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Synthetic [NiFe] Models with a Fluxional CO ligand

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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)(dppbz), and Cp*Fe(CO)(MeCN)$_2$PF$_6$ were prepared according to the reported methods.[1,2] Dichloromethane (CH_2Cl_2), diethylether, acetonitrile, *n*-hexane were HPLC-grade and typically stored over activated 4 Å molecular sieves under nitrogen. All solvents were stored under nitrogen. ^{1}H and ^{31}P NMR spectra were recorded on Bruker Avance 500 spectrometers. All NMR spectra were recorded in J. Young NMR tubes and ^{31}P NMR spectra were referenced to external 8% H_3PO_4 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)]BF$_4$ ([1'(CO)]BF$_4$). A dark-red solution of (pdt)Ni(dppe) (145 mg, 0.26 mmol) in 20 mL CH_2Cl_2 was added dropwise to a stirred solution of Cp*Fe(CO)(MeCN)$_2$BF$_4$ (100 mg, 0.26 mmol) in 20 mL of CH_2Cl_2.The resultant brown solution was heated at 40 ^oC, 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 CH_2Cl_2 at -30 ^oC. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.73−7.45 (m, 20H), 2.88 (m, 2H, PCH_2CH_2P), 2.77 (m, 1H, $SCH_2CH_2CH_2S$), 2.33 (m, 2H, PCH_2CH_2P), 2.09 (m, 2H, SCH_2), 2.02 (m, 2H, $SCH_2CH_2CH_2S$), 1.71 (m, 1H, $SCH_2CH_2CH_2S$), 1.40 (s, 15H, C_5Me_5). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 57.8. FT-IR (CH_2Cl_2, ν_{CO}): 1880 cm^{-1}. ESI-MS: calcd for [**1'**(CO)]$^+$, 781.1090; found, 781.1066. Anal. Calcd. for $C_{40}H_{45}OP_2S_2BF_4FeNi$: C, 55.27; H, 5.22. Found: C, 55.30; H, 5.27.

Oxidation of [1'(CO)]BF$_4$ to [1(CO)](BF$_4$)$_2$. To a dark green solution of [**1'**(CO)]BF$_4$ (50 mg, 0.058 mmol) in 5 mL CH_2Cl_2 was added AgBF$_4$ (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 (CH_2Cl_2, ν_{CO}): 2020 cm^{-1}.

[Cp*Fe(CO)(pdt)Ni(dppe)]BF$_4$ ([1(CO)]BF$_4$).To the dark green solution of [**1**(CO)](BF$_4$)$_2$ (20 mg, 0.021 mmol) in 5 mL CH_2Cl_2 was added Cp*$_2$Fe (8 mg, 0.024 mmol). The color changed momently to brown. The solvent was removed under reduced pressure and the residue was washed with *n*-hexane. Yield: 15 mg (82 %). FT-IR (CH_2Cl_2, ν_{CO}): 1917 cm^{-1}. ^{31}P{^{1}H} NMR (202 MHz, CH_2Cl_2): δ 43.1. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.85−7.55 (m, 20H), 3.25 (m, 2H, PCH_2CH_2P), 3.04 (m, 1H, $SCH_2CH_2CH_2S$), 3.00 (m, 2H, PCH_2CH_2P), 2.88 (m, 1H, $SCH_2CH_2CH_2S$), 2.54 (m, 2H, SCH_2), 2.50 (m, 2H, $SCH_2CH_2CH_2S$), , 1.21 (s, 15H, C_5Me_5) ESI-MS: calcd for [Cp*Fe(CO)(pdt)Ni(dppe)]$^+$, 781.1066; found, 781.1090. Anal. Calcd. for $C_{40}H_{45}OP_2S_2BF_4FeNi$: C, 55.27; H, 5.22. Found: C, 55.27; H, 5.25.

[Cp*Fe(CO)(pdt)Ni(dppbz)]BF$_4$ complexes. A dark-red solution of (pdt)Ni(dppbz) (145 mg, 0.24 mmol) in 20 mL CH_2Cl_2 was added dropwise to a stirred solution of Cp*Fe(CO)(MeCN)$_2$BF$_4$ (93 mg, 0.24 mmol) in 20 mL of CH_2Cl_2. The reaction was monitored by IR spectroscopy unless the ν_{CO} band of Cp*Fe(CO)(MeCN)$_2$BF$_4$ disappeared. After 24 h, the solution was concentrated into an approximately 5 mL CH_2Cl_2 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)]BF$_4$ and [**2'**(CO)]BF$_4$. The ratio of [**2**(CO)]BF$_4$ / [**2'**(CO)]BF$_4$ was found to be 3:1 after heating the CH_2Cl_2 solutions at 40 ^oC for 72 h. Prolonged the reaction time at 40 ^oC or increasing the temperature to 50 ^oC caused decomposition of the complexes. ESI-MS: calcd for [Cp*Fe(CO)(pdt)Ni(dppbz)]$^+$, 829.1090; found, 829.1071. Anal. Calcd. for $C_{44}H_{45}OP_2S_2BF_4FeNi$: C,57.61 ; H, 4.94. Found: C, 57.69; H, 4.97.

Compound [**2'**(CO)]BF$_4$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.75−7.43 (m, 24H), 2.70 (dt, 1H, $SCH_2CH_2CH_2S$), 2.38 (m, 1H, $SCH_2CH_2CH_2S$), 2.03 (m, 2H, PCH_2CH_2P), 1.62 (m, 2H, PCH_2CH_2P), 1.36 (s, 15 H, Cp*-CH$_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 59.0. FT-IR (CH_2Cl_2, ν_{CO}): 1880 cm^{-1}.

Compound [**2**(CO)]BF$_4$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.80−7.20 (m, 24H), 2.69 (dt, 1H, $SCH_2CH_2CH_2S$), 2.61 (m, 1H, $SCH_2CH_2CH_2S$), 2.56 (m, 2H, PCH_2CH_2P), 2.27 (m, 2H, PCH_2CH_2P), 1.17 (s, Cp*-CH$_3$), ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 46.0. FT-IR (CH_2Cl_2, ν_{CO}): 1920 cm^{-1}.

[Cp*Fe(CO)(pdt)Ni(dppbz)](BF$_4$)$_2$ ([2(CO)](BF$_4$)$_2$). Dicationic complex [**2**(CO)](BF$_4$)$_2$ was prepared by following the same procedure of [**1**(CO)](BF$_4$)$_2$ but starting from [**2**(CO)]BF$_4$. Single crystals suitable for X-ray diffraction were obtained by layering hexane into CH_2Cl_2 at -30 ^oC. Yield: 40 mg (73 %). FT-IR (CH_2Cl_2, ν_{CO}): 2022 cm^{-1}. Anal. Calcd. for $C_{44}H_{45}OP_2S_2B_2F_8FeNi$: 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 CH_2Cl_2. 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

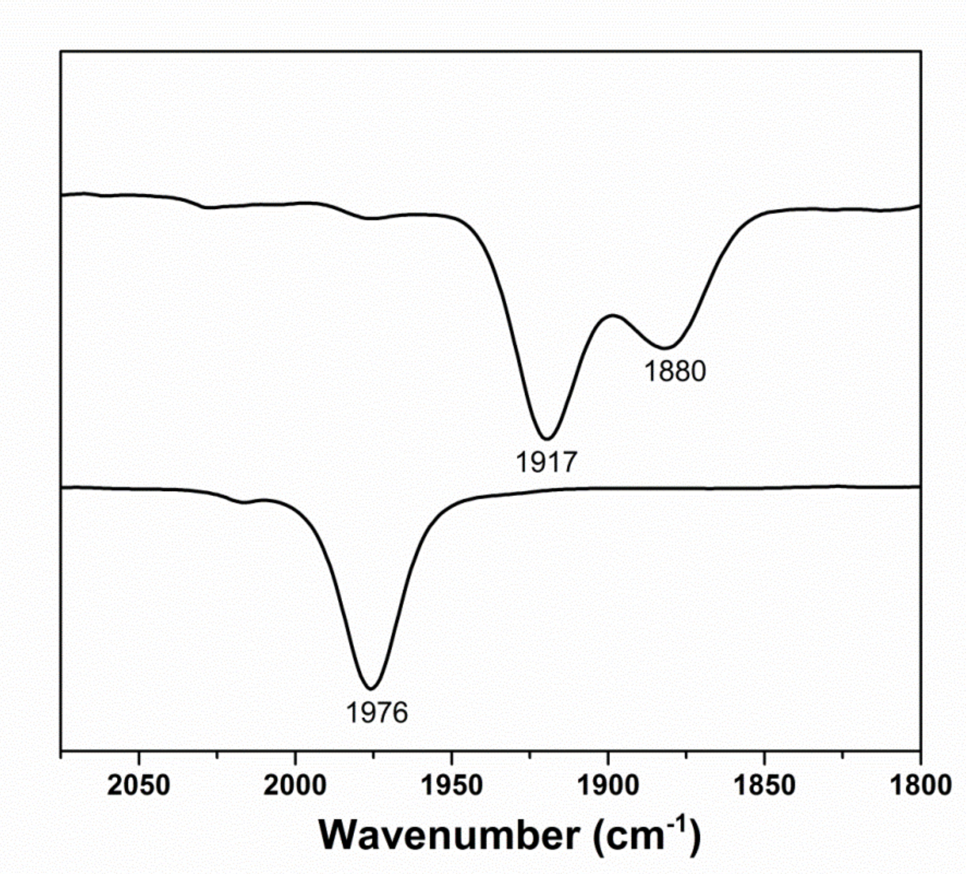


Figure S1. IR spectra collected for the reaction of Cp*Fe(CO)(MeCN)$_2$BF$_4$ with (pdt)Ni(dppe) (top), and Cp*Fe(CO)(MeCN)$_2$BF$_4$ (bottom) in CH$_2$Cl$_2$.

