

## Supplementary Material

### New Members of the $\{\text{Fe}(\text{NO})_2\}^{10}$ Dinitrosyl Iron Complexes (DNICs) bound with [thiolate, thiolate] and [amide, amide] ligations

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##### References

## Experimental Details

**General Procedures.** Manipulations, reactions, and transfers were conducted under nitrogen according to Schlenk techniques or in a glovebox (nitrogen gas). Solvents were distilled under nitrogen from appropriate drying agents (methylene chloride from  $\text{CaH}_2$ ; acetonitrile from  $\text{CaH}_2\text{-P}_2\text{O}_5$ ; diethyl ether, hexane and tetrahydrofuran(THF) from sodium benzophenone ) and stored in dried,  $\text{N}_2$ -filled flasks over  $4\text{\AA}$  molecular sieves. Nitrogen was purged through these solvents before use. Solvent was transferred to the reaction vessel via stainless cannula under positive pressure of  $\text{N}_2$ . The reagents, iron pentacarbonyl (Strem), tetraphenylphosphonium bromide ( $[\text{PPh}_4][\text{Br}]$ ), 18-crown-6-ether, nitrosonium tetrafluoroborate (Alfa Aesar), 2-mercaptobenzothiazole sodium salt, 2-hydroxybenzothiazole (TCI), ferrocenium hexafluorophosphate (Sigma-Aldrich) were used as received.  $\text{Fe}(\text{TMEDA})(\text{NO})_2$  has been prepared according to the literature procedure.<sup>1</sup>

**Physical Measurements.** Infrared spectra of the nitrosyl  $\nu(\text{NO})$  stretching frequencies were recorded on Jasco FT/IR-4100 spectrophotometer/Bruker Alpha spectrophotometer with sealed solution cells (0.1 mm) and KBr windows. UV/vis spectra were recorded on a GBC Cintra 101. X-band EPR spectrum was recorded on a Bruker EMX spectrometer equipped with a Hewlett-Packard 5246 L electronic counter. Cyclic voltammetry (CV) was carried out with a CH Instruments electrochemical analyzer 611C. A three-electrode system consisted of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a 0.1 M  $\text{Ag}/\text{Ag}^+$  reference electrode. All CV data were recorded with the scan rate of  $1\text{ V s}^{-1}$  in  $\text{CH}_3\text{CN}$  with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All potential values are reported verse ferrocene/ferrocenium ion. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

**Crystallography.** Crystallographic data and structure refinements parameters

of complexes **1-PPh<sub>4</sub>**, **2-PPh<sub>4</sub>** and **4-PPh<sub>4</sub>** are summarized in the Supplementary Material (Tables S1, S2 and S3). The crystals of complexes **1-PPh<sub>4</sub>**, **2-PPh<sub>4</sub>** and **4-PPh<sub>4</sub>** chosen for X-ray diffraction studies are measured in size 0.38 x 0.25 x 0.07 mm, 0.58 × 0.40 × 0.32 mm, and 0.40 × 0.25 × 0.25 mm, respectively. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. Unit-cell parameters were obtained by least-squares refinement. Diffraction measurements for complexes **1-PPh<sub>4</sub>**, **2-PPh<sub>4</sub>** and **4-PPh<sub>4</sub>** were carried out on a Nonius Kappa CCD and Bruker SMART Apex CCD diffractometers using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) and between 2.22 and 25.06° for complex **1-PPh<sub>4</sub>**, 2.26 and 25.04° for complex **2-PPh<sub>4</sub>**, between 1.94 and 27.50° for complex **4-PPh<sub>4</sub>**. Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on  $F^2$ . A SADABS absorption correction was made. The SHELXTL structure refinement program was employed.

