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Asymmetric Benzothiophene Condensation Facilitated by Platinum(II). The Distinct Roles of Platinum(II) and Palladium(II)

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Introduction

The coordination chemistry of the 2,6-bis(R-phenylthiomethyl)pyridine ligand series changes considerably with the nature of the R group and its position in the aromatic ring bonded to the sulfur atom.[1−3] It seems that Pd(II) or Pt(II) metal ions induce acidity to the pyridine−thioether bridging -CH_2 groups in the complexation process, rendering the ligand anionic, thus partly compensating the positive charge of the Pd(II) or Pt(II) metal ions.

Herein we describe the distinct roles of Pt(II) and Pd(II) in their reaction with 2,6-bis(2-cyanophenylthiomethyl)pyridine (**L1**).

Experimental Section

Physical Measurements. Microanalyses were performed by using a Perkin-Elmer 240B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H NMR (300.13 MHz) and $^{13}C\{^1H\}$ NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer; chemical shifts are given in ppm, and their values are referenced to an internal standard of $SiMe_4$.

Materials. The starting compounds 2-mercaptobenzonitrile[4] and 2,6-bis(bromomethyl)pyridine[5] were synthesized as reported. All syntheses were done under a dinitrogen atmosphere.

Intramolecular Condensation of 2,6-Bis(*o*-methoxycarbonylphenylthiomethyl)pyridine (L2) with K^{t}BuO. K*t*-BuO (170 mg, 1.4 mmol) was added to a solution of 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine (256 mg, 0.6 mmol) in dry THF (50 mL). The mixture was refluxed for 24 h. On cooling a red solid was isolated by filtration and washed with THF, ethyl ether, dichloromethane, and water, yield: 67 mg (24.7%). FTIR (KBr): ν_{max} 1571−1501 cm^{-1} (m, ν_{arC-C}), 1473−1427 cm^{-1} (m, ν_{arC-C}). ^1H NMR ($CDCl_3$): δ 7.34 (t, ^1J(H,H) = 7 Hz, 4$\underline{H}_{aryl}$), 7.60 (m, 3$\underline{H}_{aryl}$), 7.77 (d, ^1J(H,H) = 7 Hz, 2$\underline{H}_{aryl}$), 7.87 (d, ^1J(H,H) = 4 Hz, 2$\underline{H}_{aryl}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 105.8, 113.9, 122.7, 123.4, 124.0, 127.0, 136.0, 136.7, 137.9, 152.2, 160.2. Anal. Calcd for $C_{21}H_{11}K_2NO_2S_2$ H_2O: C, 53.71; H, 2.77; N, 2.98; S, 13.65. Found: C, 54.08; H, 3.09; N, 2.78; S, 13.51.

Synthesis of 2,6-Bis(*o*-cyanophenylthiomethyl)pyridine (L1). To methanol (30 mL) and sodium metal (0.21 g, 9.2 mmol), was added 2-mercaptobenzonitrile (1.24 g, 9.2 mmol) and the mixture was stirred for a further 10 min. The solution was then added to a solution of 2,6-bis(bromomethyl)pyridine (1.22 g, 4.6 mmol) in methanol (30 mL). The mixture was heated to 30−35 °C for 30 min and then cooled to room temperature. A white precipitate appeared which was filtered, washed with methanol, and redissolved in chloroform. The suspension was filtered again, and the filtrate was evaporated under reduced pressure to afford **L1** as a white solid, yield: 1.18 g (69%). FTIR (KBr): ν_{max}(C≡N) 2218 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.31 (s, 4H, py-C$\underline{H}_2$-S), 7.24-7.49 (m, 11H, $\underline{H}_{aryl}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 39.8 (s, py-$\underline{C}H_2$-S), 121.8 (s, $\underline{C}$≡N), 126.5−156.3 ($\underline{C}_{aryl}$). Anal. Calcd for $C_{21}H_{15}N_3S_2$: C, 67.53; H, 4.05; N, 11.25; S, 17.17. Found: C, 67.21; H, 3.92; N, 11.01; S, 16.88.

Synthesis of [PtCl(L1′)]. To a solution of **L1** (74.7 mg, 0.20 mmol) in acetone (15 mL) was added $[NH_4]_2[PtCl_4]$ (74.6 mg, 0.20 mmol) in water (5 mL). The mixture was refluxed for 10 h. On cooling a reddish solid was obtained, yield: 56.1 mg (47%). FTIR (KBr): ν_{max}(NH) 3353 cm^{-1}, (C≡N) 2228 cm^{-1}. ^1H NMR (dmso-d_6, 300 MHz): δ 4.76 (d, ^2J(H,H) = 16.8 Hz, 1H, py-C($\underline{H}_a$)(H_b)-S), 5.14 (d, ^2J(H,H) = 16.8 Hz, 1H, py-C(H_a)($\underline{H}_b$)-S), 7.00−8.21 (m, 12H, $\underline{H}_{aryl}$ and N-$\underline{H}$). Anal. Calcd for $C_{21}H_{14}ClN_3PtS_2$: C, 41.83; H, 2.34; N, 6.97; S, 10.63. Found: C, 41.64; H, 2.22; N, 6.86; S, 10.37. Brown crystals suitable for X-ray diffraction were grown from acetone by slow evaporation.