Results: ν_{CO} (cm^{-1}, CH$_2$Cl$_2$) for [(dppe)Ni(pdt)FeCp*(CO)]$^+$, 1917 and 1880.

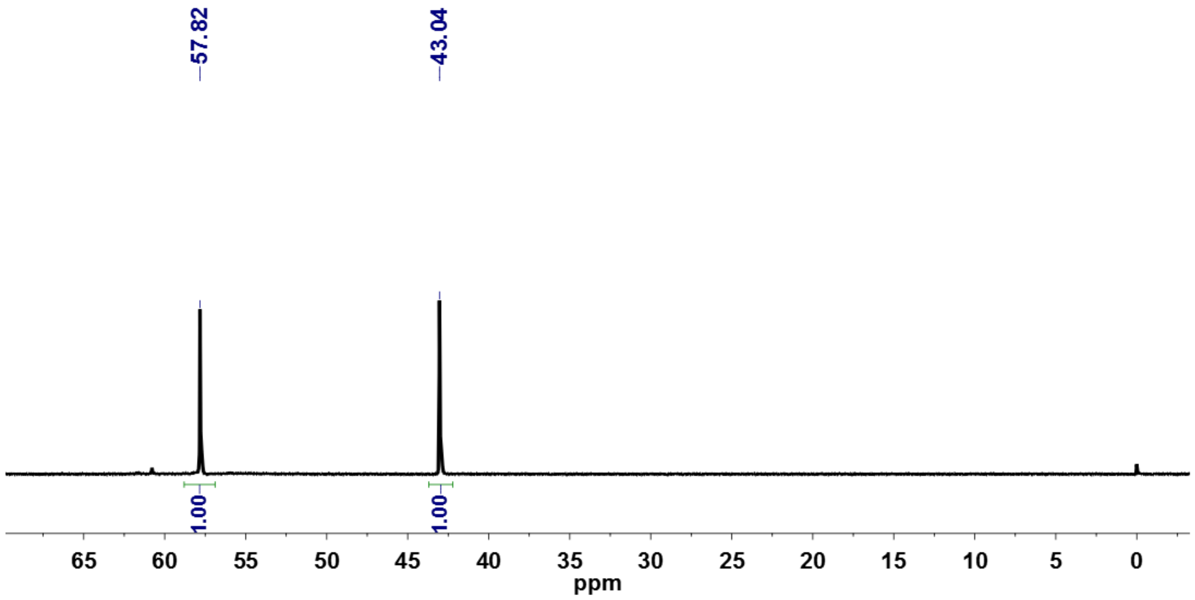


Figure S2. ^{31}P NMR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]$^+$ in CD_2Cl_2, which was referenced to external 8% H_3PO_4 as internal standard.

Results: [(dppe)Ni(pdt)FeCp*(CO)]$^+$ contains two isomers with 1:1 ratio.

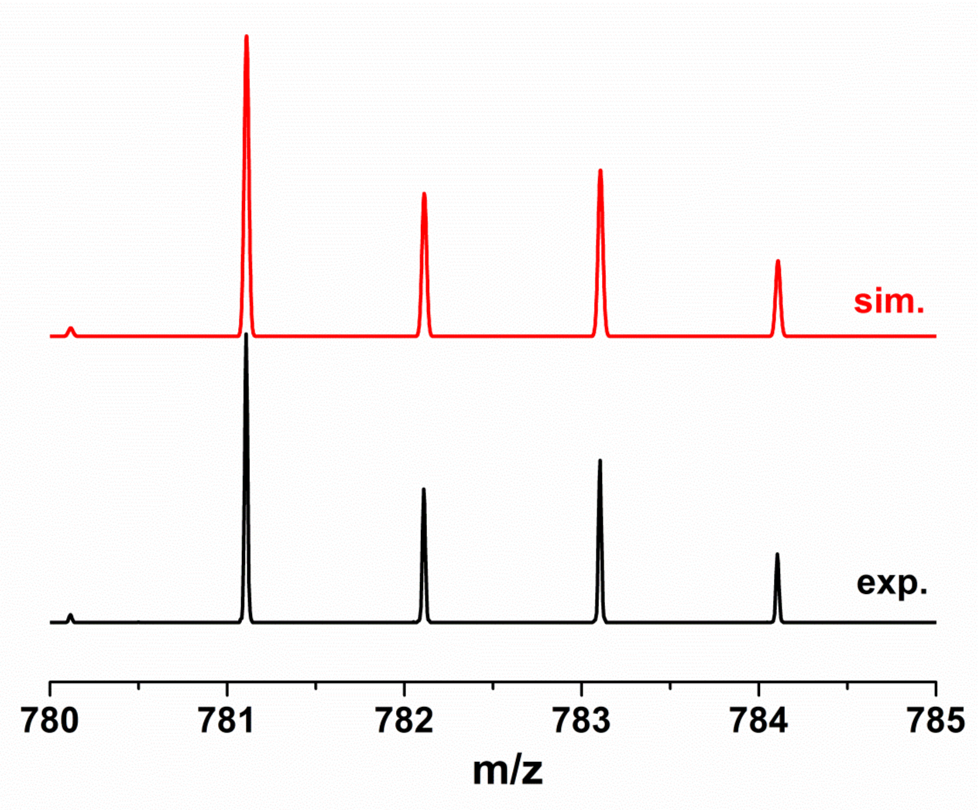


Figure S3. ESI-MS spectrum of $[(dppe)Ni(pdt)FeCp^*(CO)]^+$ in CH_2Cl_2.

Results:

Calcd for $[(dppe)Ni(pdt)FeCp^*(CO)]^+$, 781.1066; found, 781.1090.

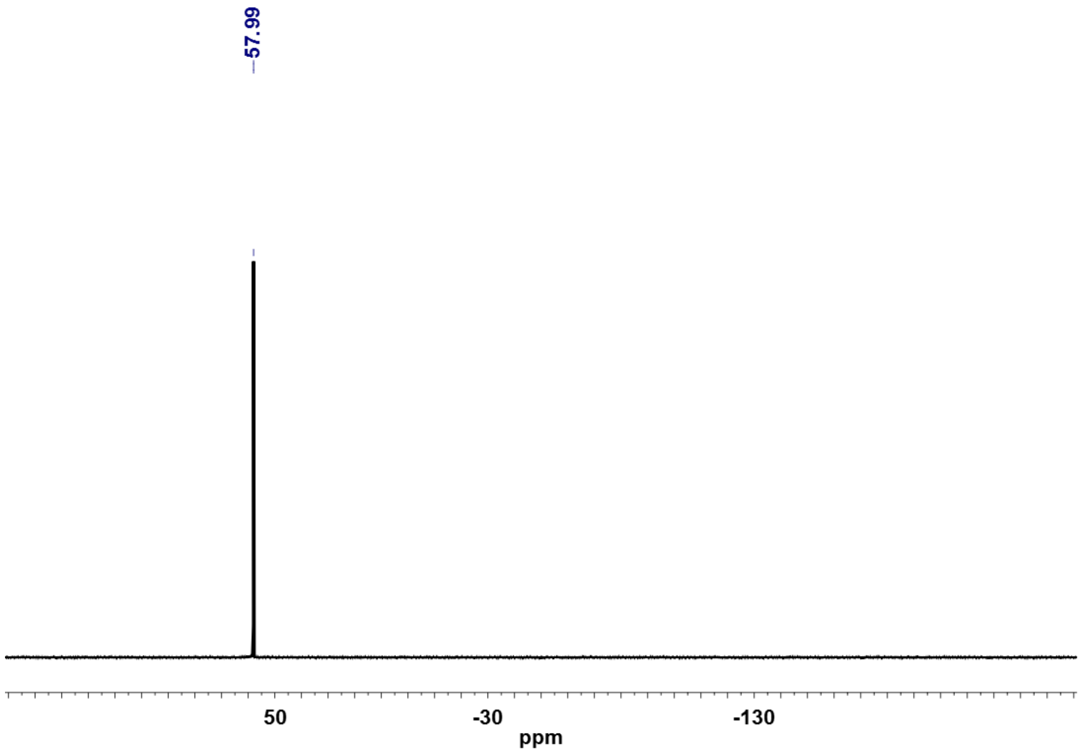


Figure S4. ^{31}P NMR spectrum of [**1’**(CO)]BF_4 in CD_2Cl_2.