**Preparation of [cation]<sub>2</sub>[Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (1) (cation = Na-18-crown-6-ether (1-Na), PPh<sub>4</sub><sup>+</sup> (1-PPh<sub>4</sub>)).** **1-Na:** The compounds Fe(TMEDA)(NO)<sub>2</sub> (0.232 g, 1 mmol), [Na][SC<sub>7</sub>H<sub>4</sub>SN] (0.398 g, 2 mmol) and 18-crown-6-ether (0.528 g, 2 mmol) were loaded into a Schlenk tube, and then 20 mL of THF was added under positive N<sub>2</sub> at ambient temperature. The reaction solution was stirred overnight and then the light green precipitates were afforded. When the upper solution was discarded via cannula under a positive pressure of N<sub>2</sub>, the residual light green solid was washed with 15 mL of THF. After drying the light green solid under vacuum, the light green solid of [Na-18-crown-6-ether]<sub>2</sub>[Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**1-Na**) (yield: 0.95 g, 92.9 %) was afforded. IR: 1684 (s), 1633 (s) cm<sup>-1</sup> (CH<sub>3</sub>CN); 1654 (s), 1609 (s) (ν<sub>NO</sub>) cm<sup>-1</sup> (KBr). Absorption spectrum (THF) [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 670 (307), 488 (781)]. **1-PPh<sub>4</sub>:**

To the CH<sub>3</sub>CN solution (10 mL) of (TMEDA)Fe(NO)<sub>2</sub> (0.232 g, 1 mmol) was added the CH<sub>3</sub>CN solution (20 mL) of [PPh<sub>4</sub>][SC<sub>7</sub>H<sub>4</sub>SN] (1.012 g, 2 mmol) dropwise under N<sub>2</sub> at ambient temperature. After storing the reaction solution without stirring for 5 days under nitrogen atmosphere at -15°C, the upper solution was discarded by cannula under positive N<sub>2</sub> pressure and then the brown crystals suitable for single-crystal X-ray diffraction was dried under vacuum to afford [PPh<sub>4</sub>]<sub>2</sub>[Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**1-PPh<sub>4</sub>**) (yield: 0.878 g, 77.9%). IR: 1661 (s), 1613 (s) cm<sup>-1</sup> (ν<sub>NO</sub>) (KBr). Anal. Calcd for C<sub>62</sub>H<sub>48</sub>FeN<sub>4</sub>O<sub>2</sub>P<sub>2</sub>S<sub>4</sub>: C, 66.07; H, 4.29; N, 4.97. Found: C, 66.51; H, 3.88; O, 4.63.

**Preparation of [cation]<sub>2</sub>[Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (2) (cation = Na-18-crown-6-ether (2-Na), PPh<sub>4</sub> (2-PPh<sub>4</sub>)).** **2-Na:** The compounds Fe(TMEDA)(NO)<sub>2</sub> (0.232 g, 1 mmol), [Na][OC<sub>7</sub>H<sub>4</sub>SN] (0.346 g, 2 mmol) and 18-crown-6-ether (0.528 g, 2 mmol) were loaded into a Schlenk flask, and then 10 mL of THF was added under positive N<sub>2</sub> at ambient temperature. The reaction solution was stirred overnight and then 40 mL of diethyl ether was added to the reaction solution. After the reaction mixture was stirred for 1 h, the light green precipitates were afforded. The upper solution was discarded via cannula under a positive pressure of N<sub>2</sub> and the residual light green solid was washed with 20 mL of diethyl ether. After drying the light green solid under vacuum, the light green solid of [Na-18-crown-6-ether]<sub>2</sub>[Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**2-Na**) (yield: 0.65 g, 65.7%) was afforded. IR: 1665 (m), 1609 (sh) (ν<sub>NO</sub>), 1627 (s) (ν<sub>CO</sub>) cm<sup>-1</sup> (CH<sub>3</sub>CN); 1664 (s), 1606 (s) (ν<sub>NO</sub>), 1623 (s) (ν<sub>CO</sub>) cm<sup>-1</sup> (KBr). Absorption spectrum (THF) [λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 712 (125), 390 (858). **2-PPh<sub>4</sub>:** To the CH<sub>3</sub>CN solution (10 mL) of (TMEDA)Fe(NO)<sub>2</sub> (0.162 g, 0.7 mmol) was added the CH<sub>3</sub>CN solution (20 mL) of [PPh<sub>4</sub>][OC<sub>7</sub>H<sub>4</sub>SN] (0.685 g, 1.4 mmol) dropwise under N<sub>2</sub> at ambient temperature. After storing the reaction solution without stirring for 5 days under nitrogen

