Metallocyclic Complexes of Palladium(II) and Platinum(II) Containing Six- and Seven-Membered Chelate Rings[1a]

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The syntheses of several new cyclometalated Pd(II) and Pt(II) complexes with ligands containing either bipyridine or the corresponding one and two C-bridged species are described. Most of these complexes contain at least one bond to the metal from an sp^3 carbon, yielding ring systems with an overall cis geometry. The ligand series has been extended to contain an sp^3-carbon bridge and a two-carbon unsaturated bridge. While Pd(II) usually undergoes facile bis-cyclometalation, the unsaturated bridge ligand does not allow the second C–Pd bond to form easily. Also, in contrast to the previously observed Pd(II) complexation, the corresponding Pt(II) complexes must be formed via the isolation and purification of each intermediate.

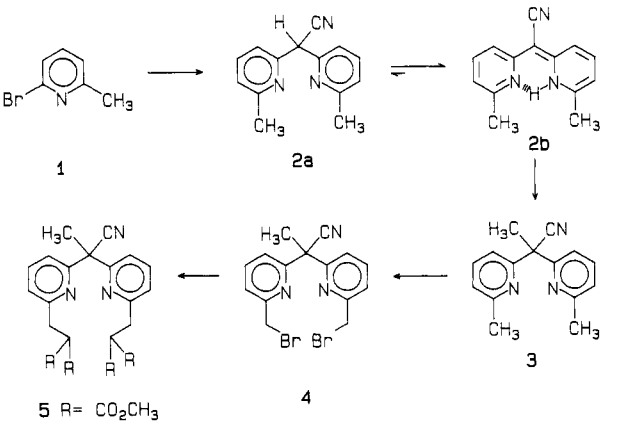
Introduction

Our interest in metallocyclic complexes of palladium(II) is well documented.[2] To date, other platinum group metals have not, however, led to successful results with these ligands[3] although several examples of cycloplatination are known in other ligand systems.[4] In addition to our achievement of incorporating platinum(II) into these ligand systems, we herein wish to report the further extension of these 5.5.5-cumulated ligands to include 5.6.5- as well as 5.7.5-cumulated ring systems, which possess a semirigid frame containing an sp^3-carbon bridge. The thrust of our ligand design has been to determine exactly which structural features cause changes in the binding locus so that either metal selectivity or molecular inclusion of a neutral guest can be achieved. In addition, the geometric constraints on carbon–metal bond formation are being investigated. We have recently shown that ring sizes other than 5-membered can also lead to successful C–Pd bond formation,[5] contrary to previously published results.[6]

Results and Discussion

1. Central Homologation. Ligand **5** was prepared via the sequence outlined in Scheme I, in which an excess of the sodio salt of acetonitrile, formed via 50% NaH and 2-bromo-6-methylpyridine (**1**) in DMF at 90 °C, leads to the formation of bis(6-methylpyridin-2-yl)acetonitrile (**2**) in 50–69% yields. The ^1H NMR spectrum of **2** shows that the methine proton is shared by the pyridine nitrogens rather than residing on the bridging carbon (δ 16.1). This

Scheme I



proton, if bound to the α-nitrile carbon, should have a chemical shift of ca. δ 6.0, based on the chemical shift of dipyridin-2-ylmethane (δ 4.33)[7] and the shielding constant for the nitrile.[8] This tautomeric mixture leads to decreased aromatic character within the pyridyl rings, as shown by the shift of H-5 from a normal region δ 7.1–6.26.

Before free radical halogenation techniques were used to functionalize the methyl groups, the methine carbon was "protected" via alkylation.[2] This was readily achieved by treatment of **2** with $MeI/K_2CO_3/DMF$ to give (70–75%) proprionitrile **3**, which was shown by NMR data to arise by C- rather than N-alkylation under these reaction conditions. The ^1H NMR spectrum shows a singlet at δ 2.20 for this methyl group, which is upfield from where the signal for the *N*-methyl derivative would appear. In addition, the ^{13}C NMR spectrum for **3** showed a signal at δ 25.1 for the methyl and at δ 50.6 for the "quaternary" center, which is in the normal range. An unexpected fragmentation of **3** was noted in the mass spectral data, namely, the initial loss of a CH_3 group rather than the more normal loss of CN (relative intensities: 100 vs 22, respectively).