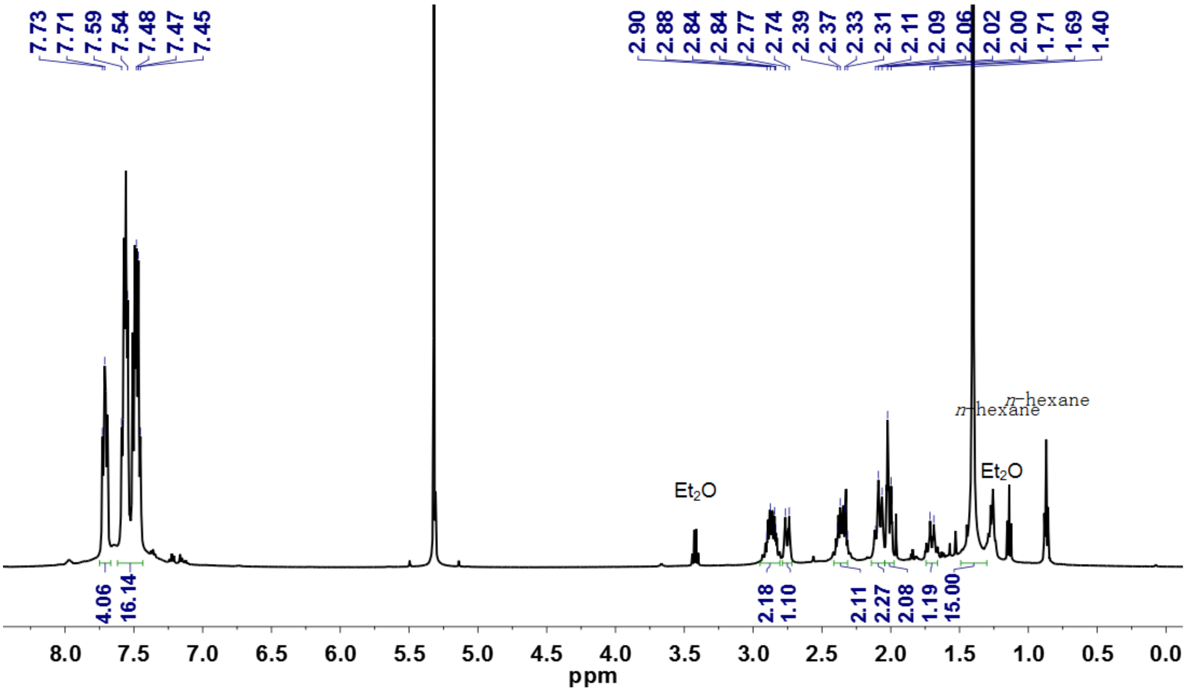


Figure S5. ^{1}H NMR spectrum of [**1'**(CO)]BF$_4$ in CD$_2$Cl$_2$.

Selected assignments:

C$_5$*Me*$_5$: δ 1.40 (15H)

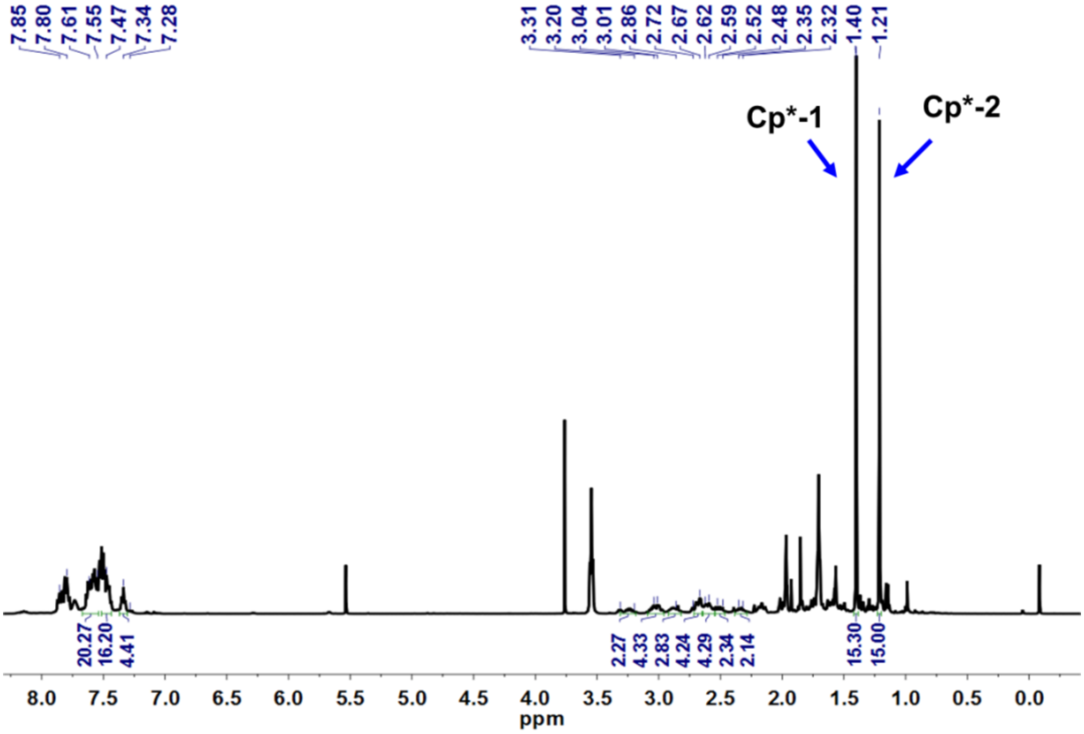


Figure S6. ^{1}H NMR spectrum of [(dppe)Ni(pdt)FeCp*(CO)]$^+$ in CD_2Cl_2.

Selected assignments:

δ 1.40 (15H) to C_5Me_5, which is consistent with the assignment in Figure S4;

δ 1.21 (15H) to C_5Me_5 of [**1**(CO)]$^+$.

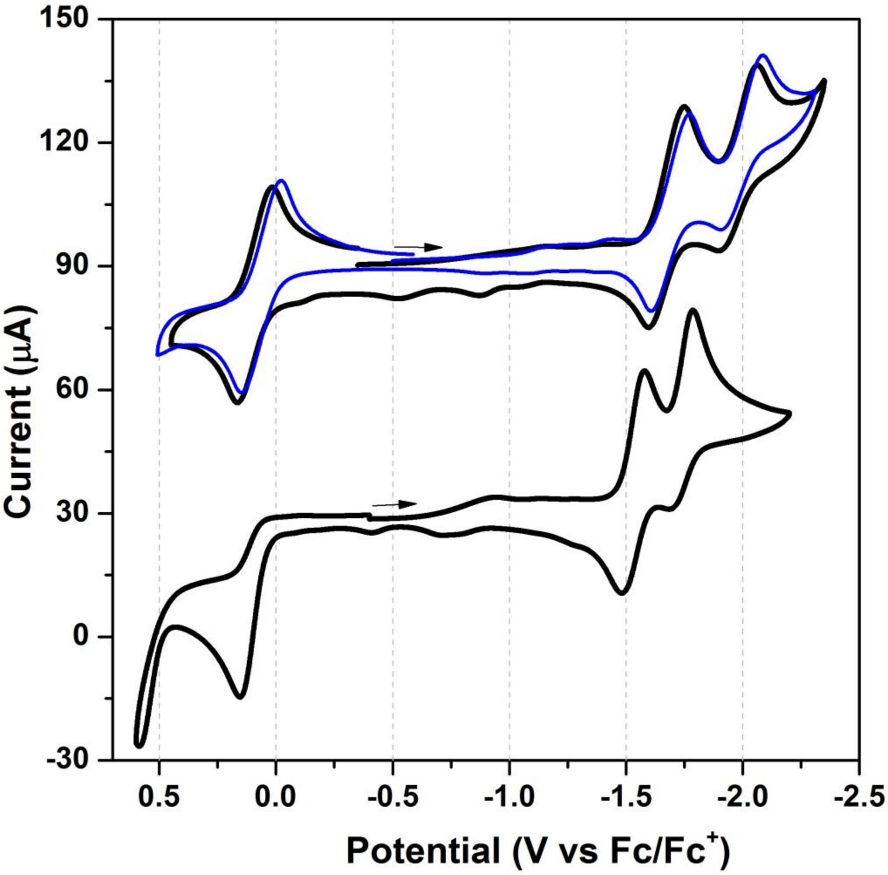


Figure S7. Cyclic voltammogram for **1'**(CO)]BF_4. Conditions: 1 mM sample in CH_2Cl_2 (top), and CH_3CN (bottom), 0.1 M *n*-Bu_4NPF_6 (black), 0.1 M *n*-Bu_4NBF_4 (blue); scan rate, 100 mV/s; potentials vs $Fc^{+/0}$.

Results:

In CH_2Cl_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_3CN, $E_{1/2}$[**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.

