SHORT COMMUNICATION

Electrochemical Preparation of Nanostructured Titanium Clusters: Characterization and Use in McMurry-Type Coupling Reactions

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The electrochemical preparation of nanostructured titanium clusters is possible by using a titanium sacrificial anode as the metal source and tetrabutylammonium bromide in THF as the electrolyte and stabilizer. Transmission electron microscopy shows the presence of spherical 3.0-nm-sized particles. THF solutions of these Ti clusters induce olefin-forming McMurry-type coupling of aldehydes and ketones.

Nanostructured transition metal clusters are of current interest as potential catalysts and advanced materials with novel optical and electronic properties[1]. They are usually prepared by chemical reduction of metal salts in the presence of such stabilizers as special ligands[1,2], polymers[1,3], or tetraalkylammonium salts[1,4]. It is generally assumed that the stabilizer forms a protective coat around the clusters, although the experimental proof of such a hypothesis has been presented only in rare cases[1,5]. For example, a recent STM/TEM study of $R_4N^+X^-$-stabilized Pd clusters showed that the surfactant does, indeed, form a monomolecular protective coat around each metal particle[5].

Recently we described two different electrochemical methods for the preparation of a variety of different transition metal clusters stabilized by tetraalkylammonium or phosphonium salts[6–10]. One of them involves sacrificial metal anodes as the metal source[6]. Accordingly, a metal sheet (e.g., palladium or nickel) is electrochemically oxidized, the corresponding metal ions then migrate the cathode where reduction back to the zero valent state takes place. Tetraalkylammonium salts serve as the electrolyte and the stabilizer, i.e., they capture the clusters and thereby prevent undesired metal powder formation (Scheme 1).

Scheme 1

$$\begin{array}{llllll}
\text{Anode:} & & M_{\text{bulk}} & \longrightarrow & M^{n+} + n\,e^- \\
\text{Cathode:} & M^{n+} + n\,e^- & + \text{ stabilizer} & \longrightarrow & M_{\text{cluster/stabilizer}} \\
\hline
\text{Sum:} & M_{\text{bulk}} & + \text{ stabilizer} & \longrightarrow & M_{\text{cluster/stabilizer}}
\end{array}$$

Alternatively, metal salts can be reduced electrochemically with formation of $R_4N^+X^-$-stabilized clusters. Using these methods, clusters[6–9] such as those of Pd, Ni, Mo, Ru, Rh, Os, and Pt and bimetallic clusters[10] (e.g., Pd/Cu, Pt/Sn, Pt/Rh) have been prepared in the size range of 2–6 nm.

We were interested in the question whether bulk titanium, e.g. a Ti sheet, can be transformed into titanium clusters electrochemically according to Scheme 1. Here we show that this is, indeed, possible and that such materials are active reagents in McMurry-type coupling.

Results and Discussion

Preparation and Characterization

All experiments were carried out in a standard electrolysis cell composed of a Ti anode and a Ti cathode, the electrolyte being 0.1 M tetrabutylammonium bromide in THF. The electrolysis was performed in an ultrasonic cleaning bath at a temperature of 28–30 °C. Application of a current density of 3 mA/cm^2 led to dissolution of the anode, and a black solution of titanium clusters was formed. Formation of insoluble metal powder was not observed[11]. The titanium clusters can be isolated in solid form for characterization. The resulting shiny black material is somewhat air-sensitive, but less so than THF solutions, which spontaneously turn yellow-green on contact with oxygen. Nanostructured TiO_2 particles are probably formed, but this needs to be studied more closely.

The ^1H- and ^{13}C-NMR spectra of the isolated clusters display slightly broadened signals, possibly due to the presence of some paramagnetic material. These spectra contain the characteristic signals of tetrabutylammonium bromide.

In the characterization of metal clusters, transmission electron microscopy (TEM) is known to be the method of choice[1,12]. However, TEM pictures of Ti clusters have not been published to date. Figure 1 shows a typical electron micrograph of the titanium clusters described in this paper. The average size of the spherical clusters is about 3.0 nm. The lattice planes of the crystallites are clearly visible.

