Supporting Information

Synthetic [NiFe] Models with a Fluxional CO ligand

Xiaoxiao Chu, Xin Yu, Sakthi Raje, Raja Angamuthu, Jianping Ma, Chen-Ho Tung and Wenguang Wang

School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, China
Laboratory of Inorganic Synthesis and Bioinspired Catalysis (LISBIC), Indian Institute of Technology Kanpur, India, Kanpur 208016
College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan, 250014, China

I. Experimental Section ................................................................. p S2
General Information and preparation of compounds ........................................ p S2

II. Supplementary Figures ............................................................. p S4
Figure S1. IR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]+ mixture ........................................ p S4
Figure S2. 31P NMR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]+ mixture ............................ p S5
Figure S3. ESI-MS of [(dppe)Ni(pdt)FeCp*(CO)]+ .................................................. p S6
Figure S4. 31P NMR spectrum of [1'(CO)]+ ....................................................... p S7
Figure S5. 1H NMR spectrum of [1'(CO)]+ ....................................................... p S8
Figure S6. 1H NMR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]+ mixture ................................ p S9
Figure S7. CV for [1'(CO)]+ ................................................................... p S10
Figure S8. CV for [(dppe)Ni(pdt)FeCp*(CO)]+ mixture ........................................ p S11
Figure S9. 31P NMR spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]+ mixture ...................... p S12
Figure S10. 1H NMR spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]+ mixture ...................... p S13
Figure S11. ESI-MS of [(dppbz)Ni(pdt)FeCp*(CO)]+ ........................................ p S14
Figure S12. Structures of [2(CO)]+ and [2'(CO)]+ .............................................. p S15
Figure S13. IR spectrum of [1'(CO)][2+] ................................................................ p S16
Figure S14. UV-vis spectra .................................................................... p S17
Figure S15. Transformation of [1'(CO)][2+] to [1(CO)][2+] monitored by UV-vis spectra .... p S18
Figure S16. IR spectra for the oxidation of [(dppe)Ni(pdt)FeCp*(CO)]+ ................. p S19
Figure S17. IR spectra for the oxidation of [(dppe)Ni(pdt)FeCp*(CO)]+ .................... p S20
Figure S18-S21. CV of [1'(CO)]+ with various amounts of acetic acid ......................... p S21
Figure S22. Comparison of the IR spectrum of [1'(CO)]+ before and after catalysis .......... p S26
Figure S23-S24. CV for the mixture of [1'(CO)]+ and [1(CO)]+ with various amounts of acetic acid .................................................................................. p S27
Scheme S1. Proposed Mechanism for H2 production by [1'(CO)]+ ......................... p S29

I. Experimental section

All manipulations were typically carried out under dry nitrogen atmosphere by using standard Schlenk
techniques. All reagents were purchased from Sigma-Aldrich, and used as received. Ni(pdt)(dppe), Ni(pdt)(dpbbz), and Cp*Fe(CO)(MeCN)2PF6 were prepared according to the reported methods.1,2 Dichloromethane (CH2Cl2), diethylether, acetonitrile, n-hexane were HPLC-grade and typically stored over activated 4 Å molecular sieves under nitrogen. All solvents were stored under nitrogen. 1H and 31P NMR spectra were recorded on Bruker Avance 500 spectrometers. All NMR spectra were recorded in J. Young NMR tubes and 31P NMR spectra were referenced to external 8% H3PO4 as internal standards. FT-IR spectra were recorded on a PerkinElmer FT-IR Spectrometer Spectrum Two (the range: from 4000 to 450 cm−1). Crystallographic data were collected using a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromatic Mo Kα radiation) at 173 K. Cyclic voltammetry was measured by a CHI 760e electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd.) under nitrogen at room temperature (electrode types: a glassycarbon electrode as working electrode, Pt wire electrode as counter electrode, and Ag wire electrode as reference electrode).

