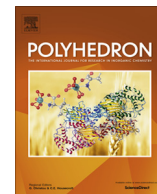




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# Iron carbonyl complexes of N,C,S-pincer ligands with a pendant thioether arm: Synthesis, structures and reactivity

Masakazu Hirotsu\*, Kiyokazu Santo, Yui Tanaka, Isamu Kinoshita

Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

## ARTICLE INFO

## Article history:

Received 30 June 2017

Accepted 8 October 2017

Available online xxxxx

## Keywords:

N,C,S-pincer ligand

Thioether

Iron carbonyl complex

C–S bond cleavage

CO substitution

## ABSTRACT

Thiolate-bridged diiron carbonyl complexes of N,C,S-pincer ligands with a pendant thioether arm were synthesized by treatment of  $[\text{Fe}(\text{CO})_5]$  with Schiff bases, which were derived from 4-formyldibenzothio-phenene and 2-(methylthio or phenylthio)aniline. Cleavage of a C–S bond in the proligands occurred during metalation. A carbonyl ligand in the complex was reversibly replaced by the thioether S atom, allowing for interconversion between the N,C,S-tridentate and S,N,C,S-tetradentate coordination modes. The diiron carbonyl complex of the S,N,C,S-tetradentate ligand reacted with dimethylphenylphosphine and 4-(dimethylamino)pyridine under moderate conditions to afford a mononuclear complex and a thio- late-bridged dimeric complex, respectively, while maintaining the S,N,C,S-tetradentate coordination mode. The dimeric complex was converted to the mononuclear complex by the reaction with dimethylphenylphosphine.

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## 1. Introduction

Polydentate ligands bearing labile and anchoring donor groups exhibit hemilabile properties in the transition metal complexes [1,2]. The ligand hemilability of complexes plays vital roles in catalysis [3–9], self-assembly [10,11], switching processes [12–18], sensing [19], and is essential for the function of many metalloproteins [20,21]. Thioether groups have been employed as labile parts of hemilabile ligands in combination with N-heterocyclic carbenes [6,7,16], phosphines [12–15], chelate ligands [4,17,18,20], or macrocyclic ligands [5]. Incorporation of the thioether groups into polydentate ligands is a promising strategy for the development of functional metal complexes.

We recently reported diiron carbonyl complexes of N,C,S-pincer ligands with a pendant coordinating group,  $[\{\text{Fe}(\mu\text{-BPT-NN-}\kappa^3\text{N,C,S}(\text{CO})_2)\text{Fe}(\text{CO})_3\}]$  (**1**) and  $[\{\text{Fe}(\mu\text{-BPT-NP-}\kappa^4\text{P,N,C,S}(\text{CO}))\text{Fe}(\text{CO})_3\}]$  (**2**), where BPT denotes a 1,1'-biphenyl-2-thiolate moiety, as shown in Fig. 1 [22]. Complexes **1** and **2** have 2-(dimethylamino)ethyl and 2-(diphenylphosphino)ethyl groups bound to N, respectively, as the pendant arm. The coordination modes of **1** and **2** differ significantly as the pendant amine N in **1** is not bound to Fe, while the phosphine P is firmly bound to Fe in **2**. Because thioether S atoms have only moderate coordination affinity toward Fe, the pendant thioether arm can impart hemilabile properties to the ligand. In

this study, we demonstrate a reversible CO/thioether substitution in analogous diiron carbonyl complexes by using N,C,S-pincer ligands with a pendant thioether group (Fig. 2), and determine the reactivity of the thioether-bound complexes.

