Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Novel reactions of homodinuclear Ni_2 complexes $[Ni(RN_{Py}S_4)]_2$ with $Fe_3(CO)_{12}$ to give heterotrinuclear $NiFe_2$ and mononuclear Fe complexes relevant to [NiFe]- and [Fe]-hydrogenases

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(1) Preparation of 2,6-bis(hydroxymethyl)-4-*i*-propylpyridine

This new precursor was prepared from the previously reported compound 2,6-bis(methoxycarbonyl)-4-*i*-propylpyridine.[1] A mixture consisting of 2,6-bis(methoxycarbonyl)-4-*i*-propylpyridine (2.373 g, 10 mmol), $NaBH_4$ (2.079 g, 55 mmol) and EtOH (100 mL) was stirred at 0 °C for 1 h, at room temperature for 1 h, and at reflux temperature for about 10 h until the fluorescence TLC analysis showed that the starting material 2,6-bis(methoxycarbonyl)-4-*i*-propylpyridine was completely consumed. To the resulting mixture was added acetone (20 mL) and then the mixture was refluxed for 1 h. After solvents were removed, a saturated aqueous Na_2CO_3 solution (20 mL) was added and then the mixture was refluxed for 1 h. After the mixture was cooled to room temperature and water (50 mL) was added, the mixture was extracted with ethyl acetate (50 mL×4) and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the drying agent and solvents, the residue was subjected to column chromatography on silica gel using $MeOH/CH_2Cl_2$ (v/v = 1:10) as an eluent to give 2,6-bis(hydroxymethyl)-4-*i*-propylpyridine (1.285 g, 71%) as a white solid, mp 73–75 °C. Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.09; H, 8.03; N, 7.62. IR (KBr disk): 3283 (s), 2964 (s), 1611 (vs), 1085 (vs), 874 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 1.18 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 2.79–2.86 (m, 1H, C*H*(CH$_3$)$_2$), 4.63 (s, 4H, 2CH$_2$), 4.81 (br.s, 2H, 2OH), 7.04 (s, 2H, C$_5$H$_2$N), ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): 23.1, 33.7 (CH(CH$_3$)$_2$), 64.5 (CH$_2$), 117.9, 159.0, 159.7 (C$_6$H$_4$) ppm. MS (ESI, CH$_2$Cl$_2$): m/z 182.2 [M$^+$].

(2) Preparation of 2,6-bis[(tosyloxy)methyl]-4-*i*-propylpyridine

This new starting material was prepared from the above-prepared precursor by using a reported procedure with some modifications.[2] To a stirred mixture consisting of 2,6-bis(hydroxymethyl)-4-*i*-propylpyridine (1.813 g, 10 mmol), CH$_2$Cl$_2$ (60 mL), and 40 % aqueous KOH solution (60 mL), tosyl chloride (3.81 g, 20 mmol) was added. The mixture was stirred at 0 °C for 1 h and at room temperature for about 4 h until the fluorescence TLC analysis showed that the starting material 2,6-bis(hydroxymethyl)-4-*i*-propylpyridine was completely consumed. After water (60 mL) was added, the resulting mixture was extracted with CH$_2$Cl$_2$ (60 mL×3) and then the combined organic phase was dried over anhydrous MgSO$_4$. After removal of the drying agent and solvents, the residue was recrystallized from CH$_2$Cl$_2$/hexane to give 2,6-bis[(tosyloxy)methyl]-4-*i*-propylpyridine (4.308 g, 88%) as a white solid, mp 59−61°C. Anal. Calcd for C$_{24}$H$_{27}$NO$_6$S$_2$： C, 58.88; H, 5.56; N, 2.86. Found: C, 58.81; H, 5.59; N, 2.96. IR (KBr disk): 2966 (m), 1609 (s), 1364 (vs), 1176 (vs), 834 (s), 554 (vs) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 1.18 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 2.43 (s, 6H, 2C$_6$H$_4$C*H*$_3$), 2.82–2.86 (m, 1H, C*H*(CH$_3$)$_2$), 5.02 (s, 4H, 2CH$_2$), 7.12 (s, 2H, C$_5$H$_2$N), 7.32, 7.79 (dd, AX system, J = 8.2 Hz, 8H, 2C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): 21.8 (C$_6$H$_4$*C*H$_3$), 23.1, 33.9 (CH(CH$_3$)$_2$), 71.7 (C$_5$H$_2$N), 119.9, 128.2, 130.0, 132.9, 145.2, 153.5, 160.2 (C$_6$H$_4$) ppm. MS (ESI, CH$_2$Cl$_2$): m/z 490.3 [M$^+$].

