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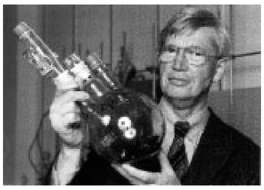
AOC

A review—How nanoparticles emerged from organometallic chemistry

Dedicated to Professor Helmut Bönnemann on the occasion of his 65th birthday



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Studied chemistry at the RWTH Aachen. Began his graduate work in Mülheim in 1964 under the supervision of Nobel Laureate Professor Karl Ziegler. Obtained his doctorate in 1967 with G. Wilke and in 1976 received his Habilitation in Industrial Chemistry. Worked for 2 years, 1978–79, in the central research laboratories of Degussa and in 1981 was appointed Professor for Industrial Chemistry at the RWTH Aachen.

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Dedication:

Und jedem Anfang wohnt ein Zauber inne.
Der uns beschützt und der uns hilft, zu leben.

Each beginning has a magic fluidism
protecting us and helping us to live.
Herrmann Hesse

KEYWORDS: nanoparticles; catalysis; colloidal; materials

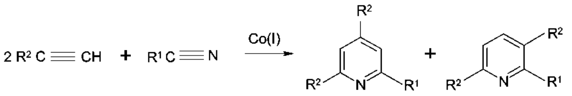
INTRODUCTION

To share the experiences of a team working at the forefront of chemical research, creating new pathways in organometallic chemistry, is always thrilling and impressive. An attempt has been made here to describe the path traced by Professor Helmut Bönnemann's group, starting from classical organometallic approaches towards nanometal particle synthesis up to the modular design of colloidal metals, catalysts, and novel materials.

The new experimental findings in the group have been documented from time to time as original publications.[1–50] In recent years, some reviews have also been published, both on the overall survey and on a critical assessment and the validity of the method.[51–57] In order to avoid repetition, we would like to take a look only at those aspects of the group's continued research efforts that have so far resulted in the greatest impact in the field of nanochemistry.

I

As happens in research, colloidal nanoparticle synthesis began in the Mülheim laboratory rather by serendipity. Up to mid-1980s, the group was actively involved in the new avenues of homogeneous organometallic catalysis. Based on cobalt(I) systems, a structure–effectivity relation was established for use in the catalytic formation of pyridines from alkynes and nitriles:[5,6]



(1)

The aim now was to develop an industrially viable process for the production of 2-vinyl pyridine, a linker material used in polymer industry. A cheap synthesis of the CpCo(I)COD (COD = cyclooctadiene) complex catalyst was needed, which was effectively achieved by a one-pot synthesis reducing $CoCl_2$ with highly activated magnesium (evolving from magnesium anthracene), an in-house speciality,[2] in the presence of cyclopentadiene and COD. In the absence of olefins, finely divided metal powders were obtained. In those days Dr Bönnemann used to end his seminars with a real 'firework' triggered by the exposure of finely divided iron kept under argon to air. This prompted an industry representative to pose the challenge of producing acicular iron metal from its oxide to be used for magnetic tape applications. The process should be performed at moderate temperatures and should be economically viable. The first attempts with calcium anthracene showed that the reduction is basically possible. However, the low solubility of the calcium anthracene, and also of the strontium- and barium-anthracenes (or the alkaline-earth metal hydrides as such), in organic solvents excluded industrial application. This shifted the group's attention towards triorganoborohydrides ('superhydrides') as reducing agents, another in-house speciality.[58]

II

Alkaliborohydrides ($LiBH_4$ or $NaBH_4$) in aqueous solutions had long been used for the reduction of transition-metal salts to X-ray amorphous metal powders. However, the drawback here was that all four atoms of the hydrogen in the reducing agent take part in the reduction process, which leaves boron to form metal borides and contaminating the product. For example, reduction of $NiCl_2$ by sodium borohydride yields a 3 : 1 molar ratio of Ni_3B and nickel (Eqn (2)), and reduction of $FeSO_4$ with $CoCl_2$ using KBH_4 results in $Fe_{44}Co_{19}B_{37}$.[59,60]

$$\begin{aligned}&10NiCl_2 + 8NaBH_4 + 17NaOH + 3H_2O\\&\quad\longrightarrow (3Ni_3B + Ni) + 5NaB(OH)_4 + 20NaCl + 17.5H_2\end{aligned} \tag{2}$$

Alkaline hydrotriorganoborates $M(BR_3H)$ may be regarded as an adduct of MH and BR_3, where the triorganoboron acts as a neutral complexing agent ('carrier') and not as a reduction agent. The presence of BR_3 provides an excellent solubility of the hydride part in organic solvents. Also, it can be regenerated. This, in the first place, led to metal nanopowders (elements of Groups 6–12 and also of Group 14) without contamination from borides:[14]

$$MX + M'(BR_3H) \xrightarrow{THF} M + M'(BR_3X) + \frac{1}{2}H_2 \uparrow \tag{3}$$

