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Facile Control of the Redox Properties of Ferrocene-Containing Dipyridyl Derivatives That Bind Platinum(II)

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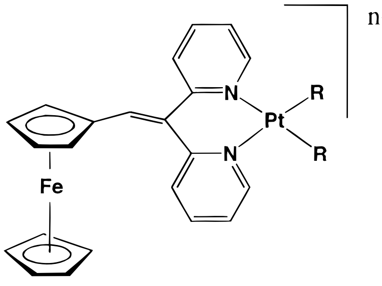
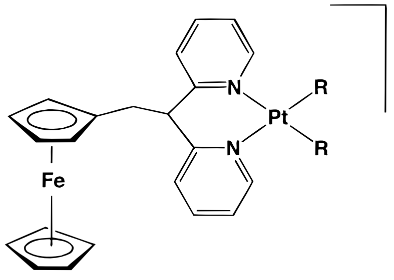
The nature of the spacer unit between the redox-active unit and the metal binding site of two new ferrocene-containing dipyridyl derivatives strongly influences the redox and spectroscopic properties of their dichloroplatinum(II) complexes, the structures of which have been determined by X-ray diffraction.

As part of the ongoing interest in electronically communicating metal centers and electrochemical sensors, the study of compounds that contain the redox-active ferrocene unit in close proximity to a second binding site continues apace.[1] These compounds may electrochemically recognize the binding of charged or neutral guest species either via through-space interactions or via various bond linkages between the receptor site and the redox-active center. There have been a number of recent examples of ferrocene complexes of platinum,[1b,2] including those that have have been designed for interaction with DNA.[3] Here we report two ferrocene-containing dipyridyl ligands that display markedly different electrochemical behavior upon complex formation with Pt(II).

By adapting a literature procedure for the synthesis of related ferrocene derivatives,[4] ligands **1** and **2** were synthesized in one and two steps, respectively, from known starting materials (see Scheme 1) and characterized by the usual spectroscopic and analytical techniques. The corresponding Pt(II) complexes **3a** and **4a** were synthesized by refluxing **1** and **2** with $[Pt(Cl)_2(NCC_5H_5)_2]$[5] in benzene.



3a
3b



4a
4b

a; **R = Cl$^-$**, n = 0
b; **R = py**, n = 2

The ^{1}H NMR spectra of compounds **1**, **2**, **3a**, and **4a** reveal interesting trends. The spectrum of ligand **1** ($CDCl_3$, 303 K) in Figure 1a shows two signals for the equivalent pairs of cyclopentadienyl (Cp) protons H_1/H_4 (3.76 ppm) and H_2/H_3 (4.14 ppm), one signal for the underivatized Cp ring (4.15 ppm), and eight signals for the pyridine protons. For the more symmetrical compound **2**, in total three Cp signals are seen for **2**, as is the case for **1**, but only four signals corresponding to

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[1] For reviews and recent advances on the complexation of charged and neutral guest species by ferrocene derivatives, see: (a) Beer, P. D.; Gale, P. A.; Chen, G. Z. *J. Chem. Soc., Dalton Trans.* **1999**, 1897. (b) Zanello, P. In *Ferrocenes: Homogeneous catalysis, organic synthesis, materials science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; Chapter 7. (c) Valério, C.; Fillaut, J. L.; Ruiz, J.; Guittard, J.; Blais, J. C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588. (d) Carr, J. D.; Coles, S. J.; Hassan, W. W.; Hursthouse, M. B.; Abdul Malik, K. M.; Tucker, J. H. R. *J. Chem. Soc., Dalton Trans.* **1999**, 57, and references therein.

[2] (a) Less, R. J.; Wicks, J. L. M.; Chatterton, N. P.; Dewey, M. J.; Cromhout, N. L.; Halcrow, M. A.; Davies, J. E. *J. Chem. Soc., Dalton Trans.* **1996**, 4055. (b) Sato, M.; Anano, H. *J. Organomet. Chem.* **1998**, *555*, 167. (c) Stang, P. J.; Olenyuk, B.; Fun, J.; Arif, A. M. *Organometallics* **1996**, *15*, 904. (d) Thomas, K. R. J.; Lin, J. T.; Lin, K. J. *Organometallics* **1999**, *18*, 5285. (e) Wong, W. Y.; Wong, W. K.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1998**, 2761.

