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Stabilization of a New Nanocomposite Family by Reduction of Gold Nanoclusters with Electron-reservoir Complexes

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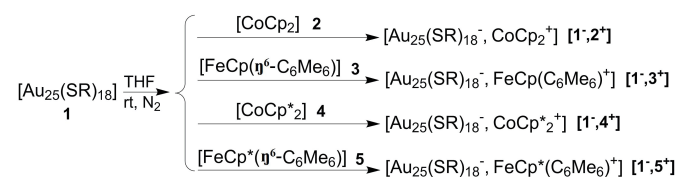
Four stable 19-electron Fe and Co sandwich electron-reservoir and three hydride reservoir complexes reduce the prototypal nanocluster $\text{Au}_{25}(\text{SR})_{18}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{Ph}$) leading to a largely increased kinetic stabilization of the anionic nanocluster form compared to previously known nanocluster anion salts; these salts represent new and robust nanocomposite anionic gold clusters with 18-electron sandwich complexes as counter cations.

Precisely defined thiolate-protected gold nanoclusters have recently attracted significant research interest because of their unique catalytic, optical, and electronic properties.¹ In this category, the spherical nanocluster $\text{Au}_{25}(\text{SR})_{18}$ ($\text{R} = (\text{CH}_2)_2\text{Ph}$), **1**,² has been the most extensively studied.¹ It is viewed as a typical “superatom”, and its neutral and anionic forms have been shown by X-ray crystal structures to contain similar cores² and are reversibly interconverted.³ Liu *et al* reported electron transfer between $[\text{Au}_{25}(\text{SR})_{18}]^- \text{TOA}^+$ ($\text{TOA}^+ = \text{N}(n\text{-C}_8\text{H}_{17})_4^+$) and $\text{TEMPO}^+ \text{BF}_4^-$, ($\text{TEMPO}^+ \text{BF}_4^- = 2,2,6,6\text{-tetramethylpiperidin-1-oxoammonium tetrafluoroborate}$),^{4a} and Chong *et al* showed that $[\text{Au}_{25}(\text{SR})_{18}]^- \text{TOA}^+$ served as electron-transfer chain catalyst⁵ for cascade reaction of 2-nitrobenzonitrile under ambient conditions.⁶ Although the nanocluster $[\text{Au}_{25}(\text{SR})_{18}]^- \text{TOA}^+$ is stable in the solid state, however, it suffers from some kinetic instability in solution, and therefore it is only stable for a few hours in CH_2Cl_2 solution under ambient conditions.^{3b} Thus, new syntheses of stable salts of $[\text{Au}_{25}(\text{SR})_{18}]^-$ in both solid state and solution are needed in order to provide access to new mixed nanocomposites and

understand the structure-property relationship at the atomic level. Therefore we have envisaged using electron-reservoir and hydride reservoir Fe and Co sandwich complexes as reducing agents of the neutral nanocluster **1** forming complex salts of the nanocluster anion **1**.

The principle of electron-reservoir complexes is that both the reduced and oxidized forms are robust and isostructural, thus readily interconverted, and that the reduced form is very electron-rich, being only oxidized at very negative redox potentials.⁷ The 19-electron complexes $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-arene})]$ ⁸ and $[\text{Co}(\eta^5\text{-C}_5\text{R}_5)_2]$ ⁹ ($\text{R} = \text{H}$ or Me) belong to this family; in particular the ring ligand permethylation (i.e. $\text{R} = \text{Me}$, arene = C_6Me_6) strengthens the bulk, robustness and reducing power of these complexes.¹⁰ The bulk of such electron-reservoir sandwich complexes not only stabilizes small nanoparticles, but also contributes to their excellent catalytic activity.¹¹ Here we are using the 19-electron complexes cobaltocene (Cp_2Co), **2**, $[\text{FeCp}(\eta^6\text{-C}_6\text{Me}_6)]$, **3**, ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), decamethyl cobaltocene, CoCp^*_2 , ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), **4** and $[\text{FeCp}^*(\eta^6\text{-C}_6\text{Me}_6)]$, **5** to stoichiometrically reduce the neutral nanocluster **1** to **1**⁻, “metallocenium”⁺ & (Scheme 1). The formal potentials of $[\text{Au}_{25}(\text{SR})_{18}]^{0/-1}$ is -0.39 V vs. ferrocene^{+0/4}, and $+0.11 \text{ V}$ vs. decamethylferrocene, FeCp^*_2 ,¹² so that **1** is exergonically reduced to **1**⁻ by these four strong organometallic reductants. The exergonicity of these reactions (Figure 1) insures fast single-electron transfer.¹³

The driving force of the electron transfer is almost exclusively governed by the respective standard redox potentials E° of the donors and acceptor (Figure 1),¹³ because the electrostatic factor in the Rehm-Weller equation is very weak due to the low charges involved and rather large sizes of the electron-



Scheme 1. Synthesis of the salts $[\text{Au}_{25}(\text{SR})_{18}]^-$, metallocenium⁺.

