Inorganic Chemistry Communications 12 (2009) 454–456

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Competition between 3d metals(II) and palladium(II) in the reaction of heterobimetallic complexes $Pd(\mu\text{-}OOCMe)_4M(OH_2)$ (M = Ni, Co, Mn) with azobenzene

Sergei E. Nefedov, Elena V. Perova, Ilya A. Yakushev, Natalia Yu. Kozitsyna, Michael N. Vargaftik *, Ilya I. Moiseev

N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prospect 31, 119991 Moscow, Russian Federation

ARTICLE INFO

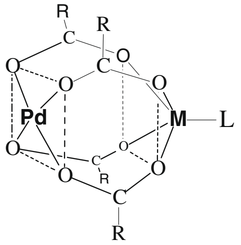
Article history:
Received 28 January 2009
Accepted 22 March 2009
Available online 31 March 2009

Keywords:
Heterobimetallic paddlewheel complexes
Palladium
Azobenzene
Ortho-metallation
X-ray structure

ABSTRACT

The reaction of $Pd^{II}(\mu\text{-}OOCMe)_4M^{II}(OH_2)$ (M = Ni, Co, Mn) with azobenzene under mild conditions produces the homonuclear complex with ortho-metallated azobenzene $(PhN{=}NC_6H_4)_2Pd_2(\mu\text{-}OOCMe)_2$ (**4**) in higher than 90 % yield as the sole Pd-containing reaction product, while the co-metals are recovered as the corresponding M^{II} acetates.

Recently we synthesized and structurally characterised a series of Pd^{II}-based heterodimetallic tetraacetate-bridged paddlewheel complexes with divalent 3d-metals [1,2].



($M = Co^{II}, Ni^{II}, Mn^{II}, Zn^{II}, Cu^{II}$;
$L = OH_2$, NCMe; R = Me, Bu^t).

The heterodimetallic complexes are prospective starting compounds for the preparation of mixed-metal materials such as nanoalloys [3] and catalysts [4] without resorting to severe high-temperature treatments. To develop the preparation procedures of these materials, we studied the chemical behaviour of the starting heterodimetallic complexes during low-temperature treatments in solutions and solid phases, in particular, the comparative reactivities of the metal partners towards N- and O-bases.

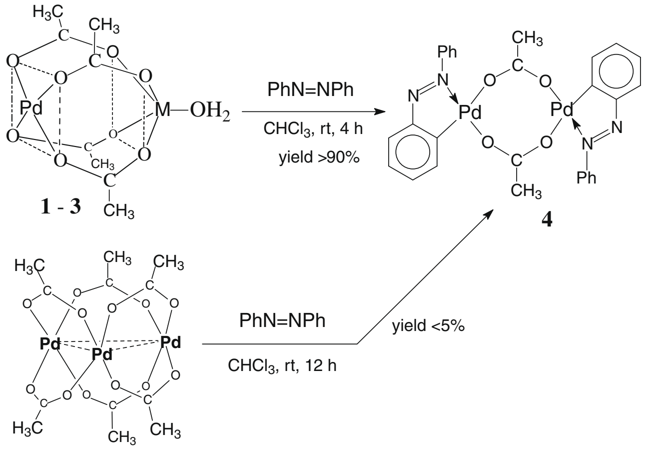
Generally, palladium(II) is a better complexation agent for N-bases than such 3d-metals as Ni^{II}, Co^{II} and Mn^{II}. However, the tetraacetate bridging system is rather strong (providing a very short, ~2.5 Å, Pd–M distance and difficult accessibility of Pd^{II} atom), whereas the axial position of the co-metal coordination sphere is rather labile and easy accessible to a nucleophilic attack. Earlier, we found that such N-donors as 1,10-phenanthroline and 2,2′-bipyridine attach to a co-metal rather than to palladium atom, keeping almost intact the acetate bridging system [5], whereas pyridine partially decomposes the heterometallic complex to form the pentanuclear bis-paddlewheel compound $[Pd(\mu\text{-}OOCMe)_4Co]_2(\mu\text{-}OOCMe)_2Pd(py)_2$ [6].

