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Synthesis of [SSSS]-type bis(thiophenol) ligand based on a trans-cyclooctane-1,2-diyl(thio) platform and an unexpected reaction with platinum complexes to produce sulfide-bis(thiolato) Pt^{II} complex

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Synthesis of [SSSS]-type bis(thiophenol) ligand based on a *trans*-cyclooctane-1,2-diyl(thio) platform and an unexpected reaction with platinum complexes to produce sulfide-bis(thiolato) Pt^{II} complex

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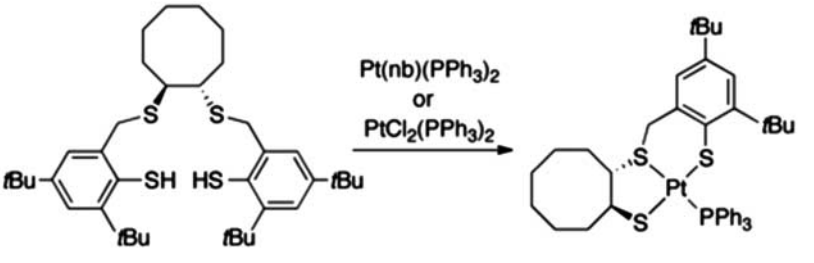
A new [SSSS]-type bis(thiophenol) ligand based on a *trans*-cyclooctane-1,2-diyl(thio) platform was prepared by the reaction of *trans*-cyclooctane-1,2-dithiol with 2 mol equiv. of 3,5-di-*tert*-butyl-2-(2-cyanoethylthio)benzyl bromide followed by deprotection. The reactions of the [SSSS]-type ligand with $[Pt(nb)(PPh_3)_2]$ (nb = norbornene) or $[PtCl_2(PPh_3)_2]$ complexes produced unexpectedly a [sulfide-bis(thiolato)]-PPh_3 Pt^{II} complex accompanying loss of one of the 2-sulfanylbenzyl groups. The structure of the Pt^{II} complex was determined by X-ray crystallography. The physical property and formation mechanism for the Pt^{II} complex are discussed.



Keywords: tetradentate sulfur ligand; tridentate sulfur ligand; platinum; cyclooctane; 1,2-dithiol

1. Introduction

A number of transition-metal complexes bearing various types of sulfur ligands have been studied so far from biological and industrial points of view (*1*), and the development of sulfur compounds being employed as an auxiliary ligand in organic synthesis is of continuous and current interest (*2–5*).

Recently, we prepared *trans*-cyclooctane-1,2-dithiol by the reaction of *cis*-cyclooctene with $(SCN)_2$ followed by the stepwise reduction with DIBAL and $LiAlH_4$ (*6*). 1,ω-Dithiols are widely

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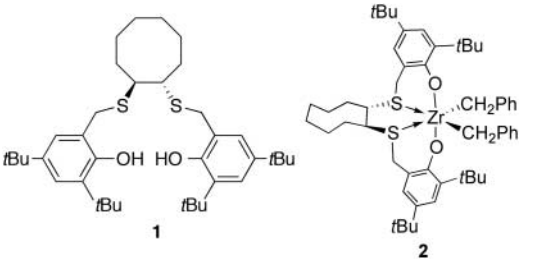
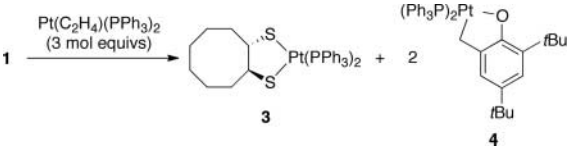
Dedicated to the memory of the late Professor Alessandro Degl'Innocenti

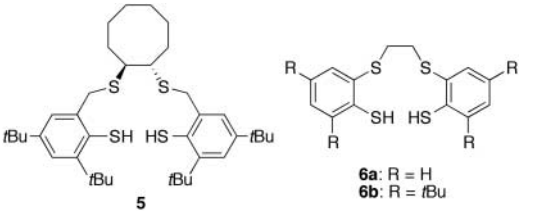
used in organic synthesis to prepare dithioacetals from aldehydes and ketones for umpolung or protection (*7*). 1,2-Dithiols convert aldehydes to 1,3-dithiolanes that, unfortunately, easily undergo cycloreversion when treated with a base. A solution for this serious problem is the introduction of a silyl group at the 2-posion as reported by Capperucci and Degl'Innocenti (*8*). On the other hand, we recently utilized *trans*-cyclooctane-1,2-dithiol in coordination chemistry by preparing a new [OSSO]-type bis(phenol) ligand **1** and showing that the zirconium complex **2**, upon activation with $B(C_6F_5)_3$ or $Ph_3C[B(C_6F_5)_4]$, performed highly active and isospecific polymerization of 1-hexene (*9–14*). Furthermore, we reported the spontaneous O–H and S–C bonds activation of 2-hydroxybenzyl sulfides with Pt^0 complexes: The reaction of **1** with 3 mol equiv. of $[Pt(C_2H_4)(PPh_3)_2]$ forms dithiolato Pt^{II} complex **3** and 1,2-oxaplatinacyle **4**(Eq. (1)) (*15*).





