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Coordination chemistry of the heterotopic 1,2-phenylenebis(thio)diacetic acid ligand: Rhodium(I), palladium(II) and nickel(II) complexes

Christiane Berghof[a,1], Ioana Georgeta Grosu[a,b,1], Peter Lönnecke[a], Santiago Gómez-Ruiz[a,c], Luminita Silaghi-Dumitrescu[b,*], Evamarie Hey-Hawkins[a,*]

[a] Universität Leipzig, Institut für Anorganische Chemie, Johannisallee 29, D-04103 Leipzig, Germany
[b] Department of Chemistry, Babeş-Bolyai University, Kogalniceanu 1, RO-400084 Cluj-Napoca, Romania
[c] Departamento de Química Inorgánica y Analítica, Universidad Rey Juan Carlos, C/ Tulipán s/n, E-28933, Móstoles (Madrid), Spain

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ABSTRACT

Starting from the heterotopic multidentate ligand 1,2-phenylenebis(thio)diacetic acid (**1**), *cis-rac*-$[PdCl_2\{1,2\text{-}(HOOCCH_2S)_2C_6H_4\text{-}\kappa^2S,S'\}]$ (**2**), *cis-rac*-$[Rh\{1,2\text{-}(HOOCCH_2S)_2C_6H_4\text{-}\kappa^2S,S'\}(cod)]BF_4$ (**3**) and *cis-rac*-$[Ni\{1,2\text{-}(OOCCH_2S)_2C_6H_4\text{-}\kappa^4O,O'S,S'\}\{cis\text{-}(C_3H_4N_2)\}_2]$ (**4**) were prepared and characterised by X-ray diffraction and conventional spectroscopic techniques. Compounds **1**–**4** show extensive hydrogen-bonded networks (XH···O, X = O, N) in the solid state.

1. Introduction

The design of functional materials including metal–organic materials (MOMs) such as metal–organic polyhedra, metal–organic frameworks (MOFs) and coordination polymers has received much interest during recent years, not only due to their diverse and interesting architectures, but also because of their applications in fields like gas storage, ion exchange, catalysis, magnetism and non-linear optics [1–5].

Although molecular self-assembly is a promising route to synthesise coordination polymers, [6,7] the controlling factors and experimental conditions for the preparation of the polymers are not yet completely understood [8,9]. In recent years, rational synthetic approaches for the assembly of the target structures from molecular building blocks have been taken into consideration. The key step in the rational approach is the design of molecular building blocks which can direct the formation of the desired architecture and functionality of the target compound. Organometallic species such as π-bonded benzoquinone manganese(II), rhodium(I) and copper(I) complexes [10–12] or hydroquinone manganese(II) complexes [13] were successfully used as bifunctional ligands (organometallo-ligands) for the rational construction of coordination polymers. Furthermore, heterobimetallic coordination polymers (e.g., Ln–Ba, Ln–Na and Ln–Ca) that retain the luminescence properties of the starting mononuclear Ln complexes were obtained by a stepwise approach [14,15], as were polymers based on ferrocenylzinc, and -calcium [16]. On the other hand, coordination polymers are widely used in catalysis [2(f), 17]. Some transition metal complexes are well known for their catalytic potential, especially those of Pd, Rh and Ni, which are successfully used as catalysts in many reactions like Suzuki–Miyaura cross-coupling [18,19], hydroformylation of terminal alkenes [20], Heck olefination [21], carbonylation [22], asymmetric Wittig olefination [23], α-arylation of acyclic ketones [24] and ethylene polymerisation [25].

Taking into account the above considerations we set out to synthesise potentially suitable mononuclear building blocks for the rational preparation of catalytically active coordination polymers. The flexible 1,2-phenylenebis(thio)diacetic acid was chosen as a hybrid multidentate ligand that contains both soft (S) and hard (O) donor sites and is thus potentially suitable for selective coordination to specific transition metals.

2. Results and discussion

The coordination chemistry of 1,2-phenylenebis(thio)diacetic acid (**1**) [26,27] towards Pd, Rh and Ni was studied (Scheme 1). Complexes **2** and **3** were obtained in high yield as orange crystals from the reaction of **1** with $[PdCl_2(cod)]$ and $[Rh(cod)_2]BF_4$

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* Corresponding authors. Tel.: +49 341 9736151; fax: +49 341 9739319.
E-mail address: hey@rz.uni-leipzig.de (E. Hey-Hawkins).

[1] Joint first authors.

