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Silver Nanocluster Redox-Couple-Promoted Nonclassical Electron Transfer: An Efficient Electrochemical Wolff Rearrangement of α-Diazoketones

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Dedicated to Professor G. S. Sudrik

Abstract: In this work we report the unique electrocatalytic role of benzoic acid protected silver nanoclusters (Ag_n, mean core diameter 2.5 nm) in the Wolff rearrangement (Scheme 1) of α-diazoketones. More specifically, the presence of a Ag_n^0/Ag_n^+ redox couple facilitates a nonclassical electron-transfer process, involving chemical reaction(s) interposed between two electron-transfer steps occurring in opposite directions. Consequently, the net electron transfer between the electron mediator (Ag_n) and α-diazoketone is zero. In-situ UV-visible studies using pyridine as a nucleophilic probe indicate the participation of α-ketocarbene/ketene as important reaction intermediates. Controlled potential coulometry of α-diazoketones using Ag_n as the anode results in the formation of Wolff rearranged carboxylic acids in excellent yield, without sacrificing the electrocatalyst.

Keywords: electrocatalysis · electrochemistry · electron transfer · ketocarbenes · silver nanoclusters

α-Carbonyl carbenes are a versatile class of reaction intermediates with boundless synthetic utility.[1,2] The central route to the synthesis of these intermediates involves α-elimination of nitrogen from α-diazocarbonyl compounds using transition-metal catalysts, like copper powder, copper(II) chelates, rhodium(II) complexes, and silver(I) salts. Our group[3] has recently shown that silver nanoclusters (Ag_n) catalyze the Wolff rearrangement[4,5] of α-diazoketones involving α-ketocarbene intermediates; it was previously thought that silver(I) ions were responsible for this catalysis.[6] Attempts to generate the α-ketocarbene intermediates by electrolysis[7,8] of α-diazocarbonyl compounds using conventional electrodes, like platinum, glassy carbon, and mercury, reveal that the removal of an electron (oxidation) or the addition of an electron (reduction) triggers the α-elimination of dinitrogen, leading to the formation of a carbene radical cation[9–11] (CRC) or a carbene radical anion[12] (CRA), respectively. A novel attempt by Jones[13] to generate α-ketocarbene intermediates by removing an electron from α-diazoketone using the triarylamine radical cation also failed to yield the specific products from these intermediates; this is perhaps most likely due to the lack of back electron transfer. Surprisingly, this could be circumvented by the use of a redox electrocatalyst that offers the unprecedented possibility of simultaneously removing one electron and providing its back-donation, following the loss of dinitrogen or vice-versa. In this way the production of α-ketocarbene intermediates from α-diazoketone could be realised. Consequently, the formation of these reaction intermediates can be confirmed either spectroscopically,[14–16] or chemically from their characteristic reactions, like the *Z*-conformation specific[17,18] Wolff rearrangement, which involves a stereospecific 1,2-carbon shift leading to the formation of ketene.[11] Accordingly, we illustrate the first successful electrochemical Wolff rearrangement of α-diazoketone,

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facilitating fine tuning of the electrode potential (Ag_n^0) with the redox potential of α-diazoketone, ultimately leading to the formation of the rearranged product in excellent yield.

Pioneering work by Murray[19] and co-workers has clearly indicated that thiol-protected gold nanoclusters (Au_n) can act as mediators in electron-transfer reactions; this result motivated us to test the above-mentioned concept. Towards this goal, we first examined the formation of Ag_n from silver(I) ions by recording the change in the open-circuit potential[20] (OCP) of the cell, made up of silver(I) benzoate coated Pt as the working electrode and Ag/AgCl as the reference electrode in aqueous acetonitrile, following the addition of Et_3N at room temperature (Figure 1, curve A). The OCP shift from 0.41 to 0.35 V within 20 minutes clearly indicates a reduction reaction. Further combined evidence from UV-visible and transmission electron microscopic (TEM) analysis of the working electrode material revealed the formation of polydispersed Ag_n (0.8–11.2 nm core diameter).[21,22] These results, along with the direction of change of the OCP indicates the transfer of an electron from Et_3N to silver(I) ions, ultimately leading to the formation of Ag_n.