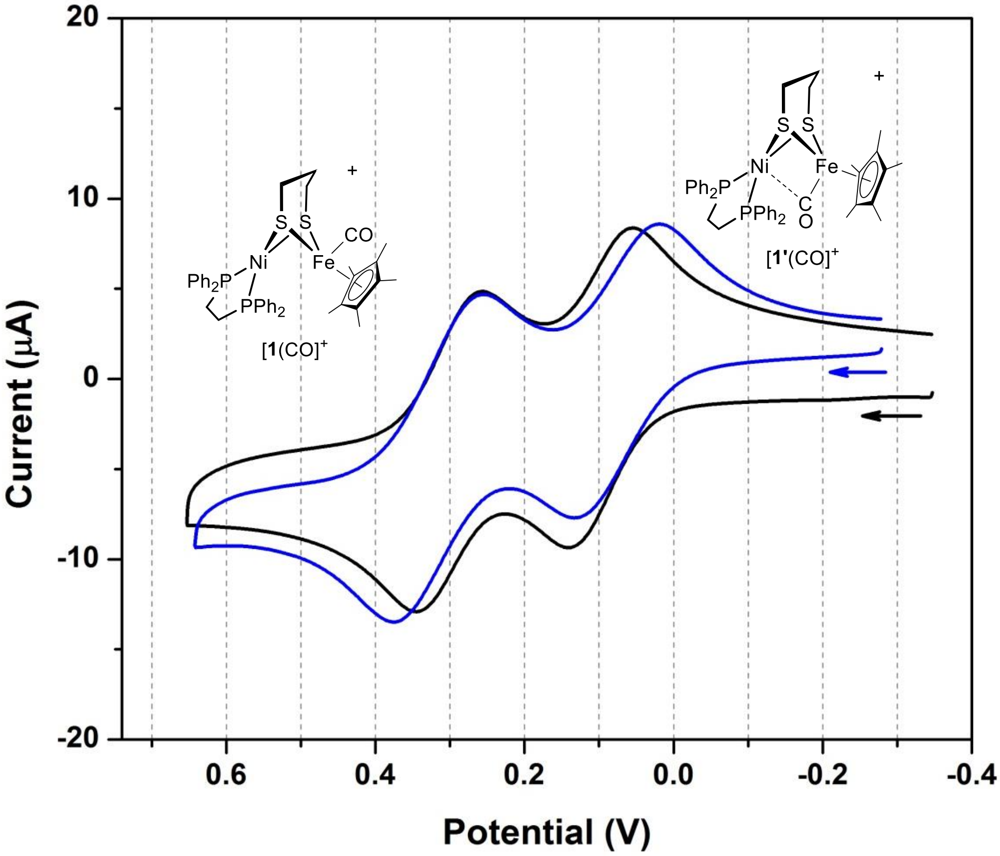


Figure S8. Cyclic voltammogram for [(dppe)Ni(pdt)FeCp*(CO)]$^+$ mixture. Conditions: 1 mM sample in CH_2Cl_2, 0.1 M *n*-Bu_4NPF_6 (black), *n*-Bu_4NBF_4 (blue); scan rate, 100 mV/s; potentials vs $Fc^{+/0}$.

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

$E_{1/2}$[**1**(CO)]$^{2+/+}$ = 0.32 V, i_{pa}/i_{pc} = 0.97;

$E_{1/2}$[**1’**(CO)]$^{2+/+}$ = 0.09 V, i_{pa}/i_{pc} = 0.98

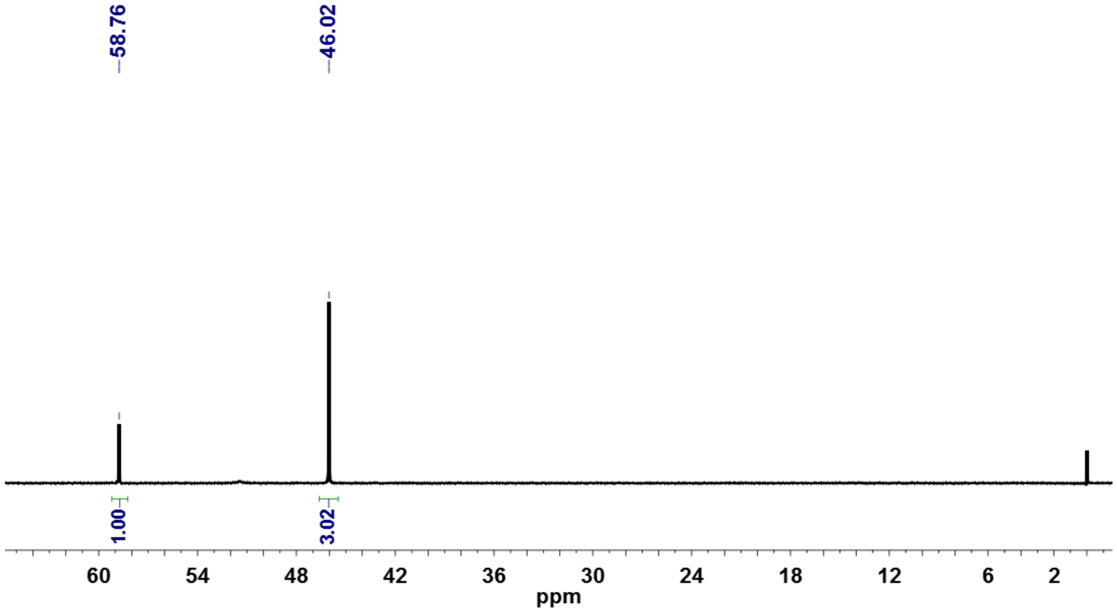


Figure S9. ^{31}P NMR spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]$^{+}$.

Assignments:

δ 58.7 to [**2'**(CO)]$^{+}$;

δ 46.0 to [**2**(CO)]$^{+}$

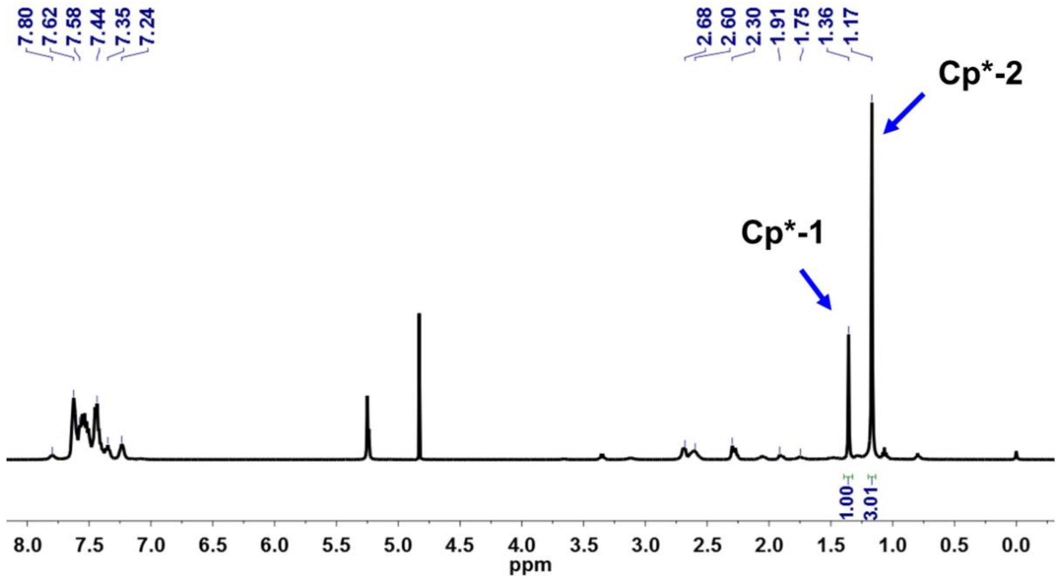


Figure S10. ^{1}H NMR spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]$^+$.