(1)

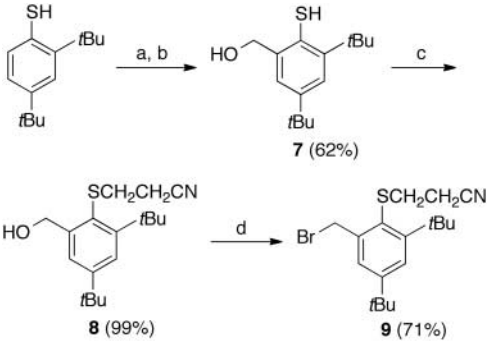
In continuation to our studies on the coordination chemistry utilizing *trans*-cyclooctane-1, 2-dithiol, we report here the preparation of persulfurated tetradentate ligand, [SSSS]-type ligand **5**, for late-transition metals. Sellmann and Sutter (*16*) reported the synthesis of a structurally related [SSSS]-type ligands **6a** by the reaction of [Fe(benzene-1,2-dithiolato)$_2$(CO)$_2$]$^{2-}$ with 1, 2-dibromoethane followed by decomplexation with hydrochloric acid in THF (*17*). In a similar manner, **6b** was also prepared. They synthesized iron (*18–23*), ruthenium (*24*, *25*), rhodium (*26*), and iron–nickel (*27*) complexes with **6** to employ them as models for active sites of enzymes (*17*). Ligands **6** are different from **5** in the manner of connection of the two inner sulfurs that are bonded directly to a thiophenol group.



2. Results and discussion

2.1. *Synthesis and structure of [SSSS]-type ligand 5*

Ligand **5** was synthesized as follows: 2,4-di-*t*-butylbenzenethiol (*28*) in ether was treated with 2 equiv. of butyllithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) and then paraformaldehyde to give 2-sulfanylbenzyl alcohol **7** in 62% yield. After the sulfanyl group in **7** was protected with a 2-cyanoethyl group (**8**, 99%) (*29*, *30*), **8** was converted to benzyl bromide **9** by treatment with PBr_3 in chloroform (71%) (Scheme 1).



Scheme 1. Synthesis of benzyl bromide **9**. Reaction conditions: (a) BuLi (2 equiv.), TMEDA (2 equiv.), Et_2O, 0°C, 7 h; (b) paraformaldehyde, rt, 15 h; (c) $BrCH_2CH_2CN$, K_2CO_3, THF, rt, 25 h; (d) PBr_3, $CHCl_3$, rt, 1.5 h.

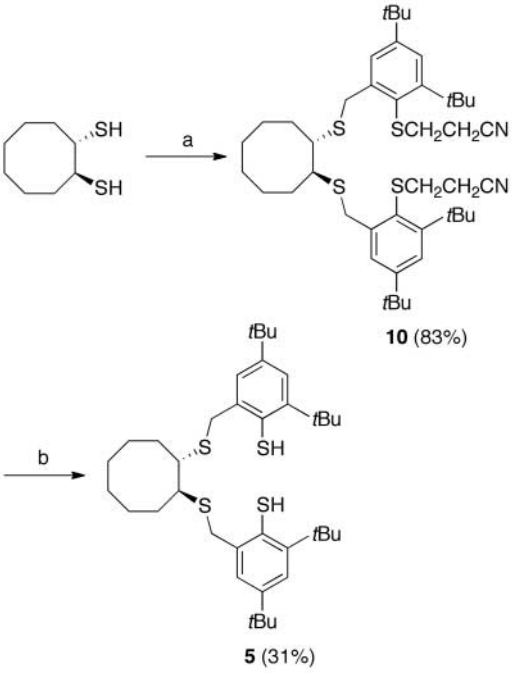
The reaction of *trans*-cyclooctane-1,2-dithiol with benzyl bromide **9** was carried out in the presence of triethylamine as the base in THF under reflux to give the protected [SSSS]-type ligand **10** in high yield (Scheme 2). Incidentally, the reaction of *trans*-cyclooctane-1,2-dithiol with the benzyl bromide derived from unprotected benzyl alcohol **7** gave a complex mixture, and as a result protection of the sulfanyl group in **7** was required.