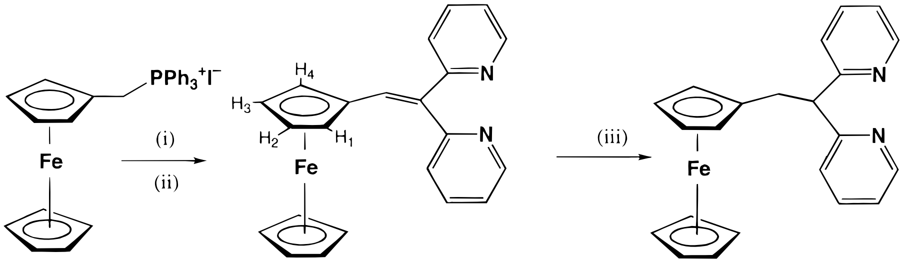
[3] (a) Ricra, X.; Caubet, A.; López, C.; Moreno, V. *Polyhedron* **1999**, *18*, 2549, and references therein. (b) Duffy, N. W.; Harper, J.; Ramani, P.; Ranatunge-Bandarage, R.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1998**, *564*, 125, and references therein.

[4] Beer, P. D.; Blackburn, C.; McAleer, J. F.; Sikanyika, H. *Inorg. Chem.* **1990**, *29*, 378.

[5] Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60.

10.1021/om000215h CCC: $19.00

Scheme 1[a]



1 **2**

[a] Reagents and Conditions: (i) n-BuLi, THF, room temp, 2 h; (ii) di-2-pyridyl ketone, THF, room temp, 24 h; (iii) H_2, Pd/C, THF, room temp, 3 h.

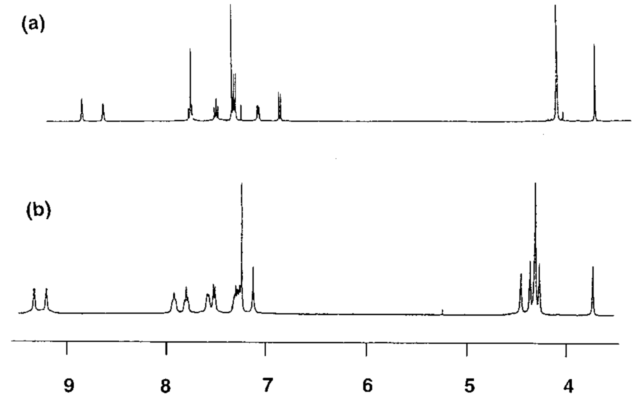


Figure 1. ^{1}H NMR spectra of (a) **1** and (b) **3a** in $CDCl_3$ at 303 K.

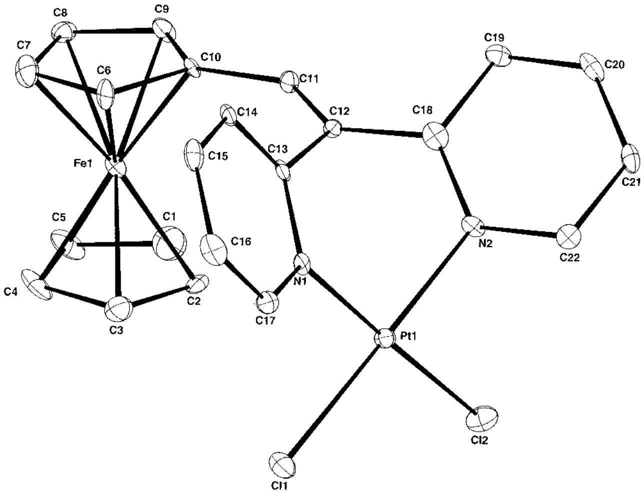


Figure 2. Molecular structure of **3a**.