Selected assignments:

δ 1.36 to C_5*Me*$_5$ of [**2'**(CO)]$^+$,

δ 1.17 to C_5*Me*$_5$ of [**2**(CO)]$^+$

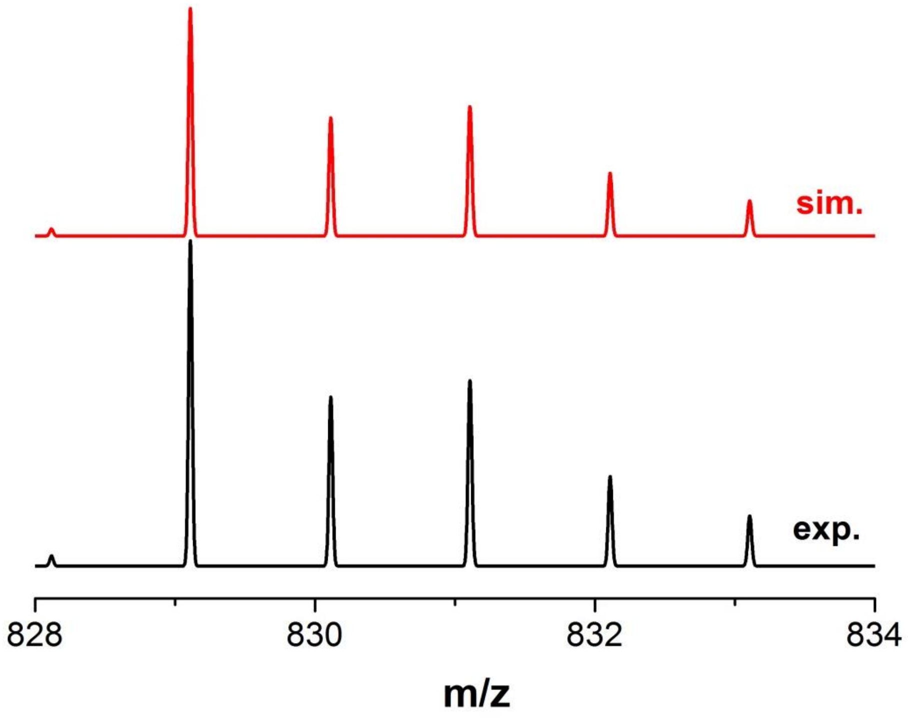


Figure S11. ESI-MS spectrum of [(dppbz)Ni(pdt)FeCp*(CO)]$^+$ in CH_2Cl_2.

Results:

Calcd for [(dppbz)Ni(pdt)FeCp*(CO)]$^+$, 829.1090; found, 829.1071.

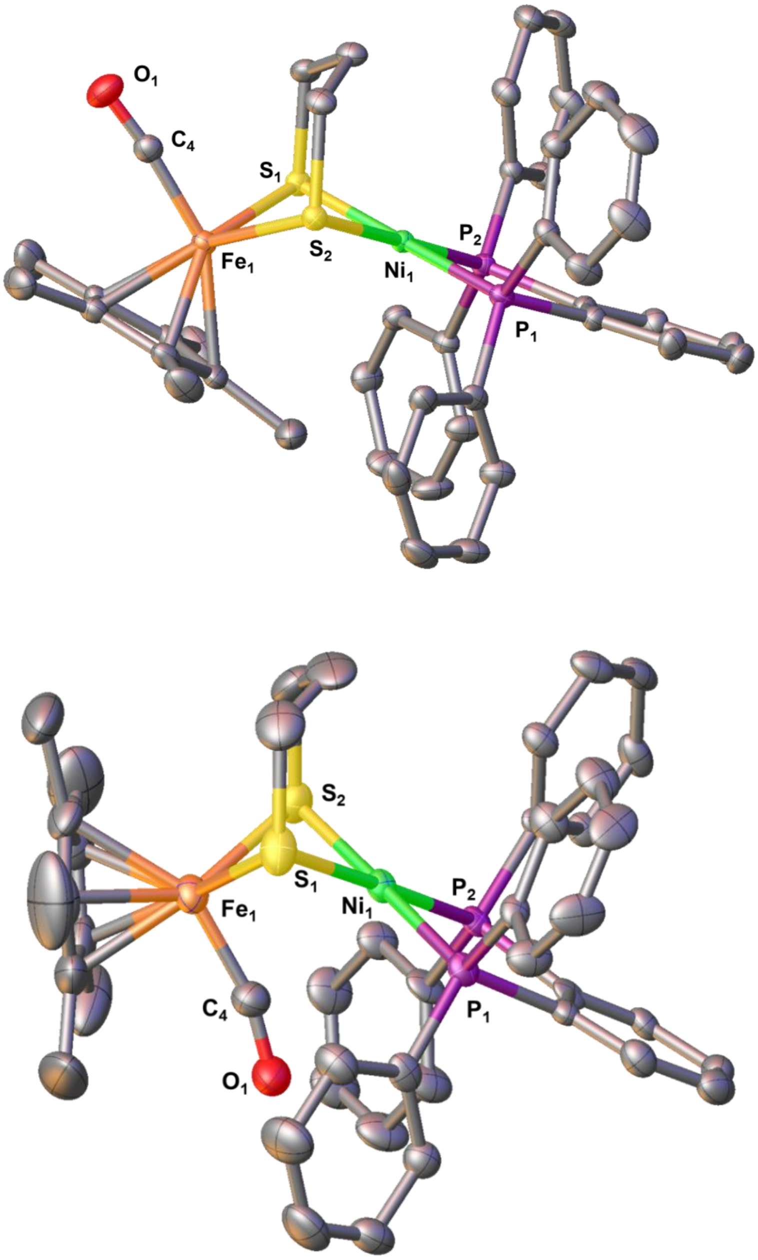


Figure S12. Structures of [**2**(CO)]$^+$ and [**2'**(CO)]$^+$ cations with 50% probability thermal ellipsoids. For clarity, tetrafluoroborate counterions have been omitted.

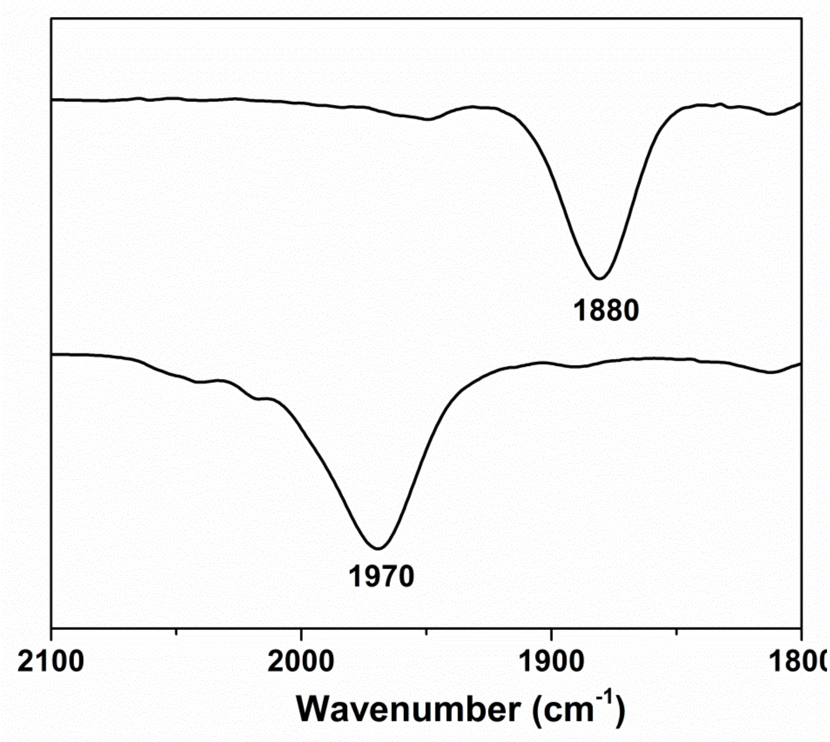


Figure S13. IR spectra of [**1’**(CO)]BF_4 in CH_2Cl_2 (up), reaction of [**1’**(CO)]BF_4 with $AgBF_4$ (bottom).

Result:

ν_{CO} of [**1’**(CO)]$^{2+}$ (cm^{-1}, CH_2Cl_2), 1970.

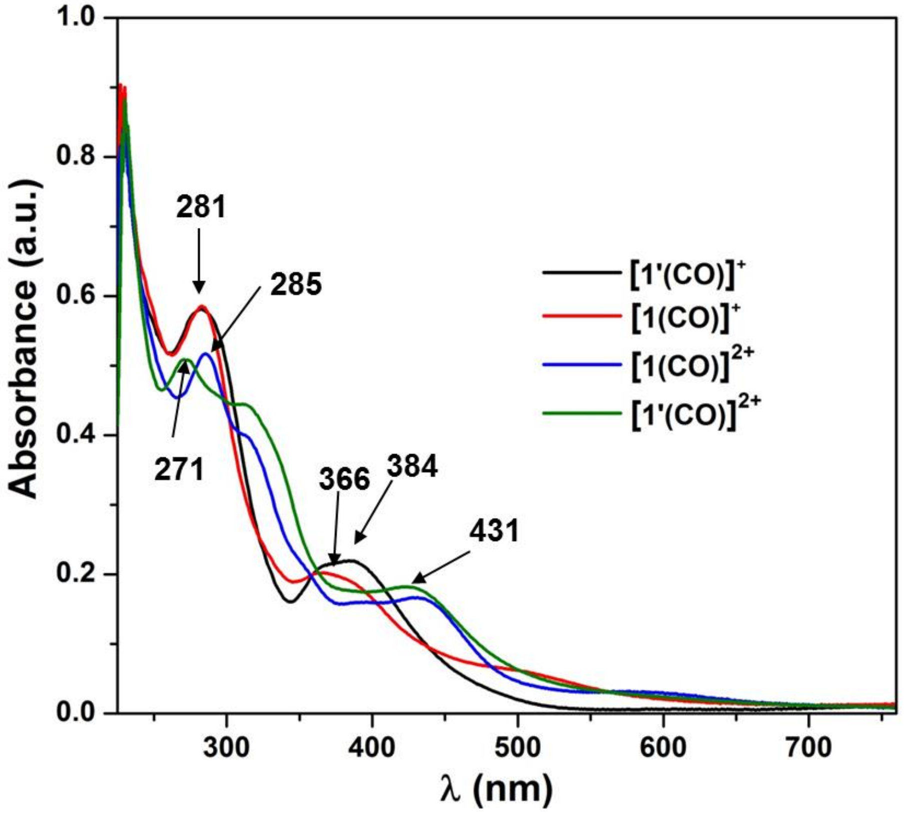


Figure S14. UV-vis spectra of [**1**(CO)]$^+$, [**1’**(CO)]$^+$, **[1**(CO)]$^{2+}$and [**1’**(CO)]$^{2+}$ in CH_2Cl_2.