Here we report on the reaction of the complexes $Pd^{II}(\mu\text{-}OOCMe)_4M^{II}(OH_2)$ (M = Ni (**1**), Co (**2**), Mn (**3**)) with azobenzene. We found that *trans*-Ph_2N_2 readily reacts with complexes **1–3** to produce the homonuclear red-brown complex $(PhN{=}NC_6H_4)_2Pd_2(\mu\text{-}OOCMe)_2$ (**4**) in chloroform at ambient temperature as the sole Pd-containing reaction product [7]:

---

* Corresponding author. Tel.: +7 495 9554865; fax: +7 495 9541279.
E-mail address: wahr36@gmail.com (M.N. Vargaftik).

1387-7003/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2009.03.012



The co-metals form no N-containing reaction products but the corresponding acetate complexes.

The X-ray diffraction [8] showed that the ortho-metallated azobenzene molecules in complex **4** are attached to two Pd^{II} atoms (Pd···Pd 2.9032(3) Å) that are linked by a couple of acetate bridges. The Pd^{II} atoms have a typical square-plane environment of the acetate O atoms as well as the N and C atoms of the ortho-palladated azobenzene ligand (Fig. 1).

In conclusion, two points are worthy of notice. First, in the metal pairs comprising complexes **1–3**, palladium confidently wins the competition with co-metals for azobenzene, while the 3d-metals turned to be inactive in ortho-metallation and transform into the corresponding M^{II} acetates. This fact seems to be not unexpected, although nickel(II) is known as the historically first metallating agent for azobenzene [9]. Another point is that heterometallic complexes **1–3** react with Ph_2N_2 much easier than homometallic $Pd_3(OOCCH_3)_6$, while the latter gives only traces (<5 %) of **4** under these conditions even after 12 h. Generally, the efficiency of ortho-palladation depends on the solvent and Pd^{II} complex ($PdCl_4^{2-}$, $PdCl_2$/$NaOOCCH_3$, etc.), normally producing the ortho-metallated azobenzene or relative N-aryl in 50–60% yield upon rather long staying or heating [10a–c]. The highest yield (91%) was achieved in the reaction of $Pd_3(OOCCH_3)_6$ with azobenzene for 6 h at 50 °C in acetic acid [10d].