To probe the involvement of electron transfer between benzoic acid protected[23] Ag_n, with a 2.5–15 nm core diameter (see Supporting Information Part 1), and α-diazoketone, we performed an analogous experiment using Ag_n-coated Pt as the working electrode. Addition of 1-diazo-2-hexanone-6-phenyl (**1a**) at room temperature (300 K) caused a shift of approximately 0.035 V in an anodic direction, as a function of time (Figure 1, curve B). This shift confirmed the occurrence of an oxidation process, while cyclic voltammetry (CV) and controlled potential coulometry (CPC) revealed the uniqueness of this phenomenon (see below). UV-visible and TEM analysis of the working-electrode material confirmed the presence of Ag_n. The invariant nature of the working-electrode material and the direction of shift in the OCP, most likely indicates the removal of an electron (oxidation) from α-diazoketone **1a** by Ag_n as being one of the important steps in the Wolff rearrangement; this reaction is represented by step iv in Scheme 1. Similar OCP experiments performed with Pt as the working electrode failed to show any noteworthy change in the OCP with time.

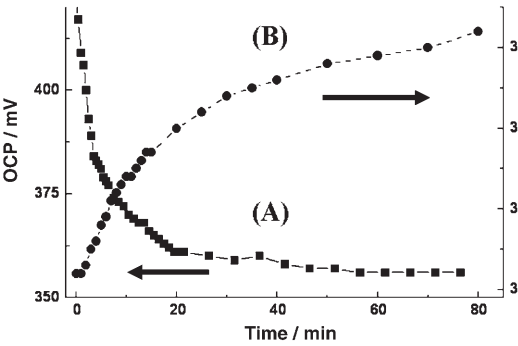
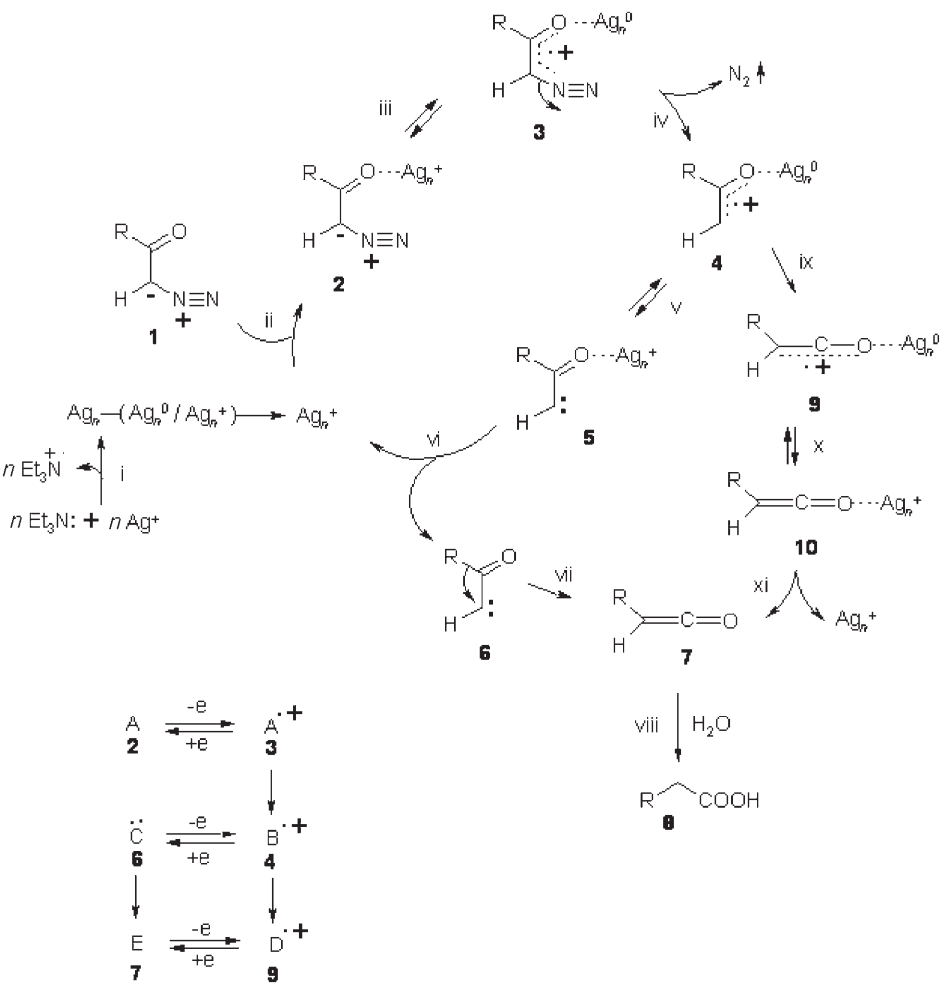


Figure 1. Plot of the open circuit potential of the cell as a function of time at constant temperature (300 K): A) Silver(I) benzoate as the working electrode and Ag/AgCl as the reference electrode in aqueous acetonitrile following the addition of triethyl amine; B) Benzoic acid protected silver nanoclusters as the working electrode and Ag/AgCl as the reference electrode in aqueous acetonitrile following the addition of α-diazoketone.



