

Mixed-Metal Palladium(II) Complexes: a Way from Heterometallic Carboxylates to Bimetallic Nanoparticles

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The paper describes some chemical transformations of the mixed-metal palladium (II) complexes, including interactions of binuclear complexes with pyridine, 1,10-phenanthroline and bipyridine; also described thermal and reductive transformations of some binuclear and pentanuclear nitrogen-containing complexes, in particular red-ox transformations in reductive media to yield mixed-metal nanomaterials. For this nanomaterials and nanoalloys also provided HREM and TEM investigations.

Keywords: Palladium, Transition Metals, Thermal Conversions, Reduction under Mild Conditions.

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1. INTRODUCTION

Palladium-based heterometallic carboxylates seem to be handy precursors of nanoalloys and mixed-metal catalysts [1]. Earlier we used for this purpose Pd^{II}-based heterobimetallic complexes containing the alkaline-earth (Ca, Sr, Ba) [2], transition (Mn^{II}, Co^{II},

Ni^{II}, Cu^{II}) [2, 3], post-transition (Zn^{II}) [3] and rare-earth (Ce^{IV}, Nd^{III}, Eu^{III}, Sm^{III}) metals [4, 5]. (Fig. 1) in which the Pd to complementary metal (M) ratio is 1:1. In this work we prepared and studied new Pd^{II}-based heterometallic carboxylates with a Pd:M ratio of 3:2.

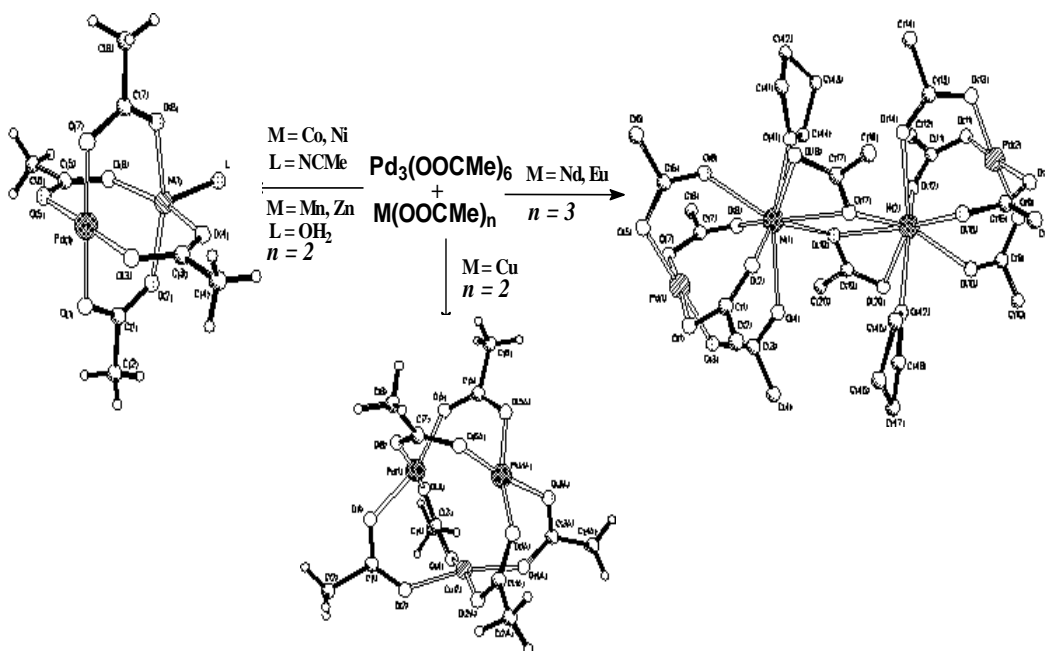


Fig. 1

2. REACTIONS WITH N-DONOR LIGANDS

With this purpose we studied a reactivity and coordination abilities of 1:1 Pd^{II}-based binuclear complexes towards N-bases, pyridine (Py), 1,10-phenanthroline (Phen) and 2,2'-bipyridine (bipy).