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Electronic Supplementary Information (ESI) available: [General data, details for the synthesis and characterizations of the gold cluster-sandwich complex nanocomposites]. See DOI: 10.1039/x0xx00000x

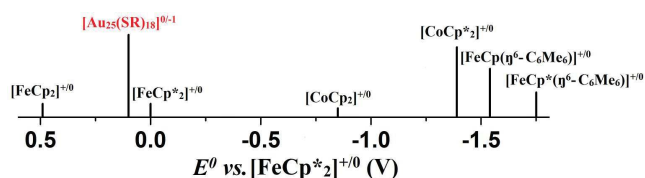


Figure 1. Standard redox potentials of Fe and Co sandwich complexes vs. $[\text{FeCp}^*_2]^{+/0}$.

transfer substrates.¹⁴ The 19-electron complexes have oxidation potentials far more negative than the reduction potential of **1**, therefore they all reduce **1** in a fast reaction. On the other hand, decamethylferrocene, FeCp^*_2 , **6**, whose redox potential is almost the same as that of **1**, does not reduce **1** at room temperature for kinetic reasons in a situation of too weak driving force. The fast reaction between **1** and 1 equiv of organometallic sandwich complex **2-5** under N_2 at rt leads to instantaneous color change from yellow brown to red brown at the equivalence point of the reaction (Figure S1).

UV-vis. absorption spectroscopy, which is a convincing physical technique to distinguish salts of diamagnetic 1^- from paramagnetic $1^{\cdot-}$,^{3b} was used before and after reduction of **1** (Figure S4). The shoulder at 630 nm in the spectrum of **1** disappears, while the characteristic absorption band of 1^- emerges at 800 nm. Simultaneously, the intensities of the 400-nm band decreases and that of the 450-nm band increases during these electron-transfer reactions.

^1H NMR was also used to characterize these four new compounds. The ^1H NMR spectra of the diamagnetic TOA^+ salt was first reproduced in CD_2Cl_2 .^{3a} The ^1H NMR spectra of the four diamagnetic salts $[1^-, \text{"metallocenium"}^+]$ present sharp peaks and are similar to that of $[1^-, \text{TOA}^+]$, except for the obvious differences for the cations (Figure S5). This contrasts with the ^1H NMR spectrum of **1** that presents broad bands due to the paramagnetism resulting from its electronic structure with an unpaired electron in the HOMO.³

The matrix assisted laser desorption ionization mass spectra (MALDI-MS) and electrospray ionization mass spectra (ESI-MS) confirm the formula of the salts $[1^-, 2^+]$, $[1^-, 3^+]$, $[1^-, 4^+]$ and $[1^-, 5^+]$. The left part of Figure 2 and Figure S6 reveal prominent peaks at $m/z = 7392.44$, 7391.91 , 7391.91 and 7392.03 Da that are assigned to the anion 1^- (cal. 7392.93 Da) of the salt $[1^-, \text{metallocenium}^+]$ (the other peaks are assigned to its fragments). On the right part of Figure 2, a peak at $m/z = 354.19$ Da is observed in positive mode of ESI-MS, showing the cation 5^+ (cal. 354.19 Da) in $[1^-, 5^+]$. In the same way, peaks at

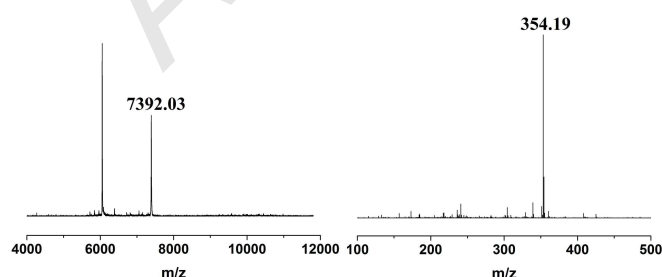


Figure 2. MALDI-MS (left) and ESI-MS (right) analysis of the $[1^-, 5^+]$.

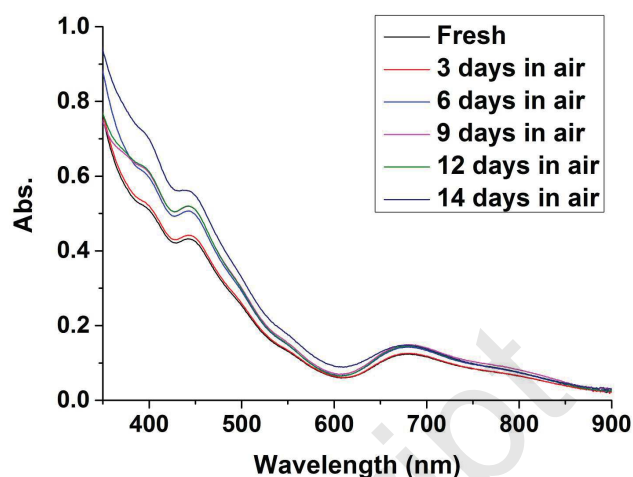


Figure 3. UV-vis. spectra of the nanocluster composite $[1^-, 5^+]$ exposed to air at rt in THF solution.

