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Synthesis and characterization of cyclometallated palladium(II) and platinum(II) complexes with amide-thiolate ligands

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Abstract

The redox reaction of bis(2-benzamidophenyl) disulfide (H_2L-LH_2) with [Pd(PPh$_3$)$_4$] in a 1:1 ratio gave mononuclear and dinuclear palladium(II) complexes with 2-benzamidobenzenethiolate (H_2L^-), [Pd(H_2L-S)$_2$(PPh$_3$)$_2$] (**1**) and [Pd$_2$(H_2L-S)$_2$ (μ-H_2L-S)$_2$(PPh$_3$)$_2$] (**2**). A similar reaction with [Pt(PPh$_3$)$_4$] produced only the corresponding mononuclear platinum(II) complex, [Pt(H_2L-S)$_2$(PPh$_3$)$_2$] (**3**). Treatment of these complexes with KOH led to the formation of cyclometallated palladium(II) and platinum(II) complexes, [Pd(L-C,N,S)(PPh$_3$)]$^-$ ([**4**]$^-$) and [Pt(L-C,N,S) (PPh$_3$)]$^-$ ([**5**]$^-$). The molecular structures of **2**, **3** and [**4**]$^-$ were determined by X-ray crystallography.
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Keywords: Palladium(II) complexes; Platinum(II) complexes; Amide ligand; Cyclometallation; S–S bond activation

1. Introduction

Cyclometallated compounds, which are generated through the activation of C–H bonds, have been extensively investigated, because of their novel and outstanding applications in organic and organometallic synthesis [1–4]. In this respect, a large number of cyclometallated complexes with azobenzene and Schiff base moieties have been reported. We have also reported cyclometallated palladium(II) and platinum(II) complexes having a rare tridentate-C,N,S Schiff base ligand [5]. However, there are only a few examples of cyclometallated complexes with amide ligands, even though amide ligands adopt a planar coordination framework as do Schiff base ligands [6–9]. In particular, little is known about the structures and properties of complexes with amide-thiolate ligands [7]. This seems to be due to the high reactivity of sulfur atoms in amide ligands, leading to sulfenate, sulfinate, or disulfide species [10,11]. Thus, we planed to apply redox reactions between low oxidation metals and disulfide compounds in order to rule out

the possibility of oxidation on sulfur atoms in reaction processes [12].

In this paper, we report that the reactions of bis(2-benzamidophenyl) disulfide with [Pd(PPh$_3$)$_4$] or [Pt(PPh$_3$)$_4$] produce palladium(II) and platinum(II) complexes with monodentate-S amide-thiolate ligands, which are converted into cyclometallated palladium(II) and platinum(II) complexes with tridentate-C,N,S amide-thiolate ligands by treatment with base. The molecular structures of some of these complexes are also reported.

2. Results and discussion

2.1. Synthesis

The reaction of bis(2-benzamidophenyl) disulfide (H_2L-LH_2) with an equimolar amount of [Pd(PPh$_3$)$_4$] in benzene under an anaerobic condition led to the formation of a mixture of two compounds (**1** and **2**) that are separated by fractional precipitation or recrystallization of a mixed sample. Complexes **1** and **2** were assigned to have a mononuclear and a dinuclear structures in [Pd(H_2L-S)$_2$(PPh$_3$)$_2$] and [Pd$_2$(H_2L-S)$_2$(μ-H_2L-S)$_2$(PPh$_3$)$_2$] (H_2L^- = 2-benzami-

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dobenzenethiolate), respectively, by the elemental analyses and the IR and ^{1}H NMR spectroscopies, along with the X-ray analysis for **2**. Similar treatment of H_2L-LH_2 with [Pt(PPh$_3$)$_4$] gave a yellow compound (**3**). It was found from the IR and ^{1}H NMR spectra and the X-ray analysis that **3** contains a single mononuclear species, [Pt(H$_2$L-S)$_2$(PPh$_3$)$_2$], which is analogous to the mononuclear **1**. Treatment of a mixture of **1** and **2** with KOH in ethanol gave a yellow solution, from which a yellow powder ([(*n*-Bu)$_4$N][**4**]) was isolated by adding (*n*-Bu)$_4$NBr. X-ray analysis demonstrated that [**4**]$^-$ is a desired cyclometallated complex, [Pd(L-*C*,*N*,*S*)(PPh$_3$)]$^-$, in which a Pd^{II} centre is coordinated by C, N, and S atoms from an amide-thiolate ligand (L^{3-}). An analogous cyclometallated complex (K[**5**]) was also obtained by treatment of **3** with KOH in ethanol, which was assigned by the elemental analysis and the IR and NMR spectroscopic studies (Scheme 1).

