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Bimetallic neutral palladium (II) bis(dithiolene) complex: Unusual synthesis, structural and theoretical study

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ABSTRACT

The unusual synthesis of the dimeric dithiolene complex $[(PPh_3)Pd(ethylene-1,2-dithiolate)]_2$ (1), containing the simplest dithiolene ligand, has been achieved through the reaction between tetrathiafulvalene (TTF) and $Pd(PPh_3)_4$. The complex shows a folded structure in the solid state, according to single crystal X-ray analysis performed on crystals grown from two different system solvents and conditions, with a central $[Pd_2S_2]$ ring folded about the S...S hinge by 67.9° . The optimized geometry at the DFT level is in excellent agreement with the experimental structure. Moreover, TD-DFT calculations allowed the assignment of the low energy band arising at 576 nm to the HOMO→LUMO transition, between frontier orbitals having mixed metal and dithiolene character.

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1. Introduction

Metal-dithiolene complexes have been extensively studied since many years for the elaboration of molecular materials with conducting, magnetic and optical properties [1], their peculiarity coming from the non-innocence of the dithiolate ligands. Indeed, the frontier orbitals of such complexes develop both on the ligands, especially the sulfur atoms, and on the metal centers [2]. This feature, combined with their propensity to engage in intermolecular S...S and metal...S interactions, thus providing excellent stacking properties in the solid state, makes them valuable building blocks for conducting and magnetic materials [3]. In addition, metal bis(dithiolene) complexes in different oxidation states show strong absorption in the near infrared region [4] from 700 nm (nickel) up to $1.6 \mu m$ (gold) depending on the nature of the metal and the substitution pattern of the dithiolene ligand [5]. The group 10 (Ni, Pd, Pt) square planar complexes show in the monoanionic or neutral species, very often obtained upon oxidation of the

initially formed dianionic compounds, these low energy absorption bands, attributed to π - π^* transitions of HOMO–SOMO and HOMO–LUMO types, respectively [6]. Accordingly, such complexes have found applications as near infrared photodetectors [7], optical switching devices [8], organic dyes [9], and organic electronics [10].

In the case of the simplest 1,2-dithiolene ligand, e.g. 1,2-ethylene-dithiolate ($S_2C_2H_2$), also considered as the “parent dithiolene”, the crystal structures of the neutral bis(dithiolene) complexes $[M(S_2C_2H_2)_2]$ ($M = Ni, Pd, Pt$) show, interestingly, dimeric units formed through $M...M$ bonds for Pd and Pt, while the Ni complex consists of isolated monomers [11]. The low energy absorption bands for these “parent complexes”, in which the oxidation from the dianion to the neutral species affects mainly the “non-innocent” ligands, appear at 720 nm (Ni) [5a], 785 nm (Pd) [5b], and 680 nm (Pt) [5c]. Neutral metal mono(dithiolene) complexes ($M = Ni, Pd, Pt$) can be obtained by formally replacing one dithiolene ligand by two monodentate or one bidentate neutral ligand, such as the phosphines. However, in this case there is no ambiguity on the oxidation state of the components, since the metal is $2+$ and the dithiolene $2-$. Accordingly, an extensive series of neutral mono(dithiolene) complexes formulated as

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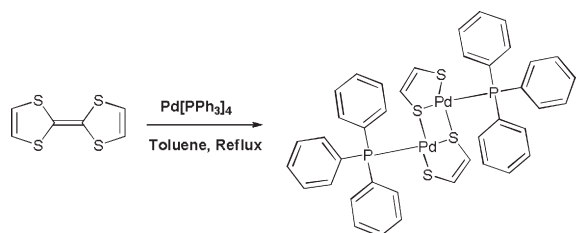
(P2)M(dithiolene) (M = Ni, Pd, Pt) have been synthesized, where P2 stands generally for two PPh₃ or one dppe ligands (dppe = 1,2-bis(diphenylphosphino)ethane) [12]. The colours of these complexes when the dithiolene is maleonitriledithiolate (mnt) vary from brown-red for Ni to orange for Pd and, finally, yellow for Pt, yet large variations are observed upon changing the substitution pattern on the dithiolene ligand. For example, the Pd complex formulated as (Ph₃P)₂Pd(S₂C₂(SMe)₂), thus containing the bis(thiomethyl)dithiolene ligand, for which the single crystal X-ray structure was described, was obtained as red-violet crystals [12c]. Note that in all the crystal structures described so far the complexes appear as monomeric units. Generally, the synthesis of these neutral mono(dithiolene) complexes involves either the reaction between the (P2)MCl₂ complex with the dithiolate [12e], the displacement of a dithiolene ligand from the neutral bis(dithiolene) complexes by phosphines [12a,b], or the displacement of a cyclooctadiene (COD) from (COD)Pt(dithiolene) by phosphines [12f,g]. However, other more specific methods have been also employed, such as the direct reaction between the Pd(PPh₃)₄ complex and the dimethyltetraathiooxalate in the case of (Ph₃P)₂Pd(S₂C₂(SMe)₂) [12c]. To our knowledge, in all but one case [12g], the dithiolene ligand was not the parent one. Surprisingly indeed in this series, only the platinum complex (Ph₃P)₂Pt(edt) (edt = 1,2-ethylene-dithiolate) was described as a bright yellow solid, although without any crystal structure analysis [12g].

