Inorganica Chimica Acta 409 (2014) 238–243

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Supramolecular chemistry of the ligand N,N'-bis(2-diphenylphosphinoethyl)phthalamide and its complexes with gold(I) and silver(I)

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ARTICLE INFO

Article history:
Received 11 July 2013
Received in revised form 9 September 2013
Accepted 13 September 2013
Available online 20 September 2013

Keywords:
Dicarboxamide–diphosphine
Gold(I)
Silver(I)
Supramolecular assembly

ABSTRACT

The dicarboxamide–diphosphine ligand N,N′-bis(2-diphenylphosphinoethyl)phthalamide, dpppa, which is prepared from 2-diphenylphosphinoethylamine and phthaloyl chloride, forms the binuclear gold(I) complex [Au_2Cl_2(μ-dpppa)], **1**, and polymeric complex [{Ag_2(μ-O_2CCF_3)$_2$(μ-dpppa)}$_n$], **2**. The ligand and both complexes **1** and **2** undergo further association through hydrogen bonding to give supramolecular polymer or network structures.

1. Introduction

There is growing interest in the use of diphosphine–carboxamide ligands in the design of catalysts or molecular materials [1–3]. The phosphine groups are typically used to bind to transition metal ions while the carboxamide groups engage in hydrogen bonding, with the role to recognize substrates for catalysis or to increase dimensionality in molecular materials [1–8]. For example, coordination polymers or network materials can be prepared by using the phosphine donors to form a primary structure through dynamic coordination chemistry or dynamic ring-opening polymerization, and by using the carboxamide groups to increase the dimensionality [9,10]. This general strategy has been developed primarily through the use of nitrogen-donors rather than phosphorus-donors, but recent work certainly indicates that phosphine-carboxamide ligands have great potential [11–17]. We have reported on the chemistry of the terephthalamide and isophthalamide derivatives dppeta [7] and dpipa [8] (Chart 1) and this work describes the synthesis and chemistry of the corresponding phthalamide derivative dpppa (Chart 1). This *ortho* substituted diphosphine ligand, N,N′-bis(2-diphenylphosphinoethyl)phthalamide, dpppa, can be compared to the *para* and *meta* substituted isomers dppeta and dpipa, and also to related *ortho* substituted diphosphine–dicarboxamide ligands such as dppbH and Trost's ligand (Chart 1) [18–20]. These are versatile diphosphine ligands which can give *cis* or *trans* chelate complexes, and they can also act as bridging ligands [7,18–21]. Several chiral ligands, which can be considered as derivatives of dpppa, have been prepared by Morimoto and used for chiral catalysis but the parent dpppa was previously unknown [22,23].

2. Results and discussion

The ligand dpppa was prepared by reaction of phthaloyl chloride with $Ph_2PCH_2CH_2NH_2$, according to Scheme 1. There is a competition between formation of dpppa and cyclization to give the phthalimide derivative 1,2-$C_6H_4(CO)_2NCH_2CH_2PPh_2$, dpppi. The yield of dpppa was improved by using excess $Ph_2PCH_2CH_2NH_2$, and the products were then separated by column chromatography. Isolated yields of dpppi and dpppa were 38% and 40% respectively. In the ^{31}P NMR spectrum, dpppa gave a singlet resonance at $\delta(^{31}P) = -21.29$ and in the ^{1}H NMR spectrum it gave multiplet resonances for the CH_2P and CH_2N protons at $\delta(^{1}H) = 2.31$ and 3.46 respectively and a resonance at $\delta(^{1}H) = 6.89$ for the NH protons. The ligand dpppi was characterized in the ^{1}H NMR spectrum by CH_2N and CH_2P resonances at δ 3.85 and 2.45 respectively and, in the ^{31}P NMR spectrum, by a singlet resonance at δ −21.46.