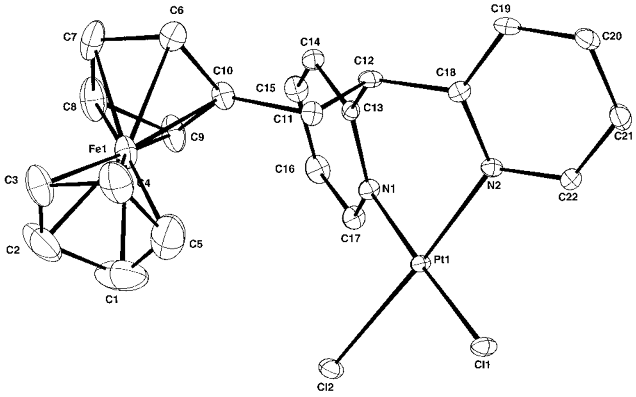


Figure 3. Molecular structure of **4a**.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 3a and 4a

3a		4a	
Pt(1)−Cl(2)	2.298(4)	Pt(1)−Cl(2)	2.306(1)
Pt(1)−Cl(1)	2.272(4)	Pt(1)−Cl(1)	2.301(1)
Pt(1)−N(2)	1.991(10)	Pt(1)−N(2)	2.020(3)
Pt(1)−N(1)	2.005(11)	Pt(1)−N(1)	2.021(3)
C(11)−C(12)	1.350(1)	C(11)−C(12)	1.547(5)
Cl(2)−Pt(1)−Cl(1)	91.1(2)	Cl(2)−Pt(1)−Cl(1)	90.79(3)
N(2)−Pt(1)−N(1)	87.7(4)	N(2)−Pt(1)−N(1)	90.80(8)
C(18)−C(12)−C(13)	114.3(8)	C(18)−C(12)−C(13)	111.7(3)
N(1)−C(13)−C(12)	116.9(10)	N(1)−C(13)−C(12)	119.2(3)
N(2)−C(18)−C(12)	117.5(10)	N(2)−C(18)−C(12)	119.1(3)

the pyridine protons are observed. Interestingly, upon complexation with Pt(II) to form **3a**, the four protons on the derivatized Cp ring of **1** become nonequivalent, as shown in Figure 1b.

An explanation for this change in the ^{1}H NMR can be found from the X-ray crystal structure of **3a** (Figure 2), which reveals that the six-membered chelate ring, formed by square-planar coordination to the Pt(II) center, is not planar but puckered. Cremer−Pople analysis[6] shows the conformation to be boat (θ and ϕ angles = 82.2° and 0.98°, respectively). The presence of such a geometry in solution would mean that, in contrast to the free ligand, free rotation about the Cp−C bond would not make the two Cp proton pairs equivalent. The crystal structure of **4a** (Figure 3) reveals a similar puckered geometry, but the symmetry of the complex is such that the Cp proton pairs on the derivatized ring remain equivalent. The Pt−Fe through-space distances for **3a** and **4a** are similar (5.20 and 5.50 Å, respectively), and in both complexes, the Cp rings are virtually eclipsed (rotation angle = 2°). Selected bond lengths and angles are depicted in Table 1. Dimethylpalladium(II) complexes of related dipyridylmethane ligands show temperature-dependent NMR spectra indicating inversion of the puckered chelate ring.[7] However, variable-temperature studies between −90 and 130 °C in $(CDCl_2)_2$ revealed no changes in the ^{1}H NMR spectra of **1**, **2**, **3a**, and **4a**.

Both **1** and **2** undergo reversible ferrocene-centered oxidations at similar potentials in CH_2Cl_2 ($E = +0.54$ and $+0.51$ V, respectively, vs decamethylferrocene

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(6) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

(7) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.

Table 2. Electrochemical Data[a] at 293 K in Dry CH_2Cl_2

	1	**2**	**3a**	**4a**
E/V	+0.54	+0.51	+0.69	+0.54

[a] Electrode potentials, E, where $E = 0.5\ (E_{pa} + E_{pc})$ were referenced to decamethylferrocene (1 mM), which was used as an internal reference. The confidence limit is ±5 mV. Pt working, Pt counter, and Ag/AgCl reference electrodes were used with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. For each voltammogram, the reversibility of the redox wave matched that of ferrocene under the same experimental conditions ($\Delta E_p = 70-100$ mV).

internal reference, 293 K). However the redox properties of the complexes are markedly different in that the ferrocene redox couple of **3a** is shifted by +150 mV compared to **1**, whereas Pt(II) complexation with **2** brings about a much smaller shift of +30 mV (Table 2).