189.07, 283.20 and 329.27 Da are present in Figure S6a, S6b and S6c, related to 2^+ (cal. 189.01 Da), 3^+ (cal. 283.11 Da), 4^+ (cal. 329.17 Da) in $[1^-, 2^+]$, $[1^-, 3^+]$ and $[1^-, 4^+]$, respectively.

UV-vis. absorption spectroscopy allowed studying the counter cation effect on the stability to air of these nanocluster anion salts in THF solution under ambient conditions. The parent cobalticinium salt $[1^-, 2^+]$ was stable in air in THF for 2 days, and the iron sandwich salt $[1^-, 3^+]$, that possess 6 methyl groups on the benzene ring, exhibited the same aerobic stability (Figure S7). This 2-day stabilization is a great progress compared to the salt $[1^-, \text{TOA}^+]$ that is stable only for a few hours at rt. However, when methyl groups are present on both ligand rings, i.e. in the cations 4^+ of $[1^-, 4^+]$ (Figure S8) and 5^+ of $[1^-, 5^+]$ (Figure 3), these salts both resisted to aerobic oxidation by O_2 from air for 14 days at rt in THF solution.

The similarity between the aerobic stability periods in solution of $[1^-, 2^+]$ and $[1^-, 3^+]$ that have in common a Cp ligand, and a large size difference of the other ligand (Cp in **2** and C_6Me_6 in **3**) is remarkable. The permethylation of only one ring in 3^+ in which the six methyl groups introduce a large additional bulk on one side of the sandwich does not bring about any aerobic stability advantage compared to cobalticinium, 2^+ . In addition the dichotomy between the aerobic stability times of the two sub-families (2 days for $[1^-, 2^+]$ and $[1^-, 3^+]$ vs. 14 days for $[1^-, 4^+]$ and $[1^-, 5^+]$) shows a key point for strong aerobic stability increase. These features indicate that the smaller Cp ligand is facing the Au_{25} cluster anion in the two former salts (Figures 4a vs. 4b), whereas both ring permethylations force one of the two permethylated Cp^* ligands to face the Au cluster in the two latter complexes (Figure 4c). This trend takes into account the large aerobic stability increase to 14 days for these two latter salts. It is the bulk of both sandwich ligands that protects the anionic Au_{25}^- core. On the other hand the bulk of only one sandwich ligand does not play a decisive role in the Au cluster protection, because it does not directly face the Au cluster anion.

This nanocluster composites $[1^-, 4^+]$ and $[1^-, 5^+]$ are also stable in air for more than half a year in the solid state under ambient

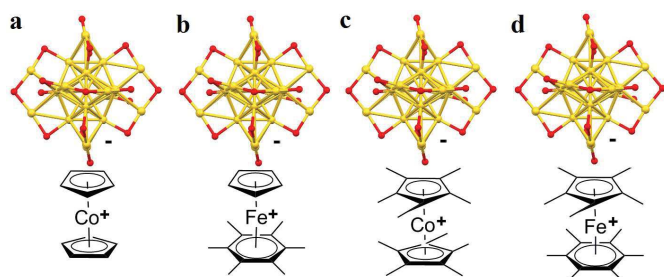


Figure 4. Proposed stabilization mode of the anion 1^- in the salts a, $[1^-, 2^+]$, b, $[1^-, 3^+]$, c, $[1^-, 4^+]$ and d, $[1^-, 5^+]$.

conditions, which surpasses the stability of $[1^-, \text{TOA}^+]$. By comparison, $[1^-, \text{Na}^+]$, synthesized by NaBH_4 reduction of **1**, is oxidized by air within a few minutes to **1** in THF solution (Figure S9).

Finally we have also examined the electron-transfer properties to **1** of the 18-electron complexes $[\text{CoCp}(\eta^4\text{-C}_5\text{H}_6)]$, **7**, $[\text{FeCp}(\eta^5\text{-C}_6\text{Me}_6\text{H})]$, **8** and $[\text{CoCp}^*(\eta^4\text{-C}_5\text{Me}_5\text{H})]$, **9** (Figure 5) that are hydride reservoirs, i.e. good reductants and reversibly interconverted by hydride transfer from the cations 2^+ , 3^+ and 4^+ respectively.¹⁵ For instance reaction of 2^+PF_6^- with NaBH_4 is known to yield **7** via a single-electron transfer pathway via **2**,¹⁶ but electron-transfer reactions of **7** yielding a salt of 2^+ are not known. The complexes **7**, **8** and **9** indeed rapidly react with **1** to form exactly the same nanocomposite salts $[1^-, 2^+]$, $[1^-, 3^+]$ and $[1^-, 4^+]$, respectively, as those obtained by reactions of **2**, **3** and **4** with **1**, as shown by UV-vis. and ^1H NMR spectroscopies and mass spectrometry (Figure S10 and S11).