2. Thermal decomposition experiments of trinuclear complexes 2a-2e.

A 50 mL three-necked flask equipped with a magnetic stir-bar, a serum cap, a N_2 inlet tube and a reflux condenser topped with a N_2 outlet tube was charged with **2a** (35 mg, 0.05 mmol) and CH_2Cl_2 (5 mL). After the stirred mixture was refluxed for 12 h, it was subjected to flash column chromatography under anaerobic conditions. First, CH_2Cl_2 eluted a brown-red band from which the unreacted **2a** (21 mg, 61%) was recovered. Then, CH_2Cl_2/acetone (v/v = 4:1) eluted a red band from which product **3a** (5 mg, 21%) was obtained.

(2) Thermal decomposition experiment of 2a in refluxing CH_2Cl_2 in air.

A 50 mL three-necked flask equipped with a condenser was charged with **2a** (35 mg, 0.05 mmol) and CH_2Cl_2 (5 mL). The mixture was refluxed for 12 h and then the resulting mixture was subjected to flash column chromatography in air. No **2a** was recovered due to its decomposition during the refluxing and isolation courses in air. CH_2Cl_2/acetone (v/v = 4:1) eluted a tiny red band from which product **3a** (2.5 mg, 10%) was obtained.

A 50 mL three-necked flask equipped with a magnetic stir-bar, two serum caps and a N_2 inlet tube was charged with **2b** (36 mg, 0.05 mmol) and CH_2Cl_2 (5 mL). After the mixture was stirred at room temperature for 12 h, it was subjected to flash column chromatography under anaerobic conditions. First, CH_2Cl_2 eluted a brown-red band from which the unreacted **2b** (24 mg, 69%) was recovered. Then, CH_2Cl_2/acetone (v/v = 4:1) eluted a red band from which product **3b** (3 mg, 12%) was obtained. Similarly, by using trinuclear complex **2c** (36 mg, 0.05 mmol), **2d** (39 mg, 0.05 mmol), or **2e** (37 mg, 0.05 mmol), the unreacted **2c** (26 mg, 72%), **2d** (27 mg, 69%), or **2e** (27 mg, 73%) was recovered and the corresponding product **3c** (2.8 mg, 11%), **3d** (4 mg, 15%), or **3e** (4 mg, 16%) was obtained.

A 50 mL three-necked flask equipped with a condenser was charged with **2b** (36 mg, 0.05 mmol) and CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 12 h then the resulting mixture was subjected to flash column chromatography. No **2b** was recovered due to its decomposition during the stirring and isolation courses in air. CH_2Cl_2/acetone (v/v = 4:1) eluted a tiny red band from which product **3b** (1.5 mg, 6%) was obtained. Similarly, by using **2c** (36 mg, 0.05 mmol), **2d** (39 mg, 0.05 mmol), or **2e** (37 mg, 0.05 mmol), no **2c, 2d** or **2e** was recovered. The corresponding product **3c** (1.2 mg, 5%), **3d** (1.6 mg, 6%), or **3e** (1.8 mg, 7%) was obtained.