The reason for this difference in electrochemical behavior is due to the conjugated π-electron system present in **3a** between the ferrocene center and the dipyridyl unit, which permits through-bond communication between the two metal centers.[1a,4] Consequently, as found with other neutral ferrocene complexes of Pt(II),[1b,2a] the electron-withdrawing nature of the bound metal center makes the ferrocene unit harder to oxidize. Through-bond effects are reduced for related compounds that contain a longer conjugated link between the ferrocene center and the metal binding site.[8]

Simple exchange of the two chloride ligands at the Pt(II) center for N-donor ligands was achieved by refluxing either **3a** or **4a** with 2 equiv of pyridine in H_2O. Filtration and subsequent addition of NH_4PF_6 resulted in the precipitation of compounds **3b** and **4b**. Cyclic voltammetry studies in CH_3CN revealed anodic shifts of +15 and +20 mV for the reversible redox couples of **3b** and **4b**, respectively, compared to those for **3a** and **4a** in the same solvent. Presumably this small difference reflects the positively charged nature of complexes **3b** and **4b** as a result of there being four neutral ligands around the Pt(II) center.

In conclusion, we have shown that the redox properties of ferrocene-containing Pt(II) complexes may be easily controlled by changing either the degree of conjugation or the ligand environment at the Pt(II) center.

Experimental Section

General Comments. Reagent grade reactants and solvents were used as received from chemical suppliers. Anhydrous solvents were dried by the usual procedures and were stored over 4 Å molecular sieves. All reactions were carried out under an inert atmosphere of nitrogen. $FeCp(CpCH_2PPh_3{}^+I^-)$[4,9] and $[Pt(Cl)_2(NCC_5H_5)_2]$[5] were prepared according to literature procedures. Di-2-pyridyl ketone was purchased from Aldrich Chemical Co. Column chromatography was performed on silica gel (Merck, grade 60). EI and LSIMS (liquid secondary ion mass spectrometry) mass spectra were carried out by the EPSRC National Mass Spectrometry Service at the University of Wales, Swansea, UK.

Preparation of [2,2-(Di-2-pyridyl)ethenyl]ferrocene, 1. A suspension of the $FeCp(CpCH_2PPh_3{}^+I^-)$ (2.00 g, 3.8 mmol) in anhydrous THF (250 mL) was treated with a solution of *n*-BuLi in hexane (2.58 mL, 4.0 mmol) dropwise. The deep red solution formed was stirred for 2 h at room temperature, and then di-2-pyridyl ketone (0.714 g, 3.8 mmol) in anhydrous THF (100 mL) was added dropwise. The reaction mixture was stirred for a further 24 h with the exclusion of light under nitrogen before water (50 mL) was added. The solvent mixture was removed under reduced pressure, extracted with CH_2Cl_2 (3 × 50 mL), and dried ($MgSO_4$), and again the solvent was removed. The crude product was purified by chromatography on silica gel (Et_2O with 5% CH_2Cl_2) to give **1** as a red solid (0.45 g, 32%). The compound may be recrystallized from CH_2Cl_2–diethyl ether to give red rhombic crystals, mp 124–125 °C. Anal. Calcd for $C_{22}H_{18}FeN_2$: C, 72.15.; H, 4.95; N, 7.65. Found: C, 71.83; H, 4.89; N, 7.62. MS (EI): m/z 366 (M^+). Acc. Mass Calcd for $C_{22}H_{18}FeN_2$: 366.0819. Found: 366.0814. ^1H NMR ($CDCl_3$, 400 MHz, 303 K): δ 8.83 (d, 1H, py-H), 8.61 (d, 1H, py-H), 7.76 (t, 1H, py-H), 7.75 (s, 1H, olefin-H), 7.51 (t, 1H, py-H), 7.33 (dd, 1H, py-H), 7.32 (d, 1H, py-H), 7.09 (dd, 1H, py-H), 6.88 (d, 1H, py-H), 4.15 (s, 5H, Cp-H), 4.14 (m, 2H, Cp-H), 3.76 (m, 2H, Cp-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 303 K): δ 159.12, 157.35, 150.21, 149.29, 136.81, 136.35, 136.15, 131.06, 125.96, 122.33, 121.27, 121.21, 80.20, 69.86, 69.59, 69.39.

