Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2013

Synthesis and Reactivity of Mononuclear Iron Models of [Fe]-Hydrogenase That Contain an Acylmethylpyridinol Ligand

Bowen Hu,[a] Dafa Chen,*[a] and Xile Hu[b]

chem_201304290_sm_miscellaneous_information.pdf
**Experimental Section**

A. **Chemicals and Reagents**

All manipulations were carried out under an inert N$_2$(g) atmosphere using a Schlenk line. Solvents were distilled from appropriate drying agents under N$_2$ before use. All reagents were purchased from commercial sources. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use. 2-tert-butoxy-6-chloropyridine was prepared as described previously.$^{[S1]}$

B. **Physical methods**

The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 spectrometer. $^1$H NMR chemical shifts were referenced to residual solvent as determined relative to Me$_4$Si ($\delta = 0$ ppm). The $^{13}$C ($^1$H) chemical shifts were reported in ppm relative to the carbon resonance of CDCl$_3$ (77.0 ppm). IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Mass spectra were performed on an Agilent 6530 Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) mass spectrometer, equipped with an ESI source. X-ray diffraction studies were carried out on a Xcalibur E X-ray single crystal diffractometer. Data collections were performed using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption.$^{[S2]}$ Solution, refinement and geometrical calculations for all crystal structures were performed by SHELXTL.$^{[S3]}$

C. **Synthetic methods**

Synthesis of 2-tert-butoxy-6-methylpyridine

2-tert-butoxy-6-methylpyridine was prepared using a similar method as described previously.$^{[S1]}$ A solution of CH$_3$MgBr/ether (3 M, 10.8 mL, 32.4 mmol) was added drop-wise to a mixture of 2-tert-butoxy-6-chloropyridine (4.0 g, 21.6 mmol) and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride (34.2 mg, 0.0648 mmol) in THF (40 mL). The mixture was stirred at room temperature for 4 h. The reaction was diluted with ether (20 mL) and quenched by addition of H$_2$O to dissolve inorganics. The organic phase was washed with H$_2$O. After drying the organic phase over Na$_2$SO$_4$ and evaporation of the solvent, the crude products were purified by silica gel column chromatography, giving 2-tert-butoxy-6-methylpyridine as a colorless oil (2.79 g, 16.9 mmol; yield 78%).

$^1$H NMR (400.13 MHz, CDCl$_3$): 7.41 (t, $J = 7.6$ Hz, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.47 (d, $J = 7.6$ Hz, 1H), 2.43 (s, 3H), 1.57 (s, 9H) ppm. $^{13}$C NMR (400.13 MHz, CDCl$_3$): 163.2, 155.7, 138.3, 115.2, 109.7, 79.1, 28.7, 24.2. MS (ESI, positive mode): Calcd for C$_{10}$H$_{15}$NO + H: 166.1232. Found: 166.1223. Anal. Calcd for C$_{10}$H$_{15}$NO: C, 72.7; H, 9.2; N, 8.5. Found: C, 73.0; H, 9.1, N, 8.2.

Synthesis of [(2-CH$_2$CO-6-t-BuOC$_5$H$_3$N)Fe(CO)$_3$I] (I)

n-BuLi (5 mL, 1.6 M, 8.0 mmol) was added into a solution of 2-tert-butoxy-6-methylpyridine (1.32 g, 8.0 mmol) in THF (50 mL) under stirring at 0 °C. After stirring for 0.5 h at this temperature, the solution was added into a solution of Fe(CO)$_5$ (1.57 g, 8.0 mmol) in THF (50 mL) at -50 °C, and the resulting solution was warmed slowly to -20 °C (about 2 h). The solution was then cooled to -60 °C, followed by adding solid I$_2$ (2.03 g, 8.0 mmol) at the same temperature. The resulting solution was kept at -60 °C for 2 hours. The solvent was then evaporated in vacuum. The residue was placed in an Al$_2$O$_3$ column. Elution with CH$_2$Cl$_2$ developed a red band, which afforded I (1.87 g, 4.1 mmol; yield: 51 %) as red crystals after recrystallization from CH$_2$Cl$_2$/ether.

