ORGANOMETALLICS

Thiolate-Bridged Nickel-Iron and Nickel-Ruthenium Complexes Relevant to the CO-Inhibited State of [NiFe]-Hydrogenase

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S Supporting Information

ABSTRACT: By employing $S(CH_2CH_2S^-)_2$ (tpdt) and O- $(CH_2CH_2S^-)_2$ (opdt) as bridging ligands, two nickel-iron and two nickel-ruthenium heterodimetallic complexes, $[Cp*M(\mu 1\kappa^3$ SSS': $2\kappa^2$ SS-tpdt)Ni(dppe)][PF₆] (1, M = Fe; 3, M = Ru) and $[Cp*M(\mu-1\kappa^3 SSO:2\kappa^2 SS-opdt)Ni(dppe)][PF_6] (2, M = Fe; 4, M =$ Ru) (Cp* = η^5 -C₅Me₅; dppe = Ph₂P(CH₂)₂PPh₂), were obtained by a one-pot synthetic method and were identified by spectroscopy and X-ray crystallography. At 1 atm of CO, the pendant oxygen atom dissociated from the iron or ruthenium center and rapidly transferred to the nickel center when a CO molecule attacked the iron or ruthenium center in 2 and 4. However, there was no similar reaction



occurring in 1 and 3 with the pendant sulfur atom. We confirmed the solid-state structure of the CO complex $[Cp*Fe(t-CO)(\mu-t)]$ $1\kappa^2 SS: 2\kappa^3 SSO-opdt)Ni(dppe)$ [PF₆] (5), which represents a possible configuration in the CO-inhibited state of [NiFe]hydrogenase and exhibits no catalytic activity in electrochemical proton reduction.

INTRODUCTION

Hydrogenases efficiently catalyze the oxidation of hydrogen and the reduction of protons for biological energy metabolism, which has inspired the development of catalysts using hydrogen as an energy source.¹ [NiFe]-hydrogenases are the most prevalent family in the three main classes of hydrogenases (FeFe, FeNi, and Fe) depending on their metal contents.² Because the active site of [NiFe]-hydrogenase features a Ni(μ_2 -S)Fe core structure,³⁻⁶ thiolate-bridged nickel—iron heterodimetallic complexes as biomimics have attracted considerable attention from bioinorganic chemists. In comparison to the large number of [FeFe]-hydrogenase model complexes,⁷ the number of [NiFe]-hydrogenase model complexes is small.⁸ Among these mimics, only a few compounds display biofunctional activity toward proton reduction⁹ and dihydrogen oxidation.¹⁰ Most of these functional models feature strong donor ligands, such as bidentate phosphine^{9b,c,10c} or Cp* (Cp* = η^5 -C₅Me₅) ligands, which can be formally viewed as a combination of three diatomic ligands such as CN⁻ and CO from the coordination number.¹¹ So far, [NiFe]-hydrogenase model complexes containing the bidentate phosphines and Cp* ligands are rare.¹²

Although several structural and functional mimics have been synthesized and the crystal structures of some intermediates in the enzymatic conversion have been determined, the catalytic mechanism of [NiFe]-hydrogenase remains controversial.¹³ To gain insight into the catalytic activity of [NiFe]-hydrogenase, chemists turned to investigations of the inhibitory effect of CO on [NiFe]-hydrogenase.¹⁴ Higuchi and co-workers produced a Ni-SCO state by X-ray crystallographic analysis, in which a CO

molecule reversibly binds to the nickel center (Figure 1).¹⁵ Lubitz and co-workers provided powerful experimental and



Figure 1. Two possible CO-inhibited forms of the active center of [NiFe]-hydrogenase.

theoretical data for the Ni-SCO state.¹⁶ Moreover, a [NiFe]hydrogenase model complex can achieve reversible coordination of CO at the nickel center.¹⁷ However, in 2011, Ogo et al. proposed a different mechanism for the inhibition of [NiFe]hydrogenase by CO.¹⁸ In this mechanism, CO as a π -acceptor ligand prefers to bind a low-spin Fe^{II} or Ru^{II} center rather than a Ni^{II} center and thus effectively inhibits H₂ oxidation of [NiFe]-hydrogenase. Studies on the activity of [NiFe]-hydrogenase model complexes with CO inhibitor are rare.¹⁷

Our group has focused on synthesizing thiolate-bridged diiron complexes as nitrogenase models for chemically biomimicking the nitrogen fixation process^{19,20} and constructing heteronuclear complexes for the structural simulation of metalloenzymes²¹ or catalytic transformations.²² Herein, to better understand the CO inhibitory effect on [NiFe]hydrogenase, we report the synthesis and reactivity toward