Synthesis of [PdCl$_2$(L1″)]. (a) To a refluxing suspension of **L1** (85.9 mg, 0.23 mmol) in methanol (50 mL) was added $[PdCl_2(CH_3CN)_2]$ (40.4 mg, 0.23 mmol) in acetonitrile (5 mL). The mixture was refluxed for 8 h. On cooling and partial evaporation, a yellowish solid was obtained. The solid was filtered and washed with diethyl ether and chloroform, yield: 58.7 mg (46%). (b) The ligand **L1** (8.8 mg, 0.02 mmol) and $K_2[PdCl_4]$ (7.7 mg, 0.02 mmol) were disolved in methanol (5 mL), and the solution was refluxed for 10 h. On cooling a yellowish solid was obtained. The solid was filtered, washed with methanol, and dried under vacuum, yield: 5 mg (38%). FTIR (KBr): ν_{max}(NH) 3262 cm^{-1}, (NH_3^+) 2664 cm^{-1}. ^1H NMR (dmso-d_6, 300 MHz): δ 7.35−8.37 (m, 15H, $\underline{H}_{aryl}$ and N-$\underline{H}$). $^{13}C\{^1H\}$ NMR (dmso-d_6, 75 MHz): δ 108.5−153.6 ($\underline{C}_{aryl}$). Anal. Calcd for $C_{21}H_{15}Cl_2N_3PdS_2$: C, 45.79; H, 2.75; N, 7.63; S, 11.64. Found: C, 45.66; H, 2.71; N, 7.47; S, 11.44.

X-ray Studies. A Rigaku AFC5S instrument was used for data collection. Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections measured after every 150 reflections showed a decay of 2.40%. The data were corrected for Lorentz and polarization effects and for decay. Corrections for ψ scan absorption and secondary extinction were also applied.

The structure was solved by direct methods and refined by least-squares techniques to an R value of 0.027 (R_w = 0.025) for 2929 independent reflections having $I > 3\sigma(I)$. The NH hydrogen atom was refined, and the remaining hydrogen atoms were included in calculated positions with fixed temperature factors. All calculations were performed using TEXSAN software.[7] Crystallographic data and structure refinement parameters are presented in Table 1.

Results and Discussion

The reaction of 2,6-bis(*o*-cyanophenylthiomethyl)pyridine (**L1**) with $[NH_4]_2[PtCl_4]$ in acetone/water yielded a reddish solid, [PtCl(**L1′**)]. The IR spectra presented two significative bands, one at 3353 cm^{-1} corresponding to N−H and a second one at 2228 cm^{-1} corresponding to C≡N. The ^1H NMR spectra presented a doublet of doublets in the zone corresponding to methylenic protons. The splitting into two doublets is consistent

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[†] On the occasion of the 80th birthday of our teacher Prof. Heribert Barrera i Costa, in recognition of his outstanding personal and professional merits.

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10.1021/ic971425y CCC: $18.00

Table 1. Crystallographic Data for [PtCl(**L1′**)]

empirical formula	$C_{21}H_{14}ClN_3PtS_2$
fw	603.02
space group	$P\bar{1}$ (No. 2)
a, Å	9.5861 (9)
b, Å	12.472 (1)
c, Å	8.2247 (8)
α, deg	100.77 (1)
β, deg	93.582 (8)
γ, deg	93.528 (9)
V, Å^3	961.4 (2)
Z	2
T, °C	21
D_c, g/cm^3	2.083
μ(Mo Kα), cm^{-1}	76.34
R^a	0.028
$R_w{}^b$	0.025

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o2|]^{1/2}$.

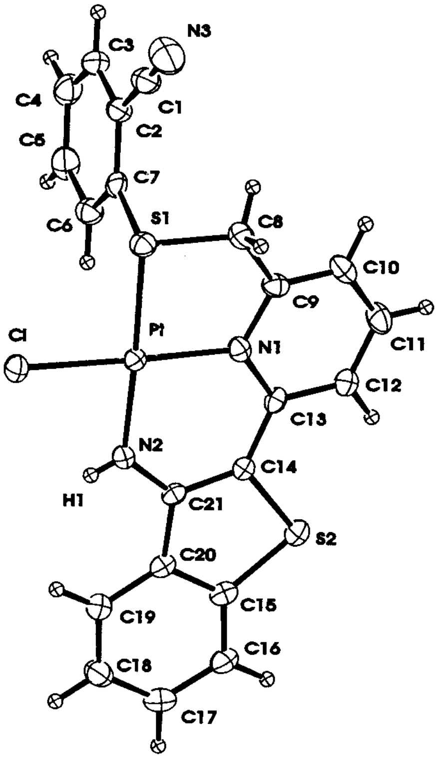


Figure 1. ORTEP diagram of [PtCl(**L1′**)].