$^1$H NMR (400.13 MHz, CDCl$_3$): 7.73 (t, $J = 8.0$ Hz, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 5.42 (d, $J = 20.0$ Hz, 1H), 4.29 (d, $J = 20.0$ Hz, 1H), 1.70 (s, 9H) ppm. IR (ν$_{CO}$, KBr, cm$^{-1}$): 2089 (s), 2045 (s), 2034 (s), 2011 (s), 2000 (s). IR (ν$_{CO}$, CH$_2$Cl$_2$, cm$^{-1}$): 2088 (s), 2040 (s), 2008 (s), 1948 (s), 1911 (s), 1898 (s), 1877 (s). Anal. Calcd for C$_{14}$H$_{14}$FeNO$_5$: C, 36.6; H, 3.1; N, 3.1. Found: C, 36.7; H, 3.1, N, 2.9.
Synthesis of \([2\text{-CH}_2\text{CO}-6\text{-t-BuOC}_5\text{H}_3\text{N})\text{Fe(CO)}_2\{\text{S-(2,6-Me}_2\text{-C}_6\text{H}_3}\}\) (2)

A newly synthesized sample of \((2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{SNa}\) (228.0 mg, 1.38 mmol), which was prepared by NaH (33.2 mg, 1.38 mmol) and \((2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{SH}\) (190.6 mg, 1.38 mmol) in THF, was mixed with complex 1 (634.0 mg, 1.38 mmol) in CH\(_2\)Cl\(_2\) (10 mL). After stirring for 0.5 h at room temperature in the dark, the solvent was evaporated in vacuum. The residue was extracted with CH\(_2\)Cl\(_2\) (4 mL). After removing the solvent of the filtrate, the residue was recrystallized from CH\(_2\)Cl\(_2\)/hexane at -30 °C in the dark to afford (430.0 mg, 0.975 mmol; yield: 71 %) as red crystals.

\(^{1}H\) NMR (400.13 MHz, CD\(_3\)CN): 7.97 (t, \(J = 8.0\) Hz, 1H), 7.24-7.20 (m, 2H), 7.07 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 8.0\) Hz, 1H), 4.44 (d, \(J = 20.0\) Hz, 1H), 4.04 (d, \(J = 20.0\) Hz, 1H), 2.30 (s, 6H), 1.58 (s, 9H) ppm. IR (\(\nu_{\text{CO}}, \text{KBr}, \text{cm}^{-1}\)): 2013 (s), 1948 (s). Anal. Calcd for C\(_{21}\)H\(_{23}\)FeNO\(_4\)S: C, 57.2; H, 5.3; N, 3.2. Found: C, 57.5; H, 5.4, N, 3.4.

Reaction of 2 with CO: Formation of \([2\text{-CH}_2\text{CO}-6\text{-t-BuOC}_5\text{H}_3\text{N})\text{Fe(CO)}_3\{\text{S-(2,6-Me}_2\text{-C}_6\text{H}_3}\}\) (3)

A solution of 2 (20 mg, 0.045 mmol) in 0.5 mL CDCl\(_3\) was added to a J Young NMR tube. The solution was frozen and the tube was evacuated under vacuum. 1 atm of CO was added and the tube was sealed. The color changed from red to yellow as soon as the solution was thawed. The NMR and IR showed \([6\text{-t-BuO-C}_5\text{H}_3\text{N-2-CH}_2\text{CO})\text{Fe(CO)}_3\{\text{S-(2,6-Me}_2\text{-C}_6\text{H}_3}\}\) (3) formed. If the tube was opened and flushed with N\(_2\), 3 would transform back to 2.

\(^{1}H\) NMR (400.13 MHz, CDCl\(_3\)): 7.72 (br s, 1H), 7.12-6.90 (m, 5H), 5.18 (d, \(J = 20.0\) Hz, 1H), 4.05 (d, \(J = 20.0\) Hz, 1H), 2.19 (s, 6H), 1.63 (s, 9H) ppm. \(^{13}C\) NMR (400.13 MHz, CDCl\(_3\)): 260.9 (CH\(_2\)C\(_O\)), 210.3 (terminal CO), 208.3 (terminal CO), 205.8 (terminal CO), 163.6, 161.5, 144.3, 141.7, 139.6, 127.2, 125.0, 114.9, 108.6, 84.4, 66.0, 28.7, 22.4. ppm. IR (\(\nu_{\text{CO}}, \text{CH}_3\text{CN}, \text{cm}^{-1}\)): 2078 (s), 2027 (s), 2001 (s).