## 2. Experimental

## 2.1. General procedures

All manipulations were performed using a glovebox under an atmosphere of oxygen-free dry nitrogen or standard Schlenk techniques under a nitrogen atmosphere. Dried solvents and  $[\text{Fe}(\text{CO})_5]$  were purchased from Kanto Chemical Co., Inc. 2-(Methylthio)aniline and 2-(phenylthio)aniline were purchased from Tokyo Chemical Industry Co., Ltd. 4-Formyldibenzothio-phenene was prepared according to a literature procedure [23]. NMR spectra were recorded on a JEOL Lambda 300, a Bruker AVANCE 300, or a Bruker AVANCE 400 FT-NMR spectrometer at room temperature. IR spectra were recorded on a JASCO FT/IR-4600 by attenuated total reflection (ATR) or KBr pellet methods. Elemental analyses were performed by the Analytical Research Service Center at Osaka City University on J-Science JM10 or Fisons EA1108 elemental analyzers. The solvent molecules in the elemental analysis samples were confirmed by  $^1\text{H}$  NMR spectroscopy. Photolysis was carried out using a 450 W high-pressure Hg lamp (Ushio UM-452) placed in a water-cooled quartz jacket.

\* Corresponding author. Fax: +81 6 6605 2522.

E-mail address: [mhiro@sci.osaka-cu.ac.jp](mailto:mhiro@sci.osaka-cu.ac.jp) (M. Hirotsu).

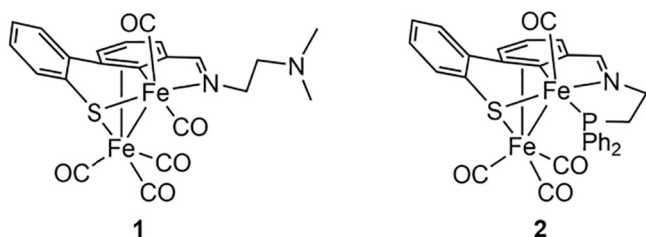


Fig. 1. Structures of diiron complexes **1** and **2**.

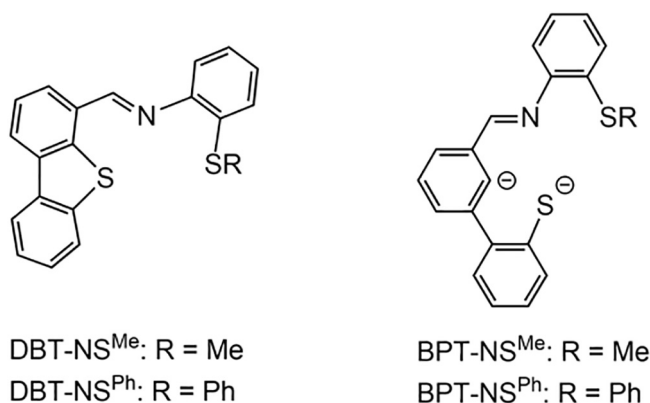


Fig. 2. Structures of dibenzothienyl Schiff bases (left) and ligands (right) with a pendant thioether arm.

## 2.2. Synthesis of ligand precursors

### 2.2.1. DBT-NS<sup>Me</sup>

Ethanol (30 mL) was purged with N<sub>2</sub> for 20 min, and then 4-formyldibenzothiophene (311 mg, 1.47 mmol), 2-(methylthio)aniline (362  $\mu$ L, 2.94 mmol) and acetic acid (1 mL) were added. The mixture was refluxed under N<sub>2</sub> for 7 h to afford a yellow solution. The volatiles were removed under reduced pressure, and the remaining yellow solid was recrystallized from dichloromethane-*n*-hexane to afford yellow crystals (354 mg, 72%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.77 (s, 1H, N=CH), 8.33 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.26–8.20 (m, 1H), 8.03–7.95 (m, 1H), 7.80 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.54–7.46 (m, 2H), 7.29–7.25 (m, 2H), 7.24–7.17 (m, 1H), 7.11 (dt, *J* = 7.5, 0.9 Hz, 1H), 2.52 (s, 3H, SMe). *Anal.* Calc. for C<sub>20</sub>H<sub>15</sub>NS<sub>2</sub>: C, 72.03; H, 4.53; N, 4.20. Found: C, 71.61; H, 4.61; N, 4.17%.

