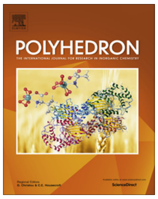
Polyhedron 134 (2017) 215–220

Contents lists available at ScienceDirect

Polyhedron

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



Reactions of metallodithiolate ligand with palladium dichloride bearing monophosphine or diphosphine

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ARTICLE INFO

Article history:
Received 20 May 2017
Accepted 18 June 2017
Available online 21 June 2017

Keywords:
Heterobimetallic
Trinuclear
Nickel
Palladium
Crystal structure

ABSTRACT

Reaction of metallodithiolate ligand Ni(bme-dach*) [bme-dach* = *N,N′*-bis(mercaptoethyl)-1,4-diazacyclohexane] with $Pd[P(4\text{-}C_6H_4CH_3)_3]_2Cl_2$ in the presence of NH_4PF_6 yielded a heterobimetallic complex {Ni(bme-dach*)$Pd[P(4\text{-}C_6H_4CH_3)_3]_2$}$[PF_6]_2$ (**1**) in 43% yield. However, reaction of Ni(bme-dach*) with Pd(dppm)Cl_2 [dppm = 1,1-bis(diphenylphosphino)methane] resulted in the formation of a mononuclear Pd complex $[Pd(dppm)_2][PF_6]_2$ (**2**) via dissociation between Pd–P bonds. Moreover, reaction of Ni(bme-dach*) with Pd(dppv)Cl_2 [dppv = *cis*-1,2-bis(diphenylphosphino)ethylene] in the presence of NH_4PF_6 afforded an expected product [Ni(bme-dach*)Pd(dppv)]$[PF_6]_2$ (**3**) in 80% yield as well as an unexpected product {Ni(bme-dach*)[Pd(dppv)Cl]$_2$}$[PF_6]_2$ (**4**) as a byproduct. The new complexes **1** and **3** were characterized by elemental analysis, ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopy. In addition, the structures of the complexes **1**–**4** were confirmed by single crystal X-ray diffraction analysis.

1. Introduction

Metallodithiolates have been widely used as ligands in coordination, bioinorganic, and organometallic chemistry due to their relationship with the active sites of natural enzymes nitrile hydratase, thiocyanate hydratase, and acetyl coenzyme A synthase (ACS) [1]. For instance, Ni(bme-daco) [bme-daco = *N,N′*-bis(mercaptoethyl)-1,5-diazacyclooctane] [2] and Ni(bme-dach) [bme-dach = *N,N′*-bis(mercaptoethyl)-1,4-diazacycloheptane] [3] were prepared by the reactions of the corresponding dithiols with Ni(acac)$_2$ (acac = acetylacetonate). Further reactions of Ni(bme-daco) or Ni(bme-dach) with other transition metal complexes yielded a great number of dinuclear complexes constructed by two bridging thiolato-S of the metallodithiolate ligands [1,4,5]. Very recently, Darensbourg and co-workers [6] reported that four Ni–Pd complexes were synthesized by the reactions of Ni(bme-dach) or Ni(bme-dach*) with Pd(dppe)Cl_2 [dppe = 1,2-bis(diphenylphosphino)ethane] or Pd(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane]. Further studies revealed that these Ni–Pd complexes can be used as catalysts for Suzuki–Miyaura coupling reactions.

Some examples of heterobimetallic Ni–Pd complexes constructed by NiN_2S_2 are shown in Fig. 1, **A**–**E**, in order to mimic the dinickel structure in the active site of ACS [7–9]. Recently, we focused on the reactions of Ni(bme-dach*) as a metallodithiolate ligand with palladium dichloride bearing monophosphine tris(4-tolyl)phosphine or diphosphine dppm, dppv with aim to synthesize heterobimetallic Ni–Pd complexes via two bridging thiolato-S. As a result, we obtained two expected products **1** and **3** by substitution of two chlorides of $Pd[(4\text{-}C_6H_4CH_3)_3]_2Cl_2$ or Pd(dppv)Cl_2 with two sulfurs of Ni(bme-dach*) as well as two unexpected products of mononuclear Pd complex **2** by dissociation of Pd–P bonds and trinuclear Ni-Pd$_2$ complex **4** by substitution of one chloride of Pd(dppv)Cl_2 with one sulfur of Ni(bme-dach*). Fortunately, the structures of the complexes **1**–**4** were determined by X-ray diffraction analysis. Herein, in this paper, we report the reactions of Ni(bme-dach*) with palladium dichloride bearing phosphine as well as the crystal structures of a mononuclear Pd complex, two dinuclear Ni–Pd complexes and a trinuclear Ni-Pd$_2$ complex constructed by a metallodithiolate ligand Ni(bme-dach*).