2.2. Molecular structures of [Pd$_2$(H$_2$L–S)$_2$(μ-H$_2$L–S)$_2$(PPh$_3$)$_2$] (2), [Pt(H$_2$L–S)$_2$(PPh$_3$)$_2$] (3) and [(n-Bu)$_4$N][Pd(L-C,N,S)(PPh$_3$)] ([(n-Bu)$_4$N][4])

The molecular structure of **2** is shown in Fig. 1, and its selected bond distances and angles are given in Table 1. In **2**, there is a crystallographic inversion centre at the midpoint of the Pd1···Pd1′ vector. Two palladium(II) atoms are bridged by two thiolato sulfur atoms from two amide-thiolate ligands (H$_2$L$^-$). The Pd···Pd separation in **2** is 3.5504(8) Å, which is indicative of the absence of a bonding interaction [5]. Each palladium(II) centre resides in a square-planar geometry that is defined by two sulfur atoms from two bridging H$_2$L$^-$ ligands, one sulfur atom from a terminal H$_2$L$^-$ ligand and one phosphorus atom from triphenylphosphine. The Pd–S$_{terminal}$ (av. 2.333(2) Å), Pd–S$_{bridging}$ (2.406(2) Å) and Pd–P (2.291(2) Å) bond distances are within the range of normal values [13,14]. Two triphenylphosphine ligands are *trans* to each other across two palladium(II) atoms. Each phenyl ring of the terminal and bridging H$_2$L$^-$ ligands is oriented so as to face a phenyl of triphenylphosphine with distances of 3.370(10) and 3.497(10) Å, respectively. In addition, amide protons form an intr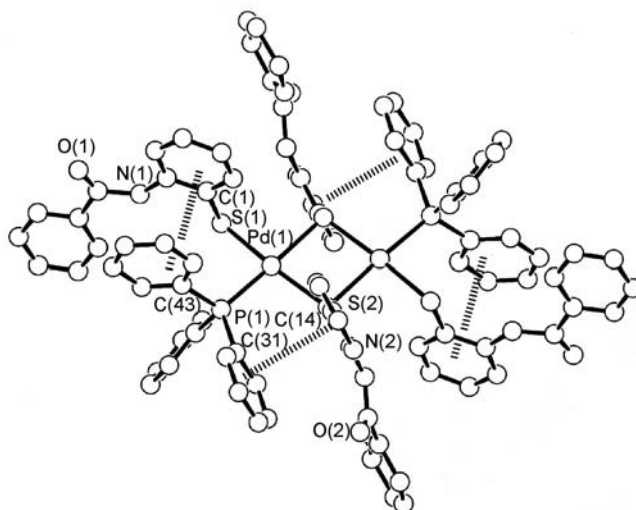aligand hydrogen bond with thiolato sulfur atoms with distances of N1–H···S1 = 2.35(6) Å and N2–H···S2 = 2.57(7) Å [15,16].

The molecular structure of **3** is shown in Fig. 2, and its selected bond distances and angles are given in Table 2. In **3**, the platinum(II) centre resides in a square-planar geometry that is defined by two sulfur atoms from two H$_2$L$^-$ ligands and two phosphorus atoms from two triphenylphosphine ligands. The two phosphorus atoms are *cis* to each other. The Pt–S bond distances (av. 2.359(9) Å) are almost the same as those of a previously reported platinum(II) complex, [Pt(PPh$_3$)$_2$(TIPT)$_2$] (HTIPT = 2,4,6-tri-isopropylbenzenethiol) (av. 2.359(4) Å) [17]. The Pt–P bond distances (av. 2.292(9) Å) are also comparable to those found in [Pt(PPh$_3$)$_2$(TIPT)$_2$] (av. 2.323(4) Å). The phenyl rings from two H$_2$L$^-$ ligands face each other with a distance of ca. 3.54 Å. In addition, two intraligand hydrogen bonds are observed between an amide and a thiolato groups with distances of N1–H···S1 = 2.291(8) Å and N2–H···S2 = 2.580(9) Å [15,16].