Deprotection of the 2-cycanoethyl groups in the protected [SSSS]-type ligand **10** was examined using the standard method (*29*, *30*) of CsOH to produce the desired [SSSS]-type ligand **5** in 31% yield. Ligand **5** was also obtained with a yield of 48% by treatment of **10** with $LiAlH_4$ in ether, but the reproducibility of the yield was unsatisfactory.

In the ^{1}H NMR spectrum of [SSSS]-type ligand **5**, a set of protons for the 3,5-di-*t*-butyl-2-sulfanylbenzyl groups and the methine protons of the cyclooctane ring were observed: δ 1.30 and 1.52 for *t*-butyl groups, δ 3.96 and 4.04 ($J_{gem} = 12$ Hz) for diastereotopic benzyl protons, δ 5.23 for sulfanyl protons, δ 7.15 and 7.38 for aromatic protons, and δ2.84 or methine protons. This observation indicates that **5** has the same C_2 symmetry on the NMR time scale in solution as previously observed for [OSSO]-type ligand **1**. This C_2 symmetry was also reflected in the ^{13}C NMR spectrum of **5**, where 15 signals were observed, from which four signals at δ 26.0 (CH_2), 26.5 (CH_2), 31.2 (CH_2), and 51.7 (CH) were assigned to carbons in the cyclooctane ring.

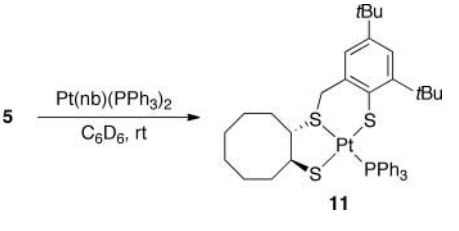
2.2. *Reaction of [SSSS]-type ligand 5 with Pt complexes*

The reaction of **5** with $[Pt(nb)(PPh_3)_2]$ (nb = norbornene) in C_6D_6 at room temperature furnished sulfide-bis(thiolato) Pt^{II} complex **11** in a low yield (21%) (Eq. (2)). We attempted, without success,



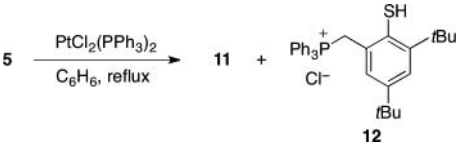
Scheme 2. Synthesis of [SSSS]-type ligand **5**. Reaction conditions: (a) **9** (2.7 mol equiv.), Et_3N, THF, reflux, 15 h; (b) CsOH, MeOH, THF, rt, 3 h.

to observe the intermediates during formation of **11** by NMR spectroscopy to result.



(2)

On the other hand, the reaction of **5** with a Pt^{II} complex, $[PtCl_2(PPh_3)_2]$, in C_6H_6 at reflux produced a small amount of colorless precipitates sparingly soluble in the solvent in addition to **11** (31%). The second product was identified as phosphonium salt **12** (3%) by NMR spectroscopy and ESI-MS (Eq. (3)).[1]



(3)

In the ^1H NMR spectrum of **11**, two methine protons appeared at δ 3.06–3.18 and 3.23–3.35 ppm as multiplets, and diastereotopic benzyl protons resonated at δ 4.11 and 4.81 ppm as a doublet of doublets due to the geminal coupling ($J_{gem} = 10$ Hz) and the coupling with one ^{31}P nucleus ($^4J_{P-H} = 6$ Hz) accompanied by the satellites due to the ^{195}Pt nucleus ($^3J_{Pt-H} = 54$ Hz). In the ^{31}P NMR spectrum, a singlet with satellites due to the ^{195}Pt nucleus ($^1J_{Pt-P} = 3700$ Hz) was observed