{[2,2-(Di-2-pyridyl)]eth-1-yl}ferrocene, 2. A mixture of triethylamine (0.09 g, 0.9 mmol) and compound **1** (0.10 g, 0.27 mmol) was dissolved in anhydrous THF (50 mL). A catalytic amount of palladium on activated carbon was added, and H_2 was passed over the solution with rapid stirring for 3 h. The solution was filtered through Celite and the solvent removed under reduced pressure to give **2** as a yellow solid (0.096 g, 97%). The compound may be recrystallized from CH_2Cl_2–diethyl ether to give yellow crystals, mp 99–100 °C. MS (EI): m/z 368 (M^+). Acc. Mass Calcd for $C_{22}H_{20}FeN_2$: 368.0975. Found: 368.0983. ^1H NMR ($CDCl_3$, 400 MHz, 303 K): δ 8.57 (d, 2H, py-H), 7.54 (t, 2H, py-H), 7.30 (d, 2H, py-H), 7.09 (dd, 2H, py-H), 4.37 (t, 1H, CH),4.07 (s, 5H, Cp-H), 3.91 (m, 2H, Cp-H), 3.86 (m, 2H, Cp-H), 3.34 (d, 1H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 303 K): δ 162.30, 149.18, 136.30, 123.29, 121.51, 86.74, 68.85, 68.54, 67.11, 58.31 (CH), 35.05 (CH_2).

{[2,2-(Di-2-pyridyl)ethenyl]ferrocenyl}dichloroplatinum(II), 3a. Compound **1** (0.030 g, 0.08 mmol) and $[PtCl_2(C_6H_5CN)_2]$ (0.040 g, 0.08 mmol) in anhydrous benzene (20 mL) was refluxed for 24 h. Pure compound precipitated out overnight and was collected by filtration, then washed with anhydrous benzene (3 × 5 mL) to give a red solid (0.047 g, 93%). The compound may be recrystallized from CH_2Cl_2–diethyl ether to give red crystals, mp 265 °C (decomp). Anal. Calcd for $C_{22}H_{18}N_2Cl_2FePt$ (+ 0.5 equiv of H_2O): C, 41.29; H, 2.99; N, 4.38. Found: C, 41.28; H, 2.77; N, 4.11. MS (EI): m/z 631 (M^+). Acc. Mass Calcd for $C_{22}H_{18}N_2Cl_2FePt$: 630.9844. Found: 630.9838. ^1H NMR ($CDCl_3$, 400 MHz, 303 K): δ 9.29 (d, 1H, py-H), 9.17 (d, 1H, py-H), 7.93 (t, 1H, py-H), 7.81 (t, 1H, py-H), 7.61 (d, 1H, py-H), 7.53 (d, 1H, py-H), 7.33 (dd, 1H, py-H), 7.29 (dd, 1H, py-H), 7.15 (s, 1H, olefin-H), 4.56 (m, 1H, Cp-H), 4.45 (m, 1H, Cp-H), 4.39 (s, 5H, Cp-H), 4.36 (m, 1H, Cp-H), 3.84 (m, 1H, Cp-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 303 K): δ 156.41, 153.86, 153.59, 153.04, 139,24, 138.22, 136.92, 131.79, 126.22, 124.40, 123.96, 122.77, 77.31, 73.03, 71.70, 71.15, 70.53, 67.52.

{[2,2-(Di-2-pyridyl)ethenyl]ferrocenyl}dipyridineplatinum(II) Hexafluorophosphate, 3b. Complex **3a** (0.050 g, 0.08 mmol) and pyridine (0.02 g, 0.25 mmol) in water (20 mL) were refluxed for 24 h. The red solution was filtered and excess NH_4PF_6 added to give a red precipitate (0.052 g, 65%), which was washed with water (3 × 5 mL). The compound can be purified by repeated recrystallization from CH_3CN–diethyl ether to give red crystals, mp 260 °C (decomp). Anal. Calcd for $C_{32}H_{28}N_4F_{12}FeP_2Pt$ (+ 1.5 equiv of H_2O): C, 37.08; H, 3.01;

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(8) (a) Beer, P. D.; Kocian, O.; Mortimer, R. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3283. (b) Chambron, J. C.; Coudret, C.; Sauvage, J. P. *New J. Chem.* **1992**, *16*, 361. (c) Bhadhade, M. M.; Das, A.; Jeffery, J. C.; McCleverty, J. A.; Navas Badiola, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2769.

