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Communication

Formation of Trinuclear Palladium Orthometalated Complexes with Unprecedented Asymmetrical (μ_3-S)(μ_3-X) Bridges (X = OH, SR, O_2CR) from μ_2-Hydroxo Dimeric Complexes and CS_2[†]

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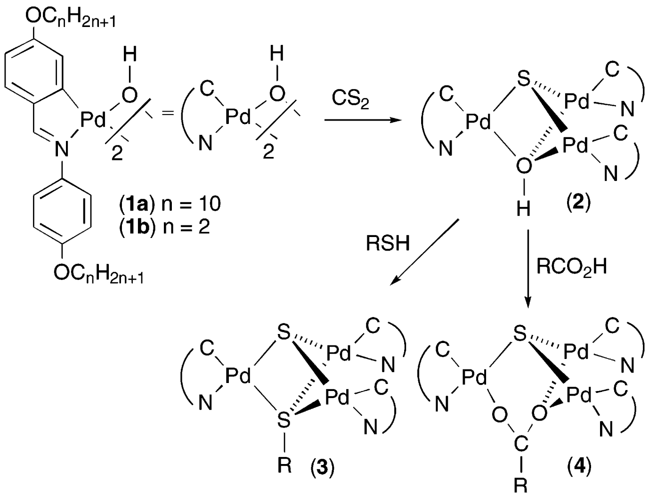
Complexes $[Pd_3(\mu_3\text{-}S)(\mu_3\text{-}X)(L)_3]$ (L = orthometalated imine), obtained by an unusual reaction of μ_2-OH dimeric complexes and CS_2, are an unprecedented type of asymmetrical bridges between metallatriangles, which force an all-cis arrangement of the three orthometalated ligands relative to the metallatriangle.

The reactivity of binuclear compounds $[Pd(\mu\text{-}OH)L^n]_2$ HL^n = $p\text{-}C_nH_{2n+1}O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}OC_nH_{2n+1}\text{-}p$ (n = 2, 6, and 10) toward protic substrates such as amines, thiols, and carboxylic acids provides a versatile entry to mesomorphic binuclear complexes (metallomesogens) with other bridges, and to mesomorphic mononuclear *N*,*N*-dialkyldithio−carbamate complexes by reaction with dialkylamines in the presence of carbon disulfide.[1] The change in molecular shape from dinuclear to mononuclear metallomesogens produces a noticeable lowering of transition temperatures, as expected from the less favorable molecular shape of the latter.[2] Pursuing our interest in novel structures to add to the still limited types of metallomesogenic materials, it was planned that the reaction of the μ-hydroxo complexes with alcohols and CS_2 might afford mononuclear xanthate complexes.[3] The outcome of the study was quite different.

When $[Pd(\mu\text{-}OH)L^{10}]_2$ (**1a**, Scheme 1) in CH_2Cl_2 was treated with 2 molar equiv of octanol and carbon disulfide at 35 °C for 7 h, a yellow compound **2a** was obtained. The ^1H NMR spectrum of **2a** showed (a) the absence of octanyloxy chains; (b) only one set of ^1H resonances for the orthometalated imine ligand; and (c) a singlet at −2.55 ppm (with intensity 1 for 3 imines) which might be due to the presence of a μ-OH group. A very weak absorption in the IR at ca. 3622 cm^{-1} was in the expected range for ν(OH). Good quality crystals suitable for a full X-ray analysis could not be obtained for this complex with long aliphatic chains, nor for its analogue **2b** with L^2, but partial resolution of poor quality crystals for **2b** revealed the existence of a Pd_3 core with two bridging ligands which, according to the elemental analysis C,H,N,S and the IR and ^1H NMR spectra, are assigned one S and one OH group, as shown in Scheme 1.

Scheme 1



The structure of **2** is further supported by those found for two derivatives (**3b** and **4b**). The hydroxo ligand of complexes **2** is easily replaced when treated with some Brönsted acids. Thus, treatment of **2b** with HSC_4H_9 (molar ratio 1:1) afforded the trinuclear complex $[Pd_3(\mu_3\text{-}S)(\mu_3\text{-}SC_4H_9)(L^2)_3]$ (**3b**), with mixed sulfide−thiolato bridges. The ^1H NMR resonances of the orthopalladated imine ligand in **3b** indicate a cis arrangement of the three imines. The upfield shift of the methylene groups of the SC_4H_9 chain is consistent with the thiolato group being cis to the imine nitrogens.[4] The X-ray structure of **3b** was determined **(**Figure 1).[5] The

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[†] Dedicated to Professor J. Vicente on the occasion of his 60th birthday.

