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SYNTHESIS OF Ag^+ -SELECTIVE DIPALLADIUM(II) METALLOHOST BASED ON *O*-ALKYLOXIME BIS(N_2SO) LIGANDS

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*Novel bis(N_2SO) ligands 2a (= H_4L^{2a}) and 2b (= H_4L^{2b}) comprising *O*-alkyloxime, thio-phenol, and phenol moieties were synthesized. The complexation of H_4L^{2a} and H_4L^{2b} with palladium(II) acetate afforded the dinuclear metallohosts $[\text{L}^{2a}\text{Pd}_2]$ and $[\text{L}^{2b}\text{Pd}_2]$, which have a recognition site consisting of two sulfur and four oxygen donor atoms. The metallohost $[\text{L}^{2b}\text{Pd}_2]$ strongly binds Ag^+ to give $[(\text{L}^{2b}\text{Pd}_2)_2\text{Ag}]^+$, whereas no detectable interaction between $[\text{L}^{2b}\text{Pd}_2]$ and hard metal cations (Na^+ , Ca^{2+} , Y^{3+} , La^{3+} , and Lu^{3+}) was observed.*

Keywords Metallohost; oxime; palladium; silver; thiol

INTRODUCTION

Metallohosts, which have a metal complex moiety in their framework, have recently attracted much interest. The metal atom is useful to form a host structure suitable for guest recognition¹ or to output signals by changing the properties of the metal upon the guest recognition.^{2,3} We have investigated the design, synthesis, and complexation behavior of a series of bis(N_2O_2) type ligands (**1** and its analogs, Scheme 1), which are expected to afford dinuclear metallohosts.^{4,5} We have demonstrated that H_2salamo (= 1,2-bis(salicylideneaminoxy)ethane)^{6,7} based on *O*-alkyloxime functionality is useful as the N_2O_2 coordination site to synthesize these types of bis(N_2O_2) ligands because of the high stability toward $\text{C}=\text{N}$ bond recombination. Upon metalation, the bis(N_2O_2) ligand affords a trinuclear complex in a cooperative fashion, in which the third metal ion sits in the central O_6 site in addition to the two metal ions in the N_2O_2 sites. The trinuclear complex acts as a metallohost based on novel transmetalation strategy, in which guest recognition takes place with concomitant release of one of the metal ions. The guest ion nicely fits into the metallohost cavity comprising six oxygen donor atoms of four phenoxo and two methoxy groups.⁴

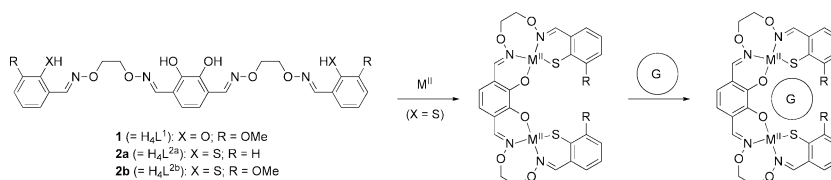
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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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If sulfur donor atoms are introduced into a host molecule instead of oxygen, the binding selectivity is expected to change. Indeed, thiacycrown ethers prefer softer metal ions such as Ag⁺, whereas the oxygen analogs bind harder cations.⁸ Thus, we introduce sulfur donor atoms into the bis(N₂O₂) framework of **1** in order to change the binding selectivity of our novel ion recognition system. We have already reported the synthesis, reactivity, and complexation ability of sulfur analogs of the salamo ligand, which have one or two thiophenol moieties instead of the phenol groups.⁹ In this article we report the synthesis of new bis(N₂SO) ligands **2a** and **2b**, which can be converted into the dinuclear metallohost (Scheme 1). The complexation ability of the metallohost is also investigated.

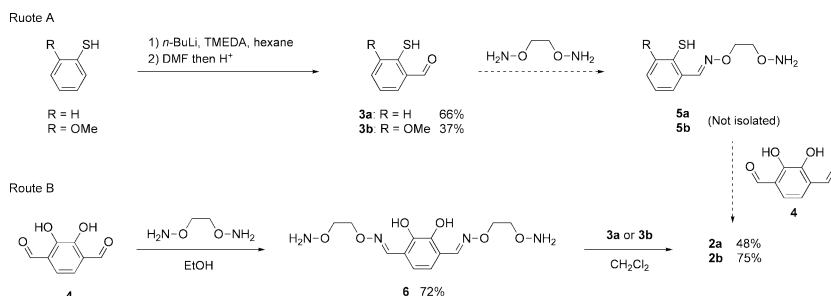


Scheme 1 Design of bis(N₂SO) ligands and the metallohost for guest recognition.