The structures of dpppi and dpppa are shown in Figs. 1 and 2. In dpppi (Fig. 1), the nitrogen atom has trigonal planar stereochemistry, while the phosphorus atom has the usual trigonal pyramidal stereochemistry. In dpppa (Fig. 2), the amide groups are roughly planar [torsion angles O(1)–C(15)–N(1)–C(14) 3°, O(2)-C(22)-N(2)-C(23) 4°], but they are significantly twisted out of the plane of the central C_6H_4 group [torsion angles O(1)–C(15)–C(16)–C(21) 38°, O(2)–C(22)–C(21)–C(16) 124°]. The result of this unsymmetrical twist of the two amide groups is that the two oxygen atoms lie

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http://dx.doi.org/10.1016/j.ica.2013.09.024

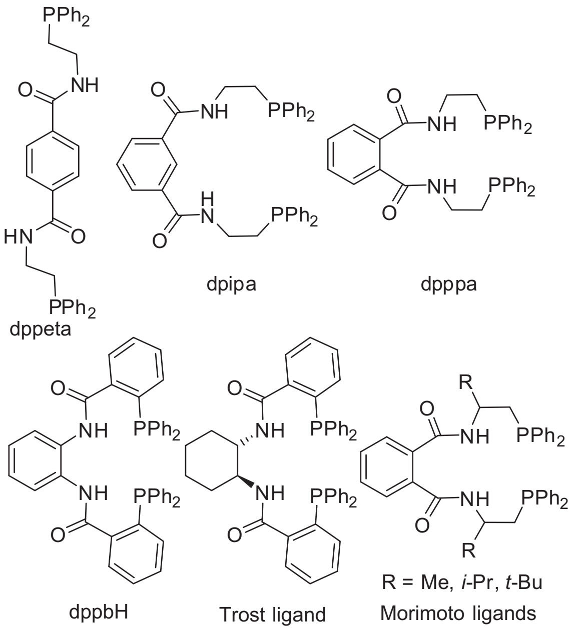
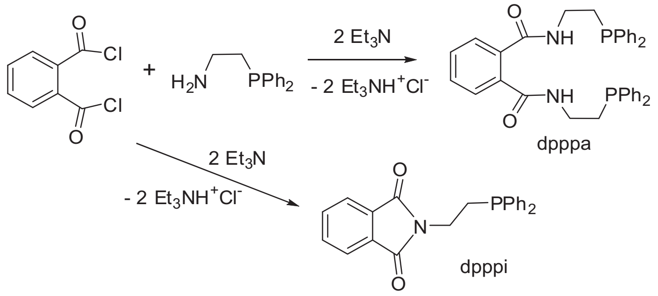


Chart 1. Some diphosphine–dicarboxamide ligands.



Scheme 1. Synthesis of the ligand dpppa.

on one side and the two NH groups on the other side of the C_6H_4 group. There is intermolecular hydrogen bonding of the type C═O···HN to give a supramolecular polymeric structure (Fig. 2b). Each molecule of dpppa forms four hydrogen bonds, using two NH donors to the neighboring molecule on one side and two C═O acceptors to the neighboring molecule on the other side (Fig. 2b).

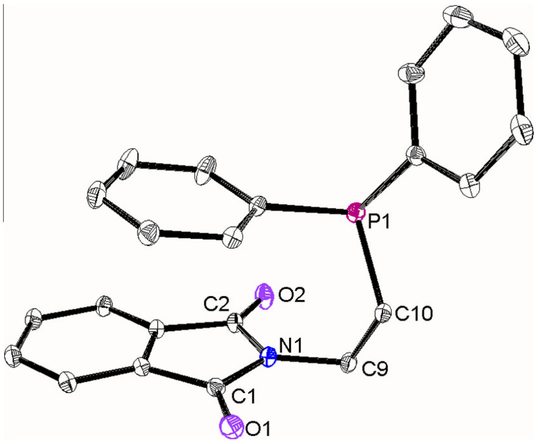


Fig. 1. The structure of dpppi, showing 30% probability ellipsoids. Selected distances: O(1)–C(1) 1.2147(8), O(2)–C(2) 1.2105(8), C(1)–N(1) 1.3958(9), N(1)–C(2) 1.3967(8), N(1)–C(9) 1.4576(9) Å.

