

Palladium-promoted Benzothiophene Condensation in NS₂ Ligands

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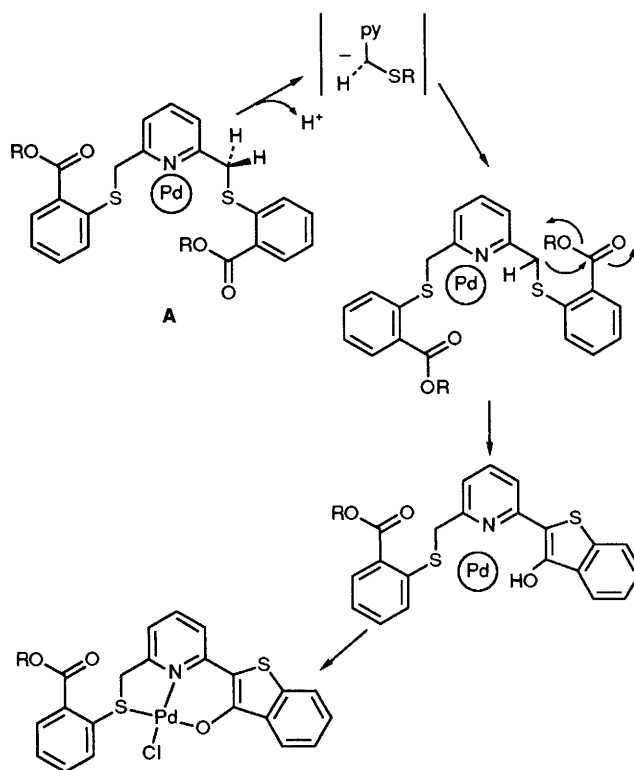
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The reaction of 2,6-bis(*o*-methoxycarbonylphenylthiomethyl)pyridine with PdCl₂ or Ru(Me₂SO)₆(BF₄)₂ in methanol produces a tridentate non-symmetrical ligand incorporating the benzothiophene fragment.

The coordination chemistry of the 2,6-bis(*R*-thiomethyl)pyridine ligand series changes considerably with the nature of the *R* group (aryl or alkyl).^{1,2} The reaction of 2,6-bis(*o*-methoxycarbonylphenylthiomethyl)pyridine (LNA) (**A** in Scheme 1) with Ru(Me₂SO)₆(BF₄)₂ in methanol yielded a red solid, which presented a doublet of doublets at δ 5.1 and 4.7 (*py*-CH₂-S, *J* 20 Hz) in the ¹H NMR spectrum. The interpretation of these signals was not straightforward on the basis of the initial structure of LNA. Attempts to grow crystals of this material were not successful and its low solubility precluded the ¹³C NMR study. In another experiment PdCl₂ (40.4 mg, 0.23 mmol) in acetonitrile (5 cm³) was added to a refluxing suspension of LNA (100 mg, 0.23 mmol) in methanol (50 cm³). The mixture was refluxed for 8 h, and on cooling and partial evaporation, a reddish crystalline solid, **1** separated out with formula C₂₂H₁₆ClNO₃PdS₂ (yield 44%). The ¹H NMR spectrum presented a doublet of doublets at δ 5.5 and 4.30 (*J* 20 Hz), which was consistent with the observed ¹H NMR spectrum of the Ru complex. Good X-ray quality crystals of this solid were obtained by slow evaporation in MeOH-CHCl₃. The molecular structure of **1** is shown in Fig. 1. One arm of the starting ligand LNA has suffered a process leading to a cycloaddition benzothiophene fragment, while the other has remained unaltered. The molecular structure of **1** shows a non-symmetrical ligand in a distorted square-planar arrangement about the palladium atom. This is surrounded by the pyridinic nitrogen, one sulfur from the arm of the unmodified ligand, one chlorine and one oxygen from the former carboxylate group. The modified arm, the benzothiophene fragment, is remarkably coplanar with the pyridine ring with only 8° between their planes. The modified ligand shows a



Scheme 1

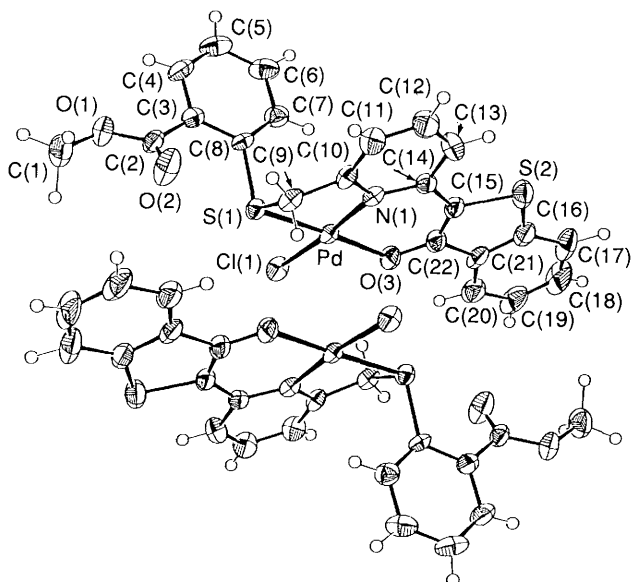


Fig. 1 Molecular structure of **1** with atomic labelling. Radii are arbitrary; H atoms have been omitted for clarity. *Crystal data:* $C_{22}H_{16}ClNO_3PdS_2$, $M = 548.345$, monoclinic, $P2_1/n$, $a = 8.165(1)$, $b = 11.716(2)$, $c = 21.550(4)$ Å, $\beta = 91.85^\circ$, $U = 2060.4(4)$ Å³, $Z = 4$, Mo-K α radiation, $2\theta_{max} = 55^\circ$, $R = 0.060$ ($R_w = 0.048$) for 3821 unique observed reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

similar coordination mode to 2,2':6',2''-terpyridine with a short Pd–N contact of 2.033(2) Å, a Pd–O of 2.001(4) Å and longer contacts [2.261(2) and 2.301(2) Å] to the terminal S and Cl donor atoms, respectively. The molecules form discrete dimeric units linked through Pd···Pd contacts of 3.23 Å. This

distance is too long to be considered the result of a Pd–Pd direct bond,^{3,4} but close enough for a Pd···Pd interaction.⁵ The disposition of the Ph–CO₂Me, almost perpendicular to the plane defined by the Pd and the pyridine–benzothiophene moiety, precludes a stacking of the resulting dimer units such as those observed in [PtL(MeCN)](PF₆).⁵ This would be possible if the benzothiophene condensation process took place in both arms of the original LNA ligand. Up to now we have not been able to do that, but more work is in progress to overcome this difficulty. Scheme 1 shows the proposed mechanisms for the benzothiophene condensation. A Pd-facilitated H⁺-dissociation process is invoked in the mechanism as a key step to explain the enhanced nucleophilicity of the carbon atom in the S–C(Ar) group. Further attack of this C anion to the C=O with loss of methanol leads to the benzothiophene containing ligand, which is in the enol form in the final complex.

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