Scheme 1. Schematic representation of the electrocatalytic role of benzoic acid protected silver nanoclusters (Ag_n, mean core diameter 2.5 nm) during the Wolff rearrangement of α-diazoketones involving two nonclassical electron-transfer pathways.

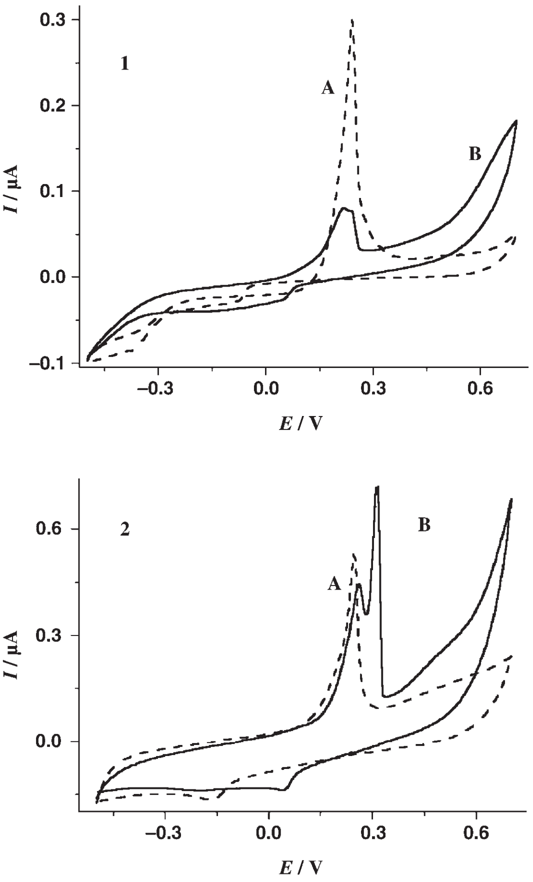


Figure 2. Superimposed CV of benzoic acid protected Ag_n in the presence (B) and absence (A) of α-diazoketone **1a** in an aqueous acetonitrile solution of $LiClO_4$ (60 mM) at 0.05 V s^{-1} (top) and 1.0 V s^{-1} (bottom). The voltammograms were recorded using a Pt microelectrode and an aqueous Ag/AgCl reference electrode.

A CV of benzoic acid protected Ag_n as a function of scan rate (ν), using a Pt microelectrode in aqueous acetonitrile revealed the presence of a redox couple with quasi-reversible electron-transfer behavior (Figure 2, curve A top and bottom and in Supporting Information Parts 2 and 3). The couple exhibits a predominant anodic peak at lower ν, indicating the preference of these morsels of silver to exist in the oxidized form. Furthermore, the couple is distinct in terms of the decrease in the ratio of the anodic to cathodic peak current (I_{pa}/I_{pc}) with increasing ν. This behavior is prominently reflected in an exponential decrease in the plot (I_{pa}/I_{pc}) versus ν. Additionally, the magnitude of separation between the anodic and cathodic peaks (ΔE_p) is higher relative to that generally observed for a quasireversible process. This enhanced magnitude[24,25] plays a crucial role in promoting coupled chemical reactions (see below). For example, the voltammogram A shown in Figure 2 (bottom panel) depicts the couple centered around 0.05 V with an anodic peak around 0.24 V and a cathodic peak around −0.14 V. The ΔE_p is approximately 0.38 V, while the ratio I_{pa}/I_{pc} is about 9.7. The origin of the couple could be ascribed to the occurrence of the electron-transfer step presented in Equation (1).

$$Ag_n^{\ +} + e^- \rightleftharpoons Ag_n^{\ 0} \tag{1}$$

An approximate estimation of the rate constant (k^o) for this process in aqueous acetonitrile based on ΔE_p is in the range 2×10^{-3} to 4×10^{-2} cm s^{-1}. It is also relevant to note that differential pulse voltammetry of stabilized Ag nanoclusters (3.3 nm core diameter) organized on the electrode surface exhibits quantized single-electron oxidative as well as reductive processes.[26] Importantly, the voltammetric features of benzoic acid protected Ag_n are independent of the concentration as well as the nature of the supporting electrolyte, despite a strong dependence on the nature of the solvent as well as the α-diazoketone **1a–e** (Table 1), indicating the occurrence of electron-transfer processes very close to the electrode surface (usually at a distance of about a few molecules).