X-ray analysis of [(*n*-Bu)$_4$N][**4**] revealed the presence of a discrete complex anion and a (*n*-Bu)$_4$N$^+$ counter cation. The structure of the complex anion [**4**]$^-$ is shown in

Fig. 1. Molecular structure of [Pd$_2$(H$_2$L-S)$_2$(μ-H$_2$L-S)$_2$(PPh$_3$)$_2$] (**2**).
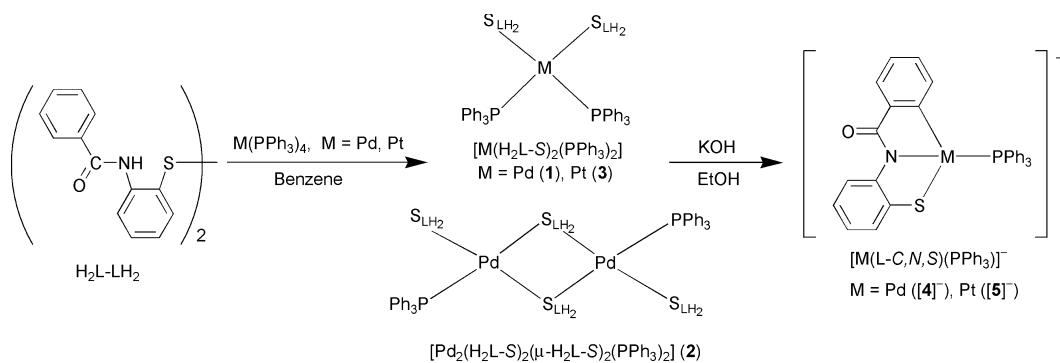
Scheme 1.

Table 1
Selected bond distances (Å) and angles (°) for [Pd$_2$(H$_2$L-S)$_2$(μ-H$_2$L-S)$_2$(PPh$_3$)$_2$] (**2**)

Pd1–S1	2.321(2)	C1···C43	3.370(10)
Pd1–S2	2.345(2)	C14···C31	3.497(10)
Pd1–S2$^{\#1}$	2.406(2)	N1–H···S1	2.35(6)
Pd1–P1	2.291(2)	N2–H···S2	2.57(7)
		Pd1···Pd1$^{\#1}$	3.5504(8)
S1–Pd1–S2	170.7(1)	S2–Pd1–P1	98.6(1)
S1–Pd1–S2$^{\#1}$	91.1(1)	S2$^{\#1}$–Pd1–P1	177.2(1)
S1–Pd1–P1	87.3(1)	Pd1–S2–Pd1$^{\#1}$	96.7(1)
S2–Pd1–S2$^{\#1}$	83.3(1)		

Symmetry transformations used to generate equivalent atoms: #1 −x, −y, −z.
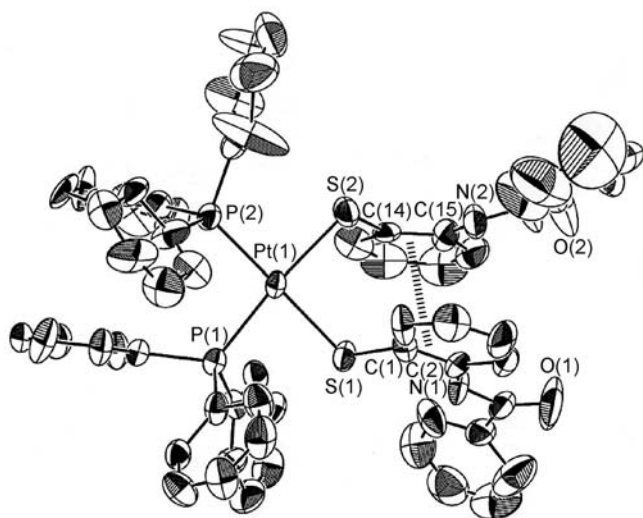

Fig. 2. Molecular structure of [Pt(H$_2$L-S)$_2$(PPh$_3$)$_2$] (**3**).