atmosphere at  $-15^{\circ}\text{C}$ , the upper solution was discarded by cannula under positive  $\text{N}_2$  pressure and then the brown crystals suitable for single-crystal X-ray diffraction was dried under vacuum to afford  $[\text{PPh}_4]_2[\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**2-PPh<sub>4</sub>**) (yield: 0.457 g, 59.6 %). IR: 1662 (s), 1637 (s) ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$  (KBr). Anal. Calcd for  $\text{C}_{62}\text{H}_{48}\text{FeN}_4\text{O}_4\text{P}_2\text{S}_2$ : C, 68.01; H, 4.42; N, 5.12. Found: C, 67.73; H, 4.05; N, 5.50.

**Reaction of  $[\text{cation}]_2[\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**1**) with  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (cation = Na-18-crown-6-ether (**1-Na**),  $\text{PPh}_4^+$  (**1-PPh<sub>4</sub>**)).** **1-Na:** The 10 mL  $\text{CH}_3\text{CN}$  solution of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (0.497 g, 1.5 mmol) was added dropwise into the 50 mL Schlenk flask containing  $\text{CH}_3\text{CN}$  solution of complex **1-Na** (1.534 g, 1.5 mmol) via a cannula under positive  $\text{N}_2$  pressure at  $0^{\circ}\text{C}$ . After being stirred for 5 h, the reaction solution was dried under vacuum to afford the brown solid. 30 mL of THF was added to dissolve the brown solid and the resulting THF solution was monitored with FTIR. The IR spectrum showing  $\nu_{\text{NO}}$  stretching frequencies at 1767 (s), 1716(s)  $\text{cm}^{-1}$  (THF) was assigned to the formation of  $[\text{Na-18-crown-6-ether}][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**3-Na**).<sup>2</sup> The THF solution was filtered through Celite to separate insoluble  $[\text{Na-18-crown-6-ether}][\text{PF}_6]$ . The brown filtrate was concentrated to 5 mL and 40 mL hexane was added to precipitate the brown solid. The brown solid was washed with 20 mL of diethyl ether twice and dried under vacuum to yield complex **3-Na** (yield: 1.03 g, 93.6 %). IR: 1773 (s), 1721 (s) ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$  ( $\text{CH}_3\text{CN}$ ); 1768 (s), 1729 (s) ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$  (KBr). Absorption spectrum (THF) [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 788 (491), 457 (2918)]. **1-PPh<sub>4</sub>:** The 5 mL  $\text{CH}_3\text{CN}$  solution of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (0.099 g, 0.3 mmol) was added dropwise into the 50 mL Schlenk flask containing  $\text{CH}_3\text{CN}$  solution of complex **1-PPh<sub>4</sub>** (0.338 g, 0.3 mmol) via a cannula under positive  $\text{N}_2$  pressure at  $0^{\circ}\text{C}$ . After being stirred for 5 h, the reaction solution was dried under vacuum to afford the brown solid. 10 mL of THF was added to dissolve the brown solid and the resulting THF solution was

monitored with FTIR. The IR spectrum showing  $\nu_{\text{NO}}$  stretching frequencies at 1767 (s), 1716(s)  $\text{cm}^{-1}$  (THF) was assigned to the formation of  $[\text{PPh}_4][\text{Fe}(\text{SC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**3-PPh<sub>4</sub>**).<sup>3</sup> The THF solution was filtered through Celite to separate insoluble  $[\text{PPh}_4][\text{PF}_6]$ . The brown filtrate was concentrated to 5 mL and 25 mL diethyl ether was added to precipitate the brown solid. The brown solid was washed with 20 mL of diethyl ether twice and dried under vacuum to yield complex **3-PPh<sub>4</sub>** (yield: 0.182 g, 76.7 %). IR: 1774 (s), 1721 (s) ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$  ( $\text{CH}_3\text{CN}$ ); 1781 (s), 1739 (s) ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$  (KBr).