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inhibitor CO of the four heterobimetallic [NiFe]-hydrogenase model complexes [Cp*M(μ -1 κ ³SSS':2 κ ²SS-tpdt)Ni(dppe)]-[PF₆] (**1**, M = Fe; **3**, M = Ru) and [Cp*M(μ -1 κ ³SSO:2 κ ²SSopdt)Ni(dppe)][PF₆] (**2**, M = Fe; **4**, M = Ru) (dppe = Ph₂P(CH₂)₂PPh₂). The reactions of **2** and **4** with CO gave the two monocarbonyl complexes **5** and **6**. Moreover, electrochemical measurements of **5** confirmed that CO has an effect on the hydrogen release function.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Nickel–Iron and Nickel–Ruthenium Heterobimetallic Complexes $[Cp*M(\mu-1\kappa^3SSS':2\kappa^2SS-tpdt)Ni(dppe)][PF_6]$ (1, M = Fe; 3, M = Ru) and $[Cp*M(\mu-1\kappa^3SSO:2\kappa^2SS-opdt)Ni(dppe)] [PF_6]$ (2, M = Fe; 4, M = Ru). The nickel–iron heterobimetallic complexes 1 and 2 were synthesized by the reaction of [Ni(tpdt)(dppe)] or [Ni(opdt)(dppe)], prepared in situ from Li₂(tpdt) or Li₂(opdt) and NiCl₂(dppe), with another building block compound, $[Cp*Fe(MeCN)_3][PF_6]$,²³ in THF under an N₂ atmosphere at room temperature (Scheme 1). In

Scheme 1. Synthesis of Ni-Fe and Ni-Ru Complexes





"Reagents and conditions: (i) 1 equiv of $NiCl_2(dppe)$, 1 equiv of NH_4PF_{67} THF, – 78 °C to room temperature, 3 h, 75%; (ii) 1 equiv of AgPF₆₇, 1 equiv of CoCp₂₇ THF, room temperature, 2 h, 65%.

addition to this one-pot synthesis, the nickel–iron dinuclear complex 1 can also be synthesized in 49% yield by the self-assembly reaction of $[Cp*Fe(tpdt)]^{24}$ and $[NiCl_2(dppe)]$ in the presence of NH_4PF_6 and subsequent reductive dechlorination.

The above two nickel-iron complexes were characterized by ¹H NMR and ESI-HRMS spectra. According to the ¹H NMR spectrum, complexes 1 and 2 are diagmagnetic, presumably consisting of low-spin Ni^{II} and Fe^{II} ions. In the ¹H NMR spectra, the Cp* methyl proton signal of 1 appears at 1.16 ppm and that of 2 appears at 0.95 ppm. The slight difference in the chemical shift is attributed to the minor change of the coordination environment of the iron center. In contrast to the Cp* signal, the resonances of the dppe ligands in 1 and 2 are similar, which appear at 7.44, 7.55 ppm and at 7.42, 7.58 ppm, respectively. The ESI-HRMS spectra exhibit the molecular ion peaks $[1 - PF_6]^+$ and $[2 - PF_6]^+$ with m/z 799.1027 (calcd 799.1019) and 783.1243 (calcd 783.1248), which confirm the compositions of 1 and 2. By replacement of the building block $[Cp*Fe(MeCN)_3][PF_6]$ with $[Cp*Ru(MeCN)_3][PF_6]$,²⁵ nickel-ruthenium complexes 3 and 4 were also synthesized using a similar method. In comparison to the nickel-iron analogues, there is no obvious change in the spectroscopic data (see the Supporting Information).

Molecular Structures of 1-4. The molecular structures of complexes 1–4 were determined by X-ray crystallography. Their ORTEP drawings are shown in Figure 2, and selected bond lengths and angles are given in Table 1. The structures of

Table 1. Selected Bond Distances (Å) and Angles (deg) in Complexes $1{-}4$

	1	2	3	4
Ni-M ^a	2.5941(8)	2.5717(9)	2.6329(9)	2.6236(7)
Ni-S1	2.1888(13)	2.1878(13)	2.1918(18)	2.1879(15)
Ni-S2	2.1787(13)	2.1804(13)	2.1798(18)	2.1888(15)
Ni-P1	2.2740(13)	2.2607(14)	2.2839(18)	2.1796(15)
Ni-P2	2.1890(14)	2.1759(14)	2.1718(19)	2.2796(14)
$M-S1^{a}$	2.2333(13)	2.2319(14)	2.2981(17)	2.2945(14)
$M-S2^{a}$	2.2256(14)	2.2191(14)	2.2998(19)	2.3102(13)
$M-X^{a,b}$	2.2192(15)	2.049(4)	2.3015(18)	2.170(4)
M-Cp* ^a	1.7617(6)	1.7462(7)	1.8821(5)	1.8423(4)
Ni-S1-M	71.83(4)	71.16(4)	71.76(5)	71.61(4)
Ni-S2-M	72.16(4)	71.53(4)	71.94(5)	71.29(4)
NiS1S2/ NiP1P2	88.68(4)	87.53(5)	89.34(6)	89.36(4)
NiS1S2/ MS1S2	27.24(5)	24.76(6)	28.46(7)	23.71(6)
$^{a}M = Fe, Ru$	$b^{b}X = S, O.$			

complexes 1 and 2 all contain a butterfly-shaped Ni(μ_2 -S)₂Fe core with dihedral angles (NiS1S2/FeS1S2) of 27.24(5) and 24.76(6)°, which are smaller than those observed in the