In comparison, CV analysis in the presence of α-diazoketone **1a** shows drastic changes in both the anodic and cathodic response of the $Ag_n^{\ 0}/Ag_n^{\ +}$ redox couple, suggesting the occurrence of a coupled chemical reaction (see Supporting Information Parts 2–4). For example, curve B in Figure 2 (top) records a significant decrease in peak current with near retention of the voltammetric pattern, indicating a decrease in the surface concentration of the original redox couple. The couple is centered around 0.14 V ($\Delta E_p = 0.18$ V, $I_{pa}/I_{pc} = 5.5$) with a larger anodic peak at 0.23 V ($I_{pa} =$ 58.8 nA) and a smaller cathodic peak around 0.05 V ($I_{pc} =$ 10.6 nA). With increasing scan rate the anodic peak shifts in the anodic direction, while the cathodic peak shifts in the cathodic direction (the magnitude of the shift is much larger

Table 1. Cyclic voltammetric features[a–c] of $Ag_n^{\ 0}/Ag_n^{\ +}$ couple in the absence and presence of α-diazoketones **1a–e**, at a scan rate, $\nu = 1$ V s^{-1}.

No.	Substrate **1** R	E_{pa1} [V]	E_{pa2} [V]	E_{pc1} [V]	E_{pc2} [V]	$E_{1/2\,Dk}$ [V]	$E_{1/2}$ [V]	Yield[d] of **8** [%]
i	–	0.24	–	–	−0.14	–	0.050	–
ii	$Ph(CH_2)_4$ (**1a**)	0.26	0.32	0.05	−0.13	0.18	0.065	94
iii	$CH_3(CH_2)_{10}$ (**1b**)	0.30	0.38	0.04	−0.14	0.21	0.080	92
iv	2-I-Ph (**1c**)	0.24	0.27	−0.04	−0.10	0.11	0.070	97
v	4-Me-Ph (**1d**)	0.16	0.45	−0.13	−0.24	0.16	−0.040	88
vi	4-MeO-Ph (**1e**)	0.19	0.52	−0.12	−0.26	0.20	−0.030	86

[a] Cyclic voltammetry was performed with a platinum working microelectrode in an electrolyte solution of 60 mM $LiClO_4$ in aqueous acetonitrile; peak potentials are measured versus an aqueous Ag/AgCl reference electrode. [b] E_{pa1} and E_{pc2} are anodic and cathodic peak potentials of the regenerated Ag_n, respectively. [c] Derivative analysis of the cyclic voltammograms of α-diazoketones **1a–e** over Ag_n clearly shows the presence of two anodic and two cathodic peaks. [d] Yield of isolated carboxylic acid **8a–e**, following controlled potential coulometry of α-diazoketones (2.5 mM) **1a–e** using Ag_n as the anode and aqueous acetonitrile as the solvent in a divided-cell assembly at 300 K.