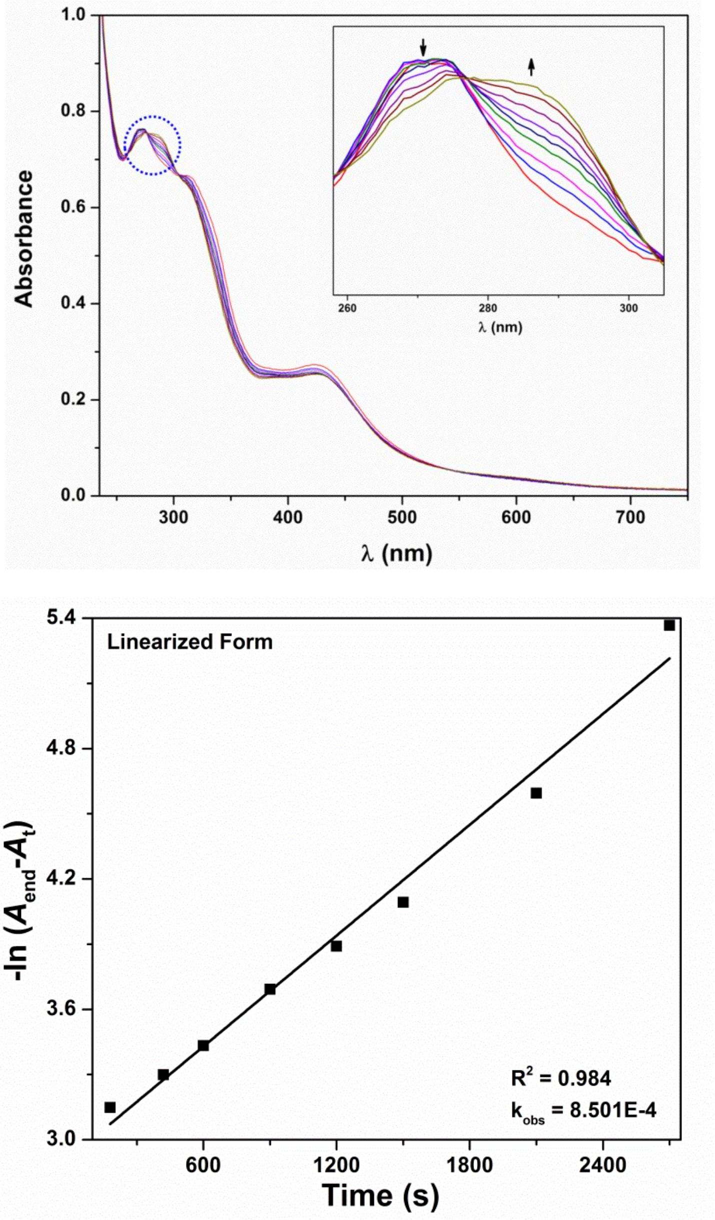
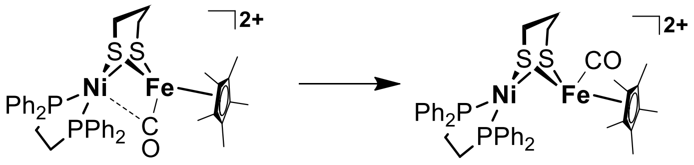


Figure S15. UV-vis spectra of the conversion from [**1'**(CO)]$^{2+}$ to [**1**(CO)]$^{2+}$ (5×10^{-4} M in CH_2Cl_2) and the absorbance of peak at 285 nm vs time.

Result:



[1'(CO)]$^{2+}$ **[1(CO)]$^{2+}$**

k_{obs} = 8.50128*10^{-4} s^{-1}

Half-life $t_{1/2}$ = 0.6932/ k_{obs} = 13.59 min.

This result is consistent with $t_{1/2}$ = 10.8 min obtained from IR spectroscopic analysis.

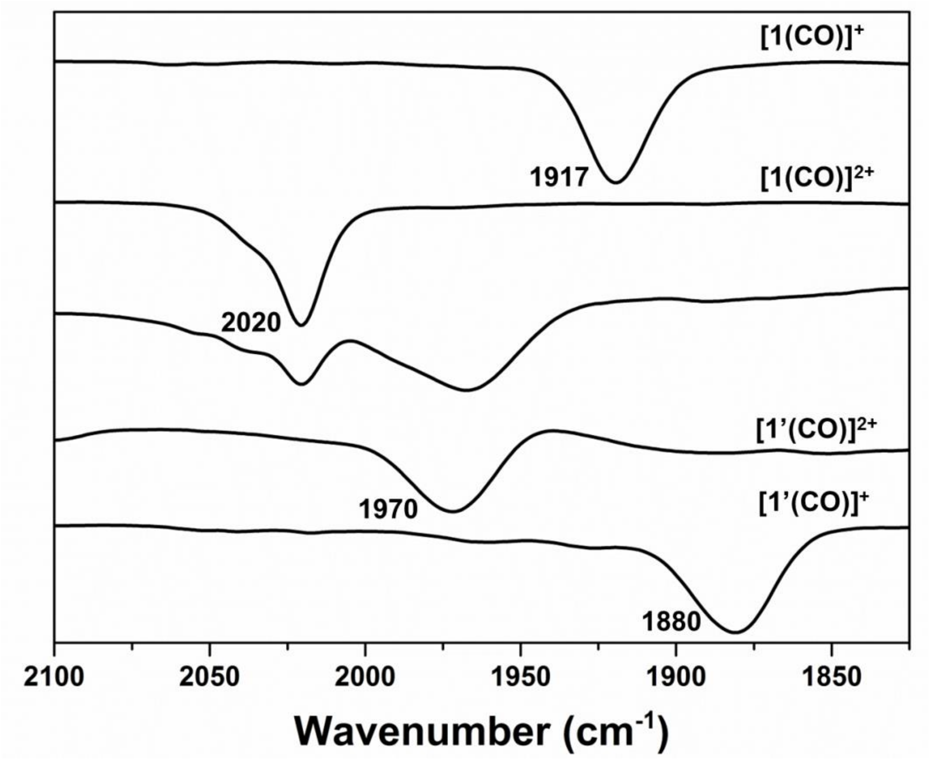


Figure S16. IR spectra of (a) [**1'**(CO)]$^+$ in CH_2Cl_2, (b) treatment of the solution (a) with $AgBF_4$ solids; the solution of b stayed at room temperature for 5 min (c) and 30 min (d); (e) treatment solution of d by Cp^*_2Fe.

Result:

[**1'**(CO)]$^+$ - e$^-$ → [**1'**(CO)]$^{2+}$;

[**1'**(CO)]$^{2+}$ → [**1'**(CO)]$^{2+}$;

[**1**(CO)]$^{2+}$+ e$^-$ → [**1**(CO)]$^+$

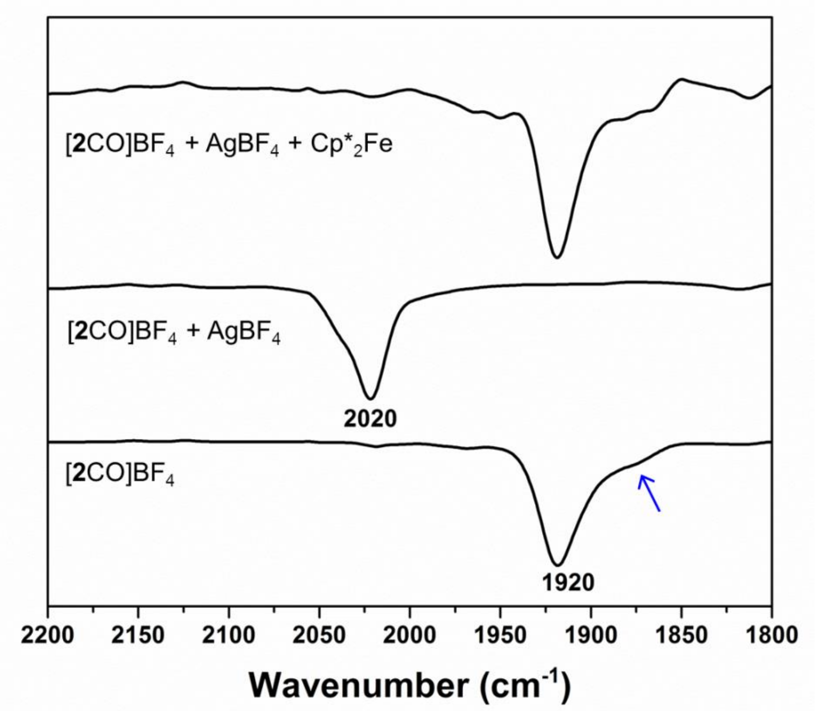


Figure S17. IR spectra of [**2**(CO)]$^+$ in CH_2Cl_2 (bottom), treatment of [**2**(CO)]$^+$ with $AgBF_4$ solids (middle), and then with Cp*$_2$Fe (up).