Reaction of 1,10-phenanthroline or 2,2'-bipyridine with the binuclear complexes gives isostructural binuclear complexes Pd(μ-OOCMe)₂(η¹-OOC-

Me)M(Phen)₂MeCN (M = Zn, Ni, Co) with three bridging acetate ligands and a short Pd–M distance (Pd···Zn 2.7004(9); Pd···Ni 2.6021(7); Pd···Co 2.6952(9)). Similar complex was obtained by the reaction of PdCo(OOCMe)₄MeCN with 2,2'-bipyridine (Pd···Co distance is 2.6748(9)) (Fig. 2).

The reaction of PdMn(μ-OOCMe)₄(OH)₂ with Phen produced Pd(μ-OOCMe)₄Mn(Phen) with four bridging acetate groups and a Pd–Mn distance of 2.8425(5). The reaction of PdZn(OOCMe)₄(OH)₂ with

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Bipy gave $(\text{Bipy})\text{Pd}(\mu\text{-OOCMe})_2\text{Zn}(\eta\text{-OOCMe})_2$, in which two acetate bridges support the binuclear structure (Fig. 3).

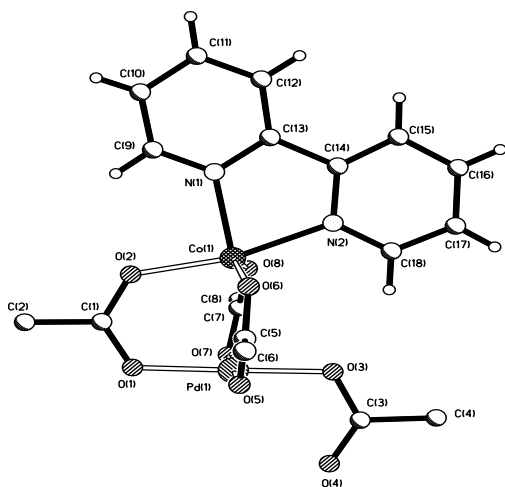


Fig. 2

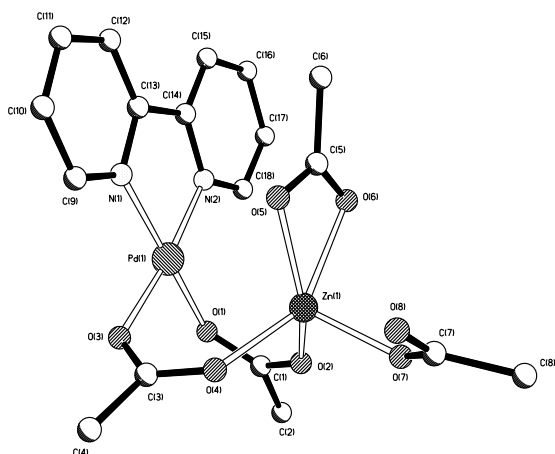


Fig. 3

Unlike these, monodentate N-donor pyridine withdraws Pd^{II} atom from some of the binuclear complexes and the $\text{Pd}(\text{Py})_2(\text{OOCMe})_2$ species formed links the residual intact binuclear complexes, producing the pentanuclear complex $[\text{PdM}(\text{OOCMe})_4]_2\text{Pd}(\text{Py})_2(\text{OOCMe})_2$ (Pd_3M_2 , $\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$) with the $\text{Pd}(\text{Py})_2(\text{OOCMe})_2$ linker (Fig. 4) [6].