**Reaction of  $[\text{cation}]_2[\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**2**) with  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (cation = Na-18-crown-6-ether (**2-Na**),  $\text{PPh}_4^+$  (**2-PPh<sub>4</sub>**)).** **2-Na:** The 8 mL  $\text{CH}_3\text{CN}$  solution of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (0.331 g, 1 mmol) was added dropwise into the 50 mL Schlenk flask containing  $\text{CH}_3\text{CN}$  solution of complex **2-Na** ((0.991 g, 1 mmol) via a cannula under positive  $\text{N}_2$  pressure at  $0^\circ\text{C}$ . After being stirred for 5 h, the reaction solution was dried under vacuum to afford the brown solid. 20 mL of THF was added to dissolve the brown solid and the resulting THF solution was monitored with FTIR. The IR spectrum showing  $\nu_{\text{NO}}$  stretching frequencies at 1786 (m), 1714(s)  $\text{cm}^{-1}$  (THF) was assigned to the formation of  $[\text{Na-18-crown-6-ether}][\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**4-Na**). The THF solution was filtered through Celite to separate insoluble  $[\text{Na-18-crown-6-ether}][\text{PF}_6]$ . The brown filtrate was concentrated to 5 mL and 40 mL diethyl ether was added to precipitate the brown solid. The brown solid was washed with 20 mL of diethyl ether twice and dried under vacuum to yield complex **4-Na** (yield 0.585 g, 83.1 %). IR: 1791 (m), 1723 (s) ( $\nu_{\text{NO}}$ ), 1634 (s) ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$  ( $\text{CH}_3\text{CN}$ ); 1786 (s), 1696 (s) ( $\nu_{\text{NO}}$ ), 1626 (s) ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$  (KBr). Absorption spectrum (THF) [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ )]: Absorption spectrum (THF) [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ )]: 721 (281), 440 (1719). **2-PPh<sub>4</sub>:** The 5 mL  $\text{CH}_3\text{CN}$  solution of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (0.099 g, 0.3 mmol) was added dropwise into the

50 mL Schlenk flask containing CH<sub>3</sub>CN solution of complex **2-PPh<sub>4</sub>** (0.329 g, 0.3 mmol) via a cannula under positive N<sub>2</sub> pressure at 0 °C. After being stirred for 5 h, the reaction solution was dried under vacuum to afford the brown solid. 10 mL of THF was added to dissolve the brown solid and the resulting THF solution was monitored with FTIR. The IR spectrum showing  $\nu_{\text{NO}}$  stretching frequencies at 1786 (m), 1718(s) cm<sup>-1</sup> (THF) was assigned to the formation of [PPh<sub>4</sub>][Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**4-PPh<sub>4</sub>**). The THF solution was filtered through Celite to separate insoluble [PPh<sub>4</sub>][PF<sub>6</sub>]. The brown filtrate was concentrated to 5 mL and 25 mL diethyl ether was added to precipitate the red-brown solid. The red-brown solid was washed with 20 mL of diethyl ether twice and dried under vacuum to yield complex **4-PPh<sub>4</sub>** (yield: 0.141 g, 61.9 %). Diffusion of diethyl ether into the THF solution of complex **4-PPh<sub>4</sub>** at -15 °C led to red-brown crystals suitable for single-crystal X-ray diffraction. IR: 1791 (m), 1723 (s) ( $\nu_{\text{NO}}$ ), 1636 (m) ( $\nu_{\text{CO}}$ ) cm<sup>-1</sup> (CH<sub>3</sub>CN); 1785 (s), 1718 (s) ( $\nu_{\text{NO}}$ ), 1636 (m), 1623 (s) ( $\nu_{\text{CO}}$ ) cm<sup>-1</sup> (KBr). EPR (THF) at 298 K:  $g = 2.031$ . Anal. Calcd for C<sub>38</sub>H<sub>28</sub>FeN<sub>4</sub>O<sub>4</sub>PS<sub>2</sub>: C, 60.40; H, 3.74; N, 7.41. Found: C, 60.71; H, 3.54; N, 7.72.

