

# Anionic palladium-induced modification in NS<sub>2</sub> ligands

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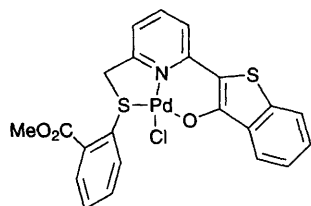
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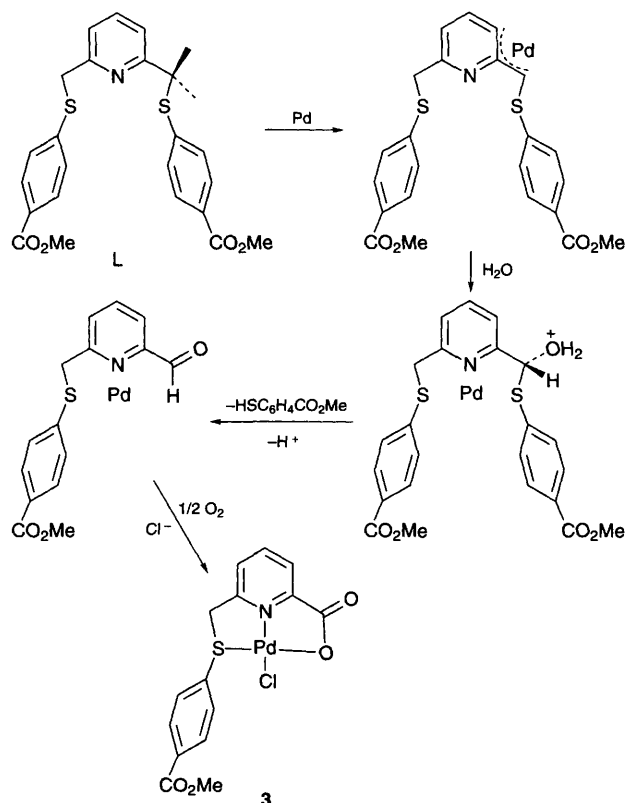
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**Palladium mediates the neutral to anionic transformation in a NS<sub>2</sub> ligand; in the process the MeO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>-arm is converted to a -CO<sub>2</sub><sup>-</sup> group.**

Palladium-mediated chemistry has emerged as an excellent synthetic strategy for a variety of useful reactions.<sup>1</sup> Most of these may be viewed as coupling reactions, rearrangements, or a combination of both, facilitated by a Pd species. How the nature of Pd influences the course of these reactions is usually unknown, though most of them can be understood by typical reactions of organometallic chemistry. Recently<sup>2</sup> we reported a palladium-promoted benzothiophene condensation on

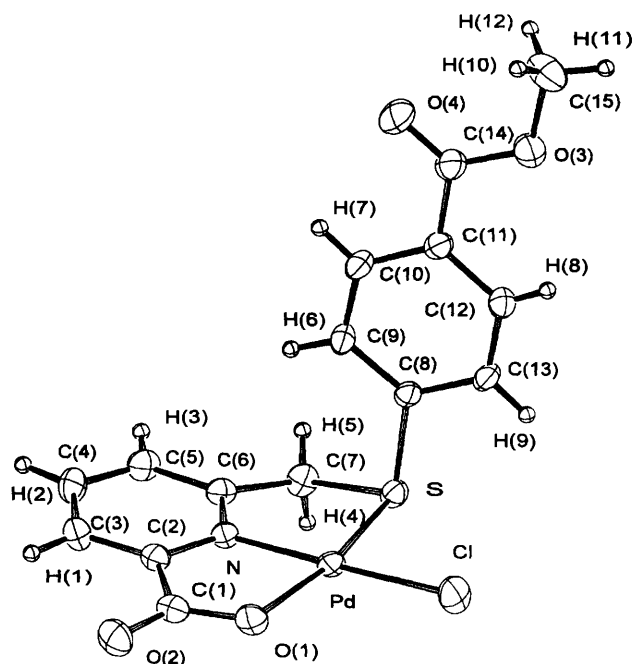


**Fig. 1** Structure of the palladium-promoted benzothiophene condensation product of **1**



**Scheme 1** Proposed mechanism for the anionic palladium-induced modification of **L**

2,6-bis(*o*-methoxycarbonylbenzylthiomethyl)pyridine **1**. As a net result of the reaction the neutral ligand molecule **1** changes to an anionic species by modification of one of the two arms to the benzothiophene moiety, see Fig. 1. Given an accessible pathway the molecule modifies itself to become negatively charged to compensate the metal charge. To do so the *ortho* disposition of the ROCO<sup>-</sup> group but not the *meta* or the *para* were appropriate. To learn more on the capacity of Pd to provide pathways aiming at the compensation of the metallic charge we studied the reaction with the *para* species, 2,6-bis(*p*-methoxycarbonylbenzylthiomethyl)pyridine **L** (Scheme 1), similar to **1**. Now, however, no analogy to the condensation found in **1** was expected. The reaction of **L** with PdCl<sub>2</sub> in MeCN, in molar ratio 2:3, yielded a red solid in reasonable yield (48%) which presented IR spectra and elemental analysis compatible with 'the expected Pd complex' with formula [(PdClL)<sub>2</sub>][PdCl<sub>4</sub>] **2**, which shows coordination of **L** *via* the two thioether groups and the nitrogen. Upon slow evaporation in the air of the resulting clear filtrate, a second compound **3** (Scheme 1) was obtained in much lower yield (4%). IR of **3** displayed two distinct C=O absorptions at 1722 and 1659 cm<sup>-1</sup>. The low solubility of this species precluded a thorough NMR study, although <sup>1</sup>H NMR