RESULTS AND DISCUSSION

Synthesis of Bis(N₂SO) Ligand

Synthesis of the ligands **2a** and **2b** was first investigated according to route A starting from the thiosalicylaldehydes **3** (Scheme 2). This route is analogous to the synthesis of **1** previously reported in the literature.⁴ 2-Mercaptobenzaldehyde (**3a**) was synthesized by the reaction of thiophenol with *n*-butyllithium followed by *N,N*-dimethylformamide, according to the literature.¹⁰ The methoxy derivative, 2-mercapto-3-methoxybenzaldehyde (**3b**),¹¹ was also prepared in a similar manner. The reaction of thiosalicylaldehydes **3a** and **3b** with 1,2-bis(aminoxy)ethane¹² gave a mixture containing compound **5**. However, the product was found to be difficult to purify. Hence, we instead prepared the central unit **6** by the reaction of dialdehyde **4**^{4d,13} and 5 equiv of 1,2-bis(aminoxy)ethane in 72% yield (route B). The bis(N₂SO) ligands **2a** and **2b** were successfully synthesized in 48% and 75% yield, respectively, by the condensation of the diamine **6** with the terminal unit **3**. These compounds were obtained as stable colorless crystals, which were characterized by ¹H ¹³C NMR and elemental analysis. We have previously reported that unsymmetrical N₂SO ligands based on two C=N nitrogen, thiophenol, and phenol groups are difficult to



Scheme 2 Synthetic routes to bis(N₂SO) ligands **2a** and **2b**.

synthesize unless an *O*-alkyloxime group is used instead of an imine group.⁹ Thiol groups may react with imine groups but not with *O*-alkyloxime groups. The low reactivity of the oxime groups also retards the C=N bond recombination, which facilitates the synthesis of the unsymmetrical salen-type ligands.

The bis(N₂SO) ligands **2a** and **2b** were stable in solution. These compounds remained unchanged in the solution at room temperature after 1 month. In the ¹H NMR spectrum of **2a**, the signals for the thiol and phenol protons were observed at 4.55 and 9.71 ppm, respectively, in CDCl₃. The thiol protons of the methoxy analog **2b** appeared at lower field (4.91 ppm), as observed for the parent N₂SO ligands.⁹

Synthesis of Bis(N₂SO)-Pd₂ Metallohost

We first investigated the metalation of the bis(N₂SO) ligands **2a** (= H₄L^{2a}) and **2b** (= H₄L^{2b}) to obtain the dinuclear metallohosts. We have previously reported that the parent mono(N₂SO) ligand gave a diamagnetic mononuclear complex upon complexation with palladium(II), while the N–O bond cleavage took place when the ligand was allowed to react with nickel(II) or copper(II).⁹ Consequently, palladium(II) is suitable for the metal to be incorporated into the metallohost.

When the N₂SO sites of ligands H₄L^{2a} and H₄L^{2b} are metalated with palladium(II), dinuclear complexes [L^{2a}Pd₂] and [L^{2b}Pd₂] are formed, respectively. In this process, four new coordination bonds were formed in each of the N₂SO moieties. This makes the metallohost molecule less flexible and fixes the conformation in a C-shaped fashion. Thus, the metallohosts were expected to have a cavity consisting of the S₂O₂ or S₂O₄ donor sets.

The palladium(II) complexes [L^{2a}Pd₂] and [L^{2b}Pd₂] were prepared in 74% and 55% yields by the reaction of palladium(II) acetate with the corresponding free ligands H₄L^{2a} and H₄L^{2b}, respectively. The methoxy derivative [L^{2b}Pd₂] is soluble in DMSO, while [L^{2a}Pd₂] without methoxy groups has low solubility. The ¹H NMR spectra in DMSO-*d*₆ showed two singlets for the oxime protons at 8.28 and 8.76 ppm for [L^{2a}Pd₂] and 8.26 and 8.80 ppm for [L^{2b}Pd₂], indicating a symmetrical structure. The formation of dinuclear complex [L^{2b}Pd₂] was confirmed by the mass spectrum (*m/z* 847.1 for [L^{2b}Pd₂Na]⁺).