The hydride reservoir complexes **7**, **8** and **9** have oxidation potentials (resp. -0.35 V, 0.04 V and -0.89 V vs. $\text{Cp}^*\text{Fe}^{+/0}$) that are less cathodic than those of the related 19-electron complexes **2**, **3**, and **4**, respectively, but about the same or more cathodic than the standard reduction potential of **1** (Figure 1). Their reactions with **1** are also driven by the irreversibility of the redox reactions, which adds to the

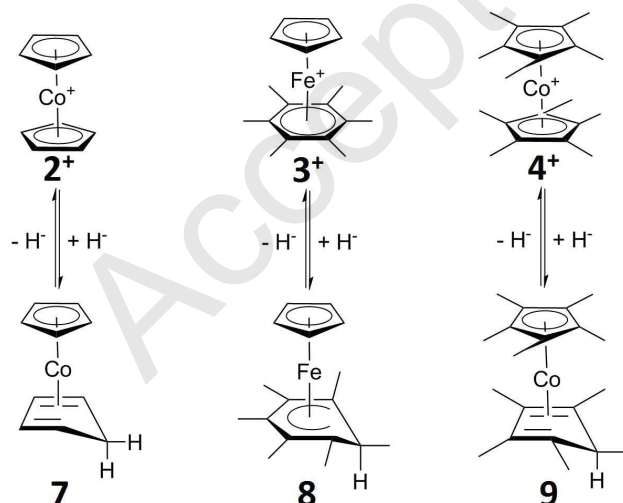


Figure 5. Three stable hydride-reservoir sandwich complexes. Their syntheses involve reactions of the organometallic cations with NaBH_4 . Hydride abstraction from the neutral complexes yielding the cations is usually conducted with a Ph_3C^+ salt.¹⁵

exergonicity to provoke fast electron transfer to **1**. For instance, 8^{15c} has the same redox potential as decamethylferrocene that does not react with **1**. The mechanism of these latter reactions is either single electron transfer to **1** followed by hydrogen atom loss or direct hydride transfer to **1** followed by hydrogen atom loss. The preserved identity of the gold cluster ligand shell disclosed by mass spectrometry discards hydride substitution of a thiolate ligand, favoring the former hypothesis. The advantages of the use of **7**, **8** and **9** over **2**, **3**, and **4** is that their synthesis is somewhat easier by reaction of the salts of the cations **2**, **3** and **4** with NaBH_4 , and **7** and **8** benefit from stability in air at rt.

In conclusion a new method of synthesis of nanocluster anions has been developed involving a strategy that uses the reduced form of electron-reservoir and hydride reservoir complexes. In this situation, the hydride reservoir complexes behave as electron-transfer reagents as the electron-reservoir complexes. Their hydride transfer properties will be illustrated later in other processes. The flexibility of this method includes the choice of the metal and the ligand bulk of the reducing agent, allowing comparison of the aerobic stabilities provided depending on the geometrical electron-reservoir parameters. The aerobic stability studies conducted by UV-vis. spectroscopy show that the best protection against the kinetic instability in air is brought about by 4^+ or 5^+ involving the largest bulk protection by permethylated Cp^* rings near the nanocluster surface. This strategy illustrates some of the applications of the concepts of electron reservoir and hydride reservoir complexes. It could be generalized to the synthesis and stabilization of most cluster anions that present reversibly interconverted redox states, affording structure-reactivity relationship studies towards catalysis, optics and molecular electronic applications.

Conflicts of interest

The authors declare no competing financial interest.

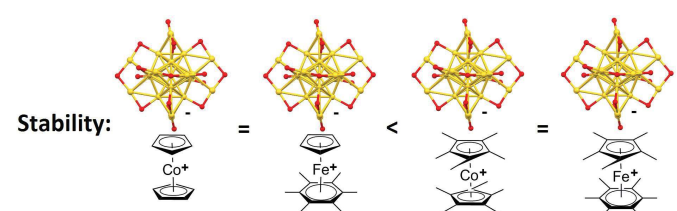
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* The significance of “metallocenium” is extended here to the monocationic Fe and Co sandwich complexes involved in this study.

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TOC:



The aerobic stabilities of four new Au₂₅ nanocluster-metal sandwich composites are provided by and related to the metal-sandwich ring sizes.