**Reaction of complex 3-PPh<sub>4</sub> with [PPh<sub>4</sub>][OC<sub>7</sub>H<sub>4</sub>SN].** The compounds, complex **3-PPh<sub>4</sub>** (0.157 g, 0.2 mmol) and [PPh<sub>4</sub>][OC<sub>7</sub>H<sub>4</sub>SN] (0.197 g, 0.4 mmol) were loaded into a Schlenk tube, and then 10 mL of THF was added under positive N<sub>2</sub> at ambient temperature. After being stirred overnight, the solution was monitored with FTIR. The IR spectrum showing  $\nu_{\text{NO}}$  stretching frequencies at 1786 (m), 1718(s) cm<sup>-1</sup> (THF) was assigned to the formation of complex **4-PPh<sub>4</sub>**. The THF solution was filtered through Celite to separate insoluble [PPh<sub>4</sub>][SC<sub>7</sub>H<sub>4</sub>SN]. The brown filtrate was concentrated to 5 mL and 25 mL diethyl ether was added to precipitate the brown solid. The brown solid was washed with 20 mL of diethyl ether twice and dried under vacuum to yield complex **4-PPh<sub>4</sub>** (yield: 0.134 g, 88.7 %).

**Reaction of complex 2-Na with [Na][SC<sub>7</sub>H<sub>4</sub>SN] and 18-crown-6-ether.** The compounds, complex **2-Na** (0.495 g, 0.5 mmol), [Na][SC<sub>7</sub>H<sub>4</sub>SN] (0.189 g, 1 mmol) and 18-crown-6-ether (0.264 g, 1 mmol) were loaded into a Schlenk flask, and then 10 mL of THF was added under positive N<sub>2</sub> at ambient temperature. After being stirred overnight, the light green precipitates were afforded. When the upper solution was discarded via cannula under a positive pressure of N<sub>2</sub>, the residual light green solid was washed with 10 mL of THF. After drying the light green solid under vacuum and identifying by FTIR (IR: 1654 (s), 1609 (s) cm<sup>-1</sup> (ν<sub>NO</sub>) (KBr)), the light green solid of [Na-18-crown-6-ether]<sub>2</sub>[Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**1-Na**) (yield: 0.44 g, 86.3 %) was afforded.