We have reported that it is difficult to obtain a dinuclear metallohost of the oxygen analog **1**, because the formation process of the trinuclear complexes of **1** with zinc(II), cobalt(II), manganese(II), and nickel(II) was highly cooperative. Even if the dinuclear metallohosts are formed, they should readily bind to an additional metal ion in the central cavity to afford the trinuclear complexes. In the case of the sulfur analogs **2** in this study, a dinuclear metallohost having a vacant cavity was obtained by using the combination of the N₂SO coordination sites and palladium(II).

Complexation Study of Dinuclear Metallohost

We investigated the complexation ability of the dinuclear metallohost [L^{2b}Pd₂], which has better solubility in DMSO. The ¹H NMR spectra of [L^{2b}Pd₂] showed no change in chemical shifts upon the addition of 1 equiv of La(OTf)₃, Lu(OTf)₃, Y(OTf)₃, Ca(ClO₄)₂, and NaClO₄. This result indicates that the metallohost [L^{2b}Pd₂] has low affinity for these hard cations. When Pb²⁺ was added to the solution, small chemical shift changes were observed.

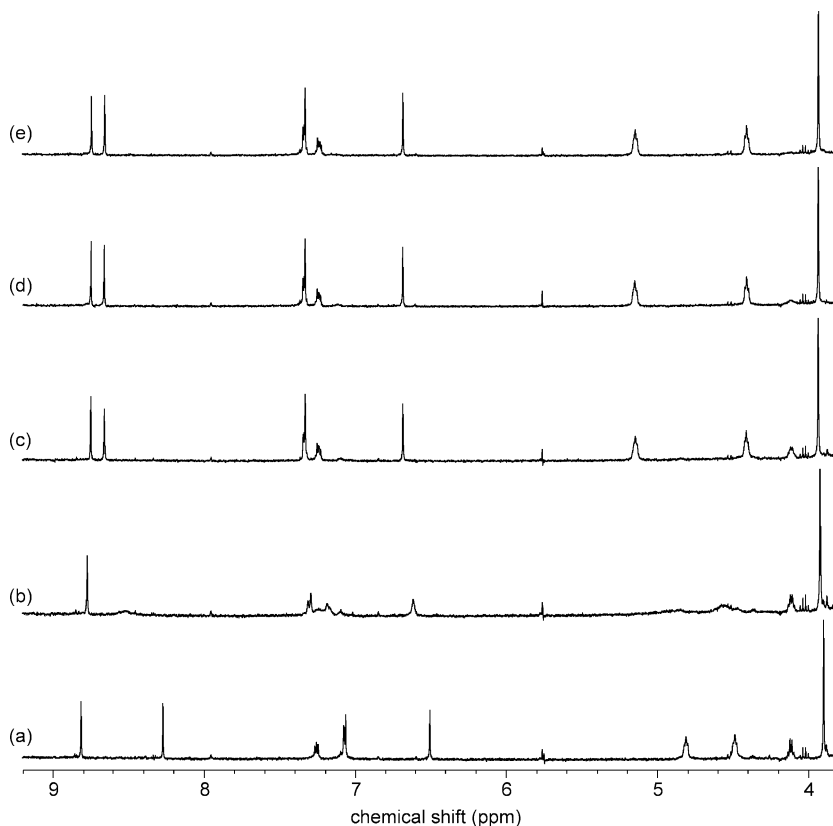
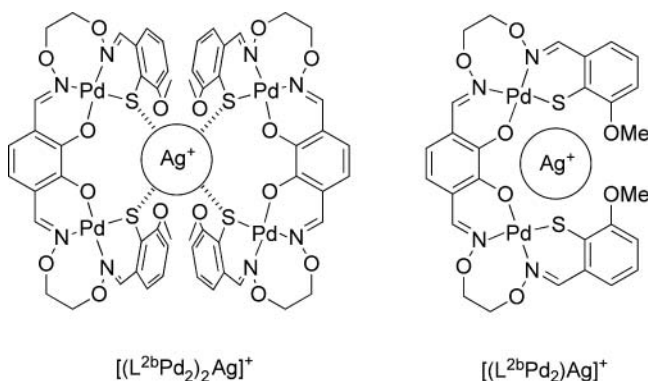


Figure 1 ^1H NMR spectra changes of $[\text{L}^{2\text{b}}\text{Pd}_2]$ by the addition of AgNO_3 in $\text{DMSO}-d_6$, $[\text{L}^{2\text{b}}\text{Pd}_2] = 1.0 \text{ mM}$, 400 MHz. (a) 0 equiv; (b) 0.25 equiv; (c) 0.5 equiv; (d) 1.0 equiv; (e) 3.0 equiv.

