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Two-dimensional nickel and palladium nanoclusters soluble in low-polarity aprotic media

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The disk-like title nanoclusters (30–100)×(15–20) Å in size were prepared by the reduction of polynuclear Ni^{II} and Pd^{II} trimethylacetato complexes with BuLi, Et_3Al or Bu^i_3Al and characterised using TEM, SAXS and EXAFS.

The colloidal nanoclusters of Group VIII metals are commonly prepared from divalent metal complexes by chemical, electrochemical or radiochemical reduction in protic (water, alcohols, acetic acid, diphase water–oil, *etc*.) media.[1] Methods for the preparation of metal colloids in aprotic solvents are scanty. Here, we report the preparation and characterization of unusual nanosized nickel and palladium colloids, which are highly soluble in low-polarity aprotic media (*viz*., THF, benzene and even hexane).

The polynuclear Ni^{II} and Pd^{II} complexes $Ni_9(OOCCMe_3)_{12}$-$(HOOCCMe_3)_4(\mu^3\text{-}OH)_3(\mu^4\text{-}OH)_3$ **1**,[2] $Pd_3[OOC^*H(Me)Et]_6$ **2**[3] and $Pd_3(OOCCMe_3)_6$ **3**,[4] whose structures have been established by X-ray diffraction, were used as starting materials in our syntheses. These compounds are highly soluble in organic solvents due to the presence of organophilic carboxylato ligands. This fact allowed us to handle complexes **1**–**3** under water-free conditions typical of organometallic synthesis. We studied the reduction of these complexes with lithium and aluminum alkylates in THF–hexane solutions.

The reactions of complexes **1**–**3** with BuLi in a THF–hexane solution† was accompanied by heat release and gas evolution and produced a dark brown transparent (in a thin layer) solution of colloidal nickel or palladium.

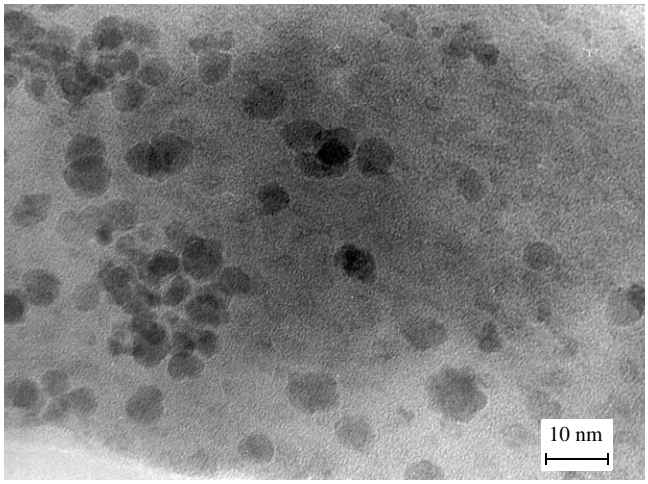

Figure 1 Transmission electron micrograph of nickel nanoclusters prepared by the reaction of complex **1** with BuLi (magnification 1.6×10⁶).

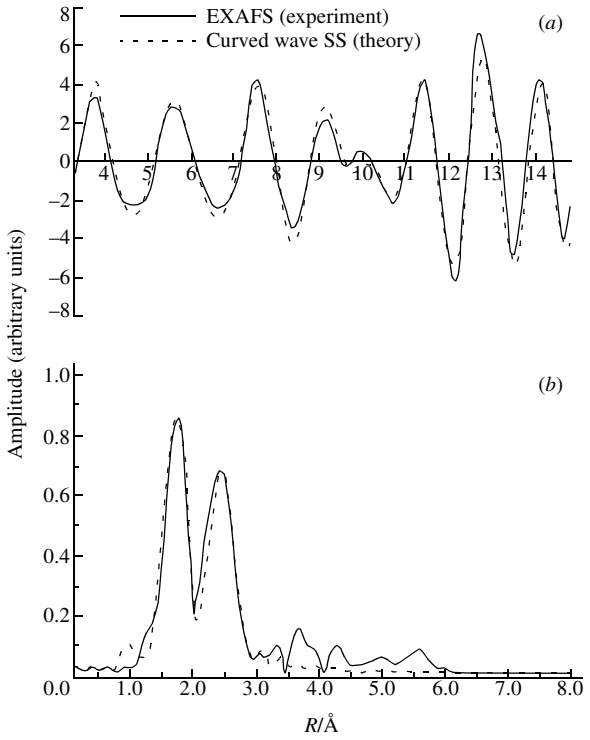

Figure 2 EXAFS data for nickel nanoclusters prepared by the reaction of complex **1** with BuLi: (*a*) Fourier transform; (*b*) RDA curve.

A small-angle X-ray scattering (SAXS) study‡ revealed nonspherical strongly asymmetric Ni and Pd nanoparticles with a mean size of ~50 Å.

Transmission electron microscopy (TEM) (Figure 1)§ showed nickel metal particles as near-regular flat circles 50–100 Å in diameter. In the TEM micrographs, individual metal particles manifest themselves as spots with a fairly low contrast and uniform blackening densities, whereas the fully or partly superimposed particles are seen as stacks, whose blackening densities

† A 1.5 M solution of BuLi (0.2–0.4 ml, ~3 mol per mole of Ni or Pd) in hexane was added rapidly to a solution of complex **1**–**3** (50 mg, 0.1–0.2 mmol based on the metal atom) in dry THF (1 cm^3) in a two-necked 5 ml flask equipped with a reflux condenser and a 10 ml gas burette with intense stirring under argon at a room temperature. Immediately upon mixing the reactants, a violent exothermic reaction occurred, resulting in a change in the solution colour to dark brown, a temperature rise to 35–40 °C and gas evolution. The solution was cooled down to a room temperature, and the gas collected was analysed by GLC. The reactions with Et_3Al and Bu^i_3Al (1.0 M solutions in hexane) were conducted analogously.