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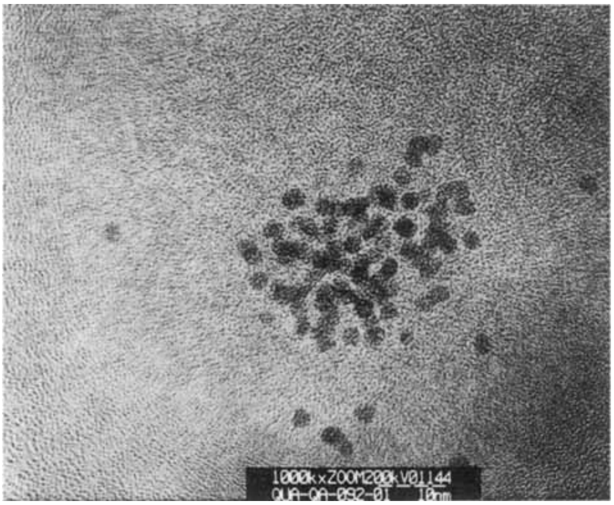
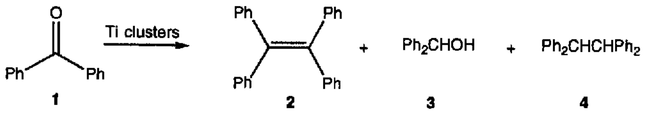
Figure 1. Electron micrograph of the titanium clusters used in reactions according to Scheme 1



The TEM study reveals valuable information concerning the inner metal core of the clusters, but not of the stabilizing mantle. The latter is probably composed of tetrabutylammonium bromide. The fact that the elemental analysis indicates the presence of a small amount of bromide other than $(C_4H_9)_4N^+Br^-$ suggests that a minor portion of the metal is present as titanium bromide of unknown oxidation state, perhaps Ti(II) (20–30%). The material described herein appears to be somewhat different from recently postulated Ti clusters prepared by the reduction of $TiCl_4$ or $TiCl_3$ using $[HBEt_3]^-K^+$[13]. These materials were reported to contain large amounts of THF and some KCl.

McMurry-Type Coupling Reactions Using of Preformed Ti Clusters

A variety of low-valent titanium reagents has been used in the olefin-forming McMurry-type coupling of carbonyl compounds[14–16], including $TiCl_3(THF)_3Mg$[17], $TiCl_4/Zn$[18], $TiCl_3(THF)_3/LiAlH_4$[19], $TiCl_3(DME)_{1.5}/Zn\text{-}Cu$[20], Ti graphite[21], and Ti powder/Me_3SiCl[22]. These reactions appear to be heterogeneous. Originally, the zero oxidation state of titanium was postulated. However, Bogdanović[23] recently showed that it is not necessary to invoke Ti(0) as the reactive species. Indeed, it was clearly demonstrated that the reduction of $TiCl_3(THF)_3$ by $LiAlH_4$ in THF affords the insoluble Ti(II) hydride $[HTiCl(THF)_{0.5}]_n$, which actually induces McMurry-type coupling reactions. We were interested in the chemical properties of the electrochemically prepared Ti clusters in the form of colloidal solutions, especially in reactions with carbonyl compounds. As a model reaction the interaction of the 3.0-nm Ti clusters with benzophenone 1 was chosen.



Reaction of benzophenone 1 with the electrochemically prepared Ti clusters in refluxing THF gave products 2–4, in addition to some starting material 1 (Table 1).

Table 1. McMurry-type coupling reaction of benzophenone using Ti clusters (7-fold excess) in refluxing THF

Reaction time [h]	Non-reacted 1 (%)	2 (%)	3 (%)	4 (%)
1.25	13	74	12	1
3.25	8	79	11	2

The results show for the first time that solutions of titanium clusters can be used to induce McMurry-type coupling reactions. It has been stated that reproducibility in classical McMurry-type reactions can be a problem[16]. In the present system yields of coupling products 2 are consistently in the range of 70–80%. However, small variations in the ratio and amounts of side products 3 and 4 may occur, and the rate of the reaction may also vary. For example, in one run a time of 25 h was required to obtain a yield of 71% of 2. These fluctuations may be the result of possible contamination by air. As noted above, treatment of the Ti clusters with oxygen causes oxidation. If partial oxidation occurs inadvertently during the transfer of the Ti clusters from the electrolysis cell to the reaction vessel, the quality of the reagent may be effected.