Synthesis of \([2\text{-CH}_2\text{CO}-6\text{-t-BuOC}_5\text{H}_3\text{N})\text{Fe(CO)}_2(\text{CH}_3\text{CN})_2]^+\text{(CF}_3\text{COO})^-\) (4)

CF\(_3\)COOH (25.9 mg, 0.227 mmol) was added into a solution of 2 (100.0 mg, 0.227 mmol) in CH\(_3\)CN (2 mL) under stirring at room temperature. The color changed from red to yellow immediately. After 1 min, the solvent was evaporated. The solid residue was washed with Et\(_2\)O (10 mL) and dried in vacuum. Compound 4 was isolated as a yellow solid in a quantitative yield (113.2 mg, 0.227 mmol). Attempts to remove the t-Bu group with excess of CF\(_3\)COOH were failed.

\(^{1}H\) NMR (400.13 MHz, CD\(_3\)CN): 7.84 (t, \(J = 8.0\) Hz, 1H), 7.11 (d, \(J = 8.0\) Hz, 2H), 4.62 (d, \(J = 20.0\) Hz, 1H), 3.66 (d, \(J = 20.0\) Hz, 1H), 1.94 (s, 6H), 1.62 (s, 9H) ppm. IR (\(\nu_{\text{CO}}, \text{KBr}, \text{cm}^{-1}\)): 2047 (s), 1988 (s). Anal. Calcd for C\(_{19}\)H\(_{20}\)F\(_3\)FeN\(_3\)O\(_6\): C, 45.7; H, 4.0; N, 8.4. Found: C, 45.9; H, 4.1, N, 8.7.

Synthesis of \([2\text{-CH}_2\text{CO}-6\text{-HOC}_5\text{H}_3\text{N})\text{Fe(CO)}_3\text{I}\] (5)

Me\(_3\)SiI (610.0 mg, 3.05 mmol) was added into a solution of 1 (400.0 mg, 0.871 mmol) in CH\(_2\)Cl\(_2\) (10 mL) under stirring at room temperature. After 12 h, H\(_2\)O (20 mL) was added into the mixture. The water phase was washed with CH\(_2\)Cl\(_2\) (20 mL \times 3) and ether (10 mL), respectively. The combined organic phase was washed with H\(_2\)O (20 mL). After drying over Na\(_2\)SO\(_4\) and evaporation of the solvent, the residue was extracted with ether (10 mL), and the filtrate was dried in vacuum. The residue was washed with hexane (40 mL) and CH\(_2\)Cl\(_2\) (1 mL), respectively. The solid residue was then extracted with ether (10 mL) again, and the filtrate was dried in vacuum. The residue was washed with hexane (20 mL) and recrystallized from ether/hexane to afford (110.0 mg, 0.273 mmol; yield: 31%) as a red solid.

\(^{1}H\) NMR (400.13 MHz, CD\(_3\)CN): 10.17 (s, 1H), 7.81(t, \(J = 8.0\) Hz, 1H), 7.08 (d, \(J = 8.0\) Hz, 1H), 6.87 (d, \(J = 8.0\) Hz, 1H), 4.46 (d, \(J = 20.0\) Hz, 1H), 4.08 (d, \(J = 20.0\) Hz, 1H) ppm. IR (\(\nu_{\text{CO}}, \text{KBr}, \text{cm}^{-1}\)): 2102 (s), 2048 (s), 2023 (s), 2014 (s). IR (\(\nu_{\text{CO}}, \text{CH}_3\text{CN}, \text{cm}^{-1}\)): 2068 (s), 2050 (s), 1996 (s). Anal. Calcd for C\(_{10}\)H\(_{20}\)FeNO\(_3\)I: C, 29.8; H, 1.5; N, 3.5. Found: C, 30.1; H, 1.5, N, 3.8.