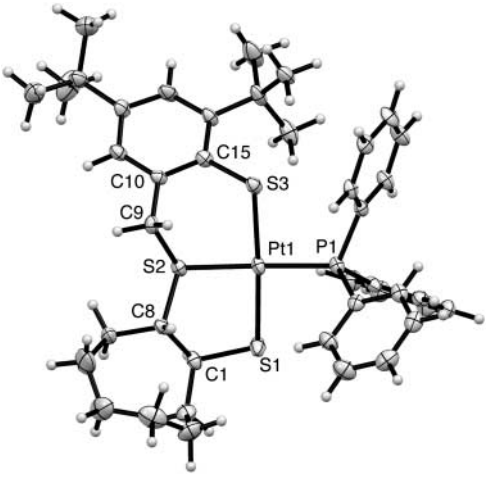
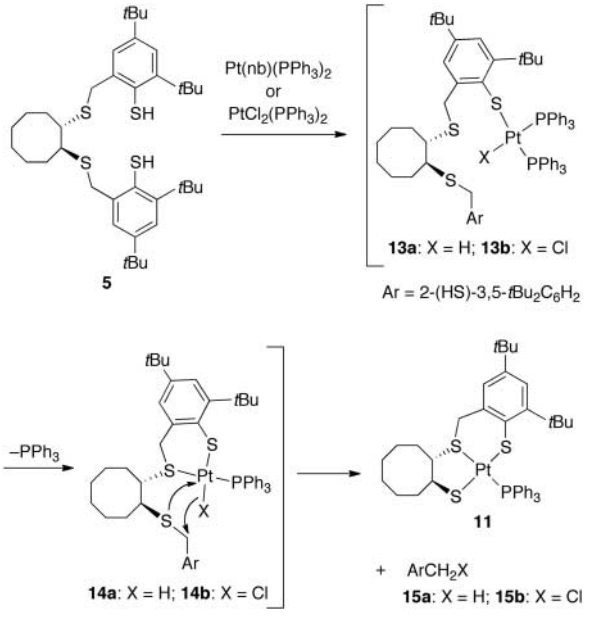


Figure 1. ORTEP drawing of sulfide-bis(thiolato) Pt^{II} complex **11**. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and bond angles (°) and torsion angles (°): Pt1–S2 2.298(1), Pt1–S1 2.322(1), Pt1–S3 2.327(1), Pt1–P1 2.265(1), S2–C8 1.831(4), C8–C1 1.524(6), C1–S1 1.839(4), S2–C9 1.826(5), S3–C15 1.785(4); S1–Pt1–S2 85.37(4), S2–Pt1–S3 91.56(4), S3–Pt1–P1 90.20(4), P1–Pt1–S1 92.91(4), S1–Pt1–S3 176.10(4); S2–Pt1–P1 178.03(4), Pt1–S2–C8 100.7(1), S2–C8–C1 103.5(3), C8–C1–S1 111.3(3), C1–S1–Pt1 104.0(1), S2–C9–C10 104.9(3), C9–C10–C15 121.1(4), C10–C15–S3 119.1(3), C15–S3–Pt1 110.3(1); S2–C8–C1–S1 58.8(3), S2–Pt1–S1–C1–7.6(1), C9–S2–Pt1–S3–33.0(1).

at δ 22.4 ppm. The structure of Pt^{II} complex **11** was finally determined by X-ray crystallography as depicted in Figure 1. The sum of bond angles around the Pt1 atom is 360.04°, and the geometry around the Pt atom is almost planar. The five-membered ring (Pt1–S1–C1–C8–S2) adopts a slightly distorted envelope form [S2–Pt1–S1–C1–7.6(1)°] and the S1–Pt1–S2 bond angle is 85.37(4)° that is smaller than the idealized 90° bond angle of square-planar tetracoordinated Pt^{II} complexes. The S2–Pt1–S3 bond angle [91.56(4)°] in the six-membered ring (Pt1–S2–C9–C10–C15–S3) is very close to 90°, and the ring strain appears to be small. The dihedral angle S2–C8–C1–S1 is 58.8(3)°. The bond length of S2(sulfide sulfur)–Pt1 [2.298(1) Å] is slightly shorter than those of S(thiolato sulfur)–Pt1 [Pt1–S1 2.322(1) Å, Pt1–S3 2.327(1) Å].