Figure 2. Molecular structures of complexes 1–4. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and counteranion PF_6^- are omitted for clarity.

enzymes (46.14–99.15°).¹² After the iron atom is replaced with a ruthenium atom, the dihedral angle (NiS1S2/RuS1S2) of 3 is slightly larger than that of 1, whereas the dihedral angle of 4 is slightly smaller than that of 2, which suggests that the dihedral angles are affected by the coordination environment of the metal center. The metal-metal distances (Fe-Ni or Ru-Ni) of 2.5717(9) - 2.6329(9) Å are suggestive of strong bonding interactions between two metal centers. The Ni-Fe distances of 2.5941(8) and 2.5717(9) Å in 1 and 2 are shorter than those in other [NiFe]-hydrogenase model complexes with a {Cp*Fe} fragment $(2.954(1)-3.182(2) \text{ Å})^{21b,26}$ and with tpdt ligand as a bridging ligand (2.8001(6) and 3.2960(5) Å).²⁷ However, the distances are close to 2.57 and 2.58 Å in the Ni-R state of the [NiFe]-hydrogenase recently reported by the Lubitz group.⁶ In the [NiFe]-hydrogenase, the nickel center binds to four sulfur atoms of cysteine in a tetrahedral geometry, whereas the nickel center adopts a square-planar arrangement and not the biomimetic geometry in most models with S₄ ligands. When the S_4 ligand is replaced with a P_2S_2 ligand set around the nickel center, the nickel-iron distances decrease and the configuration of the nickel center is similar to that in the enzyme.⁶ In complexes 1-4, the nickel centers of the NiS₂P₂ fragments all adopt distorted-tetrahedral arrangements, which indicates that the nickel center has undergone a complete tetrahedral twist after binding the square-planar precursor [NiCl₂(dppe)] to the FeCp* or RuCp* unit. The NiS₂P₂ fragments bind to the {FeCp*} or {RuCp*} units via tpdt or opdt ligands, which can provide two bridging thiolate donors and a thioether or ether donor. Because the Cp* anion can be viewed as three diatomic ligands from the electronic influences, the iron or ruthenium center can be viewed in a pseudocathedral coordination arrangement, in which the thioether or ether ligand occupies the apical position. The Ni-S bond lengths are 2.1787(13)-2.1918(18) Å in complexes 1–4, which fall in the usual range of [NiFe]-hydrogenase model complexes.⁸ The Fe-S bond lengths of 2.2191(14)-2.2333(13) Å in 1 and 2 are very close to the Ru-S bond lengths of 2.2945(14)-2.3102(13) Å in 3 and 4. Furthermore, the Fe/Ru-Cp* centroid distances in 1-4 are 1.7462(7)-1.8821(5) Å, which are shorter than those for paramagnetic nickel-iron complexes (2.007-2.029 Å).²⁶

Reactivity of Complexes 1–4 toward CO. The above complexes can be viewed as [NiFe]-hydrogenase models on the basis of the tetrahedral geometry of the nickel center and the butterfly-type nickel—iron core structure. Hence, we investigated the reactivity of complexes 1–4 toward H₂ and CO as enzymatic substrate and inhibitor, respectively. Complexes 1–4 cannot react with H₂, even under heating and elevated gas pressure. However, complexes 1, 2, and 4 can react with 1 atm of CO at room temperature. When a CH₂Cl₂ solution of 1 was exposed to 1 atm of CO at room temperature, decomposition occurred to give several mononuclear iron complexes, as identified by the ESI-MS spectrum. According to the ¹H NMR and crystallographic data, we confirmed that the main product is the known complex [Cp*Fe(dppe)(CO)][PF₆] (Scheme 2).²³

In contrast, after 2 was treated with 1 atm of CO at room temperature for 20 min, the dinuclear CO complex [Cp*Fe(*t*-CO)(μ -1 κ ²SS:2 κ ³SSO-opdt)Ni(dppe)][PF₆] (5) was obtained in 70% yield. In the infrared spectrum of 5, the strong band at 1904 cm⁻¹ is attributed to a terminal CO stretching vibration. This value is distinctly lower than the 2143 cm⁻¹ for a free CO molecule²⁸ and is close to those of iron complexes with the {Cp*FeCO} motif.^{21b} The molecular ion peak [$5 - PF_6$]⁺ at