Table 2
Selected bond distances (Å) and angles (°) for [Pt(H$_2$L-S)$_2$(PPh$_3$)$_2$] (**3**)

Pt1–S1	2.352(9)	C1···C14	3.55(5)
Pt1–S2	2.366(9)	C2···C15	3.53(5)
Pt1–P1	2.307(9)	N1–H···S1	2.291(8)
Pt1–P2	2.276(9)	N2–H···S2	2.580(9)
S1–Pt1–S2	91.7(3)	S2–Pt1–P1	170.9(3)
S1–Pt1–P1	81.6(3)	S2–Pt1–P2	89.5(3)
S1–Pt1–P2	176.9(3)	P1–Pt1–P2	97.6(3)

Fig. 3, and its selected bond distances and angles are given in Table 3. The palladium(II) centre resides in a square-planar geometry that is defined by one sulfur, one nitrogen and one carbon atom from a L$^{3−}$ ligand, besides one phosphorus atom from triphenylphosphine. Thus, the L$^{3−}$ ligand acts as a rare tridentate-*C,N,S* chelator that is derived from the cyclometallation reaction of the pendant phenyl ring. The Pd–C (2.023(6) Å) and Pd–N (2.022(5) Å) bond distances in [**4**]$^−$ are slightly longer than those in a related cyclometallated palladium(II) complex, [Pd(L′)(MeCN)] (H$_2$L′ = phenyl 2-pyridyl ketone

benzoylhydrazone) (Pd–C = 2.007(5) Å and Pd–N = 1.971(5) Å) [18].

2.3. Spectroscopic studies

The IR spectrum of each complex obtained in this study shows a carbonyl $\nu_{C=O}$ band (1661 cm^{-1} for **1**, 1676 cm^{-1} for **2**, 1667 cm^{-1} for **3**, 1655 cm^{-1} for [(n-Bu)$_4$N][**4**] and 1624 cm^{-1} for K[**5**]), which shifts to lower energy relative to the $\nu_{C=O}$ band for the starting disulfide ligand H$_2$L-LH$_2$ (1678 cm^{-1}). Each of **1** and **2** gives an amide $\nu_{N–H}$ band (3358 cm^{-1} for **1** and 3320 cm^{-1} for **2**), while two $\nu_{N–H}$ bands are observed for **3** (3352 cm^{-1} and 3304 cm^{-1}), which are compatible with the presence of weak and strong N–H···S interactions detected by the X-ray analysis (Table 2). No $\nu_{N–H}$ band is noticed for [(n-Bu)$_4$N][**4**] and K[**5**], indicative of the formation of a M–N bond (M = Pd, Pt).

The ^{1}H NMR spectra of the complexes measured in CDCl$_3$ or DMSO-d_6 are shown in Figs. S1–S3. Since the ^{1}H NMR spectrum of **1** exhibits one singlet signal at δ 8.81 due to amide protons, as does the spectrum of **3** (δ 8.71), it is reasonable to assume that **1** has a symmetrical mononuclear structure in [Pd(H$_2$L-S)$_2$(PPh$_3$)$_2$] with a *cis* configuration, which is analogous to the structure in **3** ([Pt(H$_2$L-S)$_2$(PPh$_3$)$_2$]). The relative downfield shift of amide protons for **1** and **3** would be attributed to the formation of intraligand hydrogen bonds with thiolato groups. On the other hand, two amide proton signals are observed at δ 9.24 and 8.68 in the ^{1}H NMR spectrum of **2**. This is consistent with the symmetrical structure of **2** found in crystal, which reveals the presence of two bridging and two terminal H$_2$L$^−$ ligands. As shown in Fig. S3, the ^{1}H NMR spectral feature of K[**5**] is very similar to that of [(n-Bu)$_4$N][**4**] over the whole region, showing a significant downfield shift (δ 8.80 for [**4**]$^−$ and δ 8.86 for [**5**]$^−$) for the phenyl proton adjacent to the cyclometallated atom (Fig. 3). This result implies that [**5**]$^−$ has a mononuclear structure in [Pt(L-*C,N,S*)(PPh$_3$)] bearing a cyclometallated tridentate-*C,N,S* ligand (L$^{3−}$), which is analogous to the structure in [**4**]$^−$ ([Pd(L-*C,N,S*)(PPh$_3$)]).