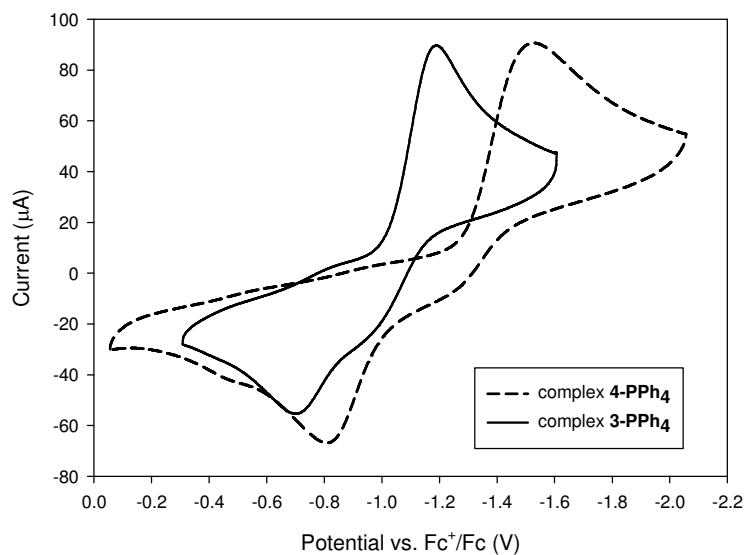
**Reaction of complex 3-PPh<sub>4</sub> with CoCp<sub>2</sub> (or Reaction of 4-PPh<sub>4</sub> with CoCp<sub>2</sub>).** Complex **3-PPh<sub>4</sub>** (0.236 g, 0.3 mmol) (or complex **4-PPh<sub>4</sub>** (0.227 g, 0.3 mmol)) and CoCp<sub>2</sub> (0.057 g, 0.3 mmol) were dissolved in THF (8 mL) and stirred overnight under nitrogen at ambient temperature. After being stirred overnight, the upper solution was discarded via cannula under a positive pressure of N<sub>2</sub>, and the residual light green solids (or light brown solids) were washed with 15 mL of diethyl ether. The IR spectrum of the light brown solids showed the ν<sub>NO</sub> stretching frequencies at 1652 (s), 1602(s) cm<sup>-1</sup> (KBr) was assigned to the formation of [PPh<sub>4</sub>][CoCp<sub>2</sub>] [Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (The IR spectrum of the light green solids showed the ν<sub>NO</sub> stretching frequencies at 1663 (s), 1636(s) cm<sup>-1</sup> (KBr) was assigned to the formation of [PPh<sub>4</sub>][CoCp<sub>2</sub>] [Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>]. After drying the light green solids under vacuum, light green solids of [PPh<sub>4</sub>][CoCp<sub>2</sub>] [Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (yield: 0.18 g, 61.4 %) (or brown solid of [PPh<sub>4</sub>][CoCp<sub>2</sub>] [Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (yield: 0.23 g, 81.2 %)) were afforded.

**Reaction of complex 3-PPh<sub>4</sub> with complex 2-PPh<sub>4</sub>.** Complex **3-PPh<sub>4</sub>** (0.157 g, 0.2 mmol) and complex **2-PPh<sub>4</sub>** (0.218 g, 0.2 mmol) were loaded into a Schlenk

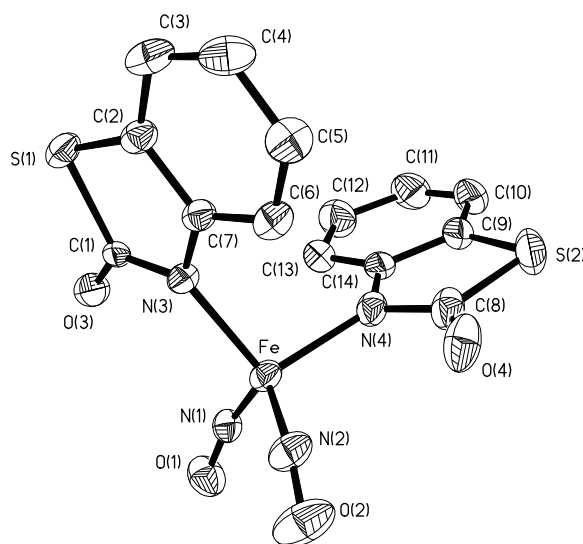


flask, and then 6 mL of THF and 2 mL of CH<sub>3</sub>CN were added under positive N<sub>2</sub> at ambient temperature. After being stirred for 3 days, 15 mL of hexane was added to the reaction mixture. When the reaction mixture was stand for several minutes, the upper red solution was transferred to the other flask via cannula under a positive pressure of N<sub>2</sub>. The residual solid was washed with 10 mL of THF and the THF solution was transferred to the above flask via cannula under a positive pressure of N<sub>2</sub>. After drying the light green solid under vacuum and identifying by FTIR (IR: 1661 (s), 1613 (s) cm<sup>-1</sup> (ν<sub>NO</sub>) (KBr)), the light green solid of complex **1-PPh<sub>4</sub>** (yield: 0.158 g, 70.2 %) was afforded. In addition, the solution of the other flask was concentrated to 5 mL and 35 mL diethyl diether was added to precipitate the red solid. The IR spectrum of the red solids showed the ν<sub>NO</sub> stretching frequencies at 1785 (s), 1718(s) cm<sup>-1</sup> (KBr) was assigned to the formation of complex **4-PPh<sub>4</sub>** and the yield was 92.7 % (0.140 g).