Scheme 2. Reactivity of Nickel–Iron Complexes 1 and 2 toward CO



m/z 811.1184 (calcd 811.1196) in the ESI-HRMS spectrum confirms the existence of the carbonyl ligand in 5. The solid-state structure of 5 was determined by X-ray crystallography (Figure 3). It is unexpected that the carbonyl ligand terminally



Figure 3. Molecular structure of complex **5**. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Fe1…Ni1 3.1648(10), 3.1618(11); Ni1–S1 2.2508(16), 2.3884(16); Ni1–S2 2.2371(15), 2.2465(16); Fe1–S1 2.3085(17), 2.3080(18); Fe1–S2 2.2994(16), 2.2960(16); Ni1–O1 2.345(4), 2.345(4); Fe1–C15 1.737(7), 1.761(8); C15–O2 1.147(8), 1.133(8); Fe1–S1–Ni1 88.24(5), 88.11(6); Fe1–S2–Ni1 88.14(6), 88.21(6); Fe1–C15–O2 171.0(6), 170.1(6); Ni1S1S2/Ni1P1P2 10.28(5), 9.67(5); Ni1S1S2/Fe1S1S2 38.84(5), 38.32(7).

binds to the iron center and not the nickel center. In the precursor complex 2, the iron center is saturated; thus, we initially proposed that CO would first bind to the nickel center. In addition, the Tatsumi group reported that a [NiFe]hydrogenase model with a saturated iron center reacted with CO to give a CO complex, in which the CO ligand was terminally bound to the nickel center.¹⁷ To verify this speculation, we performed in situ IR studies on this carbonylation process. However, the result shows only one carbonyl peak, which suggests no transfer process of the carbonyl between two metal centers. The geometry of the nickel center changes from a tetrahedron to a tetragonal pyramid. The Ni–O bond length of 2.345(4) Å is longer than two Ni–P lengths (2.1847(16), 2.1805(16) Å and 2.1786(15), 2.1795(15) Å) and Ni-S lengths (2.2508(16), 2.3884(16) Å and 2.2371(15), 2.2465(16) Å). The CO ligand was coordinated to the iron center with Fe-C lengths of 1.737(7), 1.761(8) Å and Fe-C-O angles of 170.0(6), 170.1(6)°. The C-O bond lengths of 1.147(8) and 1.133(8)

Å are almost comparable to that of a free CO of $1.128 \text{ Å}.^{28}$ The Fe–Cp* bond lengths are 1.7319(7) and 1.7353(9) Å, which are similar to those of complexes 1 and 2.

We also investigated the reactivity of the Ni-Ru complexes 3 and 4 toward CO. Under a 1 atm CO atmosphere, no cleavage of the ruthenium-sulfur bond occurred in complex 3. This result suggests that the thioether sulfur atom of the tpdt ligand coordinates tightly to the ruthenium center. Even with increasing temperature and reaction time, there is no reaction. However, nickel-ruthenium complex 4 can convert the CO complex $[Cp*Ru(t-CO)(\mu-1\kappa^2SS:2\kappa^3SSO-opdt)Ni(dppe)]$ - $[PF_6]$ (6) on exposure to 1 atm of CO. In contrast to the rapid interaction of nickel-iron complex 2 with CO, it is necessary to increase the reaction time for complete transformation from 4 to 6. Moreover, complex 6 does not react with excess CO to decompose the mononuclear complex or produce a multicarbonyl complex. In the ¹H NMR spectrum of 6, the peaks at 7.59-8.12 and 1.67 ppm are attributed to the protons of the phenyl in the dppe ligand and the methyl protons of the Cp* ligand, respectively. In the IR spectrum, the CO stretching vibration peak appears at 1903 cm⁻¹, which is very close to that of complex 5. The spectra suggest that there is no obvious change in the electronic properties of the iron and ruthenium centers in the same coordination environment. However, this value of the CO stretching vibration is 18 cm⁻¹ lower than that observed for $[Ni(xbsms)Ru(CO)Cp^*][PF_6]$ $(H_2xbsms = 1,2-bis(4-mercapto-3,3-dimethyl-2-thiabutyl)$ benzene), which indicates that the $\{P_2NiS_2\}$ subunit can be viewed as a more strongly electron donating metallodithiolate ligand²⁹ in comparison to the ${NiS_4}$ framework to increase the electron density at the ruthenium center.³⁰ The ESI-MS spectrum of 6 also confirms the existence of the carbonyl subunit.