(9) Zakaria, C. M.; Morrison, C. A.; McAndrew, D.; Bell, W.; Glidewell, C. *J. Organomet. Chem.* **1995**, *485*, 201.

Table 3. Crystallographic Data for Pt(II) Complexes 3a and 4a

	3a	4a
formula	$C_{22}H_{18}N_2Cl_2FePt(C_{0.5}HCl)$	$C_{22}H_{20}N_2Cl_2FePt(CHCl_3)$
fw	675.70	753.61
space group	triclinic ($P\bar{1}$)	monoclinic ($P2_1/c$)
a, Å	9.788(9)	18.640(4)
b, Å	10.461(3)	8.558(2)
c, Å	12.230(9)	16.072(3)
α, deg	73.80(5)	90.0
β, deg	73.44(7)	101.49(3)
γ, deg	60.76(4)	90.0
volume, Å^3	1032.7(13)	2512.4(9)
Z	2	4
density (calcd), Mg/m^3	2.173	1.992
abs coeff, mm^{-1}	7.870	6.686
F(000)	648	1448
cryst size, mm	0.3 × 0.25 × 0.1	0.3 × 0.03 × 0.03
θ_{max}, deg	25.1	26.36
index ranges	$-11 \leq h \leq 10$ $-11 \leq k \leq 11$ $-9 \leq l \leq 13$	$-23 \leq h \leq 23$ $-10 \leq k \leq 10$ $-20 \leq l \leq 20$
no. of reflns colld	4419	53 120
no. of ind reflns	2900	5136
R_{int}	0.0966	0.0557
abs corr factors/transmn factors	0.663/1.361	0.765/0.957
no. of params	271	289
goodness-of-fit on F_o^2	0.967	0.685
final R indices [$I > 2\sigma(I)$]	R1 = 0.0568 wR2 = 0.1383 (2508 reflections)	R1 = 0.0217 wR2 = 0.0739 (4683 reflections)
R indices (all data)	R1 = 0.0619 wR2 = 0.1402	R1 = 0.0258 wR2 = 0.0800
ρ_{max}/ρ_{min}, e Å^{-3}	2.697 and −3.237	0.921 and −1.090

N, 5.41. Found: C, 36.91; H, 2.69; N, 4.99. MS (LSIMS): *m/z* 864 ([M − PF_6]$^+$). Acc. Mass Calcd for $C_{32}H_{28}N_4F_6FePPt$: 864.0953. Found: 864.0958. ^{1}H NMR (CD_3CN, 400 MHz, 303 K): δ 8.82 (d, 4H, py-H), 8.26 (d, 1H, py-H), 8.16−7.99 (m, 6H, py-H), 7.86 (d, 1H, py-H), 7.72 (m, 2H, py-H), 7.63 (s, 1H, olefin-H), 7.62 (m, 2H, py-H), 7.35 (m, 2H, py-H), 4.81 (m, 1H, Cp-H), 4.66 (m, 1H, Cp-H), 4.53 (s, 1H, Cp-H), 4.43 (s, 5H, Cp-H), 4.15 (m, 1H, Cp-H). ^{13}C{^{1}H} NMR (CD_3CN, 100 MHz, 303 K): δ 156.97, 154.36, 152.30, 151.99, 151.04, 150.00, 142.24−140.93 (5C), 129.70, 128.41, 128.13, 128.08, 125.80, 125.49, 125.05, 76.77, 73.65, 72.23, 72.02, 70.17, 68.30.