3. Tables S1 and S2: Selected bond lengths (Å) and angles (°) for 2b and 3c

Table S1. Selected bond lengths (Å) and angles (°) for 2b

Ni(1)-N(1)	2.042(2)	Ni(1)-S(1)	2.2130(11)
Ni(1)-S(3)	2.2609(9)	Ni(1)-Fe(1)	2.4737(8)
Ni(1)-Fe(2)	2.4574(8)	Fe(1)-Fe(2)	2.5900(10)
Fe(1)-S(2)	2.2666(11)	Fe(2)-S(4)	2.2835(11)
N(1)-Ni(1)-Fe(1)	113.58(7)	S(3)-Ni(1)-Fe(1)	156.61(3)
S(1)-Ni(1)-Fe(1)	57.24(3)	Ni(1)-Fe(1)-Fe(2)	58.009(19)
Fe(1)-Ni(1)-Fe(2)	63.37(2)	Fe(1)-Fe(2)-S(4)	86.80(4)
Ni(1)-Fe(2)-Fe(1)	58.62(2)	Fe(2)-Fe(1)-S(2)	142.12(3)

Table S2. Selected bond lengths (Å) and angles (°) for 3c

O(1)-C(1)	1.138(2)	Fe(1)-N(1)	1.9972(15)
Fe(1)-S(4)	2.1867(7)	Fe(1)-S(2)	2.2139(8)
Fe(1)-S(1)	2.2868(7)	Fe(1)-S(3)	2.2991(7)
N(1)-Fe(1)-S(3)	90.10(5)	S(4)-Fe(1)-S(3)	89.91(2)
O(1)-C(1)-Fe(1)	178.9(2)	C(2)-S(1)-Fe(1)	102.48(6)
C(7)-S(2)-Fe(1)	104.18(6)	C(8)-S(2)-Fe(1)	97.43(6)

4. Figures S1 and S2: Molecular structures of 2b and 3c

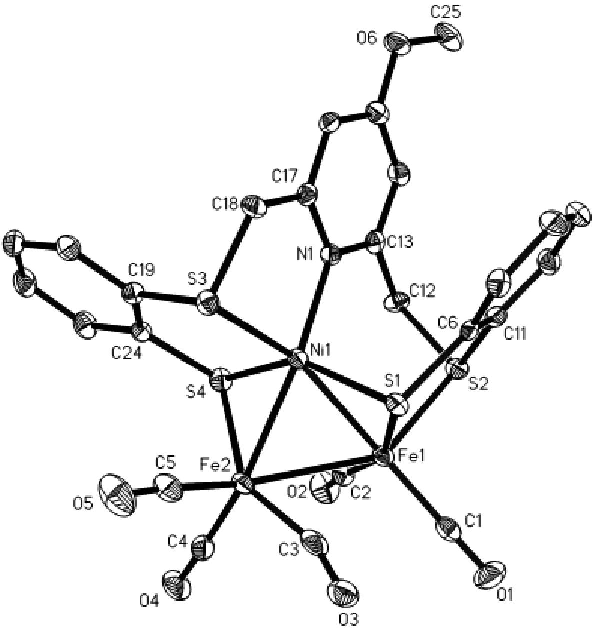


Figure S1. Molecular structure of **2b** with 30% probability level ellipsoids.