Scheme 3. Reactivity of Nickel–Ruthenium Complexes 3 and 4 toward CO



Complex **6** was further characterized by X-ray diffraction analysis. The solid-state structure of **6** is similar to that of complex **5**. The CO ligand is terminally coordinated to the ruthenium center, in which the Ru–C bond lengths and Ru– C–O bond angle are 1.854(7), 1.857(7) Å and 168.6(6)°, respectively. The Ru–C15 bond lengths of **6** are 1.854(7) and 1.857(7) Å, respectively. The C–O bond distances are 1.155(8) and 1.146(8) Å, which are very close to those of **5** (1.147(8), 1.133(8) Å). The Ni(II) center has a distortedsquare-pyramidal geometry with an ether oxygen atom occupying the apical position. Upon introduction of the CO ligand, the nickel center has undergone a complete configuration twist from tetrahedron to tetragonal pyramid. **Electrochemical Characterization.** The redox properties of complexes 1-4 were studied by cyclic voltammetry. The electrochemical data of complexes 1-4 are given in Table 2.

	1st $E_{1/2}$	2nd $E_{1/2}$ or $E_{\rm red}$
1	-0.51	-1.55
2	-0.45	-1.48
3		-1.55
4	-1.12	-1.57

^{*a*}In CH₂Cl₂ (1 mM) recorded at scan rates of 100 mV/s with ^{*n*}Bu₄NPF₆ (0.1 M) as the supporting electrolyte. All potentials are referred to the Fc^{+/0} redox couple.

Complex 1 displays a quasi-reversible reduction event at $E_{1/2} = -0.51$ V versus Fc^{+/0} and an irreversible reduction event at $E_{\rm red} = -1.55$ V, whereas complex 2 shows two quasi-reversible reduction events at $E_{1/2} = -0.45$ and -1.48 V. This result indicates that the change in the coordination sphere of iron has an effect on the redox behaviors of 1 and 2. In comparison with the nickel-iron complexes 1 and 2, the cyclic voltammograms of nickel-ruthenium compounds 3 and 4 are complicated. Complex 3 underwent one obvious reduction event at $E_{\rm red} = -1.55$ V, and complex 4 underwent two reduction processes at $E_{1/2} = -1.12$ V and $E_{\rm red} = -1.57$ V.

The electrocatalytic proton reduction properties of 1-4 were investigated. First, we examined the cyclic voltammograms of 1 and 2 in the presence of different amounts of the strong acid HBF₄, but the results showed that these two complexes are unstable under these conditions. Accordingly, the weaker acid salt $[HNEt_3][BF_4]$ was chosen as the proton source. Complexes 1 and 2 are active catalysts for electrocatalytic proton reduction on the basis of the electrochemical measurements, but the catalytic rate of 2 is slower than that of 1 according to the plot of i_c/i_p vs [HNEt₃][BF₄] (Figure S38 in the Supporting Information). For 2, upon addition of 1 equiv of $[HNEt_3][BF_4]$ to a CH_2Cl_2 solution of 2, the cyclic voltammogram had an increased cathodic current (Figure S31 in the Supporting Information). The current height of the reduction peak at -1.53 V increases linearly as the acid/catalyst concentration ratio increases (Figure 4) and as the potential is shifted toward a more negative cathodic value, which is diagnostic of the electrocatalytic proton reduction demonstrated by cyclic voltammetry. Hydrogen formation was



Figure 4. Cyclic voltammograms of 2 (1 mM in 0.1 M $^{n}Bu_{4}NPF_{6}$ in CH₂Cl₂ under Ar) with increments of [HNEt₃][BF₄] (0, 1, 5, 10, 15, 20, 30, and 40 mM).

evidenced by gas chromatographic analysis, which is consistent with electrochemical measurements. In contrast to the case for nickel–iron complexes 1 and 2, the nickel–ruthenium complexes 3 and 4 were not electrocatalysts because they are unstable in the presence of only small amounts of $[HNEt_3]$ - $[BF_4]$ according to the cyclic voltammogram.

To provide experimental evidence for the inhibitory effect of CO on the function of [NiFe]-hydrogenase, the electrocatalytic proton reduction properties of CO complex 5 were also explored. In the presence of different amounts of [HNEt₃]-[BF₄], there was no increasing trend of the reduction peak current in the cyclic voltammogram of 5. This result indicates that complex 5 is not active for the electrochemical proton reduction, because the CO ligand inhibits the substrate binding to the iron center. Meanwhile, electrocatalytic proton reduction properties of 1 and 2 under a CO atmosphere under the same conditions were also investigated. Complex 1 decomposed into unknown products under these conditions, as confirmed by the complicated cyclic voltammogram. In addition, there is no linear increase phenomenon of reduction current in the cyclic voltammogram of 2, which suggests that no catalytic process occurred. This result further proves a CO inhibitory effect on the proton reduction to hydrogen.