In contrast, the addition of Ag^+ to the solution of $[\text{L}^{2\text{b}}\text{Pd}_2]$ caused significant changes in the ^1H NMR spectra (Figure 1). When 0.25 equiv of Ag^+ is present, the spectrum of $[\text{L}^{2\text{b}}\text{Pd}_2]$ was considerably broadened, probably because the process of complexation/decomplexation with Ag^+ is slow on the ^1H NMR timescale. However, 0.5 equiv of Ag^+ caused the appearance of sharp signals, which were observed at different chemical shifts from those of the free ligand $\text{H}_4\text{L}^{2\text{b}}$. For example, two signals of the $\text{OCH}_2\text{CH}_2\text{O}$ moiety at 4.48 and 4.79 ppm shifted to 5.15 and 4.41 ppm, respectively, and the oxime protons at 8.26 and 8.80 shifted to 8.66 and 8.75 ppm, respectively. Further addition of Ag^+ caused a slight change in the chemical shifts of the oxime protons. These results clearly indicate a 2:1 stoichiometry ($[\text{L}^{2\text{b}}\text{Pd}_2]:\text{Ag}^+$), which corresponds to the 2:1 adduct $[(\text{L}^{2\text{b}}\text{Pd}_2)_2\text{Ag}]^+$ (Scheme 3).

In the ESI-MS of $[\text{L}^{2\text{b}}\text{Pd}_2]$ in the presence of 1 equiv of Ag^+ , a strong peak was observed at m/z 930.8, whose isotope pattern is consistent with $[(\text{L}^{2\text{b}}\text{Pd}_2)\text{Ag}]^+$ (Figure 2). This result indicates that the 1:1 adduct $[(\text{L}^{2\text{b}}\text{Pd}_2)\text{Ag}]^+$ is present under the highly diluted conditions for the ESI-MS measurement.

Consequently, dinuclear complex $[\text{L}^{2\text{b}}\text{Pd}_2]$ acts as a metallohost that efficiently binds to Ag^+ in the S_2O_4 cavity. The thiolato groups in the $\text{N}_2\text{SO}-\text{Pd}$ complex moieties contribute



Scheme 3 Plausible structure of the metallohost-guest complexes between $[L^{2b}Pd_2]$ and Ag^+ .

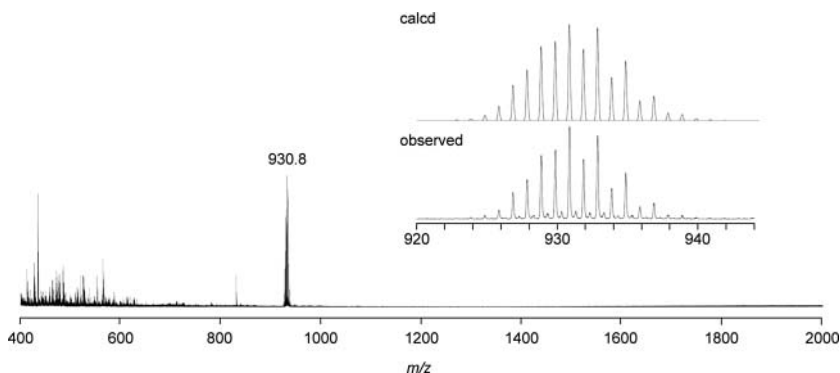


Figure 2 ESI mass spectrum of $[L^{2b}Pd_2]$ in the presence of Ag^+ . The inset shows the observed and calculated isotope patterns of $[(L^{2b}Pd_2)Ag]^+$.

to the Ag^+ -binding, probably because distance between the two thiolato groups is suitable for binding to Ag^+ .