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(5) Crystal data for **3b**·$2C\underline{H}_2Cl_2$: $C_{57}H_{67}Cl_4N_3O_6Pd_3S_2$, M = 1415.26, triclinic, space group $P\bar{1}$, a = 13.630(10) Å, b = 14.167(11) Å, c =16.393(12) Å, α = 80.885(15)°, β = 82.382(15)°, γ = 78.950(14)°, V = 3050(4) $Å^3$, Z = 2, R_1 = 0.0578, wR_2 = 0.1700. CCDC-211688.

10.1021/ic0351085 CCC: $27.50

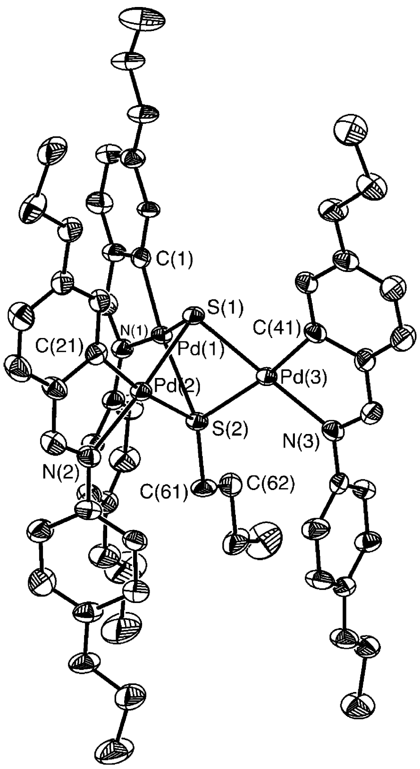


Figure 1. Molecular structure of **3b** with thermal ellipsoids (30% probability). Selected bond lengths (Å): S(1)−Pd(1) 2.304(2), S(1)−Pd(3) 2.307(3), S(1)−Pd(2) 2.314(3), S(2)−Pd(3) 2.385(2), S(2)−Pd(1) 2.407(3), S(2)−Pd(2) 2.430(3).

molecule consists of three Pd(C−N) moieties linked by one μ_3-sulfide and one μ_3-thiolate ligand. The triangle formed by the three Pd atoms in the Pd_3S_2 core of the molecule is not equilateral due to the distortion forced by the alkyl tail of the thiolato, which is oriented between the imines coordinated to Pd(1) and Pd(3). The Pd(1)−S(1)−Pd(3) angle (96.32°) is larger than the other two (Pd(1)−S(1)−Pd(2), 82.43°; Pd(2)−S(1)−Pd(3), 84.99°). The Pd(1)···Pd(3) distance (3.387 Å) is longer than the other two (Pd(1)···Pd(2), 3.091 Å; Pd(2)···Pd(3), 3.047 Å). None is suggestive of Pd···Pd interactions.

Propionic acid also displaces the hydroxo ligand of **2b** to give the corresponding trinuclear complex $[Pd_3(\mu_3\text{-S})(\mu\text{-O}_2CC_2H_5)(L^2)_3]$ **4b**. Its X-ray structure was determined (Figure 2).[6] The oxygen atom O(1) of the bridging carboxylato is coordinated to Pd(1) and Pd(2), while O(2) is bonded to Pd(3). This distorts the triangular Pd_3 core, and the Pd(2)···Pd(3) distance (3.500 Å) is longer than the other two (Pd(1)···Pd(2), 3.196 Å; Pd(2)···Pd(3), 3.145 Å).

The formation of **2** can be rationalized as shown in Scheme 2.