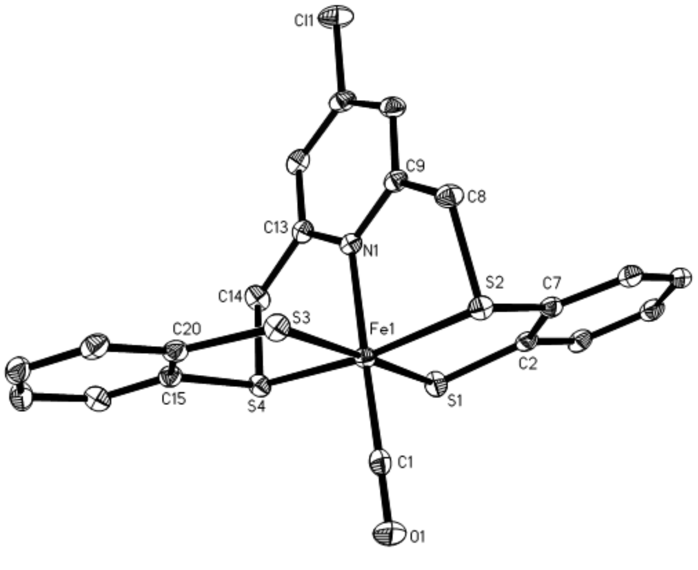
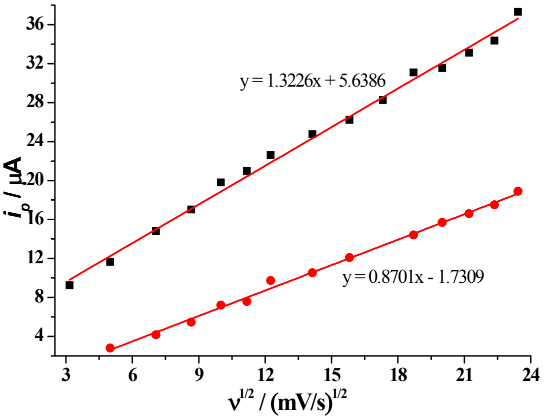
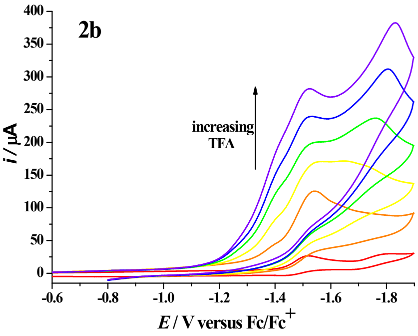


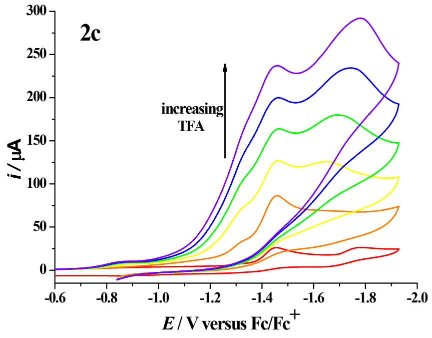
Figure S2. Molecular structure of **3c** with 30% probability level ellipsoids.

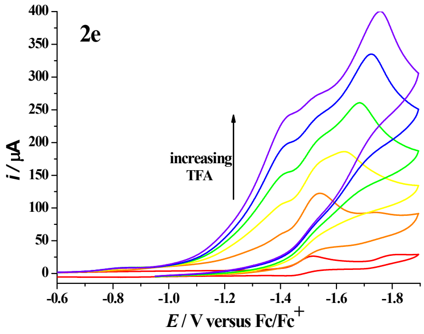
5. Figure S3: Plots of i_p versus $\nu^{1/2}$ for 2a



6. Figure S4: Cyclic voltammograms of 2b-2e with TFA

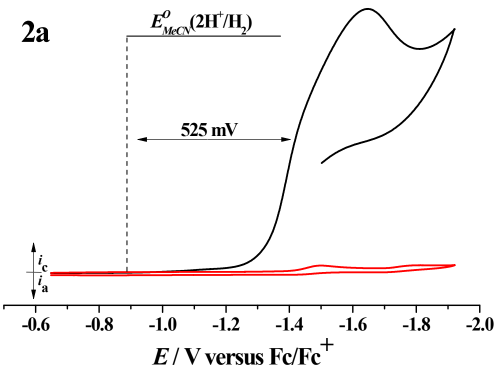

2b
increasing TFA
i / μA
400
350
300
250
200
150
100
50
0
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
E / V versus Fc/Fc+


2c
increasing TFA
i / μA
300
250
200
150
100
50
0
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
E / V versus Fc/Fc+

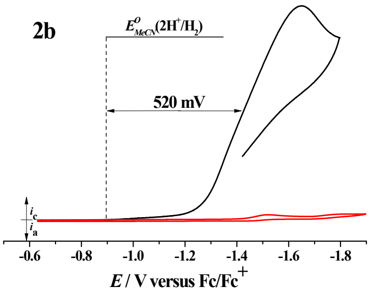

2e
increasing TFA
i / μA
400
350
300
250
200
150
100
50
0
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
E / V versus Fc/Fc+