CONCLUSION

Bis(N_2SO) ligands **2a** and **2b** based on the oxime chelate coordination moiety were synthesized. The complexation of the **2b** ($= H_4L^{2b}$) with palladium(II) acetate afforded the dinuclear metallohost $[L^{2b}Pd_2]$, which has a recognition site consisting of the two sulfur and four oxygen donor atoms. The metallohost $[L^{2b}Pd_2]$ binds strongly to Ag^+ to give $[(L^{2b}Pd_2)_2Ag]^+$, whereas interactions between $[L^{2b}Pd_2]$ and hard metal cations were not detected.

EXPERIMENTAL

All experiments were carried out under aerobic conditions unless otherwise noted. Hexane was distilled from calcium hydride prior to use. Commercial methanol, ethanol,

dichloromethane, and chloroform were used without purification. Silica gel chromatography was performed by Kanto Silica Gel 60N (spherical, neutral). Gel permeation chromatography (GPC) was performed on an LC908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns using chloroform as eluent. Melting points were determined on a Yanaco melting point apparatus and are not corrected. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX 400 or an Avance 400 spectrometer (400 and 100 MHz, respectively), using tetramethylsilane as an internal standard. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar/Pulsar *i* spectrometer.

Materials

1,2-Bis(aminooxy)ethane¹² and 2,3-dihydroxybenzene-1,4-dicarbaldehyde (**4**)^{4d,13} were prepared according to the reported procedures. 2-Mercaptobenzaldehyde (**3a**) was prepared¹⁰ and stored as a dichloromethane solution under nitrogen. 2-Methoxybenzenethiol was purchased from Wako Pure Chemical Industries Ltd.

Synthesis of 2-Mercapto-3-methoxybenzaldehyde (**3b**)

n-Butyllithium (2.6 M, in hexane, 13.4 mL, 35 mmol) was added slowly over a period of 30 min to a stirred solution of 2-methoxybenzenethiol (2.0 mL, 16 mmol) and *N,N,N',N'*-tetramethylethylenediamine (5.6 mL, 37 mmol) in hexane (50 mL) at 0°C under nitrogen atmosphere. After the reaction mixture was stirred overnight at room temperature, *N,N*-dimethylformamide (3.4 mL, 44 mmol) was added, and the mixture was stirred for further 6 h. After acidification with 1 M hydrochloric acid, the mixture was extracted with ether, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The residue was subjected to chromatography on silica gel (eluent, dichloromethane/hexane, 1:1) to afford **3b** (1.00 g, 6.0 mmol, 37%) as yellow crystals, 39–41°C,¹¹ ¹H NMR (400 MHz, CDCl₃) δ 3.96 (s, 3H), 5.71 (s, 1H), 7.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.2 Hz, 1H), 10.11 (s, 1H).

Synthesis of Dioxime **6**

A solution of dialdehyde **4** (140 mg, 0.84 mmol) in ethanol (30 mL) was added dropwise to a solution of 1,2-bis(aminooxy)ethane (465 mg, 5.1 mmol) in ethanol (70 mL) with stirring at 50–55°C. The solution was stirred at the temperature for 30 min and then concentrated to dryness. The crude product was purified by GPC to afford dioxime **6** (190 mg, 0.60 mmol, 72%) as colorless crystals, mp 102–106°C, ¹H NMR (400 MHz, CDCl₃) δ 3.97–3.99 (m, 4H), 4.39–4.41 (m, 4H), 5.52 (brs, 4H), 6.76 (s, 2H), 8.21 (s, 2H), 9.77 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 72.8 (CH₂), 73.6 (CH₂), 117.5 (C), 120.8 (CH), 145.7 (C), 151.1 (CH). Anal. Calcd for C₁₂H₁₈N₄O₆: C, 45.86; H, 5.77; N, 17.83. Found: C, 46.05; H, 5.64; N, 17.53.

Synthesis of Bis(N₂SO) Ligand **2a** (= H₄L^{2a})

A solution of dioxime **6** (65.6 mg, 0.21 mmol) in dichloromethane (2 mL) was added to a solution of 2-mercaptobenzaldehyde (**3a**, 0.42 mmol) in dichloromethane, and the resulting mixture was stirred for 3 h at room temperature. After the solution was concentrated, the residual crude product was purified by GPC to afford **2a** (55.2 mg, 0.099 mmol, 48%) as colorless crystals, mp 109–110°C, ¹H NMR (400 MHz, CDCl₃) δ 4.49–4.54