CONCLUSION

In summary, the four [NiFe]-hydrogenase model complexes $[Cp^*M(\mu-1\kappa^3SSS':2\kappa^2SS-tpdt)Ni(dppe)][PF_6]$ (1, M = Fe; 3, M = Ru) and $[Cp^*M(\mu-1\kappa^3SSO:2\kappa^2SS-opdt)Ni(dppe)][PF_6]$ (2, M = Fe; 4, M = Ru) were constructed by a one-pot synthetic method. When opdt was used as a bridging ligand, complexes 2 and 4 reacted with CO to give $[Cp^*M(t-CO)(\mu-1\kappa^2SS:2\kappa^3SSO-opdt)Ni(dppe)][PF_6]$ (5, M = Fe; 6, M = Ru). During the formation processes of 5 and 6, CO attacks the saturated iron center, and the pendant oxygen atom rapidly transfers to the nickel center. These structures are similar to the CO-inhibited state of [NiFe]-hydrogenase from the configurations of the metal centers and the coordination number. In addition, complex 2 is active for proton reduction, but complex 5 is not an active catalyst. This fact provides the experimental data for the CO inhibitory effect on hydrogen evolution.

EXPERIMENTAL SECTION

General Procedures. All manipulations were routinely conducted under an argon atmosphere, using standard Schlenk techniques. All solvents were dried and distilled over an appropriate drying agent under argon. Cp*H,³¹ [NiCl₂(dppe)],³² [Cp*Fe(MeCN)₃][PF₆],²³ [Cp*Fe(tpdt)],²⁴ and [Cp*Ru(MeCN)₃][PF₆],²⁵ were prepared according to literature procedures. Anhydrous FeCl₂ (Aldrich), S(CH₂CH₂SH)₂ (Aldrich), and O(CH₂CH₂SH)₂ (Aldrich) were used without further purification.

Spectroscopic Measurements. The ¹H NMR spectra were recorded on a Brüker 400 Ultra Shield spectrometer. Infrared spectra were recorded on a NEXVSTM FT-IR spectrometer. Elemental analyses were performed on a Vario EL analyzer. ESI-MS were recorded on a UPLC/Q-Tof micro spectrometer.

Electrochemistry. Electrochemical measurements were recorded using a BAS-100 W electrochemical potentiostat at a scan rate of 100 mV/s. Cyclic voltammetry experiments were performed in a threeelectrode cell under argon at room temperature. The working electrode was a glassy-carbon disk (diameter 3 mm), the reference electrode was a nonaqueous Ag/Ag⁺ electrode, the auxiliary electrode was a platinum wire, and the supporting electrolyte was 0.1 M "Bu₄NPF₆ in CH₂Cl₂. All potentials reported are quoted relative to the FeCp₂/FeCp₂⁺ couple. Electrocatalysis studies were performed by the stepwise addition of different amounts of $[{\rm HEt_3N}][{\rm BF_4}]$ with a microsyringe.

X-ray Crystallography Procedures. The data were obtained on a Brüker SMART APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were performed using the SADABS program.³³ Structures were solved by direct methods and were refined by full-matrix least squares on the basis of all data using F^2 in Shelx97.³⁴ All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were generated and refined in ideal positions. Crystal data and collection details for 1–6 are given in Tables S1–S3 in the Supporting Information.

Preparation of $[Cp*Fe(\mu-1\kappa^3SSS':2\kappa^2SS-tpdt)Ni(dppe)][PF_6]$ (1). NiCl₂(dppe) (265 mg, 0.5 mmol) was added to a stirred suspension of Li₂(tpdt) in THF (10 mL), prepared by the reaction of "BuLi (0.45 mL, 2.2 M solution in *n*-hexane, 1.0 mmol) and S(CH₂CH₂SH)₂ (77 mg, 0.5 mmol) at 0 °C, and the solution was stirred at room temperature for 1 h. Then, the aubergine solution gradually turned into an olive green solution when [Cp*Fe(MeCN)₃]-[PF₆] (230 mg, 0.5 mmol) was added. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane three times, extracted with CH₂Cl₂ (10 mL), and then dried in vacuo. The product, $[Cp*Fe(\mu-1\kappa^3 SSS':2\kappa^2 SS-tpdt)Ni(dppe)][PF_6]$ (1; 424 mg, 0.45 mmol, 90%), was obtained as a brownish green powder. Crystals suitable for X-ray diffraction were obtained from a saturated CH₂Cl₂ solution layered with *n*-hexane at room temperature. ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ 1.16 (s, 15 H, Cp*-CH₃), 1.59 (m, 4 H, Ph₂P(CH₂)₂PPh₂-CH₂), 2.32-2.74 (m, 8 H, tpdt-H), 7.44-7.55 (m, 20 H, Ph-H). ESI-HRMS: calcd for $[1 - PF_6]^+$ 799.1019; found 799.1027. Anal. Calcd for C40H47FeNiP2S3: C, 60.02; H, 5.92; S, 12.02. Found: C, 60.10; H, 5.86; S, 12.09.