M = transition metal, M' = alkali, alkaline-earth metal

$R = C_1–C_6$ (alkyl)

X = halide, OH, OR, CN, OCN, SCN; THF = tetrahydrofuran

As a matter of fact, acicular iron oxide and oxide–hydroxide pigments could be transformed using hydrotriorganoborates in the presence of compressed hydrogen (20–100 bar; 80 °C) to their needle-shaped metal equivalents:[61]

$$\alpha\text{-FeOOH} + 2NaBEt_3H \xrightarrow{20\text{ bar }H_2,\ 80\,^\circ C,\ 4\text{ h}} Fe_{acicular} + 2NaBEt_3OH \tag{4}$$

$$\alpha\text{-}Fe_2O_3 + 2NaBEt_3H \xrightarrow{20\text{ bar }H_2,\ 80\,^\circ C,\ 4\text{ h}} 2Fe_{acicular} + 2NaBEt_3OH \tag{5}$$

To come back to the reduction of metal salts with hydrotriorganoborates (Eqn (3)), this depends on many factors, including the difference in metal to reducing agent redox potentials, reduced metal–metal bond strength. The redox potential of sodium hydrotriethylborate in THF was electrochemically determined to be −0.77 V. Therefore, using this reducing agent, the reaction conditions for reduction of stoichiometric amounts of different transition-metal salts in organic solvents varied between −20 °C to the boiling point of the solvents, owing to changes in the redox potential differences. The side products of the reaction, like the alkali-metal halides (especially salts like LiCl, LiBr, LiI and NaI) and BR_3 are soluble in THF and thus can be separated from the transition-metal nanopowders by simple filtration. Even catalytic amounts of BR_3 added to suspended alkali-metal hydride (MH) during reduction were found to be effective in forming alkali-metal-triorganoborohydride in a relay and reduce the transition-metal halides. From X-ray diffraction and transmission electron microscopy, the grain and particle sizes of metal nanopowders were found to be between 1 and 90 nm, depending on the metal salt reduced. Tables 1, 2, and 4–6 of Ref. 14 clearly demonstrate the scope of the method. However, a big target for the group was to minimize unavoidable contamination of the metal powders with small amounts of alkali-metal halides and to increase the monodispersity. The idea was to replace the alkali metal by an organic cation, which would then bring the halides into the organic solution while the clean transition-metal powders would precipitate. Surprisingly, no precipitations were observed at all, regardless of the transition-metal salt used as starting material. This enigma was solved when the word 'colloid' came up in the laboratory and Eqn (6) drawn:

$$MX_\nu + \nu NR_4(Bet_3H) \longrightarrow M_{\mathrm{colloid}} + \nu NR_4X + \nu BEt_3 + \nu/2H_2 \uparrow \qquad (6)$$

$$M = \text{metals of the Groups 6–11};\ X = Cl, Br;\ \nu = 1, 2, 3;\ R = \text{alkyl},\ C_6\text{–}C_{20}$$

III

Without realizing that NR_4X is the colloidal 'stabilizer', a patent was filed.[62] During the reviewing process of a research publication, this view was corrected and led to the illustration given in Ref. 7, showing that $NR_4(BR_3H)$ by serendipity was selected as a combination of simultaneous reducing and stabilizing functions.

An extension of this colloidal concept led to organosols of the solvent-stabilized early transition-metal series, e.g. titanium, zirconium, niobium, and manganese, accessible by the wet-chemical reduction of the THF or thioether adducts of the corresponding metal halides with $K(BEt_3H)$. Colloidal titanium(0), Eqn (7),[9] which was characterized as a cluster of 13 atoms of titanium surrounded by six molecules of THF having a particle size of 0.8 nm, was a very efficient catalyst for the hydrogenation of titanium and zirconium sponges, as well as for a nickel hydride battery alloy, and THF-stabilized manganese exhibited antiferromagnetism.[29]

$$x[TiBr_4{\cdot}2THF] + 4xK[Bet_3H] \xrightarrow{\text{THF, 2 h,20 °C}} [Ti{\cdot}0.5THF]_x + 4xBEt_3 + 4xKBr \downarrow + 2xH_2 \uparrow \qquad (7)$$

