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Dancing of Palladacycles around a “Juggler” 2,2-Diacetyl-1,1-Ethylenedithiolato Ligand in a Trinuclear Pd(II) Complex

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A trinuclear Pd complex containing a μ^3-1,1-ethylenedithiolato ligand has been synthesized and its structure confirmed by X-ray crystallography. It is the first example of a 1,1-ethylenedithiolato complex containing an anionic carbon σ donor. This compound shows an unprecedented fluxional behavior in solution, by which the three palladacycles exchange around the dithiolene. The activation parameters for this process have been derived by NMR line shape analysis, and a mechanism is proposed.

Transition metal complexes containing unsaturated dithiolato ligands attract considerable attention because of their electronic, magnetic, and redox properties.[1] Although 1,1-ethylenedithiolato complexes have been studied[2] less than their 1,2 isomers, they show interesting photophysical properties,[3,4] including solvatochromic behavior and luminescence,[5] and are thus potential photocatalysts in light-to-chemical energy conversion.[6] Additionally, 1,1-ethylenedithiolato ligands display a great variety of coordination modes, being able to form homo-[7] or heteropolynuclear complexes[8] and clusters[9] and to stabilize high oxidation states.[10] However, there are still very few examples of organometallic 1,1-ethylenedithiolato transition metal complexes, and in all of them the organic ligand is a neutral species (cod,[11] isocyanide,[12,13] carbene,[13] vinylidene,[14] or CO[13,15,16]) or a Cp group.[17] We report here the first examples of 1,1-ethylenedithiolato complexes containing an anionic carbon σ donor, namely $C_6H_4CH_2NMe_2$-2. The high trans influence of this aryl ligand is probably responsible for the fluxional behavior in solution of the trinuclear species.

The complex $[\{Pd(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)\}_2\{\mu\text{-}S,S,O\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ (**1**) was prepared by reaction of [Pd(*C*,*N*-

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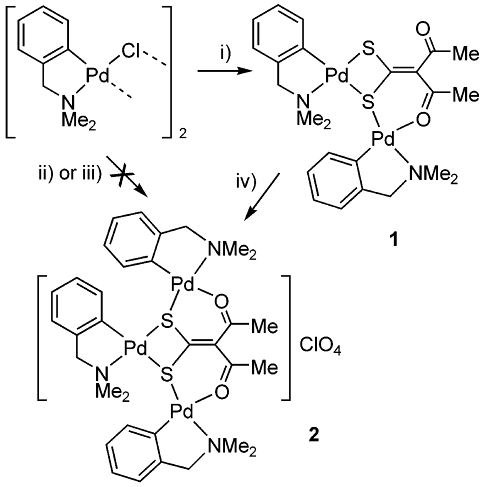
Scheme 1. Synthesis of Complexes **1** and **2**



i) + $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ - 2 TlCl; ii) + $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ + $AgClO_4$ (1:5:1:1); iii) + 1 + $AgClO_4$ (0.5:1:1); iv) + [Pd(C,N-$C_6H_4CH_2NMe_2$-2)$(NCMe)_2$]ClO_4 - 2 MeCN.

$C_6H_4CH_2NMe_2$-2)(μ-Cl)$]_2$[18] and $[Tl_2\{S_2C=C\{C(O)Me\}_2\}]$[4] (Scheme 1). The dithiolene acts as an *S*,*S* and *S*,*O* donor. The only precedent for this coordination mode in a dithiolene is found in a Re_2 complex.[15] Attempts to obtain the tripalladated species [{Pd(*C*,*N*-$C_6H_4CH_2NMe_2$-2)}$_3${μ-*O*,*S*,*S*,*O*-S_2C_2\{C(O)Me\}$_2$}]ClO_4 (**2**) by reaction of [Pd(*C*,*N*-$C_6H_4CH_2$-NMe_2-2)(μ-Cl)$]_2$ with $[Tl_2\{S_2C_2\{C(O)Me\}_2\}]$ and $AgClO_4$ (1.5:1:1), or with **1** and $AgClO_4$ (0.5:1:1) were unsuccessful (Scheme 1). However, complex **2** can be isolated in good yield by reaction of equimolar amounts of **1** and [Pd(*C*,*N*-$C_6H_4CH_2NMe_2$-2)$(NCMe)_2$]ClO_4[19] in CH_2Cl_2 (Scheme 1). The crystal structure of **2**·CH_2Cl_2 has been determined (Figure 1 and Supporting Information).[20] The 2,2-diacetyl-1,1-ethylenedithiolato ligand displays a *Z*,*Z* conformation and acts as a μ^3 bridging ligand that is *S*,*S*-chelating toward Pd(1) and *S*,*O*-chelating toward Pd(2) and Pd(3). Such a coordination mode has never been observed before for a dithiolene.

The behavior of complex **2** in solution has been investigated by variable-temperature (VT) NMR (Figure 2). At 298 K a single set of resonances is observed, suggesting a fluxional process capable of interchanging the three palladacycles, as well as the two C(O)Me groups. We propose that this process (process A, see Supporting Information) involves the cleavage of Pd−O and Pd−S bonds and rotation around a S−C bond (Scheme 2).