Preparation of $[Cp*Fe(\mu-1\kappa^3SSO:2\kappa^2SS-opdt)Ni(dppe)][PF_6]$ (2). NiCl₂(dppe) (210 mg, 0.4 mmol) was added to a stirred suspension of Li2(opdt) in THF (10 mL), prepared by the reaction of ⁿBuLi (0.36 mL, 2.2 M solution in *n*-hexane, 0.8 mmol) and O(CH₂CH₂SH)₂ (55 mg, 0.4 mmol) at 0 °C, and the solution was stirred at room temperature for 1 h. Then, the aubergine solution gradually turned into a yellow solution when [Cp*Fe(MeCN)₃][PF₆] (184 mg, 0.4 mmol) was added. All volatiles were removed under vacuum, and the residue was washed with n-hexane three times, extracted with CH₂Cl₂ (10 mL), and then dried in vacuo. The product, $[Cp*Fe(\mu-1\kappa^3SSO:2\kappa^2SS-opdt)Ni(dppe)][PF_6]$ (2; 324 mg, 0.35 mmol, 88%), was obtained as a brownish yellow powder. Crystals suitable for X-ray diffraction were obtained from a saturated CH₂Cl₂ solution layered with *n*-hexane at room temperature. ¹H NMR (400 MHz, CD_2Cl_2 , ppm): δ 0.95 (s, 15 H, Cp^*-CH_3), 1.48 (m, 4 H, Ph₂P(CH₂)₂PPh₂-CH₂), 2.66-2.70 (m, 8 H, opdt-H), 7.42-7.58 (m, 20 H, Ph-H). ESI-HRMS: calcd for $[2 - PF_6]^+$ 783.1248; found 783.1243. Anal. Calcd For C40H47FeNiOP2S2: C, 61.25; H, 6.04; S, 8.18. Found: C, 61.19; H, 6.10; S, 8.10.

Preparation of $[Cp*Ru(\mu-1\kappa^3SSS':2\kappa^2SS-tpdt)Ni(dppe)][PF_6]$ (3). NiCl₂(dppe) (289 mg, 0.55 mmol) was added to a stirred suspension of Li₂(tpdt) in THF (5 mL), prepared by the reaction of ⁿBuLi (0.5 mL, 2.2 M solution in *n*-hexane, 1.1 mmol) and S(CH₂CH₂SH)₂ (85 mg, 0.55 mmol) at 0 °C, and the solution was stirred at room temperature for 1 h. Then, the aubergine solution gradually turned into an olive green solution when [Cp*Ru-(MeCN)₃][PF₆] (277 mg, 0.55 mmol) was added. All volatiles were removed under vacuum, and the residue was washed with n-hexane three times, extracted with CH2Cl2, and then dried in vacuo. The product, $[Cp*Ru(\mu-1\kappa^3SSS':2\kappa^2SS-tpdt)Ni(dppe)][PF_6]$ (3; 415 mg, 0.42 mmol, 76%), was obtained as a brownish green powder. Crystals suitable for X-ray diffraction were obtained from a saturated CH₂Cl₂ solution layered with *n*-hexane at room temperature. ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ 1.39 (s, 15 H, Cp*-CH₃), 2.16 (m, 4 H, Ph₂P(CH₂)₂PPh₂-CH₂), 2.47-2.51 (m, 8 H, tpdt-H), 7.45-7.55 (m, 20 H, Ph-H). ESI-HRMS: calcd for $[3 - PF_6]^+$ 845.0715; found 845.0715. Anal. Calcd for C40H47RuNiP2S3: C, 56.81; H, 5.60; S, 11.37. Found: C, 56.74; H, 5.68; S, 11.30.

Preparation of $[Cp*Ru(\mu-1\kappa^3SSO:2\kappa^2SS-opdt)Ni(dppe)][PF_6]$ (4). NiCl₂(dppe) (210 mg, 0.4 mmol) was added to a stirred suspension of Li₂(opdt) in THF (10 mL), prepared by the reaction of "BuLi (0.36 mL, 2.2 M solution in n-hexane, 0.8 mmol) and O(CH₂CH₂SH)₂ (55 mg, 0.4 mmol) at 0 °C, and the solution was stirred at room temperature for 1 h. Then, the red solution gradually turned into a yellow-green solution when $[Cp*Ru(MeCN)_3][PF_6]$ (202 mg, 0.4 mmol) was added. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane three times, extracted with CH2Cl2, and then dried in vacuo. The product, $[Cp*Ru(\mu-1\kappa^3SSO:2\kappa^2SS-opdt)Ni(dppe)][PF_6]$ (4; 311 mg, 0.32 mmol, 80%), was obtained as a brownish yellow powder. Crystals suitable for X-ray diffraction were obtained from a saturated CH₂Cl₂ solution layered with n-hexane at room temperature. ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ 0.95 (s, 15 H, Cp*-CH₃), 1.50 (m, 4 H, Ph₂P(CH₂)₂PPh₂-CH₂), 2.66-2.71 (m, 8 H, opdt-H), 7.43-7.57 (m, 20 H, Ph-H). ESI-HRMS: calcd for $[4 - PF_6]^+$ 829.0944; found 829.0923. Anal. Calcd for C40H47RuNiOP2S2: C, 57.91; H, 5.71; S, 7.73. Found: C, 57.82; H, 5.64; S, 7.65.