Synthesis of \([(2\text{-CH}_2\text{CO}-6\text{-HOC}_5\text{H}_3\text{N})\text{Fe(CO)}_3\text{I}]^{+}\text{(BF}_4^-)\) (6)
AgBF₄ (48.1 mg, 0.248 mmol) was added into a solution of 5 (100.0 mg, 0.248 mmol) in CH₃CN (5 mL) under stirring. Gas (CO) was formed immediately. After 1 min, the mixture was filtered and the filtrate was dried in vacuum. The residue was washed with ether (10 mL) and dried in vacuum to afford 6 (101.0 mg, 0.242 mmol; 98 %) as a light yellow oily solid.

1H NMR (400.13 MHz, CD₃CN): 9.33 (s, 1H), 7.83 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 4.66 (d, J = 20.0 Hz, 1H), 3.89 (d, J = 20.0 Hz, 1H), 1.96 (s, 6H) ppm. IR (νCO, KBr, cm⁻¹): 2057 (s), 1999 (s). IR (νCO, CH₃CN, cm⁻¹): 2065 (s), 2010 (s).

Anal. Calcd for C₁₃H₁₂BF₄FeN₃O₄: C, 37.5; H, 2.9; N, 10.1. Found: C, 37.7; H, 3.0, N, 9.9.

Reaction of 6 with HS-(2,6-Me₂-C₆H₃) and NEt₃: Synthesis of [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₂{S-(2,6-Me₂-C₆H₃)}] (7)

HS-(2,6-Me₂-C₆H₃) (6.62~13.2 mg, 0.048~0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH₃CN (5 mL) under stirring. NEt₃ (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2011 and 1944 cm⁻¹. The intensity of the two bands decreased quickly, with the emergence of two new bands at 2063 and 1983 cm⁻¹. After about 10 mins, almost all the bands between 2100-1900 cm⁻¹ disappeared, and the color changed to black.

If HBF₄⋅Et₂O (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of 7, 6 was regenerated.

IR (νCO, CH₃CN, cm⁻¹): 2011 (s), 1944 (s).

Reaction of 7 with CO: Formation [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₃{S-(2,6-Me₂-C₆H₃)}] (7a)

HS-(2,6-Me₂-C₆H₃) (6.62~13.2 mg, 0.048~0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH₃CN (5 mL) under CO atmosphere. NEt₃ (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing four ν(CO) absorption bands at 2063, 2011, 1983 and 1944 cm⁻¹. The intensity of the peak at 2063 cm⁻¹ is about 50 % of that of the peak at 1944 cm⁻¹, indicating that about 33 % of 7 transformed to 7a.

7a: IR (νCO, CH₃CN, cm⁻¹): 2063 (s), 2011 (s), 1983 (s).

Reaction of 6 with HS-(4-NO₂-C₆H₄) and NEt₃: Synthesis of [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₂{S-(4-NO₂-C₆H₄)}] (8)

HS-(4-NO₂-C₆H₄) (7.43~14.9 mg, 0.048~0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH₃CN (5 mL) under stirring. NEt₃ (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to deep yellow immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2013 and 1953 cm⁻¹. The intensity of the two bands decreased quickly, with the emergence of two new bands at 2071 and 1992 cm⁻¹. After about 10 mins, almost all the bands between 2100-1900 cm⁻¹ disappeared, and the color changed to black.

If HBF₄⋅Et₂O (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of 8, 6 was regenerated.

IR (νCO, solid, cm⁻¹): 2014 (s), 1953 (s). IR (νCO, CH₃CN, cm⁻¹): 2063 (s), 1953 (s).

Reaction of 6 with HS-(C₆F₅) and NEt₃: Synthesis of [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₂{S-(C₆F₅)}] (9)

HS-(C₆F₅) (9.59~19.2 mg, 0.048~0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH₃CN (5 mL) under stirring. NEt₃ (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2020 and 1956 cm⁻¹. The intensity of the two bands decreased quickly, with the emergence of two new bands at 2071 and 1992 cm⁻¹. After about 10 mins, almost all the bands between 2100-1900 cm⁻¹ disappeared, and the color changed to black.

If HBF₄⋅Et₂O (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of 9, 6 was regenerated.