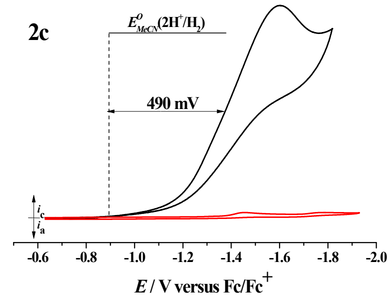
7. Figures S5 and S6: Overpotential determinations for 2a-2e

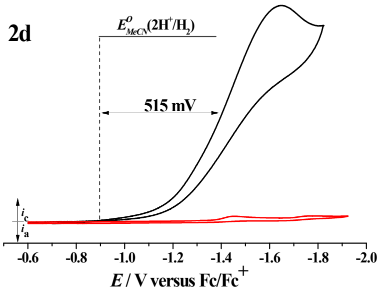
Since the pK_a and the standard redox potential are known for MeCN solutions of TFA (pK_a^{MeCN} = 12.7,[3] homoconjugation not taken into account), the $E^{o,MeCN}$(TFA/H_2) = –0.89 V vs Fc/Fc$^+$ can be calculated using Evans′ relationship.[4] The overpotential of 525 mV for the electrocatalytic proton reduction catalyzed by **2a** is measured from the potential at 0.5 (i_{pc}), where i_{pc} is the cathodic peak current in the cyclic voltammogram recorded after addition of 100 equivalents of TFA (Figure S5).

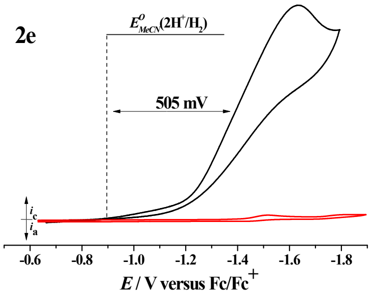


The overpotentials for **2b**-**2e** can also be calculated by Evans′ relationship (Figure S6).

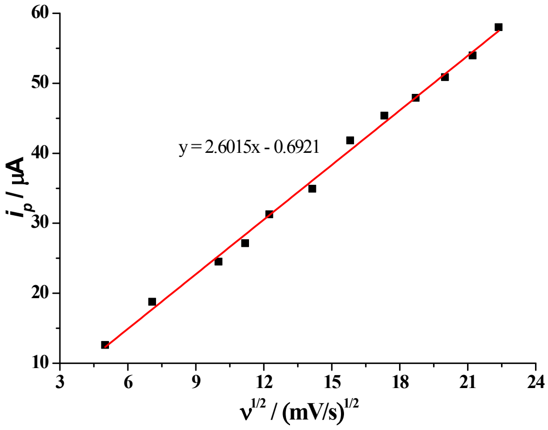




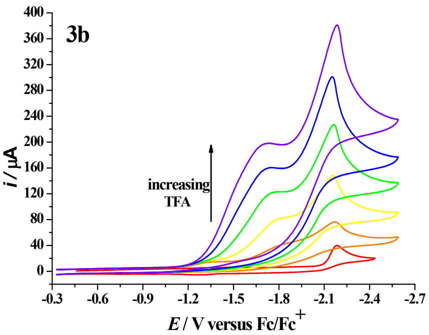


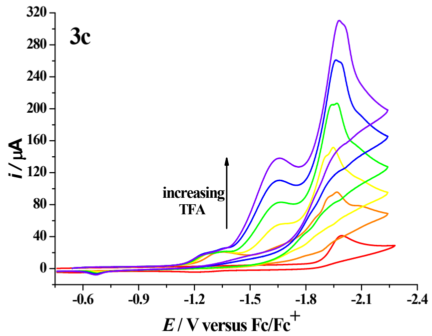


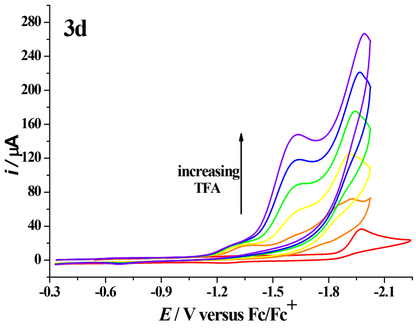
8. Figure S7: Plot of i_p versus $\nu^{1/2}$ for 3a