3. Conclusions

It was found in this study that the redox reaction between the disulfide H$_2$L-LH$_2$ and [Pd(PPh$_3$)$_4$] produces a mixture of the mononuclear [Pd(H$_2$L-S)$_2$(PPh$_3$)$_2$] (**1**) and the dinuclear [Pd$_2$(H$_2$L-S)$_2$(μ-H$_2$L-S)$_2$(PPh$_3$)$_2$] (**2**), which was successfully separated. On the other hand, only the mononuclear [Pt(H$_2$L-S)$_2$(PPh$_3$)$_2$] (**3**) was obtained for the corresponding reaction with [Pt(PPh$_3$)$_4$], which is most likely due to the stronger Pt–P bonds compared with the Pd–P bonds. Interestingly, treatment of a mixture of **1** and **2** with OH$^−$ results in the cyclometallated [Pd(L-*C,N,S*)(PPh$_3$)]$^−$ ([**4**]$^−$). The first step of this reaction is the cleavage of amide N–H bond by OH$^−$, which leads to the formation of Pd–N bond accompanied by the loss
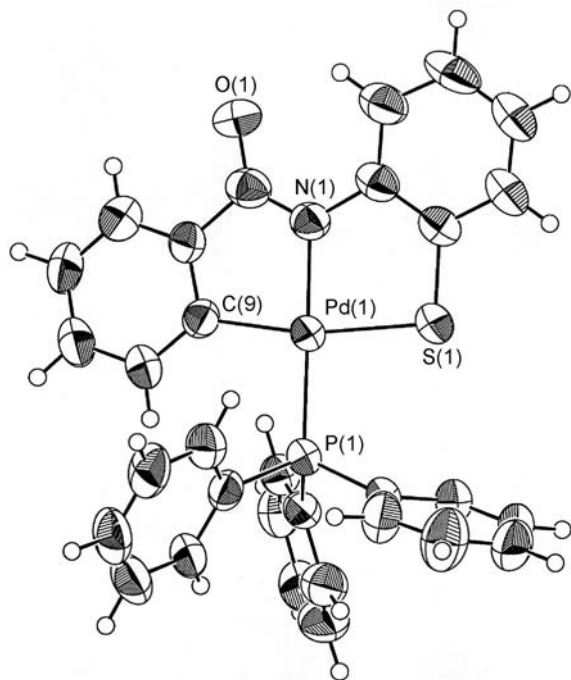
Fig. 3. Molecular structure of [Pd(L-*C,N,S*)(PPh₃)]⁻ ([**4**]⁻).

Table 3
Selected bond distances (Å) and angles (°) for [(*n*-Bu)₄N][Pd(L-*C,N,S*)(PPh₃)] ([(*n*-Bu)₄N][**4**])

Pd1–S1	2.312(2)	Pd1–N1	2.022(5)
Pd1–P1	2.243(2)	Pd1–C9	2.023(6)
S1–Pd1–P1	94.7(1)	P1–Pd1–N1	177.4(2)
S1–Pd1–N1	85.3(2)	P1–Pd1–C9	97.7(2)
S1–Pd1–C9	167.1(2)	N1–Pd1–C9	82.5(2)

of a H_2L^- and a PPh_3 ligands. The coordination of amide nitrogen atom affords the access of a pendant phenyl ring to the metal centre, followed by the C–H activation. Cyclometallation of phenyl ring caused by such short contact has been found in the corresponding Schiff base complexes [5,19,20]. The analogous cyclometallated [Pt(L-*C,N,S*)(PPh₃)]⁻ ([**5**]⁻) was also formed by treatment of **3** with OH⁻. Thus, it was evidenced that the redox reaction between a low oxidation metal (Pd^0 or Pt^0) and an amide-disulfide compound (H_2L-LH_2), followed by treatment with base, is a simple and convenient synthetic route to create cyclometallated metal complexes with amide-thiolate ligands, which does not suffer oxidation at thiolato groups.