IR (νCO, solid, cm⁻¹): 2014 (s), 1953 (s). IR (νCO, CH₃CN, cm⁻¹): 2063 (s), 1953 (s).
After about 1 h, almost all the bands between 2100-1900 cm\(^{-1}\) disappeared, and the color changed to black.

If HBF\(_4\)\(\cdot\)Et\(_2\)O (7.77 mg–23.3 mg, 0.048–0.14 mmol) was added quickly after the formation of 9, 6 was regenerated.

IR (\(\nu_{\text{CO}}, \text{solid, cm}^{-1}\)): 2024 (s), 1960 (s). IR (\(\nu_{\text{CO}}, \text{CH}_3\text{CN, cm}^{-1}\)): 2020 (s), 1956 (s).

Reaction of 6 with NaS-(C\(_6\)F\(_5\)): An alternative route to synthesize 9

NaS-(C\(_6\)F\(_5\)) (2.66 mg, 0.012 mmol) was added into a solution of 6 (5.00 mg, 0.012 mmol) in CD\(_3\)CN (0.6 mL) in a J Young NMR tube at -30 °C. The \(^1\)H NMR was measured immediately, which showed 9 formed. Some precipitate can be found in the tube after the \(^1\)H NMR measurement.

\(^1\)H NMR (400.13 MHz, CD\(_3\)CN): 7.73 (br s, 1H), 6.98-6.71 (m, 2H), 4.37 (d, \(J = 20.0 \text{ Hz}, 1\)H), 3.91 ppm.

Reaction of 9 with CO: Formation of [(2-CH\(_2\)CO-6-HOC\(_5\)H\(_3\)N)Fe(CO)\(_3\)\(\cdot\)S-(C\(_6\)F\(_5\))] (9a)

HS-(C\(_6\)F\(_5\)) (9.59–19.2 mg, 0.048–0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH\(_3\)CN (5 mL) under a CO atmosphere. NEt\(_3\) (4.85–9.79 mg, 0.048–0.096 mmol) was added into the mixture at -30 °C. The IR spectrum was recorded immediately, showing four \(\nu\) (CO) absorption bands at 2074, 2020, 1989 and 1956 cm\(^{-1}\). The intensity of the peak at 2074 cm\(^{-1}\) is about 60 % of that of the peak at 1956 cm\(^{-1}\), showing that about 38 % of 9 transformed to 9a.

9a: IR (\(\nu_{\text{CO}}, \text{CH}_3\text{CN, cm}^{-1}\)): 2074 (s), 2020 (s), 1989 (s).

Reaction of 9 with \(p\)-toluenesulfonylmethylisocyanide

HS-(C\(_6\)F\(_5\)) (9.59–19.2 mg, 0.048–0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH\(_3\)CN (5 mL). NEt\(_3\) (4.85–9.79 mg, 0.048–0.096 mmol) and \(p\)-toluenesulfonylmethylisocyanide (9.36–18.7 mg, 0.048–0.096 mmol) were added into the mixture at -30 °C, respectively. The IR spectrum was recorded immediately, showing two \(\nu\) (CO) absorption bands at 2027 and 1974 cm\(^{-1}\). The product decomposed completely in 15 mins at room temperature in the dark.

Reaction of 9 with \(t\)-BuSH and NEt\(_3\): Synthesis of [(2-CH\(_2\)CO-6-HOC\(_5\)H\(_3\)N)Fe(CO)\(_2\)(S-t-Bu)] (10)

\(t\)-BuSH (4.32–8.64 mg, 0.048–0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH\(_3\)CN (5 mL) under stirring. NEt\(_3\) (4.85–9.79 mg, 0.048–0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense \(\nu\) (CO) absorption bands at 2017 and 1974 cm\(^{-1}\). After about 3 mins, almost all the bands between 2100-1900 cm\(^{-1}\) disappeared, and the color changed to black.

If HBF\(_4\)\(\cdot\)Et\(_2\)O (7.77 mg–23.3 mg, 0.048–0.14 mmol) was added quickly after the formation of 10, 6 was regenerated.

IR (\(\nu_{\text{CO}}, \text{CH}_3\text{CN, cm}^{-1}\)): 2017 (s), 1956 (s).