2. Experimental

2.1. Materials and methods

NH_4PF_6 was available commercially and used as received. Ni(bme-dach*) [10], $Pd[P(4\text{-}C_6H_4CH_3)_3]_2Cl_2$ [11], Pd(dppm)Cl_2 [11] and Pd(dppv)Cl_2 [11] were prepared according to literature procedures. NMR spectra were obtained on a Bruker 500 MHz spectrometer. Elemental analysis were performed by a Perkin–Elmer 240C analyzer.

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http://dx.doi.org/10.1016/j.poly.2017.06.027

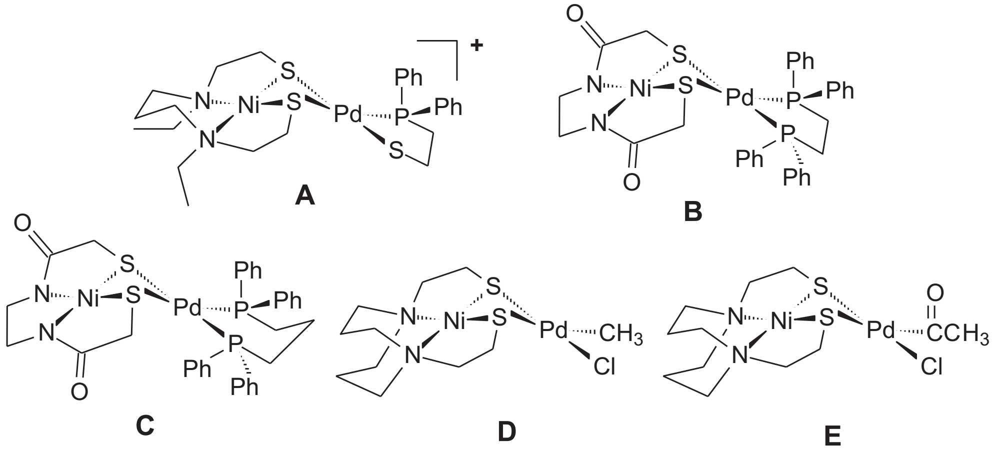

Fig. 1. Some examples of heterobimetallic Ni-Pd complexes **A**, **B**, **C**, **D**, and **E**.

2.2. Synthesis of {Ni(bme-dach*)Pd[P(4-$C_6H_4CH_3$)$_3$]$_2$}[PF_6]$_2$ (**1**)

A mixture of Ni(bme-dach*) (0.105 g, 0.4 mmol), Pd[P(4-C_6H_4-CH_3)$_3$]$_2Cl_2$ (0.314 g, 0.4 mmol), and NH_4PF_6 (0.132 g, 0.8 mmol) were dissolved in CH_3CN (20 mL) and stirred for 1 h. The solvent was reduced *in vacuo* and the residue was subjected to column chromatography using CH_3OH: CH_2Cl_2 = 1% (v/v) as eluent. From the main red band, 0.220 g (43%) of complex **1** was obtained as a red solid. Slow evaporation of complex **1** in CH_2Cl_2/hexane produced X-ray quality crystals. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.31, 7.29 (2s, 12H, Ph*H*), 7.16, 7.15 (2s, 12H, Ph*H*), 4.29 (d, *J* = 5 Hz, 2H, C*H*$_2$), 3.97 (d, *J* = 6.5 Hz, 2H, C*H*$_2$), 2.94 (d, *J* = 6.5 Hz, 2H, C*H*$_2$), 2.68 (d, *J* = 7.5 Hz, 2H, C*H*$_2$), 2.40, 2.38, 2.35 (3s, 24H, 6C*H*$_3$ and 3C*H*$_2$), 0.94 (d, *J* = 12.5 Hz, 2H, C*H*$_2$) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): δ = 23.6 (s), −144.1 (septet, J_{F-P} = 705 Hz, PF_6^-) ppm. *Anal.* Calc. for $C_{50}H_{58}F_{12}N_2NiP_4PdS_2$: C, 47.36; H, 4.61; N, 2.21. Found: C, 47.84; H, 5.10; N, 2.34%.

2.3. Synthesis of [Pd(dppm)$_2$][PF_6]$_2$ (**2**)

The procedure was similar to that used for **1**, except Pd(dppm)Cl_2 (0.224 g, 0.4 mmol) was used instead of Pd[P(4-$C_6H_4CH_3$)$_3$]$_2Cl_2$. From the main red band, ca. 0.1 g [43% yield based on Pd(dppm)Cl_2] of complex **2** was obtained as a red solid. Diffusion of Et_2O into a solution of complex **2** in CH_3CN produced X-ray quality crystals. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (t, *J* = 9.7 Hz, 8H, Ph*H*), 7.39 (s, 12H, Ph*H*), 3.09 (d, *J* = 13 Hz, 2H, C*H*$_2$) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): δ = −33.7 (s), −144.2 (septet, J_{F-P} = 698 Hz, PF_6-) ppm.