Platinum complex **11** has a dianionic tridentate [SSS]-type ligand, which represents a rather rare class of ligands in comparison with monodantate and bidentate sulfur ligands (*31–34*). A structurally related Ni^{II} complex having a triphenylphosphine and a dianionic [SSS]-tridentate ligand, [Ni(tpdt)(PPh_3)] [tpdt = ($^{-}SCH_2CH_2)_2S$], has been reported (*35*). While the tpdt ligand in [Ni(tpdt)(PPh_3)] provides a 5-5 chelation system that is different from the unsymmetric 6-5 chelation system in **11**, the central S(sulfide sulfur)-Ni bond [2.150(2) Å] is slightly shorter than the terminal S(thiolato sulfur)-Ni bond lengths [2.180(2) and 2.168(2) Å], similar to that observed in the case of **11**.

A plausible mechanism for the formation of **11** is shown in Scheme 3. Ligand **5** can react with [Pt(nb)($PPh_3)_2$] or [$PtCl_2$($PPh_3)_2$] to give hydrido-thiolato Pt^{II} complex **13a** by oxidative addition of the sulfanyl group to the Pt^0 center (*36*) or chloro-thiolato Pt^{II} complex **13b** by dehydrochlorination, respectively. Then, dissociation of a PPh_3 and coordination of the sulfide sulfur occur to form a six-membered sulfide-thiolato Pt^{II} complex **14a** or **14b**. Finally, elimination of **15a** or **15b** by an intramolecular nucleophilic attack of X and coordination of the third sulfur produces **11**. Thiophenol **15a** can further react with the remaining Pt^0 or hydrido-Pt^{II} (**13a**) complexes to form the unidentifiable byproducts. In the case of **15b**, a portion of it was trapped with dissociated PPh_3 to give phosphonium salt **12**.



Scheme 3. A plausible mechanism for the formation of **11**.

3. Conclusion

[SSSS]-type bis(thiophenol) ligand **5** unexpectedly lost one 2-sulfanylbenzyl group in the reaction with Pt^0 and Pt^{II} complexes, and the remaining part coordinated to a Pt^{II} center as a dianionic [SSS]-type tridentate ligand. This behavior is in stark contrast to that of [OSSO]-type bis(phenol) ligand **1** which loses two 2-hydroxybenzyl groups, which can be attributed to the difference in the reactivity of the SH and OH groups toward Pt complexes and in the difference between covalent radii of sulfur and oxygen that influences the geometrical strain around the Pt atom. Further studies on the reactivities of **1** and **5** toward transition metals are under investigation in our laboratory.

4. Experimental

4.1. *General procedures*

All melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. Solvents were dried by standard methods and freshly distilled prior to use. Dehydrated diethyl ether and THF were purchased from Kanto Chemical Co., Inc., and used without further purification. Column chromatography was performed with neutral silica gel (60 N, Kanto Chemical Co., Inc.). Preparative gel permeation liquid chromatography was performed on an LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: $CHCl_3$). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX-400 or AVANCE-400 (400 MHz for ^1H and 100.7 MHz for ^{13}C) or Bruker AVANCE-500 (500 MHz for ^1H and 202 MHz for ^{31}P) spectrometers using $CDCl_3$ as the solvent at room temperature. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR spectrometer. X-ray crystallography was performed with a Bruker AXS SMART diffractometer. LC–ESI–MS data were recorded by using a Hitachi NanoFrontier eLD. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University.

4.2. *Synthesis of (3,5-di-tert-butyl-2-sulfanylphenyl)methanol (7)*

A solution of TMEDA (2.2 ml, 14.8 mmol) and BuLi (9.5 ml, 1.55 M in hexane solution, 14.7 mmol) in ether (10 ml) was added to a solution of 2,4-di-*tert*-butylbenzenethiol (1.10 g, 4.95 mmol) in ether (10 ml) at 0°C under argon. After stirring for 3 h at room temperature, a suspension of paraformaldehyde (0.446 g, 14.8 mmol) in ether (10 ml) was added to the reaction mixture at 0°C, and the mixture was stirred for 15 h. Hydrochloric acid (2 M, 15 ml) was added and the mixture was extracted with ether. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give a brown oil, which was purified by silica-gel column chromatography (dichloromethane) to give **7** as a colorless solid (1.52 g, 62%). **7**: Colorless crystals, mp 103–105°C (dichloromethane–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.55 (s, 9H), 1.94 (t, $J = 6$ Hz, 1H, OH), 4.34 (s, 1H, SH), 4.81 (d, $J = 6$ Hz, 2H), 7.22 (d, $J = 2$ Hz, 1H), 7.45 (d, $J = 2$ Hz, 1H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 30.3 (CH_3), 31.3 (CH_3), 34.7 (C), 36.9 (C), 66.9 (CH_2), 124.2 (CH), 124.7 (CH), 126.9 (C), 139.9 (C), 148.6 (C), 149.4 (C); IR (KBr) $\tilde{\nu}$ 3271 (OH), 2563 (SH) cm^{-1}. Anal. Calcd for $C_{15}H_{24}OS$: C, 71.37; H, 9.58. Found: C, 71.34; H, 9.60.