Result:

[**2**(CO)]$^+$ - e$^-$ → [**2**(CO)]$^{2+}$;

[**2**(CO)]$^{2+}$ + e$^-$ → [**2**(CO)]$^+$;

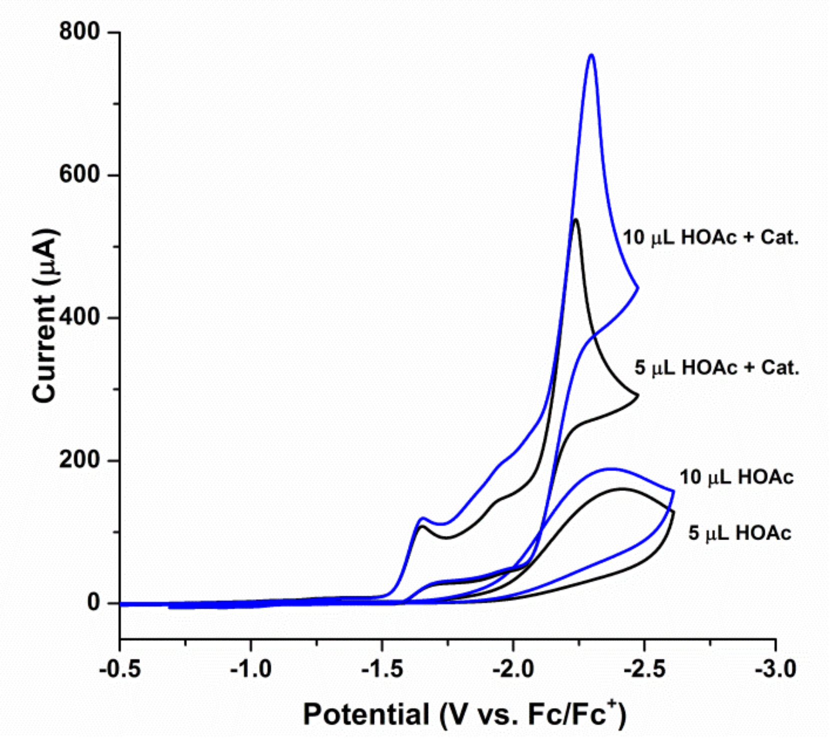


Figure S18. Comparison of cyclic voltammograms in the same concentration of CH_3COOH before and after the addition of [**1’**(CO)]BF_4 catalyst. Conditions: 1 mM sample in CH_3CN, 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte; scan rate = 100 mV/s.

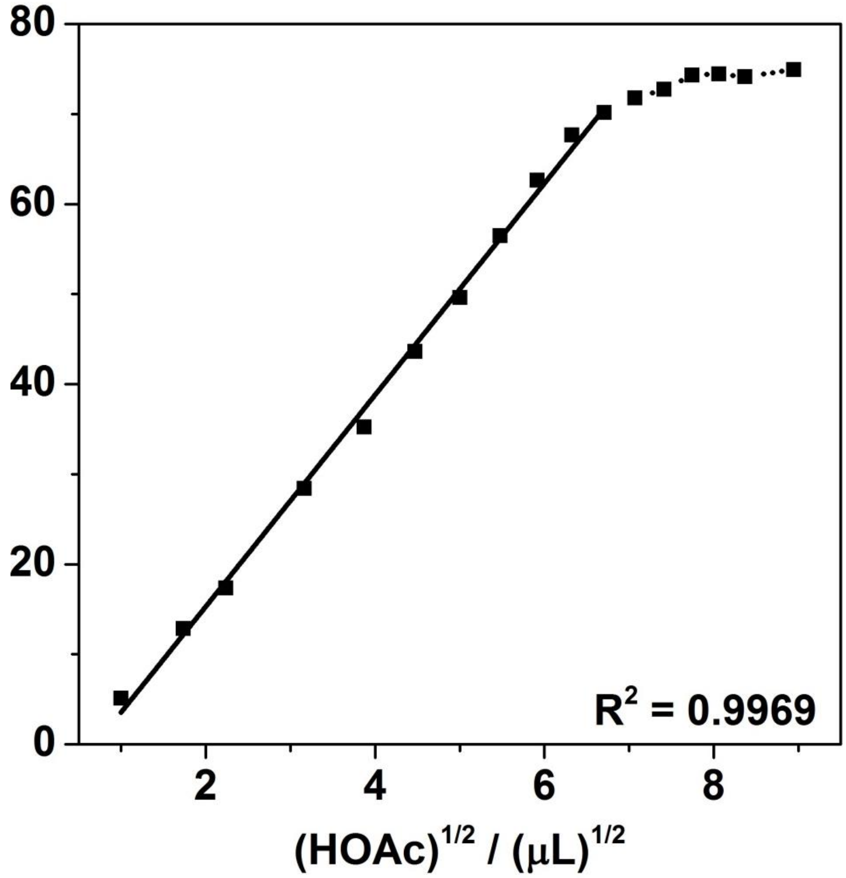


Figure S19. Plots of i_{cat}/i_p vs. $[HOAc]^{1/2}$ $(\mu L)^{1/2}$ for 1 mM [**1'**(CO)]BF_4 in 0.1 *n*-NBu_4PF_6 at the scan rate of 0.1 V/s.

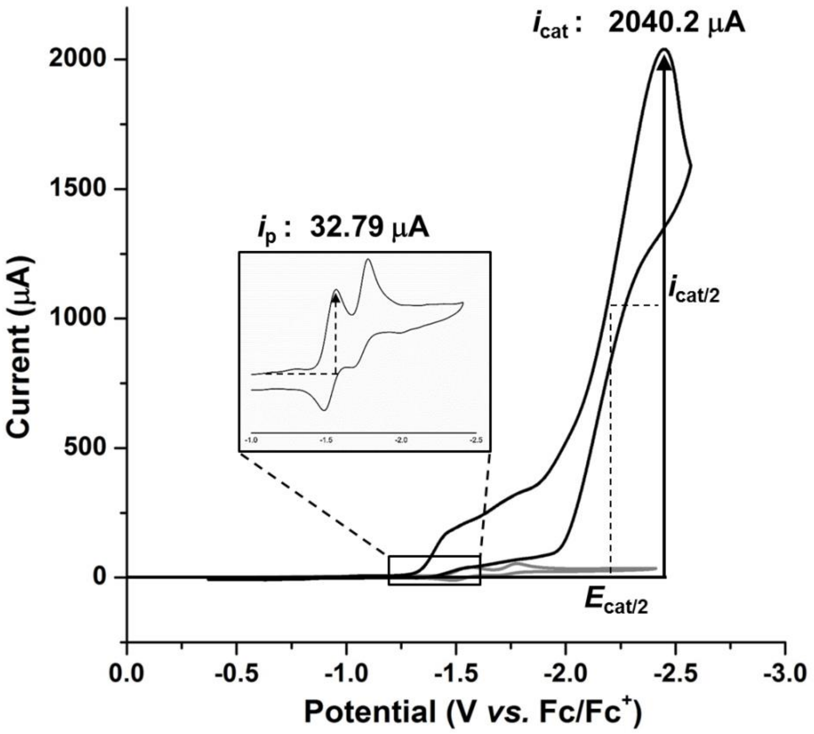


Figure S20. Cyclic voltammogram of 1 mM [**1'**(CO)]$^+$ with addition of acetic acid (35 μL) in 0.1 M *n*-NBu$_4$PF$_6$ in MeCN at a scan rate of 0.1 V.s^{-1}

Calculation of turnover frequency (TOF)

TOF = 1.94 x ν x $(i_{cat}/i_p)^2$ ν = scan rate

i_{cat} = current with added acid i_p = current of catalyst without acid

Calculation of over potential

$E_{1/2}{}^{T} = E^{o}{}_{H+/H2} - (2.303RT/F) + \varepsilon_D - (RT/2F) \ln C_1/C^{o}{}_{H2}$

$E_{1/2}{}^{T}$ = theoretical half-wave potential of acetic acid reduction in MeCN

$E^{o}{}_{H+/H2}$ = 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

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

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

$C^o{}_{H2}$ = 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)BF_4.