({[2,2-(Di-2-pyridyl)]eth-1-yl}ferrocenyl)dichloroplatinum(II), 4a. Compound **2** (0.030 g, 0.08 mmol) and [Pt(Cl)$_2$(C_6H_5N)$_2$] (0.04 g, 0.9 mmol) in anhydrous benzene (20 mL) was refluxed for 24 h. Pure compound precipitated out overnight and was collected by filtration, then washed with anhydrous benzene (3 × 5 mL) to give a yellow solid (0.046 g, 91%). The compound may be recrystallized from CH_2Cl_2−diethyl ether to give yellow crystals, mp 240 °C (decomp). Anal. Calcd for $C_{22}H_{20}N_2Cl_2FePt$ (+ 0.5 equiv $CHCl_3$): C, 38.98; H, 2.98; N, 4.04. Found: C, 38.52; H, 2.72; N, 3.97. MS (EI): *m/z* 633 (M$^+$). Acc Mass Calcd for $C_{22}H_{20}N_2Cl_2FePt$: 633.0000. Found: 633.0005. ^{1}H NMR ($CDCl_3$, 400 MHz, 303 K): δ 9.37 (d, 2H, py-H), 7.77 (t, 2H, py-H), 7.35−7.22 (m, 4H, py-H), 4.55 (d, 2H, CH_2), 4.30 (t, 1H, CH),4.21 (s, 5H, Cp-H), 4.08 (m, 2H, Cp-H), 4.06 (m, 2H, Cp-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K): δ 155.63, 154.18, 138.63, 125.76, 124.44, 83.92, 69.21, 68.57, 68.21, 61.44, 35.63.

({[2,2-(Di-2-pyridyl)]eth-1-yl}ferrocenyl)dipyridineplatinum(II) Hexafluorophosphate, 4b. Complex **4a** (0.051 g, 0.08 mmol) and pyridine (0.02 g, 0.25 mmol) in water (20 mL) were refluxed for 24 h. The solution was filtered, and excess NH_4PF_6 was added to give a yellow precipitate (0.058 g, 72%), which was washed with water (3 × 5 mL). The compound can be purified by repeated recrystallization from CH_3N−diethyl ether to give yellow crystals, mp 250 °C (decomp). Anal. Calcd for $C_{32}H_{30}N_4F_{12}FeP_2Pt$: C, 38.00; H, 2.99; N, 5.54. Found: C, 38.12; H, 2.87; N, 5.48. MS (LSIMS): *m/z* 866 ([M − PF_6]$^+$). Acc. Mass Calcd for $C_{32}H_{30}N_4F_6FePPt$: 866.1110. Found: 866.1127. ^{1}H NMR (CD_3CN, 400 MHz, 303 K): δ 8.91 (d, 4H, py-H), 8.17 (d, 2H, py-H), 8.13 (t, 2H, py-H), 8.00 (t, 2H, py-H), 7.71 (m, 4H, py-H), 7.64 (d, 2H, Py-H), 7.33 (dd, 2H, py-H), 4.90 (t, 1H, CH), 4.63 (d, 2H, CH2), 4.25 (s, 5H, Cp-H), 4.12 (m, 2H, Cp-H), 4.06 (m, 2H, Cp-H). ^{13}C-{^{1}H} NMR (CD_3CN, 100 MHz, 303 K): δ 156.87, 152.27, 151.11, 141.98, 141.79, 128.42, 128.10, 125.84, 83.40, 68.91, 68.69, 68.12, 59.17, 38.02.

Collection and Refinement of X-ray Diffraction Data for 3a and 4a. Crystals of the above compounds were mounted in random orientations on a glass wool fiber glued to a glass capillary. Data collections were performed, at 150 K in both cases, on a Nonius FAST TV area detector for **3a** and a Nonius Kappa CCD for **4a**, each equipped with a Nonius FR591 rotating anode (λMo Kα = 0.71073 Å). In each case the structures were solved by Patterson heavy atom methods, where the heavy atom positions were determined with the remaining atoms being located by successive Fourier syntheses. Hydrogen atoms were included in the refinement, but were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using DIFABS[10] for **3a** and SORTAV for **4a**.[11] Full-matrix least-squares refinement on F_o^2 converged with R1 = 0.0568 and wR2 = 0.1383 for **3a** and R1 = 0.0217 and wR2 = 0.0739 for **4a**. Geometrical and crystallographic data are summarized in Tables 1 and 3, while the molecular structures are presented in Figures 2 and 3.

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Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, full bond lengths and angles, and temperature factors for **3a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Walker, N. P. C.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158; adapted for FAST geometry by Karaulov, A. University of Wales, Cardiff, 1991.

(11) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.