4.3. *Synthesis of 3-{[2,4-di-tert-butyl-6-(hydroxymethyl)phenyl]sulfanyl}propanenitrile (8)*

A suspension of K_2CO_3 (138.9 mg, 1.00 mmol) in THF (2 ml) was added to a solution of **7** (211.2 mg, 0.84 mmol) in THF (6 ml) under argon, and then 3-bromopropionitrile (85 µl, 1.01 mmol) was added to the mixture. The reaction mixture was stirred for 25 h at room temperature. Then, the reaction was quenched by addition of hydrochloric acid (2 M, 5 ml), and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give almost pure **8** as yellow oil (22.3 mg, 0.83 mmol, 99%). The analytical sample was obtained by purification of the yellow oil with silica-gel column chromatography (dichloromethane) to give **8** as colorless oil. **8**: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.56 (s, 9H), 2.26 (br s, 1H) 2.66 (t, $J = 8$ Hz, 2H), 3.00 (t, $J = 8$ Hz, 2H), 4.97 (s, 2H), 7.42 (d, $J = 2$ Hz, 1H), 7.47 (d, $J = 2$ Hz, 1H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 17.4 (CH_2), 31.2 (CH_3), 31.7 (CH_3), 33.6 (CH_2), 35.0 (C), 37.6 (C), 65.2 (CH_2), 118.1 (C), 124.1 (CH), 124.9 (CH), 127.9 (C), 146.3 (C), 152.3 (C), 153.8 (C). Anal. Calcd for $C_{18}H_{27}NOS$: C, 70.77; H, 8.91; N, 4.59. Found: C, 70.63; H, 9.01; N, 4.51.

4.4. *Synthesis of 3-{[2-(bromomethyl)-4,6-di-tert-butylphenyl]sulfanyl}propanenitrile (9)*

A solution of PBr_3 (90%, 8.6 µl, 0.08 mmol) in chloroform (3 ml) was added to a solution of **8** (67.3 mg, 0.25 mmol) in chloroform (3 ml) at room temperature under argon. The mixture was stirred at room temperature for 1.5 h, and then the reaction was quenched with water. The mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting brown oil was purified by silica-gel column chromatography (dichloromethane) to give **9** as yellow oil (64.4 mg, 0.18 mmol, 71%). The analytical sample was obtained by purifying the yellow oil with silica-gel column chromatography (dichloromethane) to give **9** as a colorless powder. **9**: Colorless powder, mp 68–69°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.56 (s, 9H), 2.70 (t, $J = 8$ Hz, 2H), 3.11 (t, $J = 8$ Hz, 2H), 5.00 (s, 2H), 7.46–7.48 (m, 2H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 17.4 (CH_2), 31.1 (CH_3), 31.7 (CH_3), 33.0 (CH_2), 34.2 (CH_2), 34.9 (C), 37.8 (C), 117.9 (C), 125.1 (CH), 127.3 (CH), 129.0 (C), 143.7 (C), 152.4 (C), 154.2 (C). Anal. Calcd for $C_{18}H_{26}BrNS$: C, 58.69; H, 7.11; N, 3.80. Found: C, 58.85; H, 7.17; N, 3.66.

4.5. *Synthesis of trans-1,2-bis{[3,5-di-tert-butyl-2-{2-(cyanoethyl)sulfanyl}benzyl]sulfanyl} cyclooctane (10)*