## Figures

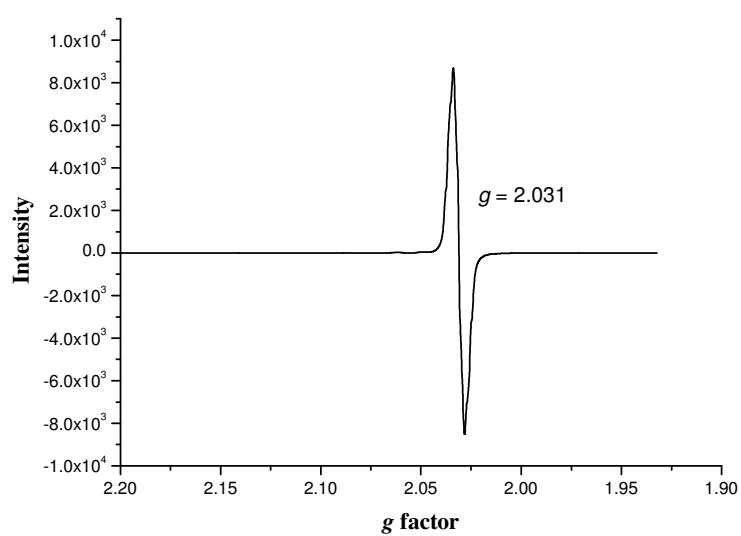


**Figure S1.** Cyclic voltammograms of 2.5 mM CH<sub>3</sub>CN solution of [PPh<sub>4</sub>][Fe(SC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**3-PPh<sub>4</sub>**) (solid line) and [PPh<sub>4</sub>][Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**4-PPh<sub>4</sub>**) (dashed line) in 0.1 M [TBA][PF<sub>6</sub>] with a glassy carbon working electrode at a scan rate of 1 V s<sup>-1</sup>.



**Figure S2.** ORTEP diagram of the anion of [PPh<sub>4</sub>][Fe(OC<sub>7</sub>H<sub>4</sub>SN)<sub>2</sub>(NO)<sub>2</sub>] (**4-PPh<sub>4</sub>**) showing 50% thermal ellipsoids for all non-hydrogen atoms. Selected bond distances (Å) and angles (deg): Fe–N(1), 1.685(2); Fe–N(2), 1.688(2); Fe–N(3), 1.992(2); Fe–N(4), 1.994(2); N(1)–O(1), 1.178(3); N(2)–O(2), 1.172(3); N(1)–Fe–N(2),

111.23(11); N(3)–Fe–N(4), 101.84(9); N(1)–Fe–N(3), 111.04(10); N(2)–Fe–N(3),  
112.12(10); Fe–N(1)–O(1), 162.8(2); Fe–N(2)–O(2), 164.3(2).



**Figure S3.** X-band EPR spectrum of  $[\text{PPh}_4][\text{Fe}(\text{OC}_7\text{H}_4\text{SN})_2(\text{NO})_2]$  (**4-PPh<sub>4</sub>**) in THF at 298 K.