than that observed for the unperturbed redox couple). A rise in peak current is also observed, although the reversal parameter I_{pa}/I_{pc} is fairly constant (~4.5). Importantly, the steep descending nature of the oxidation peak is reminiscent of processes comprising of an electron-transfer step followed by a chemical reaction. As we approach a scan rate of $1\,\mathrm{V\,s^{-1}}$, many subtle, yet significant, changes in the nature of the voltammograms are observed and some of them, like the variation of voltammetric pattern with cycle number, provide conclusive information about the electron-transfer process. For example, the forward scan of the first cycle ($\nu = 1.0\,\mathrm{V\,s^{-1}}$) depicts a more anodically shifted, steeply descending oxidation peak at 0.39 V with a very large peak current ($I_{pa2} = 4.2\,\mu\mathrm{A}$). However, the reverse scan shows a substantially suppressed reduction peak around 0.08 V, exhibiting a plateau. More significantly, the forward scan of the second cycle (represented in Figure 2 curve B, top) shows remarkable splitting[27] of the single oxidation wave into two peaks at 0.32 V ($I_{pa2} = 0.4\,\mu\mathrm{A}$) and 0.26 V ($I_{pa1} = 0.12\,\mu\mathrm{A}$). The primary oxidation wave observed in both cycles at higher positive potential, can be ascribed to the oxidation of α-diazoketone **1a**, illustrated by a marked decrease in peak current indicating a decrease in the electrode surface concentration of **1a** due to electrochemical reaction. Sequential addition of **1a** resulting in an enhancement of the peak current without altering the voltammetric pattern further substantiates this assignment. The position of the new peak observed at comparatively smaller positive potential is in fair agreement with the position of the oxidation peak of the unperturbed redox couple; this result points towards the regeneration of electrocatalytic species Ag_n^{+}. The rise in peak current with retention of voltammetric nature as presented in Figure 2 curve B (bottom), following the introduction of additional Ag_n, provides further support to this theory. The reverse scan of the second cycle shows the invariant nature of the cathodic plateau. It is relevant to note that two cathodic peaks in addition to two anodic peaks are masked due to the nature of the cathodic wave and can be clearly identified as aromatic substrates **1d** and **e** (see Supporting Information Part 5). Subsequent cycles exhibit a similar voltammetric pattern with decreasing peak current. With increasing scan rate ($\nu > 2.0\,\mathrm{V\,s^{-1}}$) the cathodic peak grows and the two well-resolved anodic peaks merge to yield a more anodically shifted redox couple with $I_{pa}/I_{pc} \approx 4$. A qualitative comparison between the anodic (predominant peak) and cathodic (smaller peak or plateau) response indicates a relatively faster oxidation process relative to the reduction process. This analysis is in agreement with the observed movement of the OCP in an anodic direction following the introduction of **1a** to a cell containing Ag_n as the working electrode (see above). The zero-current curve-crossing phenomena[25] frequently observed for square schemes with a thermodynamically easier second electron-transfer step, rather than first electron transfer, is notably absent. All these characteristic features collectively suggest the occurrence of a nonclassical electron-transfer process initiated by oxidation of α-diazoketone.[26] In this type of process, the net electron transfer from the redox couple to the substrate is zero.

Voltammetric analysis (see Table 1 and Supporting Information Part 5) of a group of α-diazoketones **1b–e** in aqueous acetonitrile using a Ag_n electrode evokes very similar electrochemical responses indicating the occurrence of nonclassical electron-transfer processes (see above). The variation in the structure of α-diazoketone induces subtle, yet informative, changes in voltammetric features, leading to a better understanding of the reactivity and selectivity pattern of these substrates. For example, in the case of aromatic α-diazoketone **1c**, the iodo group is *ortho* to the α-diazocarbonyl function and consequently the latter cannot stay in plane with the aromatic π-system owing to steric reasons. This substrate reacts vigorously at much lower temperature (~298 K) in the presence of Ag_n to give Wolff rearranged products in excellent yield. This behavior can be understood in terms of perfect matching of the half-wave potential of the substrate **1c** over the Ag_n electrode ($E_{1/2\mathrm{Dk}}$) and the half-wave potential of Ag_n ($E_{1/2}$). More significantly, a change of substrate from **1c** to **1a**, **1b**, **1d**, and **1e**, can increase the anodic peak potential (E_{pa2}), which corresponds to the oxidation of α-diazoketone, thus indicating the relative order of thermodynamic difficulty in removing an electron from α-diazoketone. Additionally, the difference between $E_{1/2\mathrm{Dk}}$ and $E_{1/2}$ increases in the same way confirming the experimental observation of Wolff rearrangement.[28] As mentioned earlier, the first substrate in this order (**1c**) reacts rapidly in the presence of Ag_n (in the absence of any electrochemical bias) at room temperature (298 K), causing Wolff rearrangement, while the last substrate in this series (**1e**) requires thermal activation at 333 K.

In sharp contrast, the CV of α-diazoketone **1a** using a Pt working microelectrode (see Supporting Information Part 6) shows a broad wave around 1.3 V ($\nu = 5\,\mathrm{V\,s^{-1}}$); this response is characteristic of a reaction, controlled by an irreversible electron-transfer step. Analysis of the voltammetric behavior at different scan rates confirms the occurrence of an EC scheme (an electrochemical reaction followed by a chemical reaction). These striking differences in the nature of the voltammograms of α-diazoketone, in the presence and absence of Ag_n, signify the electrocatalytic activity of Ag_n.