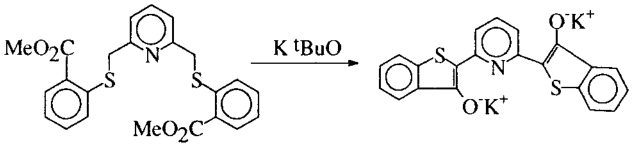
with a nonequivalence of the geminal protons (CH_2 became CH_aH_b). The ^{1}H NMR and IR spectra were not consistent with the original structure of **L1**. The molecular structure of [PtCl(**L1′**)] was determined by an X-ray diffraction study. The structure of this complex consists of a nonsymmetrical ligand in a slightly distorted square-planar arrangement about the platinum atom (see Figure 1). One arm of the starting **L1** ligand has suffered a process leading to a benzothiophene fragment, while the second one has remained unaltered. The platinum is surrounded by the pyridinic nitrogen, one sulfur from the unmodified arm of the ligand, one chlorine, and the enamine nitrogen from the modified arm of the original **L1**. Some selected bond parameters are given in Table 2. There are no exceptional features in the bonding parameters of [PtCl(**L1′**)].

According to literature, benzothiophene condensation can also be obtained upon reaction of the adequate precursor with a base. Some related examples are exemplified in Madelung synthesis[7] and benzothiophene formation.[8]

Table 2. Selected Bond Parameters for [PtCl(**L1′**)]

Distances (Å)	
Pt−Cl	2.317(2)
Pt−S(1)	2.266(2)
Pt−N(1)	2.036(4)
Pt−N(2)	1.966(5)
S(1)−C(7)	1.807(6)
S(1)−C(8)	1.820(6)
S(2)−C(14)	1.764(6)
S(2)−C(15)	1.753(6)
N(1)−C(9)	1.388(7)
N(1)−C(13)	1.374(7)
N(2)−C(21)	1.342(7)
N(3)−C(1)	1.143(8)
Angles (deg)	
Cl−Pt−S(1)	90.85(6)
Cl−Pt−N(1)	178.2(1)
Cl−Pt−N(2)	87.7(2)
S(1)−Pt−N(1)	87.4(1)
S(1)−Pt−N(2)	176.4(2)
N(1)−Pt−N(2)	94.0(2)
Pt−S(1)−C(7)	107.3(2)
Pt−S(1)−C(8)	97.5(2)
C(7)−S(1)−C(8)	100.6(3)
C(14)−S(2)−C(15)	91.3(3)
Pt−N(1)−C(9)	117.2(4)
Pt−N(1)−C(13)	124.0(4)
C(9)−N(1)−C(13)	118.8(5)
Pt−N(2)−C(21)	126.2(4)
N(3)−C(1)−C(2)	178.8(8)

Scheme 1. Benzothiophene Condensation Employing K^{t}BuO



The reaction of aryl cyanides under either acidic or basic conditions leads to the synthesis of aromatic carboxylic acids.[9] As **L1** contains two aryl cyanide groups, to ascertain the differences between the known base method and the transition metal one described here, we performed the reaction between ligand 2,6-bis(*o*-methoxycarbonylphenylthiomethyl)pyridine[1a] **(L2)** and strong bases (LiBu, K^{t}BuO). The difference between **L2** and **L1** is the R group bonded to the phenyl ring: R = $-COOCH_3$ for **L2** and R = −CN for **L1**. The result was a very insoluble and deep red solid which had no signal of methylene hydrogens in the ^{1}H NMR spectrum. The ester band in the IR spectrum was not observed, either. Thus, it was concluded that **L2** had suffered a benzothiophene condensation at the two arms of the ligand. This is represented in Scheme 1.