‡ Measured with a KRM-1 X-ray unit (Russia) using CuKα radiation.

§ JEM 2010 electron microscope (JEOL, Japan). Specimens were prepared by the deposition of a colloid metal solution onto an amorphous carbon film with a standard copper grid. All operations, including the transfer of the solution from the Schlenk tube to the microscope chamber, were conducted under argon. TEM images were recorded with a magnification of (0.5–2.0)×10⁶ at a minimum electron-beam current (≤ 10 μA) to prevent the heating of the specimens during the TEM study. In some experiments, bouncing the paramagnetic Ni nanoclusters apart from the electron beam hampered the TEM recording.

are proportional to the number of stacked particles. This pattern is different from those commonly observed in TEM and HREM studies of three-dimensional nanoclusters,[5] suggesting the nickel particles to be flat and disk-shaped. Based on photogrammetric analysis, the thickness of the particles can tentatively be assessed at 15–20 Å. The palladium metal particles are similar in shape to the nickel nanoclusters but somewhat smaller in size (30–70 Å in diameter and ~15 Å in thickness).

The EXAFS spectra (Figure 2)¶ of nickel nanoclusters in a THF solution and the solid state are identical. The radial distribution curves calculated from the EXAFS spectra revealed only one short Ni–Ni distance (2.5 Å) with the average coordination number of 0.7 and the Ni–light atom (Ni–C and/or Ni–O) distance of 1.9 Å with the average coordination number of 4. These values are inconsistent with those expected for the Chini[8] dense-packed clusters shaped as a cuboctahedron or icosahedron (M_{309}, M_{561}, M_{1415}, *etc*.). For the latter clusters, the average metal–metal coordination number should be at least 6, and that for the metal–light atom of the external ligand should be at most 1.[5] Meanwhile, the EXAFS data for the Ni nanoparticles agree well with a model of the flat metal disk about 3–5 metal–metal distances in thickness and Bu and/or RCOO ligands linked to the metal atoms at the disk surface. The occurrence of alkyl and/or branched carboxylate groups at the surface of the Ni and Pd colloidal clusters is supported by their high solubility and long-term (for at least six months) stability in low-polarity organic media (THF–hexane mixtures, benzene, toluene, *etc*.) under anaerobic conditions.

According to GC and GC/MS analysis,†† the gas evolved during the reduction of complexes **1**–**3** by BuLi contains *n*-butane and but-1-ene, whose formation can be attributed to the reactions

$$\sim[M]–OOCR + BuLi = \sim[M]–Bu + RCOOLi;$$
$$2 \sim[M]–Bu = C_4H_{10} + C_4H_8 + 2M^0,$$

where ~M–OOCR is a fragment of the polynuclear Ni^{II} or Pd^{II} complex.

In the liquid reaction products *n*-butyl *tert*-butyl ketone was found by GC/MS. It can be formed by both the reaction of BuLi with the coordinated pivalic acid (in the case of complex **1**)

$$BuLi + Bu^tCOOH \rightarrow LiOH + BuCOBu^t,$$

and the reaction of the Ni^{II} (Pd^{II}) pivalate with BuLi

$$BuLi + Pd(OCOBu^t)_2 \rightarrow Pd + Li_2O + BuCOBu^t.$$

Alkyl complexes of divalent Group VIII metals, which do not contain stabilising ligands like PR_3 or CO, readily undergo redox decomposition to alkyl radicals or cations and zero-valent metal atoms. For example, $PdCl_2$ reacts with the Grignard compound to produce Pd^{II} alkylhalide:[9]

$$PdCl_2 + EtMgBr = EtPdX + MgX_2 \ (X = Cl, Br),$$

which rapidly decomposes to Pd metal, ethane and ethylene:

$$2EtPdX \rightarrow C_2H_6 + C_2H_4 + 2PdX \rightarrow Pd^0 + 2X^-.$$

An analogous reaction involving intermediate alkyl radicals was found in the interaction of Ni^{II} acetylacetonate with triethylaluminum:[10,11]

$$Ni(acac)_2 + Et_3Al \rightarrow Et_2Ni \rightarrow Ni^0 + C_2H_4 + C_2H_6.$$

The TEM, SAXS and EXAFS data for the Ni and Pd nanoclusters that form in the reactions of complex **1** with Et_3Al and **3** with Bu^i_3Al are similar to those for the nanoclusters prepared by reduction with BuLi.

The above metal nanoclusters are close in nature to the colloidal nickel used by K. Ziegler in his early studies of catalytic olefin polymerization.[12]

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¶ The Ni and Pd K-edge EXAFS spectra of Ni and Pd adsorption were recorded on an EXAFS spectrometer at the Siberian Centre of Synchrotron Radiation (Novosibirsk) in a transmission mode with the energy of electrons in a storage ring of 2 GeV and an average current of 80 mA. The oscillating region of the spectra was extracted by the VIPER program.[6] The spectra were fitted using the EXCURV92 program.[7]

†† GC: Varian 3600 chromatograph (50 m OV-1capillary column, room temperature for gases; 60 °C for liquid reaction products); GC/MS: Automass 150 (Delsi Nermag, France, 50 m OV-1 capillary column, electron ionization, 70 eV).

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