1. i_p value:

i_p x initial volume / final volume = 32.79 μA x 5 mL / 5.035 mL = 32.56 μA

2. the ratio of i_{cat}/i_p.

i_{cat}/i_p = 2040.2 μA / 32.56 μA = 62.66

3. Calculation of TOF.

k_{obs}(TOF) = 1.94 x ν x $(i_{cat}/i_p)^2$ = 1.94 x 0.1 V/s x $(62.66)^2$ = 761 s^{-1}

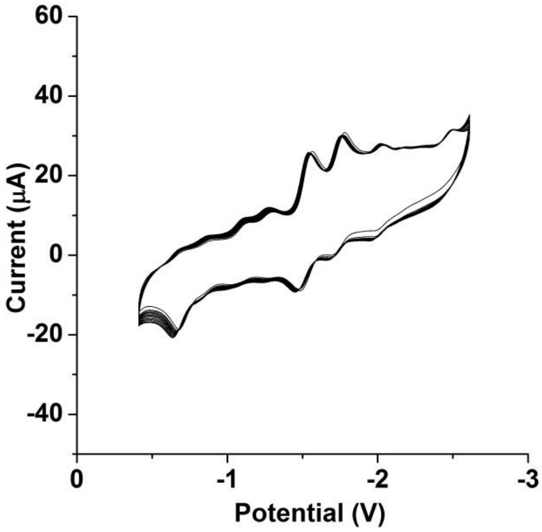


Figure S21. Cyclic voltammograms for [**1’**(CO)]$^+$ in MeCN solution with 50 scans.

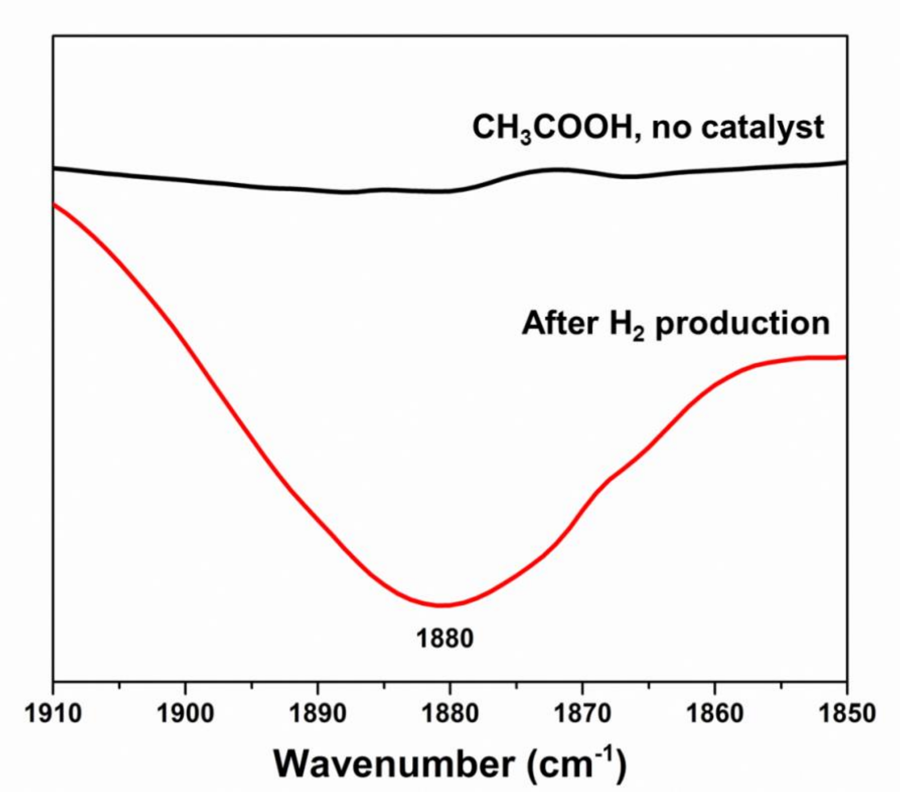


Figure S22. IR spectrum of [**1'**(CO)]$^+$ after electrochemical catalysis.

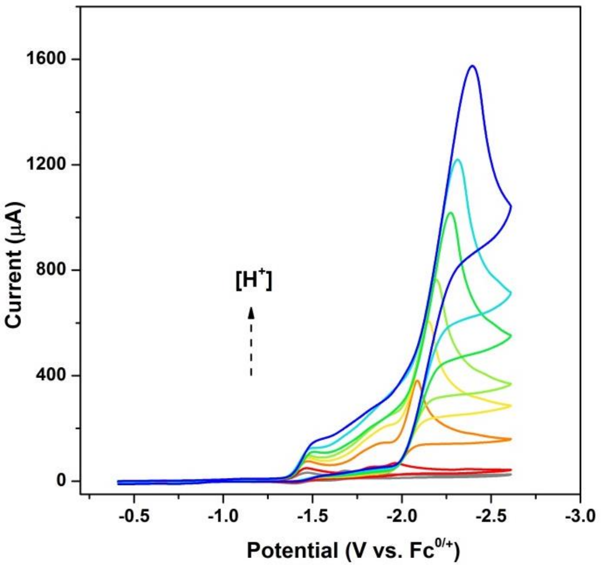


Figure S23. Cyclic voltammograms of [**1**(CO)]$^+$ and **[1'**(CO)]$^+$ (1 mM) with various amounts of acetic acid added. 0.1 *n*-NBu_4PF_6 in MeCN was employed as the supporting electrolyte; scan rate = 100 mV$^{\cdot}$ s^{-1}.

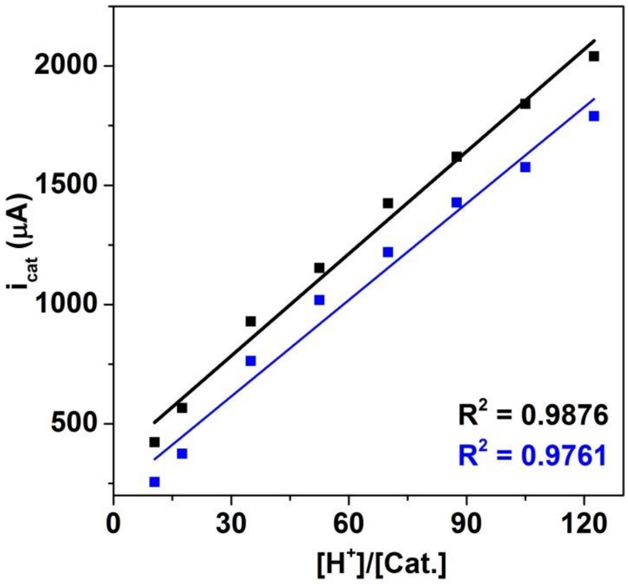
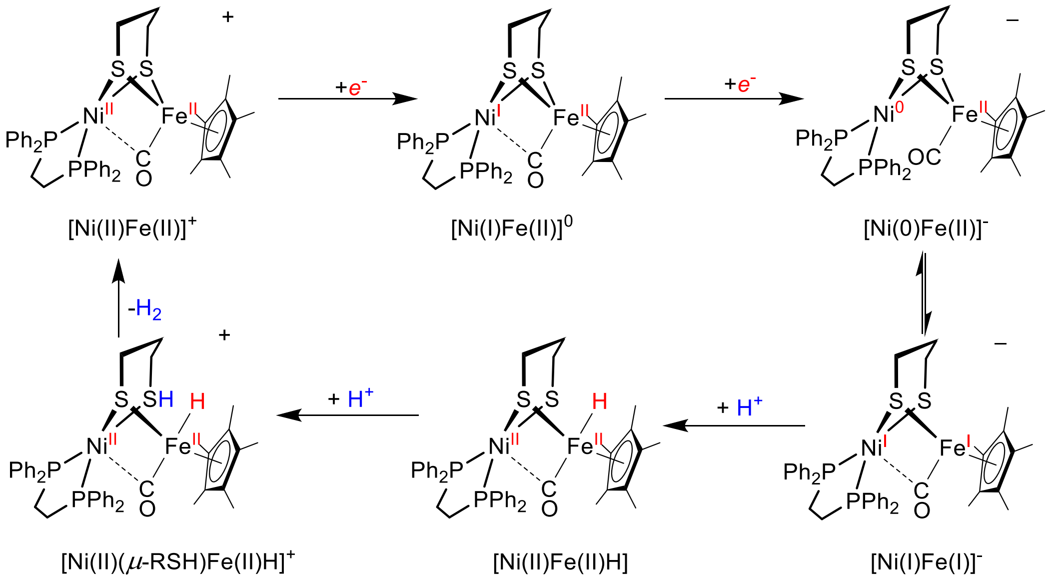


Figure S24. Plots of i_{cat} vs. [H$^+$]. For the mixture of [**1**(CO)]$^+$ and **[1’**(CO)]$^+$: y= 13.48*x +210.0 (blue plots); for **[1’**(CO)]$^+$, y= 14.28*x +356.3 (black plots).



Scheme S1. Proposed Mechanism for H_2 production by [**1'**(CO)]$^+$.

Reference

(1) M. Shmidt, G. Hoffmann, *J. Organomet. Chem.,* 1977, **124***,* C5-C8.

(2) C. Daniel, A. Didier, *Organometallics*, 1984, **3**, 1094–1100.