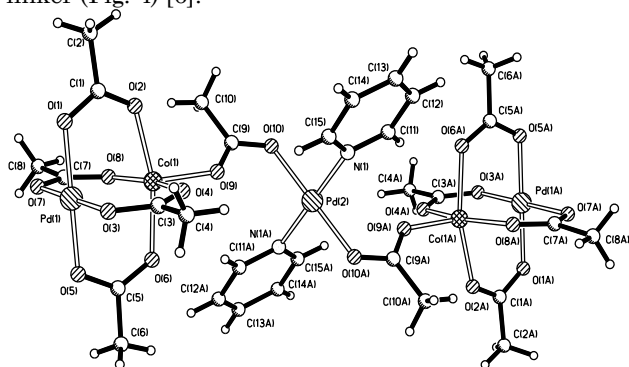


Fig. 4

3. REDUCTIVE THERMOLYSIS OF PENTANUCLEAR COMPLEXES

The obtained pentanuclear complexes $[\text{PdM}(\text{OAc})_4]_2\text{Pd}(\text{Py})_2(\text{OOCMe})_2$ ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$) were thermally decomposed in a 10% $\text{H}_2\text{-He}$ stream, by heating from room temperature to 600°C with the heating rate $20^\circ\text{C}/\text{min}$. XRD of the solid products showed that in all cases at least one non-segregated phase corresponding to a nanoalloy.

3.1 Electron micrographs of the solid products of reduction

The nanomaterials obtained by reduction of the pentanuclear complexes were studied by SEM and HREM, (see Fig. 5, HREM for Pd_3Co_2) and (Fig. 6, SEM for Pd_3Co_2 , Fig. 7 SEM for Pd_3Mn_2).

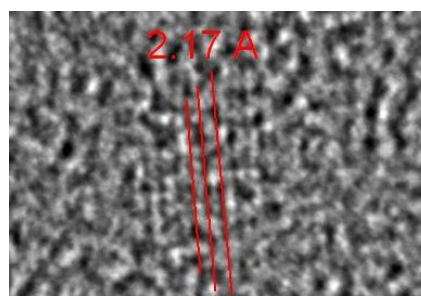


Fig. 5

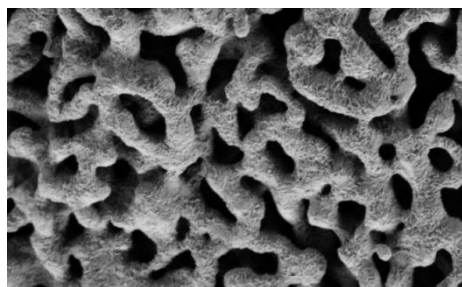


Fig. 6

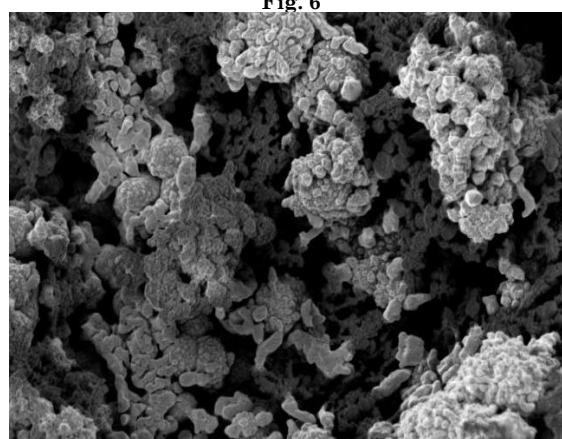


Fig. 7

3.2 Unexpected formation of bipyridine

Study of the gas-phase products of the thermal decomposition of the pentanuclear $\text{Pd}_3\text{M}_2(\text{Py})_2(\text{OAc})_{10}$ and mononuclear $\text{Pd}(\text{Py})_2(\text{OAc})_2$ complexes (Finnigan MAT

INCOS 50 mass-spectrometer, direct probe input, heating 50–250 °C) unexpectedly revealed the formation of bipyridine, the mononuclear Pd(Py)₂(OAc)₂ (Table 1).

Table 1

Complex	Yield, %
[PdCo(OOCMe) ₄] ₂ Pd(C ₅ H ₅ N) ₂ (OOCMe) ₂	0.32
[PdNi(OOCMe) ₄] ₂ Pd(C ₅ H ₅ N) ₂ (OOCMe) ₂	1.47
[PdZn(OOCMe) ₄] ₂ Pd(C ₅ H ₅ N) ₂ (OOCMe) ₂	3.26
[PdMn(OOCMe) ₄] ₂ Pd(C ₅ H ₅ N) ₂ (OOCMe) ₂	11.5
Pd(C ₅ H ₅ N) ₂ (OOCMe) ₂	1.68

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