## Tables

**Table S1.** Crystal data and structure refinement for complex **1-PPh<sub>4</sub>**.

Empirical formula	C <sub>62</sub> H <sub>48</sub> Fe N <sub>4</sub> O <sub>2</sub> P <sub>2</sub> S <sub>4</sub>	
Formula weight	1127.07	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 <sub>1</sub> /n	
Unit cell dimensions	a = 10.6617(2) Å	α = 90°.
	b = 36.6398(6) Å	β = 96.0940(10)°.
	c = 14.0069(3) Å	γ = 90°.
Volume	5440.77(18) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.376 Mg/m <sup>3</sup>	
Absorption coefficient	0.538 mm <sup>-1</sup>	
F(000)	2336	
Crystal size	0.38 x 0.25 x 0.07 mm <sup>3</sup>	
Theta range for data collection	2.22 to 25.06°.	
Index ranges	-12 ≤ h ≤ 12, -38 ≤ k ≤ 43, -16 ≤ l ≤ 12	
Reflections collected	17171	
Independent reflections	9448 [R(int) = 0.0631]	
Completeness to theta = 24.86°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9648 and 0.8397	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	9448 / 0 / 676	
Goodness-of-fit on F <sup>2</sup>	1.034	
Final R indices [I > 2σ(I)]	R1 = 0.0522, wR2 = 0.1127	
R indices (all data)	R1 = 0.0974, wR2 = 0.1354	
Largest diff. peak and hole	0.280 and -0.381 e.Å <sup>-3</sup>	

**Table S2.** Crystal data and structure refinement for complex **2-PPh<sub>4</sub>**.

Empirical formula	C <sub>62</sub> H <sub>48</sub> Fe N <sub>4</sub> O <sub>4</sub> P <sub>2</sub> S <sub>2</sub>	
Formula weight	1094.95	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 23.4730(5) Å	α = 90°.
	b = 13.4520(3) Å	β = 119.0330(10)°.
	c = 19.3090(5) Å	γ = 90°.
Volume	5330.8(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.364 Mg/m <sup>3</sup>	
Absorption coefficient	0.475 mm <sup>-1</sup>	
F(000)	2272	
Crystal size	0.58 x 0.4 x 0.32 mm <sup>3</sup>	
Theta range for data collection	2.26 to 25.04°.	
Index ranges	-23 ≤ h ≤ 26, -15 ≤ k ≤ 15, -13 ≤ l ≤ 22	
Reflections collected	12513	
Independent reflections	4446 [R(int) = 0.0486]	
Completeness to theta = 25.04°	94.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7552 and 0.596	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4446 / 0 / 339	
Goodness-of-fit on F <sup>2</sup>	1.011	
Final R indices [I > 2σ(I)]	R1 = 0.0463, wR2 = 0.1232	
R indices (all data)	R1 = 0.0608, wR2 = 0.1344	
Largest diff. peak and hole	0.681 and -0.558 e.Å <sup>-3</sup>	

**Table S3.** Crystal data and structure refinement for complex **4-PPh<sub>4</sub>**.

Empirical formula	C <sub>38</sub> H <sub>28</sub> Fe N <sub>4</sub> O <sub>4</sub> P S <sub>2</sub>	
Formula weight	755.58	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 15.5535(8) Å	α = 90°.
	b = 16.8415(8) Å	β = 90°.
	c = 26.5880(12) Å	γ = 90°.
Volume	6964.6(6) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.441 Mg/m <sup>3</sup>	
Absorption coefficient	0.646 mm <sup>-1</sup>	
F(000)	3112	
Crystal size	0.40 x 0.25 x 0.25 mm <sup>3</sup>	
Theta range for data collection	1.94 to 27.50°.	
Index ranges	-20 ≤ h ≤ 20, -21 ≤ k ≤ 16, -34 ≤ l ≤ 18	
Reflections collected	34619	
Independent reflections	7993 [R(int) = 0.0674]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8551 and 0.7821	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7993 / 0 / 451	
Goodness-of-fit on F <sup>2</sup>	1.042	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0506, wR <sub>2</sub> = 0.1063	
R indices (all data)	R <sub>1</sub> = 0.0769, wR <sub>2</sub> = 0.1172	
Largest diff. peak and hole	0.632 and -0.375 e.Å <sup>-3</sup>	

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