It is now clear that stabilizers not only prevent particles from becoming agglomerated or oxidized, they also serve as a controller of particle shape and size. Owing to the increased number of coordinatively unsaturated atoms at the surface, the nanoparticles possess excess surface free energy comparable to the lattice energy, which forces them to agglomerate. The incentive for using tetraammonium protecting agents is the formation of surface-active, sterically bulky NR_4^+ salts right at the reduction center in high local concentration that prevent particle agglomeration to yield mono-dispersed colloidal particles. In most cases, the resulting colloids can be purified and isolated in solid form by treatment of the colloidal solutions with solvents having different polarity (e.g. technical ethanol for platinum) or can be loaded uniformly on any support ('precursor concept'). Further, these isolated particles can be re-dissolved in various solvents in high concentration of the metal (up to unimolar solutions). As stated before, trialkylboron can be recovered unchanged from the reaction mass and no borides contaminate the desired product (Eqn (6)). Easy removal of NR_4X salts from the surface allows one to obtain clean metal surfaces accessible by substrate molecules during catalysis. This approach, initially thought as a model system to provide colloidal nanoparticles, is now realized as one of the promising methods for generating highly active catalysts because of the moderations, both in terms of metal composition and their morphologies, that can be brought about during synthesis (now known as the Bönnemann method). Bi-, and pluri-metallic colloidal particles can be obtained in the form of intermetallics, truly alloyed, layered metallics, and core–shell-type compositions.

While having the protecting group as part of the reducing agent is one way of synthesizing colloidal nanoparticles, addition of stoichiometric amounts of protecting agent to transition-metal salts, before reduction, forms an alternate way of obtaining colloidal nanoparticles. This 'double salt pathway' (Eqn (8)) provides the option of using a variety of reducing agents to generate colloidal nanoparticles.[10,14,52]

$$(NR_4)_wMX_vY_w + v\mathrm{Red} \longrightarrow M_{\mathrm{colloid}} + v\mathrm{RedX} + w\mathrm{NR_4Y} \qquad (8)$$

$$\mathrm{M} = \text{metals; Red} = \mathrm{H_2, HCOOH, K, Zn, LiH, LiBEt_3H, NaBEt_3H, KBEt_3H}$$

$$\mathrm{X,Y} = \mathrm{Cl, Br}$$

$$v, w = 1\text{–}3 \text{ and R} = \text{alkyl, } C_6\text{–}C_{12}$$

The advantages of the tetraalkylammoniumborate method, therefore, may be summarized as follows: it is generally applicable to salts of metals in Groups 7–11 of the periodic table; it yields extraordinarily stable metal colloids dispersible in high metal concentration in a number of organic solvents, which are easy to isolate as re-dispersible powders and the particle size distribution is monodisperse; the synthesis is suitable for multi-gram preparations and easy to scale up, and, even more importantly, the method is very reproducible (see tables 9–16 of Ref. 14 for the efficiency of this synthesis and also the catalytic activity of some of the supported catalysts). Over the years, this method has been widely accepted as one of the most appropriate pathways of generating truly zero-valent transition metal nanoparticles.

The chemical reduction of transition-metal salts in the presence of hydrophilic surfactants provides straightforward access to nanostructuresd mono- and bi-metallic hydrosols (Eqn (9)).[63,64] This synthesis can be performed even in aqueous solutions. Mono- and bi-metallic nanoparticles stabilized by hydrophilic cationic-, anionic- or nonionic-type surfactants serve as precursors for heterogeneous metal colloid catalysts effective for hydrogenation or oxidation of organic substrates. It has even been possible to incorporate a hydrophilic chiral protecting agent to result in enantioselective catalysts.

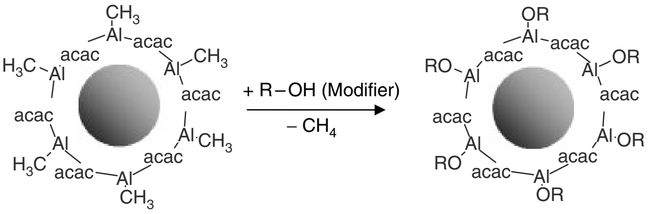
$$\underset{\text{THF soluble}}{C_{12}H_{25}N(CH_3)_2(C_3H_6\text{–}SO_3)\cdot LiBEt_3H + PtCl_2} \longrightarrow \underset{\text{Water soluble}}{Pt_{\mathrm{colloid}}\cdot C_{12}H_{25}N(CH_3)_2(C_3H_6\text{–}SO_3)} \qquad (9)$$

Formation of colloidal nanoparticles can also be effected by the decomposition of susceptible zero-valent transition-metal complexes in solution.[65–67] The controlled decomposition of low-valent complexes, eventually in the presence of stabilizers, yields very clean nanoparticulate precursors. Surface-doped bi- or pluri-metallic systems are generated by subsequent reduction of two or more different metal complexes to have decoration or coating of preformed metal cores. A prerequisite here is the availability of appropriate starting complexes. Core–shell nanoparticles, comprising a non-noble metal core and noble-metal shell electrocatalyst, were generated by having the 'carrier particles' (non-noble metal, cobalt) pretreated with strong reducing agents (e.g. organometallics) and subsequent addition of noble metals (gold) in the form of a salt or low-valent complex to cover the surface of the carrier with a thin layer of the catalytically active noble metal.[68]