[Cp*Fe(CO)(pdt)Ni(dppe)]BF4 ([1′(CO)]BF4). A dark-red solution of (pdt)Ni(dppe) (145 mg, 0.26 mmol) in 20 mL CH2Cl2 was added dropwise to a stirred solution of Cp*Fe(CO)(MeCN)2BF4 (100 mg, 0.26 mmol) in 20 mL of CH2Cl2. The resultant brown solution was heated at 40 °C, and the conversion was monitored by IR spectroscopy. After 24 h, the mixture was concentrated, and hexane (30 mL) was added. A brown precipitate was collected by filtration. Yield: 170 mg (75%). Single crystals suitable for X-ray diffraction were obtained by layering hexane into CH2Cl2 at -30 °C. 1H NMR (500 MHz, CD2Cl2): δ 7.73−7.45 (m, 20H), 2.88 (m, 2H, PCH2CH2P), 2.77 (m, 1H, SCH2CH2CH2S), 2.33 (m, 2H, PCH2CH2P), 2.09 (m, 2H, SCH2), 2.02 (m, 2H, SCH2CH2CH2S), 1.71 (m, 1H, SCH2CH2CH2S), 1.40 (s, 15H, C5Me5). 31P{1H} NMR (202 MHz, CD2Cl2): δ 57.8. FT-IR (CH2Cl2, νCO): 1880 cm−1. ESI-MS: calcd for [1′(CO)]+, 781.1090; found, 781.1066. Anal. Calcd. for C40H46OP2S2BF4FeNi: C, 55.27; H, 5.22. Found: C, 55.30; H, 5.27.

Oxidation of [1′(CO)]BF4 to [1(CO)](BF4)2. To a dark green solution of [1′(CO)]BF4 (50 mg, 0.058 mmol) in 5 mL CH2Cl2 was added AgBF4 (12 mg, 0.062 mmol), the color changed to red brown immediately. Then the solution was stirred at room temperature for 1 h until the color became dark green. The conversion was monitored by FI-IR spectra. The solvent was removed under reduced pressure and the green residue was washed with n-hexane. Yield: 38 mg (68%). FT-IR (CH2Cl2, νCO): 2020 cm−1.

[Cp*Fe(CO)(pdt)Ni(dppe)]BF4 ([1(CO)]BF4). To the dark green solution of [1(CO)](BF4)2 (20 mg, 0.021 mmol) in 5 mL CH2Cl2 was added Cp∗2Fe (8 mg, 0.024 mmol). The color changed momentarily to brown. The solvent was removed under reduced pressure and the residue was washed with n-hexane. Yield: 15 mg (82%). FT-IR (CH2Cl2, νCO): 1917 cm−1. 31P{1H} NMR (202 MHz, CD2Cl2): δ 43.1. 1H NMR (500 MHz, CD2Cl2): δ 7.85−7.55 (m, 20H), 3.25 (m, 2H, PCH2CH2P), 3.04 (m, 1H, SCH2CH2CH2S), 3.00 (m, 2H, PCH2CH2P), 2.88 (m, 1H, SCH2CH2CH2S), 2.54 (m, 2H, SCH2), 2.50 (m, 2H, SCH2CH2CH2S), 1.21 (s, 15H, C5Me5) ESI-MS: calcd for [Cp*Fe(CO)(pdt)Ni(dppe)]+, 781.1066; found, 781.1090. Anal. Calcd. for C40H46OP2S2BF4FeNi: C, 55.27; H, 5.22. Found: C, 55.27; H, 5.25.
**Supporting Information**

[Cp*Fe(CO)(pdt)Ni(dppbz)]BF₄ complexes. A dark-red solution of (pdt)Ni(dppbz) (145 mg, 0.24 mmol) in 20 mL CH₂Cl₂ was added dropwise to a stirred solution of Cp*Fe(CO)(MeCN)₂BF₄ (93 mg, 0.24 mmol) in 20 mL of CH₂Cl₂. The reaction was monitored by IR spectroscopy unless the νCO band of Cp*Fe(CO)(MeCN)₂BF₄ disappeared. After 24 h, the solution was concentrated into an approximately 5 mL CH₂Cl₂ and 30 mL of n-hexane was added. A brown precipitate was collected by filtration. Yield: 175 mg (73.4 %). The product isolated contains two isomers [2(CO)]BF₄ and [2'(CO)]BF₄. The ratio of [2(CO)]BF₄ / [2'(CO)]BF₄ was found to be 3:1 after heating the CH₂Cl₂ solutions at 40 °C for 72 h. Prolonged the reaction time at 40 °C or increasing the temperature to 50 °C caused decomposition of the complexes. ESI-MS: calcd for [Cp*Fe(CO)(pdt)Ni(dppbz)]⁺, 829.1090; found, 829.1071. Anal. Calcd. for C₄₄H₄₅OP₂S₂BF₄FeNi: C, 57.61 ; H, 4.94. Found: C, 57.69; H, 4.97.