The formal insertion of CS_2 into the Pd−OH bond should produce a hydrosulfide intermediate, which will react with a new molecule of the starting dimer affording **2**. Insertion reactions of CS_2 into M−X bonds,[7] including M−OR bonds,[8] have been reported. The formation of M−SH (M = Mo, Re) from M−OH and CS_2 has also been reported very recently.[9] Dimeric hydrosulfide-bridged palladium complexes can be formed by reaction of hydroxo-bridged complexes and SH_2.[10,11] However, in our case the use of SH_2 led to uncontrolled reactions producing decomposition of **1** to

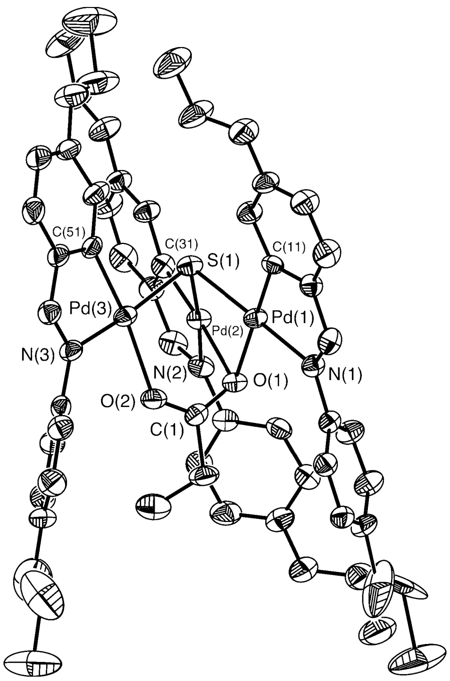
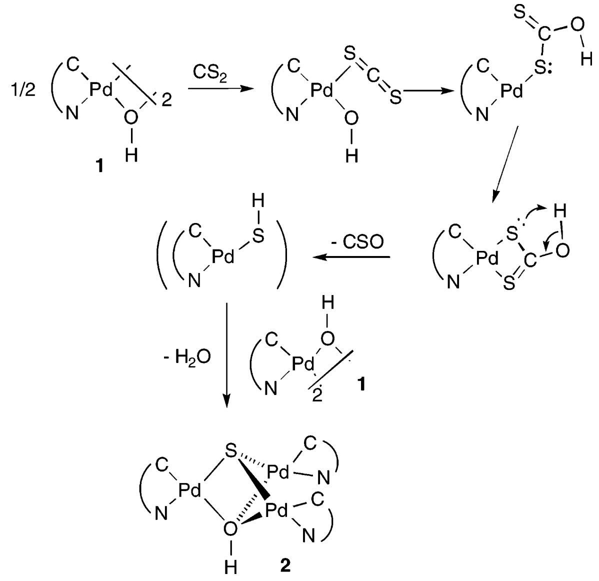


Figure 2. Molecular structure of **4b** with thermal ellipsoids (30% probability). Selected bond lengths (Å): S(1)−Pd(2) 2.254(2), S(1)−Pd(1) 2.286(2), S(1)−Pd(3) 2.296(2), O(1)−Pd(1) 2.215(5), O(1)−Pd(2) 2.237(5), O(2)−Pd(3) 2.195(5).

Scheme 2 Proposed Mechanism for the Synthesis of **2**



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(6) Crystal data for **4b**: $C_{54}H_{59}N_3O_8Pd_3S$, $M = 1229.30$, triclinic, space group $P\bar{1}$, $a = 13.041(5)$ Å, $b = 13.205(6)$ Å, $c = 15.361(6)$ Å, $\alpha = 94.995(10)°$, $\beta = 91.463(9)°$, $\gamma = 95.415(10)°$, $V = 2622.0(19)$ Å^3, $Z = 2$, $R_1 = 0.0465$, $wR_2 = 0.1139$. CCDC-211687.

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unidentified solids. The smooth generation of hydrosulfide from CS_2 seems crucial for the success of the synthesis.

Homobridged $Pd_3(\mu_3\text{-}S)_2$ cores are known,[12] but these heterobridged cores reported here were unknown. They are interesting because they force an all-cis arrangement (relative to the metallatriangle) of the three orthometalated imine ligands. The preference for a cis arrangement of C and S(sulfide) observed is probably associated with the destabilization inherent to isomers placing in mutually trans positions ligands with a high trans influence.[13] Cis arrangement in molecules containing a repeated unit (in our case the imine group) is interesting in the fields of NLO[14,15] and liquid crystals,[1,14,16] because it favors a larger molecular hyperpolarizability.

In summary, an unusual reaction leads to the formation of a novel structural type of trimetallic complexes, which arranges the substituents in an all-cis parallel alignment. This kind of alignment should produce a reinforcement of the contributions of the molecular fragments to the molecular hyperpolarizability. The use of imines (or related ligands) with suitable donor and acceptor groups should produce interesting materials. Further studies on these systems are under way.

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Supporting Information Available: Synthetic procedures, NMR, IR, and elemental analysis data, and two crystallographics files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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