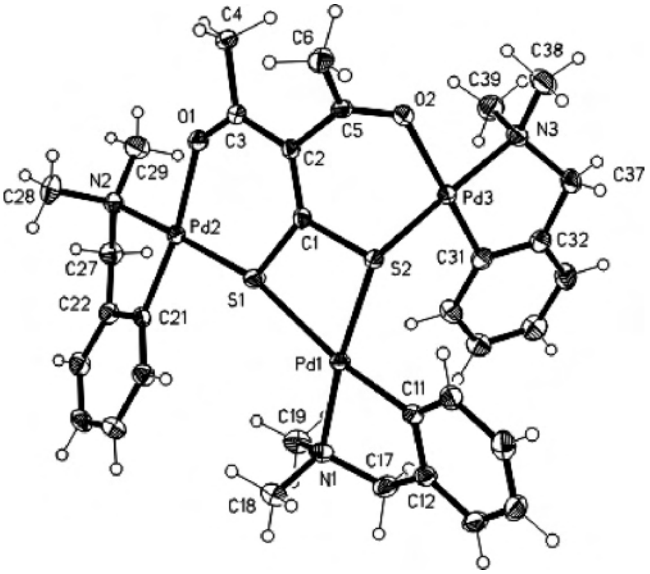


Figure 1. Crystal structure of **2**, omitting the solvent and the anion.

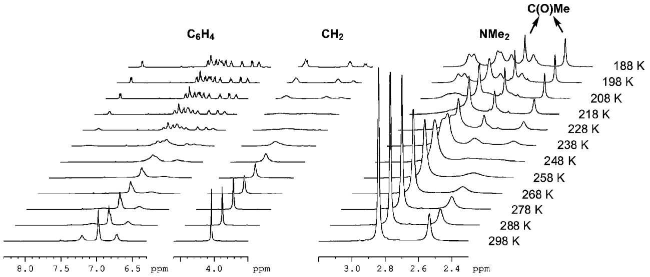
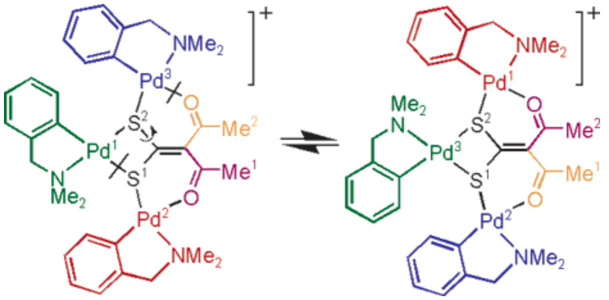


Figure 2. VT ^1H NMR Spectra of **2** (CD_2Cl_2, 600 MHz, 298−188 K).

Scheme 2. One of the Steps of the Proposed Mechanism for the Fluxional Process A in **2**. The Colors Characterize the Position of the Groups in the Molecule.



When the temperature is decreased, the resonances of the different groups resolve (see Supporting Information for the full assignment). At 178 K, the resonances of the CH_2NMe_2 protons are still broad, suggesting the presence of a second fluxional process which interchanges the two methylene protons, as well as the two methyl groups within each palladacycle (process B). This exchange is probably based on sulfur inversion, a common process in organosulfur transition metal complexes, as it is favored by the metal electronegativity and π-conjugation effects.[21]

A line shape analysis of the NMe_2 and C(O)Me resonances[22] has allowed the estimation of the activation energies for both processes, A and B (Table 1). Figure 3 shows the simulated spectra for the six temperatures at which the two processes could be simultaneously simulated.[23]

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(20) Crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into dichloromethane solutions of **2**. Data were recorded at −140 °C on a Bruker SMART 1000 CCD diffractometer to a 2θ(max) of 61° using Mo Kα radiation. The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using rigid methyl groups or a riding model.

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(22) Using gNMR 5.0, Adept Scientific, Inc. See Supporting Information for details.

Table 1. Activation Parameters for the Fluxional Processes in **2**[a]

	E_a[b]	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$	$\Delta G^{\ddagger}_{298K}$[b]
process A	33.0(0.9)	31.0(0.7)	−72(3)	52.5(0.2)
process B	30.9(1.5)	29.0(1.2)	−64(5)	48.1(0.3)

[a] Standard deviations in parentheses. [b] In kJ·mol^{-1}. [c] In J·K^{-1}·mol^{-1}.

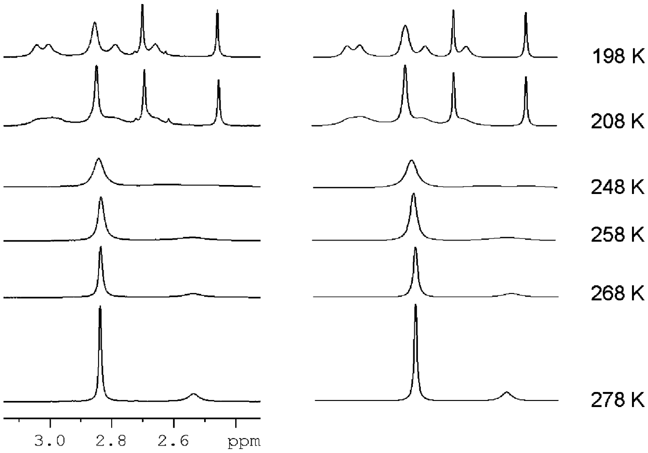

Figure 3. Experimental (left) and simulated (right) ^{1}H spectra of **2**.

$\Delta G^{\ddagger}$ values found for sulfur inversion in Pd complexes are around 50 kJ·mol^{-1},[21] in very good agreement with our results. The negative values of $\Delta S^{\ddagger}$ might be due to the steric interactions in the transition state.[24] The low activation energy for process A can be explained by the large trans influence of the aryl group, which weakens the Pd−O and Pd−S bonds to be cleaved. Although this process could take place via tricoordinated T- or Y-shaped intermediates,[25,26] the negative value of $\Delta S^{\ddagger}$ points to an associative mechanism, involving the solvent or adventitious water.[25,27]

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Supporting Information Available: Experimental procedures and complete characterization data for compounds **1** and **2**. Details of the crystal structure analyses, NMR line shape analysis, proposed fluxional mechanism, and CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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