4. Experimental

4.1. General

The reagents were purchased from commercial sources and not purified further. Bis(2-benzamidophenyl) disulfide (H_2L-LH_2) was synthesized by the modified method reported in [21].

4.2. Synthesis of complexes

4.2.1. [Pd(H₂L–S)₂(PPh₃)₂] (**1**) and [Pd₂(H₂L–S)₂-(μ-H₂L–S)₂(PPh₃)₂] (**2**)

To a solution of H_2L-LH_2 (0.51 g, 1.12 mmol) in 50 ml of degassed benzene under an argon atmosphere was added [Pd(PPh₃)₄] (1.18 g, 1.02 mmol). The reaction mixture was stirred for 1 h at room temperature, and the resulting red precipitate of a mixture of **1** and **2** (0.97 g) was collected by filtration. When the filtrate was allowed to stand in a refrigerator for 2 days, a red powder of a mixture of **1** and **2** (68 mg) was again precipitated, which was filtered off. The second filtrate was further allowed to stand in a refrigerator for 2 days. The precipitated red powder of **1** was collected by filtration. Yield: 35 mg. A pure sample of **2** was obtained by recrystallization of the first red precipitate (32 mg) from CH_2Cl_2/*n*-hexane. Yield: 10 mg. Single crystals of **2** suitable for a structure determination were grown by slow diffusion of pentane into a CH_2ClCH_2Cl solution of **2**. Anal. Calcd. for [Pd(H₂L-*S*)₂(PPh₃)₂]·1.5C₆H₆, C₇₁H₅₉N₂O₂P₂PdS₂: C, 70.78; H, 4.94; N, 2.33. Found: C, 70.88; H, 5.02; N, 2.30%. Anal. Calcd. for [Pd₂(H₂L-*S*)₂(μ-H₂L-*S*)₂(PPh₃)₂]·0.25CH₂Cl₂, C₈₈.₂₅H₇₀.₅Cl₀.₅N₄O₄P₂Pd₂S₄: C, 63.40; H, 4.25; N, 3.35. Found: C, 63.35; H, 4.30; N, 3.49%. IR ($\tilde{v}$ cm⁻¹): 3358vw (N–H), 1661 m (C=O) for **1**, 3320vw (N–H), 1676 m (C=O) for **2**. ¹H NMR (CDCl₃): δ 8.81 (s, 2H, NH), 7.97 (d, 2H, Ph CH), 7.65–7.10 (m, 42H, Ph CH), 6.84 (t, 2H, Ph CH), 6.60 (t, 2H, Ph CH) for **1**, 9.24 (s, 2H, NH), 8.68 (s, 2H, NH), 8.20 (d., 2H, Ph CH), 8.05 (d, 2H, Ph CH), 7.66 (d, 2H, Ph CH), 7.45–6.90 (m, 58H, Ph CH), 6.82 (t, 2H, Ph CH) for **2**.

4.2.2. [Pt(H₂L–S)₂(PPh₃)₂] (**3**)

To a solution of H_2L-LH_2 (0.18 g, 0.39 mmol) in 40 ml of degassed benzene under an argon atmosphere was added [Pt(PPh₃)₄] (0.48 g, 0.39 mmol). The reaction mixture was stirred at room temperature for 2 h, followed by allowing to stand in a refrigerator for 4 h. The resulting yellow powder of **3** was collected by filtration. Yield: 0.24 g. Single crystals of **3** suitable for a structure determination were grown by slow diffusion of pentane into a CHCl₃ solution of **3**. Anal. Calcd. for [Pt(H₂L-*S*)₂(PPh₃)₂], C₆₂H₅₀N₂O₂P₂PtS₂: C, 63.31; H, 4.28; N, 2.38. Found: C, 63.37; H, 4.53; N, 2.35%. IR ($\tilde{v}$ cm⁻¹): 3352 w, 3304 w (N–H), 1667 m (C=O). ¹H NMR (CDCl₃): δ 8.71 (s, 2H, NH), 8.04 (d, 2H, Ph CH), 7.79 (d, 2H, Ph CH), 7.65–7.10 (m, 40H, Ph CH), 6.69 (t, 2H, Ph CH), 6.55 (t, 2H, Ph CH).