Reaction of 6 with CH\(_3\)CH\(_2\)SH and NEt\(_3\): Synthesis of [(2-CH\(_2\)CO-6-HOC\(_5\)H\(_3\)N)Fe(CO)\(_2\)(SCH\(_2\)CH\(_2\)CH\(_3\))] (11)

CH\(_3\)CH\(_2\)CH\(_2\)SH (3.65–7.30 mg, 0.048–0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH\(_3\)CN (5 mL) under stirring. NEt\(_3\) (4.85–9.79 mg, 0.048–0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense \(\nu\) (CO) absorption bands at 2008 and 1947 cm\(^{-1}\). After about 3 mins, almost all the bands between 2100-1900 cm\(^{-1}\) disappeared, and the color changed to black.

If HBF\(_4\)\(\cdot\)Et\(_2\)O (7.77 mg–23.3 mg, 0.048–0.14 mmol) was added quickly after the formation of 11, 6 was regenerated.

IR (\(\nu_{\text{CO}}, \text{CH}_3\text{CN, cm}^{-1}\)): 2008 (s), 1947 (s).
Reaction of 6 with HOCH₂CH₂SH and NEt₃: Synthesis of [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₂(SCH₂CH₂OH)] (12)

HOCH₂CH₂SH (3.74~7.48 mg, 0.048~0.096 mmol) was added into a solution of 6 (20.0 mg, 0.048 mmol) in CH₃CN (5 mL) under stirring. NEt₃ (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2006 and 1937 cm⁻¹. After about 10 mins, almost all the bands between 2100-1900 cm⁻¹ disappeared, and the color changed to black.

IR (νCO, CH₃CN, cm⁻¹): 2006 (s), 1937 (s).

Reaction of 5 with CH₃COOAg: Synthesis of [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₂(CH₃COO)] (13) and/or [(2-CH₂CO-6-HOC₅H₃N)Fe(CO)₂(CH₃CN)₂]+(CH₃COO)⁻ (13a)

CH₃COOAg (41.2 mg, 0.248 mmol) was added into a solution of 5 (50.0 mg, 0.124 mmol) in CH₂Cl₂ (5 mL) under stirring. Gas (CO) was formed immediately. After 5 mins, the mixture was filtered and the filtrate was dried in vacuum. The residue was washed with ether (10 mL) and dried in vacuum to afford 13 (35.0 mg, 0.114 mmol, 92 %) as yellow oily solid. When dissolved in CH₃CN, parts of 13 transformed to 13a.

13: ¹H NMR (400.13 MHz, CDCl₃): 7.67 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 4.01 (d, J = 20.0 Hz, 1H), 3.92 (d, J = 20.0 Hz, 1H), 2.41 (s, 3H) ppm. IR (νCO, solid, cm⁻¹): 2042 (s), 1972 (s). IR (νCO, CH₂, cm⁻¹): 2051 (s), 1986 (s). MS (ESI, negative mode): Calcd for C₁₁H₉FeNO₆ - H: 305.9701. Found: 305.9706. Anal. Calcd for C₁₁H₉NFeO₆: C, 43.0; H, 3.0; N, 4.6. Found: C, 42.7; H, 3.2, N, 4.3.

Mixture of 13 and 13a: ¹H NMR (400.13 MHz, CD₃CN): 7.73 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), [4.20 (d, J = 20.0 Hz), 4.05 (d, J = 20.0 Hz) (1H in total)], [3.85 (d, J = 20.0 Hz), 3.82 (d, J = 20.0 Hz) (1H in total)], 1.96 (m) ppm. IR (νCO, CH₃CN, cm⁻¹): 2054 (s), 2044 (sh), 1994 (s), 1979 (sh).

Reaction of 13 with HS-(C₆F₅) and NEt₃: An alternative route to synthesize 9

HS-(C₆F₅) (13.0~26.0 mg, 0.065~0.130 mmol) was added into a solution of 13 (20.0 mg, 0.065 mmol) in CH₂Cl₂ (5 mL) under stirring. NEt₃ (6.57~13.1 mg, 0.065~0.130 mmol) was added into the mixture at -30 °C. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2022 and 1958 cm⁻¹. CH₃CN (53.3 mg, 0.65 mmol) was then added to the solution, and there was no change of the ν(CO) absorptions, which meant that CH₃CN did not coordinate with Fe center.