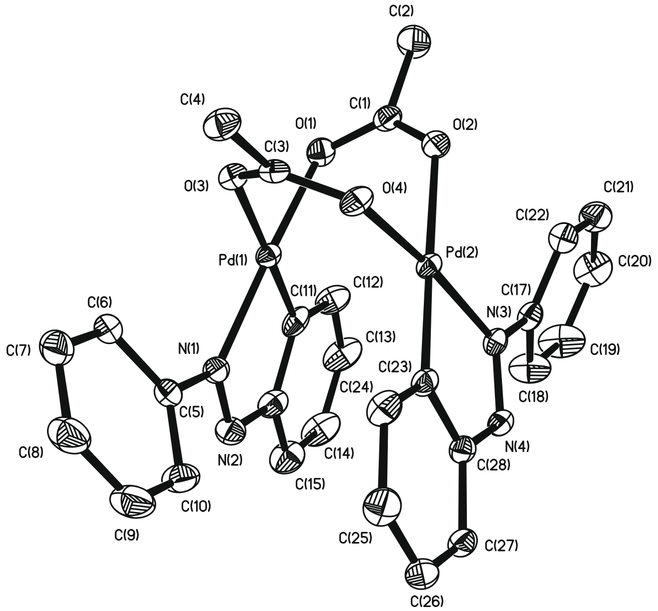


Fig. 1. Crystal structure of complex **4** with thermal ellipsoids at the 30% probability level (H atoms are omitted for clarity). Selected bond distances (Å): Pd(1)–C(11) 1.948(3), Pd(1)–N(1) 2.031(2), Pd(1)–O(1) 2.037(2), Pd(1)–O(3) 2.147(2), Pd(2)–C(23) 1.951(3), Pd(2)–N(3) 2.030(2), Pd(2)–O(4) 2.043(2), Pd(2)–O(2) 2.139(2), N(1)–N(2) 1.271(3), N(1)–C(5) 1.426(4), N(2)–C(16) 1.377(4), N(3)–N(4) 1.277(3), N(3)–C(17) 1.423(4), N(4)–C(28) 1.399(3).

Our results demonstrate a benefit of the Pd^{II}-based heterometallic vs. homometallic complexes in ortho-metallation reactions. The nature of this effect is still unclear. Our preliminary kinetic study [14] suggested a complicated reaction mechanism of the formation of heterometallic complexes **1–3**.

Acknowledgements

We thank for financial support the Russian Foundation for Basic Research (Projects Nos. 08-03-01063, 08-03-90455, 08-03-01150 and 09-03-00514), the Foundation of President of the Russian Federation (program for support of leading Russian scientific schools NSh-1733.2008.3) and the Foundation of the Russian Academy of Sciences (programs for Basic Research "Purposeful synthesis of inorganic substances and creation of related functional materials" and "Theoretical and experimental investigation of the nature of chemical bonding and mechanisms of important reactions and processes").

Appendix A. Supplementary material

CCDC 718271 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.03.012.

References

[1] N.Yu. Kozitsyna, S.E. Nefedov, F. Dolgushin, N.V. Cherkashina, M.N. Vargaftik, I.I. Moiseev, Inorg. Chim. Acta 359 (2006) 2072–2086.

[2] S.E. Nefedov, N.Yu. Kozitsyna, M.N. Vargaftik, I.I. Moiseev, Polyhedron 28 (2009) 172–180.

[3] (a) N.S. Sobal, M. Giersig, Aust. J. Chem. 58 (2005) 307–310;
(b) J.L. Fernandez, D.A. Walsh, A.J. Bard, J. Am. Chem. Soc. 127 (2005) 357–365.

[4] (a) M. Heemeier, A.F. Carlsson, M. Naschitzki, M. Schmal, M. Bäumer, H.-J. Freund, Angew. Chem. Int. Ed. 41 (2002) 4073–4076;
(b) O.P. Tkachenko, A.Yu. Stakheev, L.M. Kustov, I.V. Mashkovsky, M. van den Berg, W. Grünert, N.Yu. Kozitsyna, Zh.V. Dobrokhotova, V.I. Zhilov, S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, Catal. Lett. 112 (2006) 155–161;
(c) M.N. Vargaftik, I.V. Mashkovsky, A.Yu. Stakheev, O.P. Tkachenko, G.N. Baeva, L.M. Kustov, M. van den Berg, W. Grünert, N.Yu. Kozitsyna, S.E. Nefedov, I.I. Moiseev, EUROPA CAT VIII, Turku/Abo, Finland 2007, Books of theses, pp. 2–138.

[5] (a) S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, Inorg. Chem. Commun. 9 (2006) 755–757;
(b) S.E. Nefedov, private communication.

[6] S.E. Nefedov, I.A. Yakushev, N.Yu. Kozitsyna, Zh.V. Dobrokhotova, V.N. Ikorsky, M.N. Vargaftik, I.I. Moiseev, Inorg. Chem. Commun. 10 (2007) 948–951.

