

## 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<sup>II</sup>-based heterobimetallic complexes containing the alkaline-earth (Ca, Sr, Ba) [2], transition (Mn<sup>II</sup>, Co<sup>II</sup>,

Ni<sup>II</sup>, Cu<sup>II</sup>) [2, 3], post-transition (Zn<sup>II</sup>) [3] and rare-earth (Ce<sup>IV</sup>, Nd<sup>III</sup>, Eu<sup>III</sup>, Sm<sup>III</sup>) 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<sup>II</sup>-based heterometallic carboxylates with a Pd:M ratio of 3:2.

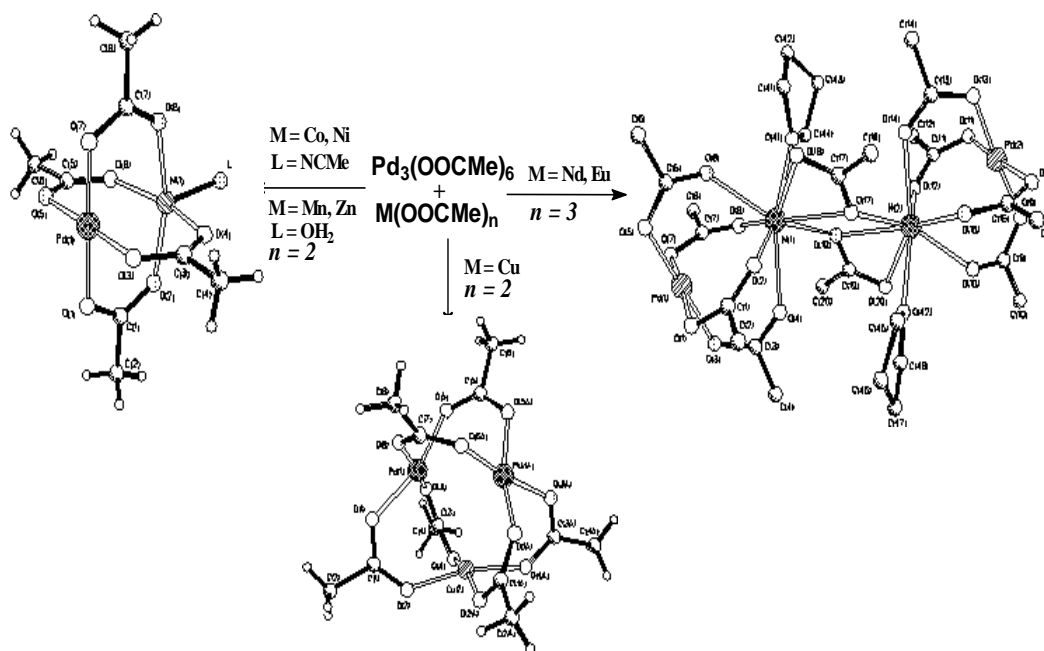


Fig. 1

### 2. REACTIONS WITH N-DONOR LIGANDS

With this purpose we studied a reactivity and coordination abilities of 1:1 Pd<sup>II</sup>-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)<sub>3</sub>(η<sup>1</sup>-OOC-

Me)M(Phen)<sub>2</sub>MeCN (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)<sub>4</sub>MeCN with 2,2'-bipyridine (Pd···Co distance is 2.6748(9)) (Fig. 2).

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

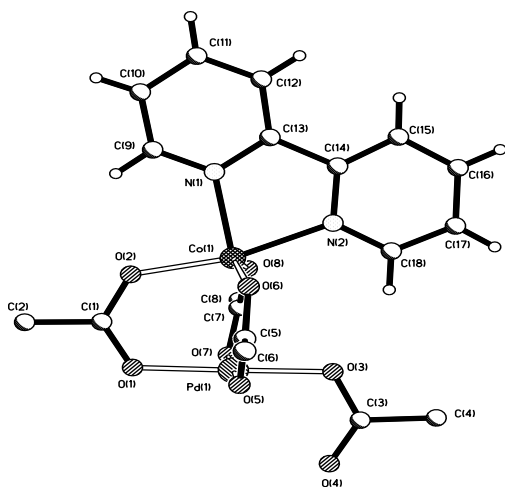


Fig. 2

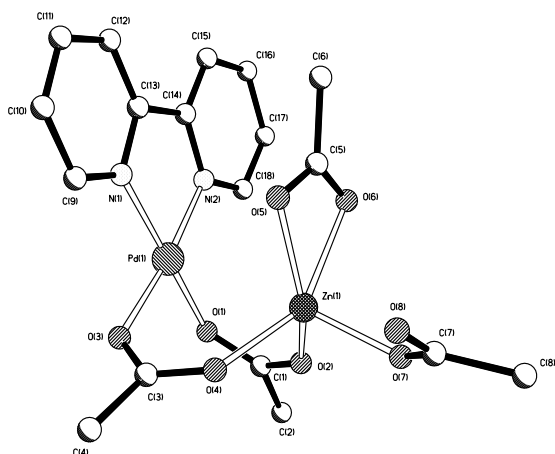


Fig. 3

Unlike these, monodentate N-donor pyridine withdraws  $\text{Pd}^{\text{II}}$  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  $[\text{PdM}(\text{OOCMe})_4]_2\text{Pd}(\text{Py})_2(\text{OOCMe})_2$  ( $\text{Pd}_3\text{M}_2$ ,  $\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$ ) with the  $\text{Pd}(\text{Py})_2(\text{OOCMe})_2$  linker (Fig. 4) [6].