Compound [2'(CO)]BF₄. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.75–7.43 (m, 24H), 2.70 (dt, 1H, SCH₂CH₂CH₂S), 2.38 (m, 1H, SCH₂CH₂CH₂S), 2.03 (m, 2H, PCH₂CH₂P), 1.62 (m, 2H, PCH₂CH₂P), 1.36 (s, 15 H, Cp*-CH₃). ³¹P(¹H) NMR (202 MHz, CD₂Cl₂): δ 59.0. FT-IR (CH₂Cl₂, νCO): 1880 cm⁻¹.

Compound [2(CO)]BF₄. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.80–7.20 (m, 24H), 2.69 (dt, 1H, SCH₂CH₂CH₂S), 2.61 (m, 1H, SCH₂CH₂CH₂S), 2.56 (m, 2H, PCH₂CH₂P), 2.27 (m, 2H, PCH₂CH₂P), 1.17 (s, Cp*-CH₃). ³¹P(¹H) NMR (202 MHz, CD₂Cl₂): δ 46.0. FT-IR (CH₂Cl₂, νCO): 1920 cm⁻¹.

[Cp*Fe(CO)(pdt)Ni(dppbz)][BF₄]₂ ([(2(CO))(BF₄)]₂). Dicationic complex [2(CO)](BF₄)₂ was prepared by following the same procedure of [1(CO)](BF₄)₂ but starting from [2(CO)]BF₄. Single crystals suitable for X-ray diffraction were obtained by layering hexane into CH₂Cl₂ at -30 °C. Yield: 40 mg (73 %). FT-IR (CH₂Cl₂, νCO): 2022 cm⁻¹. Anal. Calcd. for C₄₄H₄₅OP₂S₂B₂F₆FeNi: C, 52.63 ; H, 4.52. Found: C, 52.71; H, 4.63.

**EPR Experiments.** EPR samples were prepared in a glovebox. The sample concentration was approximately 2 mM in CH₂Cl₂. EPR spectra were recorded by using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation.
II. Supplementary Figures

Figure S1. IR spectra collected for the reaction of Cp*Fe(CO)(MeCN)$_2$BF$_4$ with (pdt)Ni(dppe) (top), and Cp*Fe(CO)(MeCN)$_2$BF$_4$ (bottom) in CH$_2$Cl$_2$.

Results: $\nu_{\text{CO}}$ (cm$^{-1}$, CH$_2$Cl$_2$) for [(dppe)Ni(pdt)FeCp*(CO)]$^+$, 1917 and 1880.
Figure S2. $^{31}$P NMR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]$^+$ in CD$_2$Cl$_2$, which was referenced to external 8% H$_3$PO$_4$ as internal standard.

Results: [(dppe)Ni(pdt)FeCp*(CO)]$^+$ contains two isomers with 1:1 ratio.
Figure S3. ESI-MS spectrum of [(dppe)Ni(pdt)FeCp*(CO)]⁺ in CH₂Cl₂.

Results:
Calcd for [(dppe)Ni(pdt)FeCp*(CO)]⁺, 781.1066; found, 781.1090.
Figure S4. $^{31}$P NMR spectrum of $[1'(CO)]BF_4$ in $CD_2Cl_2$. 
Figure S5. $^1$H NMR spectrum of [1′(CO)]BF$_4$ in CD$_2$Cl$_2$.

Selected assignments:

C$_5$Me$_5$: $\delta$ 1.40 (15H)
Figure S6. $^1$H NMR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]$^+$ in CD$_2$Cl$_2$.

Selected assignments:

$\delta$ 1.40 (15H) to C$_5$Me$_5$, which is consistent with the assignment in Figure S4;

$\delta$ 1.21 (15H) to C$_5$Me$_5$ of [1(CO)]$^+$. 
Figure S7. Cyclic voltammogram for $1'(CO)BF_4$. Conditions: 1 mM sample in CH$_2$Cl$_2$ (top), and CH$_3$CN (bottom), 0.1 M n-Bu$_4$NPF$_6$ (black), 0.1 M n-Bu$_4$NBF$_4$ (blue); scan rate, 100 mV/s; potentials vs Fc$^+/0$.