In both cases, either by Pt (II) or a base, the crucial step for the condensation is the elimination of a -CH_2- proton.[10] Although the mechanism is different the process takes place in both cases. As we have reported earlier,[1a] this is the second case in pyridine derivatives where such process has been observed with no addition of a base, and the first one with a starting CN group. In other reported examples,[11] the addition of the metal was not

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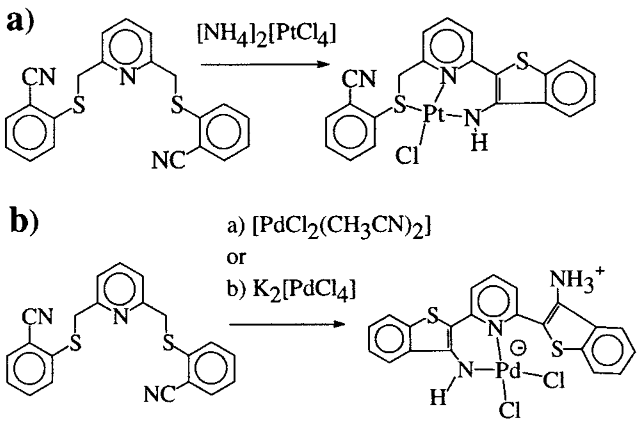
Scheme 2. Benzothiophene Condensation in [PtCl(**L1′**)] and in [PdCl$_2$(**L1″**)]



sufficient for the abstraction of the H-C from the methylene group, and it was necessary to add a supplementary deprotonating agent as Na$_2$CO$_3$. In this case, the process must probably begin with Pt(II)-allyl formation. Thus Pt(II) is responsible for the enhanced nucleophilicity of the carbon atom in the methylene group. Further attack of this carbanion to the C≡N group leads to the benzothiophene containing ligand, which is in the enamine form in the final complex. Scheme 2a) exemplifies the benzothiophene condensation.

The reaction of **L1** with Pt(II) was also conducted in a deuterated medium (D$_2$O/acetone), to know more about the process mechanism.[12] By doing so, it was expected that we know the source of the enamine hydrogen, either intramolecular or intermolecular. It turned out to be the last one since deuterium had been introduced in the enamine's group, but, in addition, deuterium exchange had also taken place at the remaining methylene group. This was confirmed by the ^{1}H NMR where no methylene signal appeared at the end of the experiment. Although only one arm of the ligand had experienced the benzothiophene condensation, the Pt(II) was enhancing the lability of all methylene protons in the molecule. For further evidence, the [PtCl(**L1′**)] complex was stirred with D$_2$O/acetone at room temperature for 3 days; Figure 2, showing the ^{1}H NMR spectra at the methylene region, it is clear that D/H exchange has taken place.

The reaction of **L1** with [PdCl$_2$(CH$_3$CN)$_2$] in acetonitrile/methanol yielded a yellowish solid, [PdCl$_2$(**L1″**)] where, apparently, the two arms of the ligand **L1** have been altered.

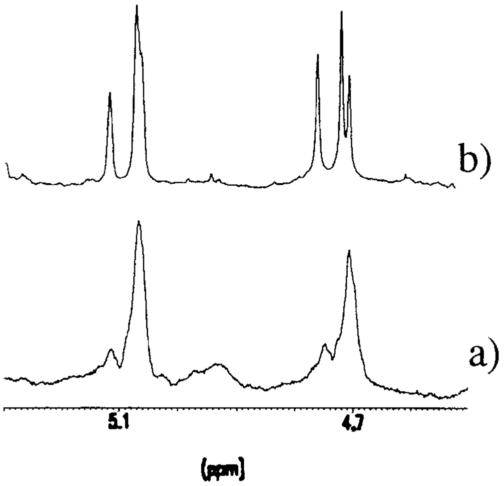


Figure 2. ^{1}H NMR spectra at the methylene region for [PtCl(**L1′**)] (b) and after stirring in D$_2$O/acetone for 3 days at room temperature (a).

According to the experimental data (IR, ^{1}H NMR, ^{13}C{^{1}H} NMR) it has been observed the total disappearance of the −C≡N and methylene groups. Instead, new resonances of aromatic protons in the ^{1}H NMR spectrum have appeared. In the case cited before[1a] only one of the two arms of the ligand **L2** had been modified in the complexation process with [PdCl$_2$(CH$_3$CN)$_2$]. In the present study it seems that the ligand is more adequate to be entirely modified by Pd(II), producing a system with five connected aromatic rings. The proposed benzothiophene condensation is shown in Scheme 2b).

To discard any influence of the ancillary ligands in the number of arms modified, the reaction of K$_2$[PdCl$_4$] with **L1** was also performed. The result was again [PdCl$_2$(**L1″**)]. As a further experiment the already described modification of **L2** with [PdCl$_2$(CH$_3$CN)$_2$], leading to a monobenzothiophene rearrangement, was also conducted with K$_2$[PdCl$_4$]. The end product proved to be equal in both cases. Thus it seems that the rearrangement of each ligand is due mostly to the nature of the metal ion itself, while the nature of the ancillary ligands does not alter the end product.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for complex [PtCl(**L1′**)] is available free of charge via the Internet at http://pubs.acs.org.

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