4.2.3. [(*n*-Bu)₄N][Pd(L-C,N,S)(PPh₃)] ([(*n*-Bu)₄N][**4**])

An ethanolic solution of KOH (0.035 g, 0.63 mmol) was added to a solution of a mixture of **1** and **2** (0.20 g) in 20 ml of ethanol under an argon atmosphere. The reaction mixture was refluxed for 2 h to give a yellow solution, which was concentrated to ca. 10 ml with a rotary evaporator. The addition of (*n*-Bu)₄NBr (0.22 g) dissolved in a small

amount of ethanol to the concentrated solution afforded a yellow powder of [(n-Bu)$_4$N][**4**], which was collected by filtration. Yield: 0.14 g. Single crystals of [(n-Bu)$_4$N][**4**] suitable for a structure determination were obtained by recrystallization of the yellow powder from hot ethanol. Anal. Calcd. for [(n-Bu)$_4$N][Pd(L-*C,N,S*)(PPh$_3$)] · 0.2 KBr, C$_{47}$H$_{59}$Br$_{0.2}$K$_{0.2}$N$_2$OPPdS: C, 65.55; H, 6.90; N, 3.25. Found: C, 65.37; H, 7.11; N, 3.30%. IR ($\tilde{v}$ cm^{-1}): 1655 m (C=O). ^{1}H NMR (DMSO-*d*$_6$): δ 8.80 (d, 1H, Ph$_{C,N\text{-chelate}}$ CH), 7.65–7.55 (m, 6H, Ph$_{PPh3}$ CH), 7.50–7.35 (m, 9H, Ph$_{PPh3}$ CH), 7.16 (d, 1H, Ph$_{N,S\text{-chelate}}$ CH), 6.70 (d, 1H, Ph$_{C,N\text{-chelate}}$ CH), 6.67 (t, 1H, Ph$_{N,S\text{-chelate}}$ CH), 6.54 (t, 1H, Ph$_{C,N\text{-chelate}}$ CH), 6.42 (t, 1H, Ph$_{C,N\text{-chelate}}$ CH), 6.36 (t, 1H, Ph$_{N,S\text{-chelate}}$ CH), 6.20 (d, 1H, Ph$_{N,S\text{-chelate}}$ CH) [22].

4.2.4. K[Pd(L-C,N,S)(PPh$_3$)] (K[5])

To a solution of **3** (0.22 g, 0.19 mmol) in 20 ml of ethanol under an argon atmosphere was added an ethanolic solution of KOH (0.039 g, 0.70 mmol). The reaction mixture was refluxed for 2 h to give a yellow solution, which was concentrated to ca. 5 ml with a rotary evaporator. The concentrated solution was allowed to stand in a refrigerator for 2 h, and the resulting yellow powder of K[**5**] was collected by filtration. Yield: 0.13 g. Anal. Calcd. for K[Pd(L-*C,N,S*)(PPh$_3$)] · 2.5H$_2$O, C$_{31}$H$_{28}$KNO$_{3.5}$PPtS: C, 48.50; H, 3.68; N, 1.82. Found: C, 48.50; H, 4.13; N, 1.50%. IR ($\tilde{v}$ cm^{-1}): 1624 m (C=O). ^{1}H NMR (DMSO-*d*$_6$): δ 8.86 (d, 1H, Ph$_{C,N\text{-chelate}}$ CH), 7.70–7.55 (m, 6H, Ph$_{PPh3}$ CH), 742 (s(br), 9H, Ph$_{PPh3}$ CH), 7.11 (d, 1H, Ph$_{N,S\text{-chelate}}$ CH), 6.73 (d, 1H, Ph$_{C,N\text{-chelate}}$ CH), 6.66 (t, 1H, Ph$_{N,S\text{-chelate}}$ CH), 6.50 (t, 1H, Ph$_{C,N\text{-chelate}}$ CH), 6.44 (t, 1H, Ph$_{C,N\text{-chelate}}$ CH), 6.36 (t, 1H, Ph$_{N,S\text{-chelate}}$ CH), 6.26 (d, 1H, Ph$_{N,S\text{-chelate}}$ CH) [22].