We describe herein the unexpected synthesis of the [(Ph₃P)Pd(edt)]₂ dimeric complex **1**, together with its spectroscopic and structural characterization. DFT and TD DFT calculations have been performed in order to support the experimental geometry and to explain the electronic structure of this unprecedented dimeric dithiolene complex.

2. Results and discussion

2.1. Synthesis and characterization

We noticed initially the formation of the title compound [(Ph₃P)Pd(edt)]₂ (**1**), identified after single crystal X-ray analysis (*vide infra*), as traces of by-product during our attempts of Stille type coupling between TTF-SnMe₃ and various halogenated aromatic substrates in the presence of the standard Pd(0) catalyst Pd(PPh₃)₄ [13]. Puzzled by this observation we decided to rationalize the formation of **1** and assumed that the direct reaction between TTF and Pd(PPh₃)₄ would afford **1**, in the absence of any other obvious reaction paths (Scheme 1).



Scheme 1. Synthesis of **1**.

Indeed, after refluxing during 48 h an equimolar mixture of TTF and Pd(PPh₃)₄ in toluene, the only product which has been isolated after chromatographic work-up was the dimeric dithiolene complex **1**. Clearly, the yield of this reaction is low, yet the unreacted TTF is fully recovered, while the excess of palladium complex affords black colloidal palladium together with phosphine and phosphine-oxide. The complex **1** was obtained as an air stable dark violet crystalline solid which was first characterized by spectroscopic methods. ³¹P NMR spectrum shows a sharp single peak at 30.26 ppm, indicative of PPh₃ ligands symmetrically coordinated to a Pd-dithiolate fragment [14]. ¹H NMR is in agreement with a 1:1 ratio between an edt and a PPh₃ ligand, although the chemical shift of one of the vinylic protons is somewhat puzzling, since it appears rather shielded, at 4.46 ppm, when compared with the other proton at 6.28 ppm, the usual value for this type of proton. The explanation for this upfield shift lies very likely in the location of the corresponding proton in the anisotropy cone of one phenyl ring of the PPh₃ ligand. This assumption is supported by the crystal structure (*vide infra*) of the complex, showing clearly the short distance (2.63–2.65 Å) between the proton and the centroid of one phenyl ring. An important result was the observation of the molecular peak of the dimer in MALDI-TOF, indicating the presence and stability of the species also in solution and not only in the crystal structure.

At the present stage, the formation of **1** is hard to explain through a reaction mechanism. One can speculate that in an initial step the unsaturated Pd(PPh₃)₂ fragment, generated by decoordination of two phosphines upon heating, coordinates to the outer double bond of TTF, as it was observed for the Pt(PPh₃)₂ fragment, for which η² complexes [(PPh₃)₂Pt(η²-TTF)] and [(PPh₃)₂Pt(η²-o-Me₂TTF)] have been evidenced, including a single crystal X-ray structure for the latter [15]. Interestingly, the coordination of the Pt center took place exclusively to the unsubstituted double bond, thus suggesting that the steric hindrance of the Me groups very likely hampers the η² coordination. Accordingly, the initial occurrence in our case of a η² complex [(PPh₃)₂Pd(η²-TTF)] (or bis-η² complex [(PPh₃)₂Pd(η²-TTF-η²)Pd(PPh₃)₂]) does not seem unlikely, all the more since when we heated Me₄-TTF (TMTTF), with both double bonds substituted by methyl groups, with Pd(PPh₃)₄ in toluene no dithiolene complex was formed and only the precipitation of black colloidal Pd was observed. The same result was obtained when TTF-tetra(methylcarboxylate) (TTF(COOMe)₄), an electron poorer donor, was heated in the presence of Pd(PPh₃)₄. In such hypothesized η² complex, [(PPh₃)₂Pd(η²-TTF)], the Pd center, perpendicular to the TTF mean plane, would be in favorable situation to interact with the neighboring S atoms and eventually to migrate on them, followed by the insertion in one of the C–S bonds. Then a reductive elimination of a carbene species would generate the monomeric [(PPh₃)₂Pd(edt)] complex which further dimerizes in the reaction conditions, upon loss of a phosphine ligand, to afford the most stable species **1**.

As already mentioned, the complex **1** was obtained as a dark violet crystalline solid. Solutions of **1** in methylene

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