2.4. Synthesis of [Ni(bme-dach*)Pd(dppv)][PF_6]$_2$ (**3**) and {Ni(bme-dach*)[Pd(dppv)Cl]$_2$}[PF_6]$_2$ (**4**)

The procedure was similar to that used for **1**, except Pd(dppv)Cl_2 (0.230, 0.4 mmol) was used instead of Pd[P(4-$C_6H_4CH_3$)$_3$]$_2Cl_2$. From the first red band, 0.340 g (80%) of complex **3** was obtained as a red solid. From the second red band, ca. 4 mg of complex **4** was obtained as a byproduct. Diffusion of Et_2O into a solution of **3** or **4** in CH_3CN produced X-ray quality crystals. **3**: ^1H NMR (500 MHz, CD_3COCD_3): 8.01–7.66 (m, 20H, Ph*H*), 7.75 (s, 2H, C*H*=C*H*), 4.18, 4.09 (2s, 4H, 2C*H*$_2$), 3.13 (s, 2H, C*H*$_2$), 2.83 (s, 2H, C*H*$_2$), 2.70–2.63 (m, 4H, 2C*H*$_2$), 2.31, 2.29 (2s, 2H, C*H*$_2$), 1.81 (s, 2H, C*H*$_2$) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, CD_3COCD_3, 85% H_3PO_4): 72.8 (s, dppv-P), −144.3 (septet, J_{F-P} = 699 Hz, PF_6-) ppm. *Anal.* Calc. for $C_{34}H_{38}F_{12}N_2NiP_4PdS_2$: C, 38.68; H, 3.63; N, 2.65. Found: C, 39.03; H, 4.02; N, 2.89%.

2.5. X-ray structure determination

A single crystal of **1**–**4** was mounted on a Bruker D8 QUEST CCD diffractometer. Data were collected at 296(2) K using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) in the ω-ϕ scanning mode. Data collection, reduction and absorption correction were performed by SADABS program [12]. The structure was solved by direct methods using the SHELXS-97 program [13] and refined by full-matrix least-squares techniques SHELXL-97 [13] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of the complexes **1**–**4**

As shown in Scheme 1, reaction of Ni(bme-dach*) with Pd[P(4-$C_6H_4CH_3$)$_3$]$_2Cl_2$ and NH_4PF_6 in CH_3CN resulted in the formation of complex **1** by substitution of the two chlorides in Pd[P(4-C_6H_4-CH_3)$_3$]$_2Cl_2$ with two sulfurs of Ni(bme-dach*). In contrast, reaction of Ni(bme-dach*) with Pd(dppm)Cl_2 gave a mononuclear Pd complex **2** which was confirmed by X-ray diffraction analysis. Another product of this reaction may be {[Ni(bme-dach*)]$_2$Pd}(PF_6)$_2$ deduced by chemical equation which cannot be separated from the reaction. Although complex **2** was reported previously [14], its crystal structure is still unknown. Treatment of Ni(bme-dach*) with Pd(dppv)Cl_2 in the presence of NH_4PF_6 in CH_3CN gave an expected product of a heterobimetallic Ni–Pd complex **3** in 80% yield by substitution of two chlorides in Pd(dppv)Cl_2 with two sulfurs of Ni(bme-dach*) as well as an unexpected product of a trinuclear Ni–Pd_2 complex **4** as a byproduct by substitution of one chloride in Pd(dppv)Cl_2 with one sulfur of Ni(bme-dach*).

The new complexes **1** and **3** are air-stable red solids, soluble in polar solvents such as CH_3CN and acetone, which have been characterized by elemental analysis and NMR spectra. $^{31}P\{^1H\}$ NMR resonances for complexes **1** (23.6 ppm) and **3** (72.8 ppm) are consistent with their precursors Pd[(4-$C_6H_4CH_3$)$_3$]$_2Cl_2$ (21.6 ppm) and Pd(dppv)Cl_2 (71.6 ppm), respectively. In addition, the $^{31}P\{^1H\}$ NMR chemical shift for complex **3** is similar to those of [Ni(bme-dach)Pd(dppe)][PF_6]$_2$ (65.0 ppm) or [Ni(bme-dach*)Pd(dppe)][PF_6]$_2$ (68.0 ppm) [6], but significantly different from those of [Ni(bme-dach)Pd(dppp)][PF_6]$_2$ (3.7 ppm) or [Ni(bme-dach*)Pd(dppp)][PF_6]$_2$ (4.3 ppm) [6].