4.3. Physical measurements

The infrared spectra were measured on a JASCO FT/IR-5000 spectrophotometer using the nujol mulls and the NMR spectra on a JEOL EX 270 instrument. Tetramethylsilane was used as the internal standard (δ 0). Elemental analyses were performed at Osaka University.

4.4. X-ray structure analysis

The crystallographic date of **2**, **3** and [(n-Bu)$_4$N][**4**] are listed in Table 4. Each of a red crystal of **2**, a yellow crystal of **3** and a yellow crystal of [(n-Bu)$_4$N][**4**] was sealed in a Lindemann glass-capillary tube with the mother liquor. X-ray diffraction data were collected on a Mac Science MXC3 diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature; the θ–2θ scans were used. The intensities of three standard reflections for each complex were measured every 100 reflections. Over the course of data collection the standards of **2** decreased by 24.3% and a linear correction factor was applied to account for this. The standards of **3** and [(n-Bu)$_4$N][**4**] showed no significant decay effects. The structure of **2** was solved by direct methods using PATTY in DIRDIF and those of **3**

Table 4
Crystallographic data of complexes

	[Pd$_2$(H$_2$L-*S*)$_2$(μ-H$_2$L-*S*)$_2$-(PPh$_3$)$_2$]·3C$_5$H$_{12}$ (**2**)	[Pt(H$_2$L-*S*)$_2$(PPh$_3$)$_2$]·1.5CHCl$_3$ (**3**)	[(n-Bu)$_4$N][Pd(L-*C,N,S*)(PPh$_3$)]·2C$_2$H$_5$OH ([(n-Bu)$_4$N][**4**])
Empirical formula	C$_{103}$H$_{106}$N$_4$O$_4$P$_2$Pd$_2$S$_4$	C$_{63.5}$H$_{51.5}$Cl$_{4.5}$N$_2$O$_2$P$_2$PtS$_2$	C$_{51}$H$_{71}$N$_2$O$_3$PPdS
Formula weight	1867.05	1355.32	929.60
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
Unit cell dimensions			
a (Å)	13.997(7)	29.32(1)	10.173(5)
b (Å)	14.904(6)	15.338(6)	27.298(9)
c (Å)	11.839(5)	12.731(4)	9.522(5)
α (°)	101.64(3)		96.86(3)
β (°)	101.57(4)	96.69(3)	104.03(4)
γ (°)	66.11(3)		81.95(3)
V (Å^3)	2192(2)	5687(3)	2530(2)
Z	1	4	2
D_{calc} (Mg m^{-3})	1.42	1.58	1.22
μ (mm^{-1})	0.58	2.66	0.47
Number of unique reflections measured	9201	10869	10005
Number of reflections in refinement	7462 ($I > 2.0\ \sigma(I)$)	7501 ($I > 2.0\ \sigma(I)$)	8567 ($I > 2.0\sigma(I)$)
R^{a}	0.071	0.088	0.081
$R_w{}^{b}$	0.086	0.098	0.097

^{a} $R = \sum \|F_o| - |F_c\| / \sum |F_o|$.
^{b} $wR = \left[\sum w(|F_o|^2 - |F_c|^2)^2 \right] / \sum \left[w(F_o^2)^2 \right]^{1/2}$.

and [(*n*-Bu)$_4$N][**4**] were solved by direct methods using SIR 92 and refined anisotropically for all non-hydrogen atoms with full-matrix least-squares calculations. Hydrogen atoms were located at fixed positions (C–H 0.96 Å). Atomic scattering factors and anomalous scattering coefficients were taken from [23]. All calculations were performed using the CRYSTAN-GM software [24].

Acknowledgements

Appendix A. Supplemental material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 299784–299786. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: int. code +44 1223 336 033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk. ^{1}H NMR spectra of complexes **1**, **2**, **3**, [(*n*-Bu)$_4$N][**4**] and K[**5**] are available (Figs. S1–S3). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.051.

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