Preparation of $[Cp*Fe(t-CO)(\mu-1\kappa^2SS:2\kappa^3SSO-opdt)Ni-$ (dppe)][PF₆] (5). Under 1 atm of CO, a solution of $[Cp*Fe(\mu 1\kappa^3$ SSO: $2\kappa^2$ SS-opdt)Ni(dppe)][PF₆] (2; 464 mg, 0.5 mmol) in THF (10 mL) was stirred at room temperature for 20 min. During this time, the solution changed gradually from brownish green to brownish vellow. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane three times and then dried in vacuo. The product, $[Cp*Fe(t-CO)(\mu-1\kappa^2SS:2\kappa^3SSO-opdt)Ni(dppe)][PF_6]$ (5; 343 mg, 0.35 mmol, 70%), was obtained as a brownish yellow powder. Crystals of 5 suitable for X-ray diffraction were obtained from a saturated CH₂Cl₂ solution layered with n-hexane at room temperature. ¹H NMR (400 MHz, CD_2Cl_2 , ppm): δ 1.51 (s, 15 H, Cp*-CH₃), 1.80-3.40 (m, 4 H, Ph₂P(CH₂)₂PPh₂-CH₂), 2.67-2.81 (m, 8 H, opdt-H), 7.55–7.93 (m, 20 H, Ph-H). IR (KBr): $\tilde{\nu}_{CO}$ 1904 ¹. ESI-HRMS: calcd for $[5 - PF_6]^+$ 811.1196; found 811.1184. cm^{-1} Anal. Calcd For C₄₁H₄₇FeNiO₂P₂S₂: C, 60.61; H, 5.83; S, 7.89. Found: C, 60.52; H, 5.90; S, 7.97.

Preparation of $[Cp*Ru(t-CO)(\mu-1\kappa^2SS:2\kappa^3SSO-opdt)Ni-$ (dppe)][PF₆] (6). Under 1 atm of CO, a solution of $[Cp*Ru(\mu 1\kappa^3$ SSO: $2\kappa^2$ SS-opdt)Ni(dppe)][PF₆] (6; 292 mg, 0.3 mmol) in THF (10 mL) was stirred at room temperature for 12 h. During this time, the solution gradually changed from brownish green to brownish yellow. All volatiles were removed under vacuum, and the residue was washed with n-hexane three times and then dried in vacuo. The product, $[Cp*Ru(t-CO)(\mu-1\kappa^2SS:2\kappa^3SSO-opdt)Ni(dppe)][PF_6]$ (6; 220 mg, 0.22 mmol, 73%), was obtained as a brownish-yellow powder. Crystals of 6 suitable for X-ray diffraction were obtained from a saturated CH₂Cl₂ solution layered with *n*-hexane at room temperature. ¹H NMR (400 MHz, CD_2Cl_2 , ppm): δ 1.67 (s, 15 H, Cp*-CH₃), 2.82–3.37 (m, 4 H, Ph₂P(CH₂)₂PPh₂-CH₂), 2.15–2.42 (m, 8 H, opdt-H), 7.59–8.12 (m, 20 H, Ph-H). IR (KBr): $\tilde{\nu}_{CO}$ 1903 cm⁻¹. ESI-HRMS: calcd for $[6 - PF_6]^+$ 857.0894; found 857.0716. Anal. Calcd for C₄₁H₄₇RuNiO₂P₂S₂: C, 57.42; H, 5.52; S, 7.48. Found: C, 57.48; H, 5.44; S, 7.41.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b01035.

X-ray crystallographic data and spectroscopic data (PDF)

- X-ray crystallographic data for 1 (CIF)
- X-ray crystallographic data for 2 (CIF)
- X-ray crystallographic data for 3 (CIF)
- X-ray crystallographic data for 4 (CIF)
- X-ray crystallographic data for 5 (CIF)
- X-ray crystallographic data for 6 (CIF)

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Notes

The authors declare no competing financial interest.

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