D. Crystallographic Details for 2

A total of 4644 reflections (-12 < h < 12, -13 < k < 8, -12 < l < 11) were collected at T = 293(2) K in the range of 2.94 to 25° of which 2898 were unique (R_int = 0.0395); MoKα radiation (λ = 0.71073 Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 1.520 and –0.542 eÅ⁻³, respectively. The least squares refinement converged normally with residuals of R(F) = 0.0898, wR(F²) = 0.2337 and a GOF = 1.098 (β=2σI). C₂₁H₂₃FeNO₄S, Mw = 441.31, space group P2(1), Monoclinic, a = 10.2510(18), b = 11.4645(10), c = 10.414(2) Å, β = 114.51(2)°, V = 1113.63(6) Å³, Z = 2, ρ calc = 1.316 Mg/m³. CCDC 963961 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References
Figure S1. IR spectrum of 1 in the solid state.

Figure S2. IR spectrum of 1 in CH₂Cl₂.
**Figure S3.** IR spectrum of 2 in the solid state.

**Figure S4.** IR spectrum of 3 in CH$_3$CN.
Figure S5. IR spectrum of 4 in the solid state.

Figure S6. IR spectrum of 5 in the solid state.
Figure S7. IR spectrum of 5 in CH₃CN.

Figure S8. IR spectrum of 6 in the solid state.
Figure S9. IR spectrum of 6 in CH$_3$CN.

Figure S10 IR spectrum of 7 in CH$_3$CN.
**Figure S11.** Reaction of 7 with CO

**Figure S12.** IR spectra of 7 or a mixture with 7a: (A) 7 in CH\textsubscript{3}CN; (B) 2 mins later of 7 in CH\textsubscript{3}CN at -30 °C; (C) 7 in the presence of CO (a mixture of 7 and 7a).
**Figure S13.** IR spectrum of 8 in the solid state.

**Figure S14.** IR spectrum of 8 in CH$_3$CN.
Figure S15. IR spectrum of 9 in the solid state.

Figure S16. IR spectrum of 9 in CH$_3$CN.
Figure S17. IR spectrum of 9 in CH$_2$Cl$_2$.

Figure S18. Reaction of 9 with CO.
Figure S19. IR spectra of 9 or a mixture with 9a: (A) 9 in CH$_3$CN; (B) 20 mins later of 9 in CH$_3$CN at room temperature; (C) 9 in the presence of CO (a mixture of 9 and 9a).

Figure S20. Reaction of 9 with p-toluenesulfonylmethylisocyanide in CH$_3$CN.
Figure S21. IR spectrum of 10 in CH$_3$CN.

Figure S22. IR spectrum of 11 in CH$_3$CN.
Figure S23. IR spectrum of 12 in CH$_3$CN.

Figure S24. IR spectrum of 13 in the solid state.
**Figure S25.** IR spectrum of 13 in CH$_2$Cl$_2$.

**Figure S26.** IR spectrum of 13 and 13a in CH$_3$CN.
Figure S27. $^1$H NMR spectrum of 2-tert-butoxy-6-methylpyridine in CDCl$_3$. 
Figure S28. $^{13}$C NMR spectrum of 2-tert-butoxy-6-methylpyridine in CDCl$_3$. 
Figure S29. $^1$H NMR spectrum of 1 in CDCl$_3$. 
Figure S30. $^1$H NMR spectrum of 2 in CD$_3$CN.
Figure S31. $^1$H NMR spectrum of 3 in CDCl$_3$. 
Figure S32. $^{13}$C NMR spectrum of 3 in CDCl$_3$. 
Figure S33. $^1$H NMR spectrum of 4 in CD$_3$CN.
Figure S34. $^1$H NMR spectrum of 5 in CD$_3$CN.
Figure S35. $^1$H NMR spectrum of 6 in CD$_3$CN.
Figure S36. $^1$H NMR spectrum of 9 in CD$_3$CN.
Figure S37. $^1$H NMR spectrum of 13 in CDCl$_3$. 
Figure S38. $^1$H NMR spectrum of 13 and 13a in CD$_3$CN.