### 2.2.2. DBT-NS<sup>Ph</sup>

4-Formyldibenzothiophene (200 mg, 0.94 mmol) and 2-(phenylthio)aniline (210 mg, 1.04 mmol) were placed in a round-bottom flask, and ethanol (40 mL) and acetic acid (0.5 mL) were added. The mixture was purged with N<sub>2</sub>, and then refluxed under N<sub>2</sub> for 8 h. The volatiles were removed under reduced pressure, and the remaining yellow solid was recrystallized from dichloromethane-*n*-hexane at 10 °C to afford a yellow solid (151 mg, 40%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.28 (s, 1H, N=CH), 7.92 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.91 (ddd, 1H), 7.59 (ddd, 1H), 7.53–7.45 (m, 2H), 7.28–7.11 (m, 5H), 7.01–6.93 (m, 4H), 6.92–6.84 (m, 1H), 6.78 (dd, *J* = 7.7, 1.4 Hz, 1H). *Anal.* Calc. for C<sub>25</sub>H<sub>17</sub>NS<sub>2</sub>: C, 75.91; H, 4.33; N, 3.54. Found: C, 75.47; H, 4.35; N, 3.50%.

## 2.3. Synthesis and reactions of complexes

### 2.3.1. Photoreaction of DBT-NS<sup>Me</sup> with [Fe(CO)<sub>5</sub>]

A quartz glass sample tube with a Teflon valve was charged with DBT-NS<sup>Me</sup> (100 mg, 0.30 mmol), [Fe(CO)<sub>5</sub>] (176 mg, 0.90

mmol) and THF (30 mL). The yellow solution was irradiated with a high-pressure Hg lamp for 10 h: the solution was degassed by two freeze–pump–thaw cycles after 5 h irradiation. The resulting blue-purple solution was placed under CO (1 atm) and left at room temperature overnight to give a purple solution. The volatiles were removed under reduced pressure, and the residue was recrystallized from THF-*n*-hexane to afford a dark purple solid (40 mg). The <sup>1</sup>H NMR spectrum showed the solid contained [(Fe( $\mu$ -BPT-NS<sup>Me</sup>- $\kappa^3$ N,C,S)(CO)<sub>2</sub>)Fe(CO)<sub>3</sub>] (**3**) and [(Fe( $\mu$ -BPT-NS<sup>Me</sup>- $\kappa^4$ S,N,C,S)(CO))Fe(CO)<sub>3</sub>] (**4**) in a 3.8:1 ratio. *Anal.* Calc. for (C<sub>25</sub>H<sub>15</sub>Fe<sub>2</sub>NO<sub>5</sub>-S<sub>2</sub>)<sub>0.79</sub>(C<sub>24</sub>H<sub>15</sub>Fe<sub>2</sub>NO<sub>4</sub>S<sub>2</sub>)<sub>0.21</sub>·0.12C<sub>4</sub>H<sub>8</sub>O·0.07C<sub>6</sub>H<sub>14</sub>: C, 51.94; H, 2.87; N, 2.36. Found: C, 52.27; H, 2.96; N, 2.38%.