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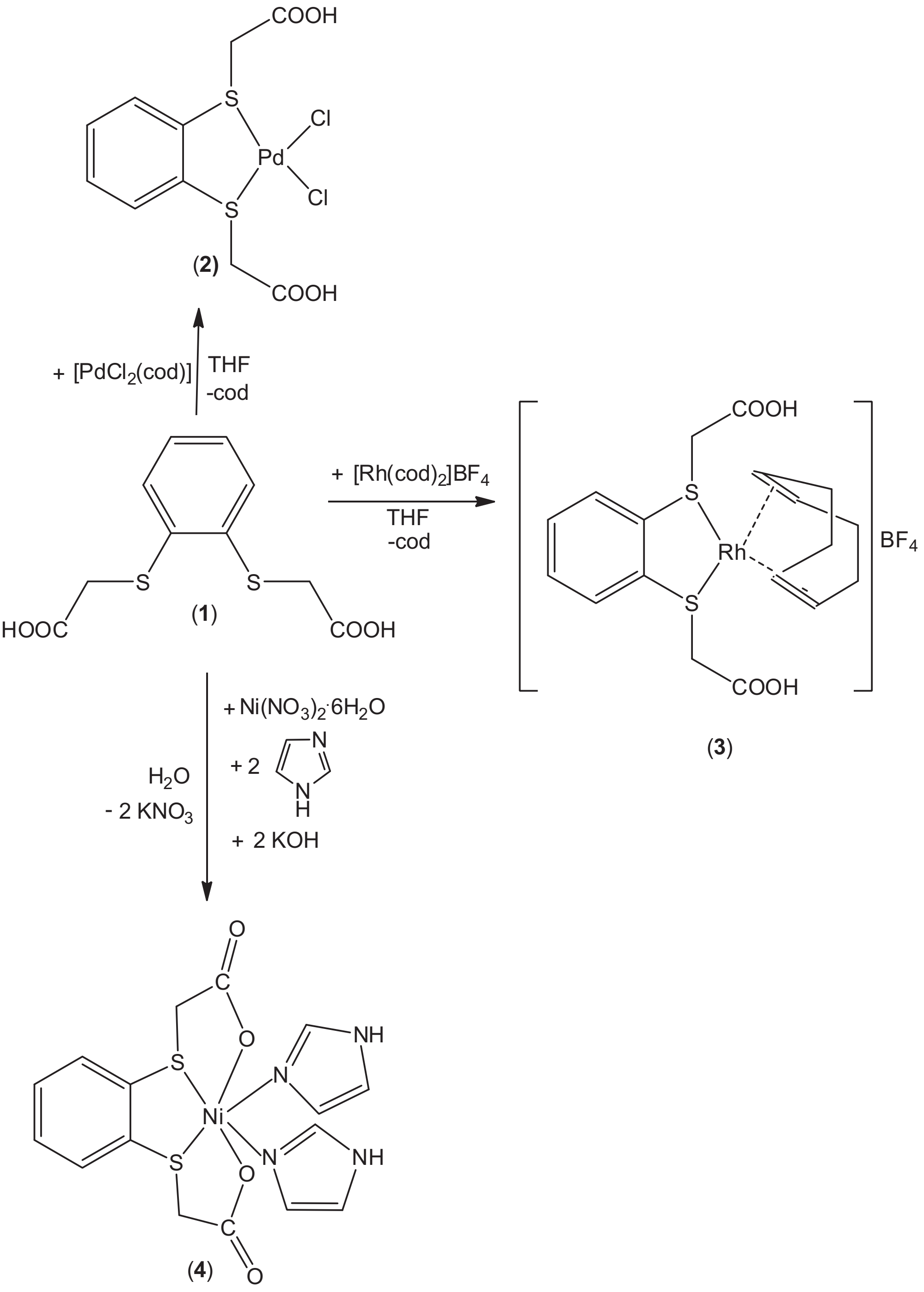

Scheme 1.

(cod = 1,5-cyclooctadiene), respectively, in refluxing THF by displacement of one cod group of the starting material by the two sulfur atoms of the ligand, which coordinate at the metal centre in a chelating manner leading to the formation of the *cis* isomers. In these complexes the carboxylic acid groups remain uncoordinated, and it might thus be possible to employ them in further coordination to construct extended networks. However, deprotonation reactions could also result in the formation of S,O-chelate complexes, as was observed in the case of nickel(II).

Thus, the mixed ligand nickel(II) complex **4**, which provides different donor groups for further coordination, was obtained by treating **1** with $Ni(NO_3)_2 \cdot 6H_2O$ in water in the presence of two equivalents of KOH as base to deprotonate the carboxyl groups and two equivalents of imidazole as co-ligand.

Complexes **2** and **3** were characterised by ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy, mass spectrometry and elemental analysis. Complex **4** has very low solubility in common solvents and was only characterised by IR spectroscopy, magnetic measurements and elemental analysis. Furthermore, single crystals suitable for X-ray crystallography could be obtained for ligand **1** and complexes **2**–**4**.

Complex **4** exhibits antiferromagnetic behaviour, the Weiss constant (Θ) has the value of -0.27 K, the effective magnetic moment is $\mu_{\text{eff}} = 3.08$ μB.