Another simple experiment was peformed by introducing 1,4-dihydroxybenzene (DHB) into a aqueous acetonitrile solution of Ag_n; this experiment answered the curious question about the fate of an electrocatalyst assuming electron acceptance (step iii, Scheme 1) as the sole process. The yellow tinge of the solution instantaneously turned purple along with the formation of a silver mirror surface following the addition of DHB at room temperature. Analysis of the solution revealed the formation of 1,4-benzoquinone, an oxidation product of DHB. CV analysis suggests that the peak potential of the anodic peak of DHB (−0.12 V vs Ag/AgCl, $\nu = 5\,\mathrm{V\,s^{-1}}$) and the cathodic peak of Ag_n (−0.20 V) are in reasonably good agreement with the occurrence of a facile electron-transfer process. However, the cathodic peak potential of DHB (−0.28 V) and the anodic peak of Ag_n

(0.29 V) differ considerably, and consequently, Ag_n accepts an electron from DHB. This leads to the formation of bulk silver along with 1,4-benzoquinone, thus indirectly emphasizing the necessity of a back electron donation by Ag_n^0 to regenerate the electrocatalyst species Ag_n^+, along with the formation of ketene intermediate.

The in situ UV-visible spectrum (see Supporting Information Part 7) recorded by applying an anodic bias (0.5 V vs Ag/AgCl), using a Ag_n electrode, to a solution of α-diazoketone **1a** in an electrolyte solution of 0.1 M tetrabutylammoniumtetrafluoroborate in dichloromethane containing pyridine as the nucleophilic probe, exhibits the presence of a strong absorption band around $\lambda = 418$ nm, indicating the involvement of either α-ketocarbene intermediate **6** or ketene **7**. However, it is difficult to pinpoint the species due to close proximity of bands arising from α-ketocarbene–pyridine ylide[14–16] and ketene–pyridine ylide.[29]

With the help of information obtained from various electrochemical experiments and the in-situ UV-visible analysis (see below), we propose two nonclassical electron-transfer pathways involving different reaction intermediates (which requires further confirmation) for the Wolff rearrangement (Scheme 1). The CPC response of α-diazoketones **1a**–**e** over Ag_n further substantiates this procedure of electron swapping (see below). The E(↑), C, E(↓)—electron transfer reactions preceding (↑) and following (↓) chemical reaction(s) in opposite directions—pathway represented by steps iii, iv, and v, respectively, leads to the formation of α-ketocarbene intermediate **6**, which spontaneously rearranges to ketene **7**. The E(↑), C, C, E(↓) pathway involves the rearrangement of CRC **4** culminating in direct realization of ketene **7**.

The CPC response of α-diazoketones **1a**–**e** (2.5 mM) at an appropriate potential (see Table 1 and Supporting Information Part 8) ultimately gives Wolff rearranged carboxylic acids **8a**–**e** in excellent and reproducible yield. A divided-cell assembly made up of a Ag_n-coated Pt plate as anode and a graphite plate as cathode were used in aqueous acetonitrile. UV-visible and TEM analysis of the anodic material revealed the invariant nature of the electrocatalyst. In contrast, CPC of α-diazoketone **1a** using Pt as the anode gave uncharacterizable, neutral products.

In conclusion, we have revealed a unique nonclassical process, which involves electron transfer preceding and following chemical reaction(s) in opposite directions, with special emphasis on the mediating role of silver nanoclusters, during the Wolff rearrangement of α-diazoketones. Apart from providing an efficient preparative electrochemical route for the Wolff rearrangement without loosing the electrocatalyst, this method has potential as an elegant homologation of the naturally occurring α-amino acids to β-amino acids—the key building blocks of proteinogenic β-peptides.[30] We believe that a similar procedure of electron swapping is involved in the generation of copper and rhodium carbenoids,[1,2] some of the well-known intermediates in cyclopropanation and C–H insertion reactions, respectively, from α-diazocarbonyl compounds. In addition, we hope that the occurrence of this nonclassical electron-transfer process is generic to several reactions catalyzed by metal nanoclusters;[31,32] further studies are essential to reveal this.

Experimental Section

For experimental details, please see the Supporting Information.

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