The coupling reaction of 1 was also attempted *during* the process of electrolysis at 28–30°C. After 18 h complete consumption of the carbonyl compound was observed with formation of olefin 2 (85%) and compound 4 (15%).

Acetophenone was also treated with the preformed Ti clusters (7-fold excess) in refluxing THF. In a typical run (25 h), 72% of (*Z*)-2,3-diphenyl-2-butene and 10% of the *E* isomer were formed, in addition to 15% of side-products. *Z* Selectivity in the McMurry coupling of acetophenone is generally observed in conventional forms of the reaction[16]. Finally, the preformed Ti clusters react with benzaldehyde under similar conditions to afford (*E*)-stilbene (90%) and (*Z*)-stilbene (10%).

In summary, bulk titanium can be transformed into titanium clusters in a simple electrochemical process. Under typical conditions 3-nm-sized particles are obtained, as shown by TEM analysis. These air-sensitive colloids induce McMurry-type coupling in solution, which is of theroretical interest.

Experimental

Electrochemical Preparation of Ti Clusters: All operations were performed under inert gas (Ar) by using dry solvents. A standard electrolysis cell (300 ml capacity) was constructed by using titanium shets (4 × 5 cm^2) as the anode and cathode, about 1 cm apart. The electrolyte [200 ml of a 0.1 M $(C_4H_9)_4N^+Br^-$ solution in THF] was added and the electrolysis cell immersed in an ultrasonic cleaning both. At 28–38°C a current density of 3 mA/cm^2 (current flow: 7200 C) was applied, resulting in a brown color within 30 min. After about 6 h the solution is black. The solution could be used directly for McMurry-type reactions. For the purpose of characterization the clusters were isolated as follows. The cluster solution was cooled to about −70 °C, causing the major portion of the excess ammonium salt to precipitate. Following filtration through a cooled (−70 °C) glass frit (D4), the solvent was removed in vacuo and the residue washed with 50 ml of pentane, providing a crystalline black solid (1.3 g). High-resoluton TEM analysis showed clusters having an average size of 3.0 nm. Energy Dispersive X-Ray (EDX) analysis demonstrated the presence of titanium and bromine. ^{1}H- and ^{13}C-NMR spectra of the solid material in [D_8]THF contained the typical peaks of $(C_4H_9)_4N^+Br^-$, although slightly broadened. The NMR spectra in [D_2]dichloromethane did not show the presence of any appreciable amount of THF. – Elemental analysis (%): C 33.4, H 6.1, Br 30.7, N 2.3, Ti 27.8. The black solid was dissolved in THF and the solution then cooled again to separate more ammonium salt. Following removal of THF a black solid was obtained; it contained 37.5% titanium.

Typical McMurry-Type Coupling Reaction: The mixture of a Ti cluster solution obtained as described above (about 0.5 mmol Ti in 10–20 ml THF) and a ketone or aldehyde (0.07 to 0.1 mmol) was refluxed under argon. After certain time intervals (Table 1) samples were taken for analysis. In doing so, the mixtures were treated with aqueous 0.5 M HCl (1 ml). The aqueous phase was extracted with diethyl ether (0.5 ml) and the volume of the combined organic phases reduced to about 500 µl. Gas chromatographic analysis showed the presence of the expected olefins and small amounts of side products (Table 1).

McMurry-Type Coupling Reaction of Benzophenone During Electrolysis: Electrolysis of a solution of THF (92 ml), $(C_4H_9)_4N^+Br^-$ (3.27 g), and benzophenone (133 mg) was carried out in a similar manner. After 3 h the electrolysis was stopped. This corresponded to a current flow of 320 C. Following the usual workup GC analysis showed the presence of starting material **1** (10%), tetraphenylethylene (**2**) (57%), **3** (17%), and **4** (15%). On the basis of the current flow this means that a major portion of the coupling and reduction processes probably occurs electrochemically.

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