IV

Organoaluminum compounds had been used in this very institute since the days of Nobel Laureate Professor Dr Karl Ziegler, under whose supervision Bönnemann began his graduate work in 1964. During the discovery of polymerization reactions catalyzed by aluminum organics, as early as 1954, Karl Ziegler[69] assumed 'colloidal nickel' in triethylaluminum to be the crucial co-catalyst that directs the controlled dimerization of ethene towards the selective formation of butene. This so-called 'nickel effect' was the basis of the subsequent discovery of the Ziegler catalysts and was later elucidated in great detail by G. Wilke and his group,[70] of which Bönnemann was a part when doing his PhD work. Using today's knowledge and analytical tools on nanometal clusters and colloids, it was in fact confirmed (1999) that Ziegler's early view was right, in that colloidal nickel is formed in solution when a trace of nickel acetylacetonate is added to triisobutylaluminum.[71] This prompted the group to, straight away, use aluminum alkyls as colloidal stabilizers ('reductive stabilizers').

'Reductive stabilization' by organoaluminum compounds was used for the preparation of various mono- and bi-metallic nanoparticles.[45,47,48] The mechanism of nanoparticle formation through its seed was exemplified in the reduction of $Pt(acac)_2$ (acac = acetylacetonate) using $Al(CH_3)_3$.[47] Colloids of zero-valent elements of Groups 6–11 of the periodic table were all prepared in the form of stable, isolable organosols using organoaluminum systems. The catalyst precursors obtained by reductive stabilization give particles in an ultrafine powder form having solubility properties to be tailored at will. The essence here is that very fine nanoparticles (0.8–2 nm) having reactive aluminum alkyl groups (e.g. $Al\text{-}C_2H_5$ or $Al\text{-}CH_3$) in their protective shell are formed. These Al–C bonds in the shell are readily modified using different proton-active organic/inorganic modifiers, such as alcohols, organic acids or inorganic substrates, e.g. SiO_2. Bi-functional molecules are used to build an inter-link between two metal cluster units, and even a three-dimensional cross-linked network can be generated this way (Eqn (10)).[43,45]



(10)

Modifiers: alcohols, carboxylic acids, silanols, sugars, polyalcohols, polyvinylpyrrolidone, surfactants, silica, alumina, etc.[43,45]

It was experimentally proved that, with appropriate modification, the colloids are dispersible in a wide range of lipophilic and hydrophilic solvents (solubility exceeding 100 mmol of metal per liter). It is also possible to surface oxidize the reactive aluminum organics to result in ultrafine metal powders with a thin layer of alumina protecting them.

A novel size-selective preparation route leading to air-stable 'monodisperse' colloidal cobalt nanoparticles for magnetic applications is obtained via the thermolysis of $Co_2(CO)_8$ in the presence of aluminum alkyls.[49,50] The size of the resulting particles is found to vary on the metal to aluminum-alkyl ratio and the nature of the alkyl chain in the aluminum organic. With suitable modifications to these particles, even air-stable cobalt particles are generated. X-ray absorption near-edge structure measurements have proved that this preparation pathway results in long-term stable zero-valent superpara magnetic cobalt particles. In addition, these measurements show that the chemical nature of the surfactant used exerts a significant influence on the stability and the local electronic and geometric structure of the nanoparticles analyzed.

V

The question of utility comes to any synthetic product, and this is the case with nanoparticles. In recent years a number of technological applications for nanoparticles have been realized and visualized. Owing to their extremely large surface areas the priority of their use is in catalysis. In order to generate efficient catalysts from the colloidal nanoparticles, the 'precursor' concept was developed in Bönnemann's group.[19,52,72] This enabled the uniform carpet-like coating of the colloidal precursors on any support (egg-shell type), which can then be converted into an active catalyst system by removal of the protective shell. Reactive annealing, also regarded as 'conditioning', has been effectively applied to remove the protective shell, leaving the clean surface metal particles on the support, without compromising on the particle size of the original particles. The catalysts thus generated have found applications in fine chemical production, electrocatalysis and as hydrogen storage catalysts.[22–24,30]

In conclusion, modulations in the design of precursors, catalysts and materials provide ample opportunity for generating materials of prime importance in various aspects of catalysis and materials science. However, it remains to be seen how the practical applications of these materials develop over the next few years.

Acknowledgements

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