, Q. Tang, S.-F. Yuan, D-.e. Jiang, Q.-M. Wang *J. Am. Chem. Soc.* **2015**, *137*, 652-655.
19 X.-K. Wan, Z.-J. Guan, Q.-M. Wang *Angew. Chem. Int. Ed* **2017**, *56*, 11494-11497.
20 Z. Lei, J.-J. Li, X.-K. Wang, W.-H. Zhang, Q.-M. Wang *Angew. Chem. Int. Ed.* **2018**, *130*, 8775.
21 P. Maity, H. Tsunoyama, M. Yamamuchi, S. Xie, T. Tsukuda *J. Am. Chem. Soc.* **2011**, *133*, 20123-20125.
22 M. Sugiuchi, Y. Shichibu, T. Nakanishi, T. Hasegawa, K. Konishi *Chem. Comm.* **2015***, 51*, 13519-13522.
23 J.-Q. Wang, Z.-J. Guan, W.-D. Liu, Y. Yang, Q.-M. Wang *J. Am. Chem. Soc.* **2019**, *141*, 2384-2390.
24 Y. Wang, H. Su, C. Xu, G. Li, L. Gell, S. Lin, Z. Tang, H. Häkkinen, N. Zheng *J. Am. Chem. Soc.* **2015**, *137*, 4324-4327.
25 G. Salassa, A. Sels, F. Mancin, T. Bürgi *ACS Nano* **2017**, *11*, 12609-12614.
26 Y.-R. Luo, J.-P. Cheng in *CRC Handbook of Chemistry and Physics, 100th Edition* (Ed: J.R. Rumble), CRC Press/Taylor & Francis, Boca Raton, **2019**, pp. 9-73-9-104.
27 Li, J.-J.; Guan, Z.-J.; Lei, Z.; Hu, F.; Wang, Q.-M. *Angew. Chem. Int. Ed.* **2019**, *58*, 1083-1087.



New ligand-exchange reactions are reported for thiolate- and acetylide-protected gold nanoclusters, which are rationalized through bond strengths and enthalpy arguments.