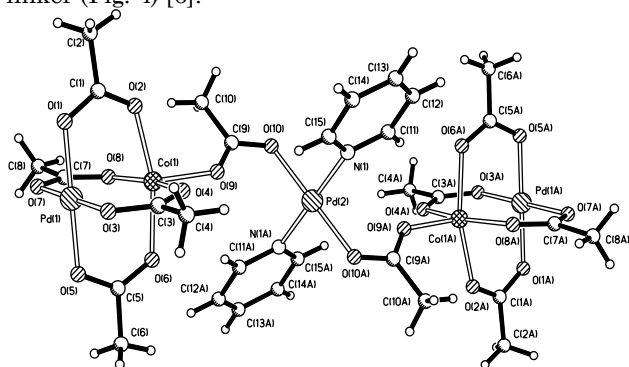


Fig. 4

### 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  $600^\circ\text{C}$  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  $\text{Pd}_3\text{Co}_2$ ) and (Fig. 6, SEM for  $\text{Pd}_3\text{Co}_2$ , Fig. 7 SEM for  $\text{Pd}_3\text{Mn}_2$ ).

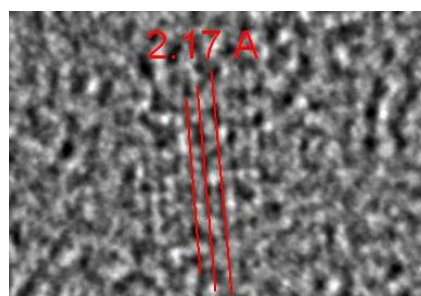


Fig. 5

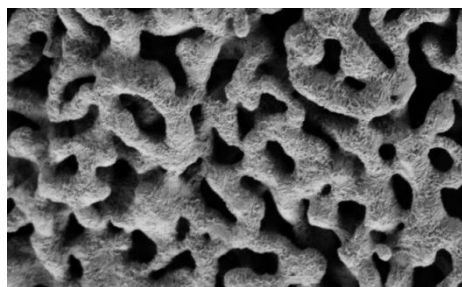


Fig. 6

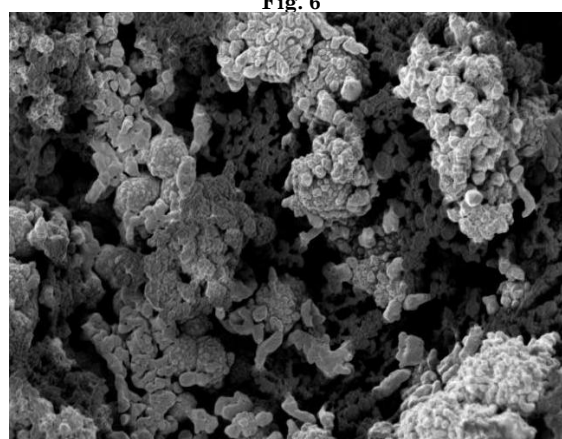


Fig. 7

#### 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)<sub>2</sub>(OAc)<sub>2</sub> (Table 1).

Table 1

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

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## REFERENCES

1. N.Yu. Kozitsyna, S.E. Nefedov, Zh.V. Dobrokhotova, V.N. Ikorsky, I.P. Stolyarov, M.N. Vargaftik, I.I. Moiseev, *Nanotechnologies in Russia* **3**, Nos 3-4, 166 (2008).
2. N.Yu. Kozityna, S.E. Nefedov, I.A. Yakushev, Z.V. Dobrokhotova, M.N. Vargaftik, I.I. Moiseev, *Mendeleev Comm.* **17**, No 5, 261-263 (2007).
3. N.Yu. Kozitsyna, S.E. Nefedov, N.V. Cherkashina, V.N. Ikorski, M.N. Vargaftik, I.I. Moiseev, *Russ. Chem. Bull.* **54**, 2215 (2005).
4. N.Yu. Kozitsyna, S.E. Nefedov, F.M. Dolgushin, N.V. Cherkashina, M.N. Vargaftik, I.I. Moiseev, *Inorg. Chim. Acta* **359**, 2072 (2006).
5. N.Yu. Kozitsyna, S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, *Mendeleev Commun.* **15**, 223 (2005).
6. S.E. Nefedov, I.A. Yakushev, N.Yu. Kozityna, Zh.V. Dobrokhotova, V.N. Ikorsky, M.N. Vargaftik, I.I. Moiseev, *Inorg. Chem. Comm.* **10**, 948–951 (2007).