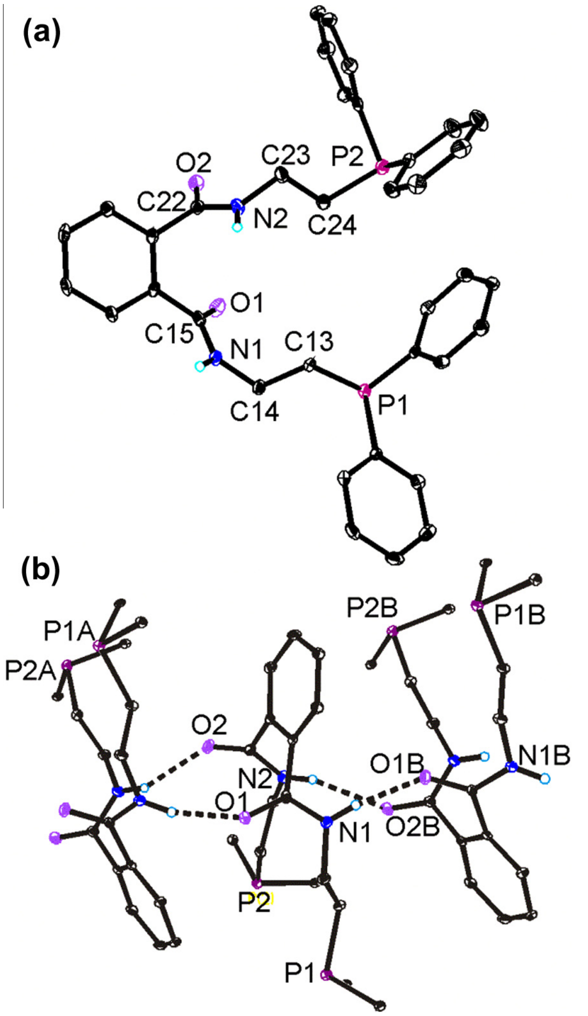
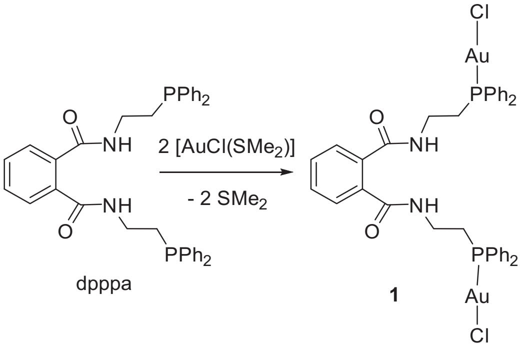


Fig. 2. The structure of the ligand dpppa: (a) the molecular structure (30% probability ellipsoids); (b) part of the supramolecular polymeric structure formed by intermolecular hydrogen bonding (only the *ipso* carbon atoms of the phenyl groups are shown). Selected distances: O(1)–C(15) 1.234(4), N(1)–C(15) 1.324(4), O(2)–C(22) 1.233(4), N(2)–C(22) 1.347(5) Å. Hydrogen bond distances: N(1)···O(1B) 2.770(4), N(2)···O(2B) 3.049(4) Å. Symmetry equivalent molecules: *x*, 1 − *y*, −½ + *z*; *x*, 1 − *y*, ½ + *z*.



Scheme 2. Synthesis of complex 1.

The ligand dpppa reacted with two equivalents of $[AuCl(SMe_2)]$ to give the gold(I) complex $[Au_2Cl_2(\mu\text{-dpppa})]$, **1**, as shown in