A solution of **9** (293.2 mg, 0.80 mmol) in THF (8 ml) was added to a solution of *trans*-cyclooctane-1,2-dithiol (52.0 mg, 0.29 mmol) in THF (5 ml) at room temperature under argon, and then triethylamine (0.12 ml, 0.86 mmol) was added to the reaction mixture. The mixture was heated under reflux for 15 h, and the reaction was quenched by addition of hydrochloric acid (2 M, 5 ml). The mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the residual yellow oil was purified by silica-gel column chromatography (dichloromethane) to give **10** as yellow oil (184.4 mg, 0.25 mmol, 83%). **10**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 20H), 1.53 (s, 20H), 1.77–1.83 (m, 4H), 2.08–2.14 (m, 4H), 2.61 (t, $J = 8$ Hz, 4H), 2.93–3.11 (m, 6H), 4.14 (d, $J = 12$ Hz, 2H), 4.28 (d, $J = 12$ Hz, 2H), 7.37 (d, $J = 2$ Hz, 2H), 7.45 (d, $J = 2$ Hz, 2H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 17.4 (CH_2), 26.0 (CH_2), 29.7 (CH_2), 30.5 (CH_2), 31.2 (CH_3), 31.7 (CH_3), 33.4 (CH_2), 34.9 (C), 36.1 (CH_2), 37.7 (C), 51.1 (CH), 118.3 (C), 123.4 (CH), 126.4 (CH), 128.7 (C), 143.9 (C), 151.6 (C), 153.5 (C). HRMS (ESI, positive mode): Calcd. for $C_{44}H_{66}N_2NaS_4$: $[M+Na]^+$ 773.40011. Found: 773.40130.

4.6. *Synthesis of trans-1,2-bis[(3,5-di-tert-butyl-2-sulfanylbenzyl)sulfanyl]cyclooctane (5)*

4.6.1. *With CsOH*

A solution of $CsOH{\bullet}H_2O$ (22.9 mg, 0.136 mmol) in MeOH (1 ml) was added to a solution of **10** (38.8 mg, 0.052 mmol) in THF (2 ml) under argon. The mixture was stirred for 3 h at room temperature, and hydrochloric acid (2 M, 1 ml) was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to silica-gel column chromatography (dichloromethane/hexane 1/1) to give **5** as colorless crystals (10.1 mg, 31%). **5**: Colorless crystals, mp 133–135°C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 20H), 1.52 (s, 20H), 1.75–1.81 (m, 4H), 2.08–2.14 (m, 4H), 2.84 (br s, 2H), 3.96 (d, $J = 12$ Hz, 2H), 4.04 (d, $J = 12$ Hz, 4H), 5.23 (s, 2H), 7.15 (s, 2H), 7.38 (s, 2H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 26.0 (CH_2), 26.5 (CH_2), 30.6 (CH_3), 31.2 (CH_2), 31.4 (CH_3), 34.7 (C), 37.1 (C), 39.9 (CH_2), 51.7 (CH), 123.7 (CH), 126.2 (CH), 127.9 (C), 136.8 (C), 148.2 (C), 149.9 (C). Anal. Calcd for $C_{38}H_{60}S_4$: C, 70.75; H, 9.37. Found: C, 70.68; H, 9.46.

4.6.2. *With $LiAlH_4$*

A suspension of $LiAlH_4$ (3.8 mg, 0.10 mmol) in ether (2 ml) was added to a solution of **10** (8.3 mg, 0.01 mmol) in ether (1 ml) at 0 °C under argon. The mixture was stirred for 3 h at room temperature, and the reaction was carefully quenched by addition of hydrochloric acid (2 M, 5 ml). The mixture was extracted with ether, and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting yellow oil was purified by silica-gel column chromatography (dichloromethane/hexane = 1/1) to give **5** as colorless crystals (3.4 mg, 48%).

4.7. *Reaction of [SSSS]-type ligand 5 with $[Pt(nb)(PPh_3)_2]$*

A solution of **5** (11.0 mg, 0.017 mmol) and $[Pt(nb)(PPh_3)_2]$ (14.0 mg, 0.017 mmol) in C_6D_6 (0.5 ml) was made to stand at room temperature overnight. The solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (dichloromethane), and