Results:

In CH$_2$Cl$_2$, $E_{1/2}[1'(CO)]^{2+/+} = 0.09$ V, $i_{pa}/i_{pc} = 0.97$; $E_{1/2}[1'(CO)]^{+/0} = -1.67$ V, quasi-reversible; $E_{1/2}[1'(CO)]^{0/-} = -1.99$ V, quasi-reversible.

In CH$_3$CN, $E_{1/2}[1'(CO)]^{2+/+} = 0.16$ V, irreversible; $E_{1/2}[1'(CO)]^{+/0} = -1.53$ V, quasi-reversible; $E_{1/2}[1'(CO)]^{0/-} = -1.75$ V, quasi-reversible.
Figure S8. Cyclic voltammogram for [(dppe)Ni(pdt)FeCp*(CO)]⁺ mixture. Conditions: 1 mM sample in CH₂Cl₂, 0.1 M n-Bu₄NPF₆ (black), n-Bu₄NBF₄ (blue); scan rate, 100 mV/s; potentials vs Fc⁺/₀.

Combining with the results in Figure S7, the assignments are:

\[ E_{1/2}[\text{1(CO)}^{2+/+}] = 0.32 \text{ V}, \frac{i_{pa}}{i_{pc}} = 0.97; \]
\[ E_{1/2}[\text{1'(CO)}^{2+/+}] = 0.09 \text{ V}, \frac{i_{pa}}{i_{pc}} = 0.98 \]
Figure S9. $^{31}$P NMR spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]^+.

Assignments:

$\delta$ 58.7 to [2'(CO)]^+;

$\delta$ 46.0 to [2(CO)]^+
Figure S10. $^1$H NMR spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]$^+$.  

Selected assignments:

$\delta$ 1.36 to $C_5Me_5$ of $[2'(CO)]^+$.

$\delta$ 1.17 to $C_5Me_5$ of $[2(CO)]^+$.
Figure S11. ESI-MS spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]⁺ in CH₂Cl₂.

Results:
Calcd for [(dppbz)Ni(pdt)FeCp*(CO)]⁺, 829.1090; found, 829.1071.
Figure S12. Structures of [2(CO)]⁺ and [2′(CO)]⁺ cations with 50% probability thermal ellipsoids. For clarity, tetrafluoroborate counterions have been omitted.
**Figure S13.** IR spectra of [1'(CO)]BF₄ in CH₂Cl₂ (up), reaction of [1'(CO)]BF₄ with AgBF₄ (bottom).

**Result:**

ν_{CO} of [1'(CO)]^{2+} (cm⁻¹, CH₂Cl₂), 1970.
Figure S14. UV-vis spectra of \([1\text{CO}]^+, [1'\text{CO}]^+, [1\text{CO}]^{2+}\) and \([1'\text{CO}]^{2+}\) in \(\text{CH}_2\text{Cl}_2\).
Figure S15. UV-vis spectra of the conversion from \([1'(CO)]^{2+}\) to \([1(CO)]^{2+}\) (5×10^{-4} M in CH₂Cl₂) and the absorbance of peak at 285 nm vs time.

Result:

\[ k_{\text{obs}} = 8.50128 \times 10^{-4} \text{ s}^{-1} \]

Half-life \( t_{1/2} = 0.6932 / k_{\text{obs}} = 13.59 \text{ min.} \)

This result is consistent with \( t_{1/2} = 10.8 \text{ min obtained from IR spectroscopic analysis.} \)
Figure S16. IR spectra of (a) $[1'\text{(CO)}]^+$ in CH$_2$Cl$_2$, (b) treatment of the solution (a) with AgBF$_4$ solids; the solution of b stayed at room temperature for 5 min (c) and 30 min (d); (e) treatment solution of d by Cp*$_2$Fe.

Result:

$[1'\text{(CO)}]^+ - e^- \rightarrow [1'(\text{CO})]^{2+}$;

$[1'(\text{CO})]^{2+} \rightarrow [1'(\text{CO})]^{2+}$;

$[1(\text{CO})]^{2+} + e^- \rightarrow [1(\text{CO})]^+$
Figure S17. IR spectra of [2(CO)]$^+$ in CH$_2$Cl$_2$ (bottom), treatment of [2(CO)]$^+$ with AgBF$_4$ solids (middle), and then with Cp*$_2$Fe (up).