### 2.3.2. [(Fe( $\mu$ -BPT-NS<sup>Me</sup>- $\kappa^4$ S,N,C,S)(CO))Fe(CO)<sub>3</sub>] (**4**)

A quartz glass sample tube with a Teflon valve was charged with DBT-NS<sup>Me</sup> (150 mg, 0.45 mmol), [Fe(CO)<sub>5</sub>] (268 mg, 1.37 mmol) and THF (30 mL). The yellow solution was degassed by two freeze–pump–thaw cycles, and then the valve was closed. The solution was irradiated with a high-pressure Hg lamp for 8 h: the solution was degassed after 4 h irradiation. The resulting red-purple solution was degassed by two freeze–pump–thaw cycles, and then heated at 60 °C for 8 h: the solution was degassed after 4 h heating. The resulting dark blue solution was evaporated under reduced pressure, and the residue was recrystallized from THF-*n*-hexane to afford dark blue crystals (110 mg, 41%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.96 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.81 (s, 1H, N=CH), 7.12–7.05 (m, 2H), 6.96 (dd, *J* = 6.9, 1.1 Hz, 1H), 6.88–6.72 (m, 5H), 6.69 (ddd, *J* = 7.6, 7.4, 1.3 Hz, 1H), 6.47 (td, *J* = 7.4, 1.5 Hz, 1H), 2.43 (s, 3H, SMe). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  217.9 (Fe(CO)<sub>3</sub>), 212.4 (CO), 164.5, 160.5, 160.1, 147.5, 145.3, 140.2, 137.4, 135.8, 132.0, 129.4, 129.1, 128.93, 128.81, 128.75, 127.3, 126.6, 124.2, 116.3, 28.7 (br, SMe). IR (KBr):  $\nu_{\text{CO}}$ /cm<sup>-1</sup> 2002, 1931, 1904, 1886, 1863. *Anal.* Calc. for C<sub>24</sub>H<sub>15</sub>Fe<sub>2</sub>NO<sub>4</sub>S<sub>2</sub>·0.1C<sub>4</sub>H<sub>8</sub>O·0.4C<sub>6</sub>H<sub>14</sub>: C, 53.75; H, 3.60; N, 2.34. Found: C, 53.66; H, 3.68; N, 2.38%.

### 2.3.3. Reaction of **4** with CO

A sample tube with a Teflon valve was charged with **4** (30 mg, 0.054 mmol) and THF (20 mL). The blue-purple solution was degassed by two freeze–pump–thaw cycles, and then CO (1 atm) was admitted after removing the cooling bath. After 10 min at room temperature, the ratio of **3** and **4** was 1.2:1 (<sup>1</sup>H NMR). The solution was heated at 60 °C for 3 h to give a red-purple solution. The ratio of **3** and **4** was 8.5:1 (<sup>1</sup>H NMR). All volatiles were removed under reduced pressure, and the remaining residue was recrystallized twice from THF-*n*-hexane at –30 °C to afford dark purple crystals containing **3** and **4** in a 32:1 ratio (16 mg, ca. 50% for **3**).

Data for **3**. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.04–7.90 (1H for two isomers), 7.44–7.26 (2H), 7.00–6.85 (3H), 6.82–6.71 (3H), 6.67–6.59 (2H), 6.42–6.32 (1H), 1.87, 1.85 (s, 3H, SMe). IR (ATR):  $\nu_{\text{CO}}$ /cm<sup>-1</sup> 2028, 1996, 1966, 1879.

### 2.3.4. [(Fe( $\mu$ -BPT-NS<sup>Ph</sup>- $\kappa^4$ S,N,C,S)(CO))Fe(CO)<sub>3</sub>] (**5**)

A quartz glass sample tube with a Teflon valve was charged with DBT-NS<sup>Ph</sup> (100 mg, 0.25 mmol), [Fe(CO)<sub>5</sub>] (149 mg, 0.76 mmol) and THF (30 mL). The yellow solution was degassed by two freeze–pump–thaw cycles, and then the valve was closed. The solution was irradiated with a high-pressure Hg lamp for 16 h, during which time the reaction solution was degassed every 4 h. The resulting deep purple solution was heated at 60 °C for 16 h, during which time the reaction solution was degassed every 4 h. The resulting blue-purple solution was evaporated under reduced pressure, and the residue was recrystallized from THF-*n*-hexane to afford dark blue crystals (64 mg, 41%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.94 (s, 1H, N=CH), 7.53–7.48 (m, 2H), 7.21–7.17 (m, 1H), 7.03–6.67 (m, 10H), 6.60

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