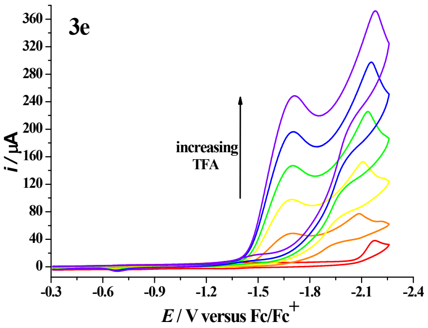


9. Figure S8: Cyclic voltammograms of 3b-3e with TFA





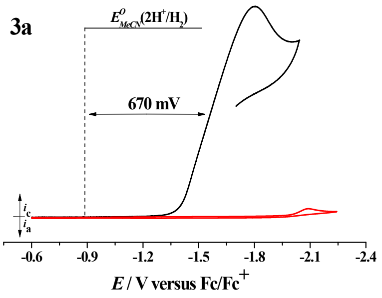

3d
i / μA
280
240
200
160
120
80
40
0
increasing
TFA
-0.3
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
E / V versus Fc/Fc$^+$


3e
i / μA
360
320
280
240
200
160
120
80
40
0
increasing
TFA
-0.3
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
E / V versus Fc/Fc$^+$

10. Figure S9: Overpotential determinations for 3a-3e

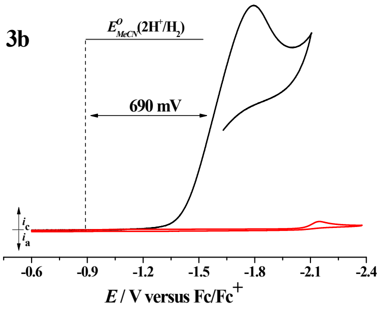
The overpotentials for **3a**-**3e** can also be calculated by Evans′ relationship (Figure S9).

3a



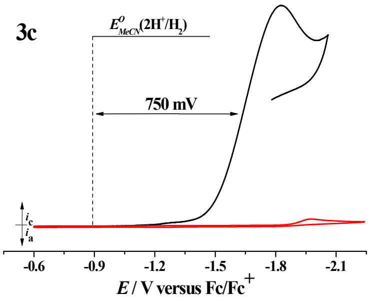
$E^{o}_{MeCN}(2H^{+}/H_{2})$
670 mV
i_c
i_a
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
E / V versus Fc/Fc^{+}

3b



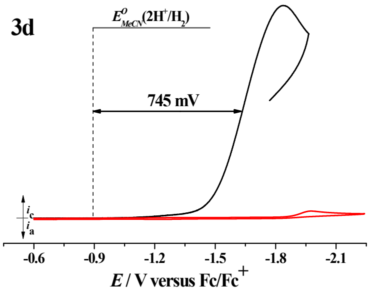
$E^{o}_{MeCN}(2H^{+}/H_{2})$
690 mV
i_c
i_a
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
E / V versus Fc/Fc^{+}

3c



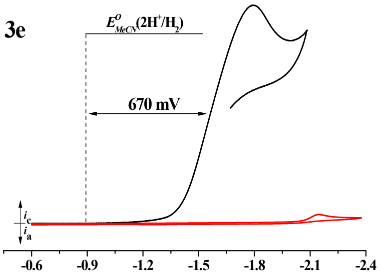
$E^{o}_{MeCN}(2H^{+}/H_{2})$
750 mV
i_c
i_a
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
E / V versus Fc/Fc^{+}

3d



$E^{o}_{MeCN}(2H^{+}/H_{2})$
745 mV
i_c
i_a
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
E / V versus Fc/Fc^{+}

3e



$E^{o}_{MeCN}(2H^{+}/H_{2})$
670 mV
i_c
i_a
-0.6
-0.9
-1.2
-1.5
-1.8
-2.1
-2.4

11. References

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4 G. A. N. Felton, R. S. Glass, D. L. Lichtenberger and D. H. Evans, *Inorg. Chem*. 2006, **45**, 9181-9184.