[7] Synthesis of **4**. Azobenzene (0.18 g, 1 mmol) and **1** (210 mg, 0.5 mmol) were stirred in 20 ml of chloroform for 4 h at room temperature, the reaction solution was evaporated to dryness and the residue was washed with hexane (5×10 ml) to remove the unreacted azobenzene. The residue was dissolved in 10 ml of benzene and the red-brown solution that formed was filtered. The residual light-green powder, insoluble in organic solvents, contained nickel and traces of palladium (ICP analysis). Anal.: Found (%): C, 22.58; H, 5.04; N, 0.12. $NiC_4H_{14}O_8$. Calc. (%): C, 19.31; H, 5.67). To the solution was added 10 ml of heptane, the solution was concentrated to 5 ml and stored at 5 °C for 24 h. The formed red-brown rhombic crystals of **4** were separated by decantation, washed with cold hexane and dried in an Ar flow. Yield 160 mg, 92% based on Pd. Parallel syntheses with complexes **2** and **3** as the starting materials gave identical (by X-ray) samples of **4** in 94% and 90% based on Pd, respectively. Anal. for **4**: Found (%): C, 48.77; H, 3.19; N, 8.27. $PdC_{14}H_{12}N_2O_2$. Calc. (%): C, 48.50; H, 3.49; N, 8.08. IR (KBr), ν/cm^{-1}: 3451br, *s*, 3053w, 2924m, 2853w, 1744w, 1652w, 1577vs, 1560vs, 1482w, 1458m, 1444m, 1413vs, 1372m, 1346m, 1308m, 1261m, 1243m, 1168w, 1159w, 1019m, 918m, 860m, 840m, 762s, 759s, 708s, 689vs, 622s, 594s, 550m, 433w.

[8] X-ray structure analysis of **4**: Bruker Apex II, CCD-detector $\lambda(\mathrm{Mo}\,K\mathit{a}) = 0.71073$ Å, graphite monochromator, ω-scanning, $2\theta_{\max} = 52°$. $C_{28}H_{24}N_4O_4Pd_2$, $M = 693.31$, orthorhombic, space group $Pna2(1)$, $a = 21.3796(8)$ Å, $b = 9.9655(4)$ Å, $c = 12.7265(5)$ Å, $V = 2711.49(18)$ Å^3 (160 K), $Z = 4$, $D_{\mathrm{calc}} = 1.698$ g/cm^3, 21,168 measured reflections, 5265 [$R(\mathrm{int}) = 0.0214$] independent reflections with $F^2 > 2\sigma(I)$, $\mu = 1.367$ cm^{-1}, $R_1 = 0.0177$, $wR_2 = 0.0433$. Corrections for absorption were made by SADABS [11]. The structure was solved by the direct method and refined by the full-matrix least squares method for F^2 with anisotropic parameters for all non-hydrogen atoms. All calculations were performed with the use of the SAINT [12] and SHELXTL-97 [13] program packages.

[9] J.P. Kleinmann, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 1544–1545.

[10] (a) A.C. Cope, R.W. Siekman, J. Am. Chem. Soc. 87 (1965) 3272–3273;
(b) J. Vicente, I. Saura-Llamas, M.G. Palin, P.G. Jones, M.C.R. Arellano, Organometallics 16 (1997) 826–833;
(c) S.A. Kurzeev, G.M. Kazankov, A.D. Ryabov, Inorg. Chim. Acta 340 (2002) 192–196;
(d) I. Aiello, A. Crispini, M. Ghedini, M. La Deda, F. Barigelletti, Inorg. Chim. Acta 308 (2000) 121–128.

[11] G.M. Sheldrick, SADABS, Bruker AXS Inc., Madison, WI-53719, USA, 1997.

[12] SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software, Bruker AXS Inc., Madison, WI-53719, USA, 1998.

[13] G.M. Sheldrick, SHELXTL-97 V5.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.

[14] N.S. Akhmadullina, N.V. Cherkashina, N.Yu. Kozitsyna, I.P. Stolarov, E.V. Perova, A.E. Gekhman, S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, Inorg. Chim. Acta (2008), doi:10.1016/j.ica.2008.09.042.