the crude material was purified by recrystallization from a mixed solvent of dichloromethane and hexane to give **11** as yellow crystals (3.2 mg, 21%). **11**: Yellow crystals, mp 160–163°C decomp. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.27 (s, 9H), 1.48–1.94 (m, 9H), 1.99–2.16 (m, 2H), 2.22–2.33 (m, 1H), 3.06–3.18 (m, 1H), 3.23–3.35 (m, 1H), 4.11 (dd, $J = 10$, 6 Hz, $^3J_{Pt-H} = 54$ Hz, 1H), 4.81 (dd, $J = 10$, 6 Hz, $^3J_{Pt-H} = 54$ Hz, 1H), 7.05 (d, $J = 2$ Hz, 1H), 7.35 (d, $J = 2$ Hz, 1H), 7.35–7.45 (m, 10H), 7.65–7.74 (m, 5H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 25.5 (CH_2), 25.7 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 29.4 (CH_2), 30.2 (CH_3), 31.4 (CH_3), 34.4(C), 35.9 (CH_2), 37.2 (C), 40.1 (CH_2), 45.3 (d, $J_{P-C} = 5$ Hz, CH), 63.1 (CH), 124.1 (d, $J_{P-C} = 62$ Hz, CH), 127.8 (d, $J_{P-C} = 11$ Hz, CH), 129.1 (d, $J_{P-C} = 58$ Hz, C), 130.5 (CH), 130.6 (CH), 134.9 (d, $J_{P-C} = 11$ Hz, CH), 136.8 (C), 146.0 (C), 150.9 (C) (an aromatic quaternary carbon was not observed probably because of broadening); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ 22.4 (s, $^1J_{Pt-P} = 3700$ Hz). HRMS (ESI, positive mode): Calcd. for $C_{41}H_{51}NaPS_3Pt$: $[M + Na]^+$ 888.2431. Found: 888.2429.

X-ray crystallographic analysis: Yellow single crystals of **11** were grown by slow evaporation of the saturated hexane–dichloromethane solution at –20°C. The intensity data were collected at 90 K employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), and the structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX–97) (*37*): *Crystallographic data:* $C_{41}H_{51}PPtS_3$ (866.06), yellow crystals, $0.29 \times 0.20 \times 0.15$ mm^3, 90 K, monoclinic, $P2_1/c$, $a = 13.7792(6)$, $b = 21.0969(9)$, $c = 14.1768(6)$ Å, $\beta = 113.7800(10)°$, $V = 3771.3(3)$ Å^3, $Z = 4$, $d_{calc} = 1.525$ g cm^{-3}, 7023 unique data, 421 parameters, R_1 ($I > 2\sigma(I)$) = 0.0324, wR_2 (all data) = 0.0781, GOF = 1.030: CCDC 922457 contains the supplementary crystallographic data of **11**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.8. *Reaction of [SSSS]-type ligand 5 with [PtCl$_2$(PPh$_3$)$_2$]*

A solution of **5** (9.7 mg, 0.015 mmol) and [$PtCl_2(PPh_3)_2$] (11.8 mg, 0.015 mmol) in benzene (2 ml) was refluxed under argon for 7 h. After cooling to room temperature, the colorless precipitates were collected by filtration to give phosphonium salt **12** (0.2 mg, 3%). The filtrate was evaporated to dryness, and the residue was subjected to silica-gel column chromatography (dichloromethane) to give **11** as yellow crystals (4.1 mg, 31%) and an unidentified material (see Note 1) (4.0 mg). **12**: Colorless crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (s, 9H), 1.37 (s, 9H), 4.46 (s, 1H), 5.78 (d, $^1J_{P-H} = 14$ Hz, 2H), 6.94 (t, $J = 2$ Hz, ^{1}H), 7.34 (t, $J = 2$ Hz, 1H), 7.57–7.68 (m, 12H), 7.72–7.80 (m, 3H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 25.4 (s). HRMS (ESI, positive mode) Calcd. for $C_{33}H_{38}PS$: $[M]^+$ 497.2426. Found: 497.2468.

Note

1. In this reaction, we isolated another platinum complex: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 18H), 1.25 (s, 18H), 4.13 (dd, $J = 7$, 6 Hz, $J_{Pt-H} = 54$ Hz, 2H), 7.09 (d, $J = 2$ Hz, 2H), 7.29 (d, $J = 2$ Hz, 2H), 7.35–7.47 (m, 9H), 7.72–7.82 (m, 6H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 30.2 (CH_3), 31.4 (CH_3), 34.4 (C), 37.1 (C), 43.7 (CH_2), 124.2 (d, $J_{P-C} = 55$ Hz), 127.7 (d, $J_{P-C} = 11$ Hz), 127.9 (d, C, $J_{P-C} = 59$ Hz), 130.5 (CH), 130.6, (CH), 135.2, (d, $J_{P-C} = 10$ Hz), 136.6 (C), 146.3 (C) (an aromatic quaternary carbon was not observed probably because of broadening); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.0 (s, $J_{Pt-P} = 3686$ Hz). We have not determined the structure but will report it elsewhere in the future.

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