Result:

\[ \text{[2(CO)]}^+ - e^- \rightarrow [2(CO)]^{2+}; \]

\[ [2(CO)]^{2+} + e^- \rightarrow [2(CO)]^+; \]
Figure S18. Comparison of cyclic voltammograms in the same concentration of CH$_3$COOH before and after the addition of [1'(CO)]BF$_4$ catalyst. Conditions: 1 mM sample in CH$_3$CN, 0.1 M n-Bu$_4$NP$_6$ as the supporting electrolyte; scan rate = 100 mV/s.
Figure S19. Plots of $i_{ca}/i_p$ vs. [HOAc]$^{1/2}$ ($\mu$L)$^{1/2}$ for 1 mM $[1'(CO)]BF_4$ in 0.1 n-NBu$_4$PF$_6$ at the scan rate of 0.1 V/s.
**Figure S20.** Cyclic voltamogram of 1 mM [1'(CO)]⁺ with addition of acetic acid (35 μL) in 0.1 M n-NBu₄PF₆ in MeCN at a scan rate of 0.1 V.s⁻¹

**Calculation of turnover frequency (TOF)**

\[
\text{TOF} = 1.94 \times v \times \left( \frac{i_{\text{cat}}}{i_p} \right)^2
\]

\( v \) = scan rate
\( i_{\text{cat}} \) = current with added acid
\( i_p \) = current of catalyst without acid

**Calculation of over potential**

\[
E_{1/2}^T = E^{o\ H+/H_2} - (2.303RT/F) + \varepsilon_D - (RT/2F) \ln \left( \frac{C_1}{C_0\ H_2} \right)
\]

\( E_{1/2}^T \) = theoretical half-wave potential of acetic acid reduction in MeCN
\( E^{o\ H+/H_2} \) = Standard reduced hydrogen potential (V)
\( R \) = perfect gas constant (8.314 J/(mol*K))
\( T \) = temperature (298.15 K)
\( F \) = faraday constant (96500 C/mol)
\( pK_a \) = acid dissociation constant
Supporting Information

\( \varepsilon_D \) = the rate of diffusion about product with reactant (V)

\( C_1 \) = the concentration of acetic acid (mol/L)

\( C_{oH_2} \) = the concentration of dissolved hydrogen equal to under pressure of \( 10^5 \) Pa (mol/L)

Over-potential = \( E_{1/2}^T - E_{cat/2} \)

\( E_{cat/2} \) = the observed half-wave potential of acetic acid reduction with 1'(CO)BF₄.

1. \( i_p \) value:

\[ i_p \times \text{initial volume} / \text{final volume} = 32.79 \ \mu\text{A} \times 5 \ \text{mL} / 5.035 \ \text{mL} = 32.56 \ \mu\text{A} \]

2. the ratio of \( i_{cat/i_p} \).

\[ i_{cat/i_p} = 2040.2 \ \mu\text{A} / 32.56 \ \mu\text{A} = 62.66 \]

3. Calculation of TOF.

\( k_{obs}(\text{TOF}) = 1.94 \times v \times (i_{cat/i_p})^2 = 1.94 \times 0.1 \ \text{V/s} \times (62.66)^2 = 761 \ \text{s}^{-1} \)
Figure S21. Cyclic voltammograms for [1'(CO)]⁺ in MeCN solution with 50 scans.
Figure S22. IR spectrum of [1¹(CO)]⁺ after electrochemical catalysis.
Figure S23. Cyclic voltammograms of $[1(\text{CO})]^+$ and $[1'(\text{CO})]^+$ (1 mM) with various amounts of acetic acid added. 0.1 $n\text{-Bu}_4\text{PF}_6$ in MeCN was employed as the supporting electrolyte; scan rate = 100 mV·s$^{-1}$. 
Figure S24. Plots of $i_{\text{cat}}$ vs. [H$^+$]. For the mixture of [I(CO)]$^+$ and [I'(CO)]$^+$: $y = 13.48x + 210.0$ (blue plots); for [I'(CO)]$^+$, $y = 14.28x + 356.3$ (black plots).
Scheme S1. Proposed Mechanism for H₂ production by [1'\((\text{CO})\)]⁺.

Reference