**Fig. 2** ORTEP diagram of **3**. Selected intramolecular distances (Å) and angles (°): Pd–Cl 2.284(1), Pd–S 2.258(1), Pd–O(1) 2.055(3), Pd–N 1.956(3), S–C(7) 1.825(5), S–C(8) 1.794(4), O(1)–C(1) 1.296(5), O(2)–C(1) 1.211(5), Cl–Pd–S 93.08(5), Cl–Pd–O(1) 98.62(9), Cl–Pd–N 178.5(1), S–Pd–O(1) 168.24(8), S–Pd–N 87.0(1), O(1)–Pd–N 81.2(1), Pd–S–C(7) 97.1(1), Pd–S–C(8) 102.0(1), C(7)–S–C(8) 103.7(2), Pd–O(1)–C(1) 113.8(3), Pd–N–C(2) 115.9(3), Pd–N–C(6) 122.3(3), C(2)–N–C(6) 121.7(3).

confirmed the presence of the full  $\text{MeCO}_2\text{C}_6\text{H}_4\text{SCH}_2-$  arm in the molecule. The unusual constitution of complex **3** was determined by an X-ray diffraction study† which confirmed the existence of one unaltered arm but also a  $-\text{CO}_2^-$  unit directly bonded to the pyridine backbone, see Fig. 2. The  $\text{Pd}^{\text{II}}$  cation shows a normal but slightly distorted square-planar coordination sphere with no short  $\text{Pd}\cdots\text{Pd}$  contacts. The efficiently chelating carboxylic group partially compensates the charge of  $\text{Pd}^{\text{II}}$ . Although the benzothiophene condensation was not feasible, ligand L is modified to an anion.‡ There are three possible sources of the  $-\text{CO}_2^-$  group: (i)  $\text{CO}_2$  either from the air or from the  $-\text{C}_6\text{H}_4\text{CO}_2\text{Me}$  moiety, (ii) carbonylation following a metallation, (iii) nucleophilic attack by water on a palladium-allylic complex. The attack of  $\text{CO}_2$ , although reported,<sup>3,4</sup> has been excluded since an experiment done under a  $\text{CO}_2$  atmosphere did not enhance the yield of **3**. A carbonylation process would require a  $\text{C}_6\text{H}_4\text{CO}_2\text{Me}$  decarbonylation, metallation and carbonylation. Although examples of individual steps of this process have been reported<sup>5,6</sup> the spatial arrangement of the arm does not seem to favour this mechanism. We feel that the nucleophilic attack by water on the allylic complex as shown in Scheme 1 is most probable and is analogous with the Wacker process<sup>7</sup> for aldehyde formation. The main step would be the formation and later attack of the palladium-allylic complex. Many points, however, remain unclear, such as  $\text{O}_2$  participation in the synthesis, and are the object of current investigations. Despite the low yield of **2** this result provides some clues as to how Pd, upon complexation, can induce ligand modifications to lower the charge of the complex.

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#### Footnotes

† A yellow crystal suitable for X-ray analysis was grown from acetonitrile by slow evaporation. Triclinic, space group  $P\bar{1}$  (no. 2),  $a = 8.148(2)$ ,  $b = 13.608(2)$ ,  $c = 7.788(2)$  Å,  $\alpha = 102.81(1)$ ,  $\beta = 109.20(1)$ ,  $\gamma = 96.78(1)^\circ$ ,  $U = 777.9(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $M_r = 444.18$ ,  $D_c = 1.896$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) =$

$14.96$  cm<sup>-1</sup>,  $F(000) = 440$ . The data set was collected on a Rigaku AFC5S diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å) at 294 K. The intensities were corrected for Lorentz and polarization effects. An experimental absorption correction based on three  $\psi$ -scans (transmission coefficient 0.88–1.00) was also applied.<sup>8</sup> The structure was solved by direct methods and refined by least-squares techniques to  $R = 0.028$  ( $R_w = 0.034$ ) and GOF = 1.19 for 2268 independent reflections having  $I > 3\sigma(I)$ . Heavy atoms were refined with anisotropic and hydrogen atoms with fixed isotropic displacement parameters (1.2 times that of the host atom) except methyl hydrogen atoms, which were included in calculated positions with fixed displacement parameters. All calculations were performed using TEXSAN (MSC) software.<sup>9</sup> Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ An impurity in ligand L of the asymmetric ligand found in complex **3** is discounted because of a non-realistic pathway for its synthesis, the purity of the NMR and IR spectra of L and the absence of reports of complexes containing this asymmetric ligand with transition metals other than Pd.

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