(m, 8H), 4.55 (s, 2H), 6.76 (s, 2H), 7.14–7.22 (m, 4H), 7.32 (dd, $J = 7.4, 1.6$ Hz, 2H), 7.53 (dd, $J = 7.4, 1.6$ Hz, 2H), 8.23 (s, 2H), 8.44 (s, 2H), 9.71 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 72.7 (CH_2), 73.3 (CH_2), 117.6 (C), 120.7 (CH), 125.7 (CH), 129.5 (C), 129.6 (CH), 129.8 (CH), 131.5 (CH), 132.1 (C), 145.8 (C), 149.4 (CH), 151.2 (CH). Anal Calcd for $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_6\text{S}_2\cdot\text{H}_2\text{O}$: C, 54.53; H, 4.93; N, 9.78. Found: C, 54.66; H, 5.02; N, 9.56.

Synthesis of Bis(N_2SO) Ligand **2b** (= H_4L^{2b})

A solution of dioxime **6** (15.4 mg, 0.049 mmol) in dichloromethane (2 mL) was added to a solution of 2-mercapto-3-methoxybenzaldehyde (**3b**, 17.8 mg, 0.11 mmol) in dichloromethane (2 mL), and the resulting mixture was stirred for 4.5 h at room temperature. After the solution was concentrated, the residue was subjected to column chromatography on silica gel (eluent, dichloromethane:hexane, 1:1 then 1:0) to afford **2b** as colorless crystals (22.5 mg, 0.037 mmol, 75%), mp 128–130°C, ^1H NMR (400 MHz, CDCl_3) δ 3.91 (s, 6H), 4.49–4.54 (m, 8H), 4.91 (s, 2H), 6.76 (s, 2H), 6.85 (dd, $J = 8.0, 0.9$ Hz, 2H), 7.10 (t, $J = 8.0$ Hz, 2H), 7.22 (dd, $J = 8.0, 0.9$ Hz, 2H), 8.23 (s, 2H), 8.43 (s, 2H), 9.68 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.2 (CH_3), 72.5 (CH_2), 73.3 (CH_2), 111.1 (CH), 117.6 (C), 120.7 (CH), 121.4 (CH), 122.3 (C), 125.1 (CH), 129.8 (C), 145.8 (C), 148.8 (CH), 151.2 (CH), 154.7 (C). Anal Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_8\text{S}_2$: C, 54.71; H, 4.92; N, 9.11. Found: C, 54.40; H, 4.92; N, 8.64.

Synthesis of Metallohost [L^{2a}Pd_2]

A solution of ligand H_4L^{2a} (30.9 mg, 0.056 mmol) in dichloromethane (25 mL) was added to a solution of palladium(II) acetate (23.8 mg, 0.11 mmol) in methanol (25 mL). After the solution was allowed to stand at room temperature, brown precipitates were collected to give [L^{2a}Pd_2] (30.1 mg, 0.039 mmol, 74%) as brown powder, ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 4.48 (brt, 4H), 4.74 (brt, 4H), 6.50 (s, 2H), 7.07 (t, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 2H), 7.57 (d, $J = 7.4$ Hz, 2H), 7.64 (d, $J = 7.4$ Hz, 2H), 8.28 (s, 2H), 8.76 (s, 2H). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_6\text{Pd}_2\text{S}_2\cdot 1.5\text{CH}_2\text{Cl}_2$: C, 37.08; H, 2.83; N, 6.29. Found: C, 36.71; H, 3.16; N, 6.47.

Synthesis of Metallohost [L^{2b}Pd_2]

A solution of ligand H_4L^{2b} (36.4 mg, 0.059 mmol) in chloroform (100 mL) was added to a solution of palladium(II) acetate (30.9 mg, 0.14 mmol) in chloroform (100 mL). After the solution was allowed to stand at room temperature, brown precipitates were collected to give [L^{2b}Pd_2] (27.0 mg, 0.033 mmol, 55%) as brown powder, ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 3.89 (s, 6H), 4.48 (brt, 4H), 4.79 (brt, 4H), 6.49 (s, 2H), 7.05–7.07 (m, 4H), 7.23–7.26 (m, 2H), 8.26 (s, 2H), 8.80 (s, 2H). Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_8\text{Pd}_2\text{S}_2\cdot 2\text{CH}_2\text{Cl}_2$: C, 36.27; H, 3.04; N, 5.64. Found: C, 35.95; H, 3.06; N, 5.62.

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