Functionalization of the α-methyl moieties was then successfully achieved via NBS bromination[9] to give the bis(bromomethyl) derivative **4** in 50–67% yields. Integration of the ^1H NMR spectrum of the crude reaction mixture indicated that bromomethyl moieties constituted

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(2) (a) Newkome, G. R.; Puckett, W. E.; Kiefer, G. E.; Gupta, V. K.; Fronczek, F. R.; Pantaleo, D. C.; McClure, G. L.; Simpson, J. B.; Deutsch, W. A. *Inorg. Chem.* **1985**, *24*, 811. (b) Newkome, G. R.; Kiefer, G. E.; Frere, Y. A.; Onishi, M.; Gupta, V. K.; Fronczek, F. R. *Organometallics* **1986**, *5*, 348. (c) Newkome, G. R.; Onishi, M.; Puckett, W. E.; Deutsch, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4551. See for overall review: Evans, D. W.; Newkome, G. R. *Coord. Chem. Rev.*, in press.

(3) For recent exception, see: Newkome, G. R.; Evans, D. W.; Fronczek, F. R. *Organometallics*, to be submitted for publication.

(4) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451.

(5) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Fronczek, F. R. *Organometallics* **1983**, *2*, 1247.

(6) Matsuda, S.; Kikkawa, S.; Omae, I. *Kogyo Kagaku Zasshi* **1966**, *69*, 646 (*Chem. Abstr.* **1966**, *65*, 18612e). Since this report several examples of complexes containing other than 5-membered cyclometalation rings have been reported, several of which are included in the following reviews: Reference 4 and: Constable, E. C. *Polyhedron* **1984**, *3*, 1037.

(7) Ohsawa, A.; Kawaguchi, T.; Igeta, H. *J. Org. Chem.* **1982**, *47*, 3497.

(8) Silverstein, R. M.; Bassler, G. C.; Morill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1974; p 220.

(9) Offermann, W.; Vögtle, F. *J. Org. Chem.* **1979**, *44*, 710.

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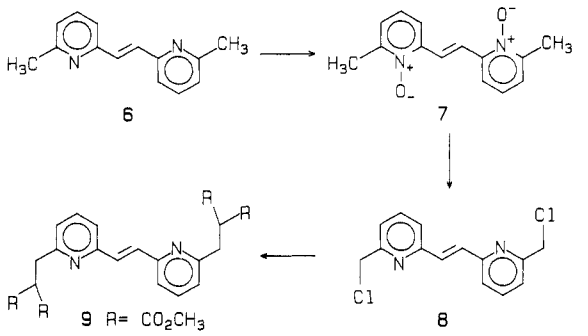
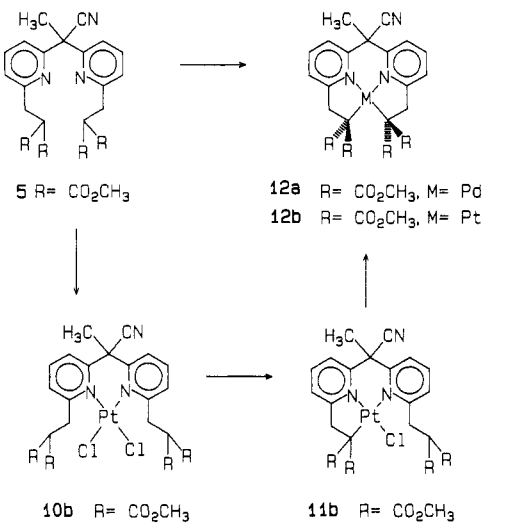
Scheme II



Scheme III



86% of the brominated product (δ 4.52), while the remainder of the methyl groups were dibrominated (δ 6.63).

Transformation of **4** into the bis(malonate) **5** was accomplished in high yields (85–92%; 27% from **1**) upon treatment with anhydrous K_2CO_3 and excess dimethyl malonate in DMF. The ^1H NMR spectrum of **5** showed the usual pattern (doublet with a triplet further downfield) for a monosubstituted malonate derivative. A comparative study of the CPK models of **5** to that of the corresponding dipyridyl ketone[2b] indicated that the bite of **5** should be slightly smaller, due to the change in hybridization of the bridging carbon from sp^2 to sp^3. This should be offset by the increased N-ligandophilicity caused by the bridging saturated carbon, as opposed to the carbonyl carbon. The ease of preparation of this ligand[2b] should allow a more detailed study of the 5.6.5-tricyclic ring system.

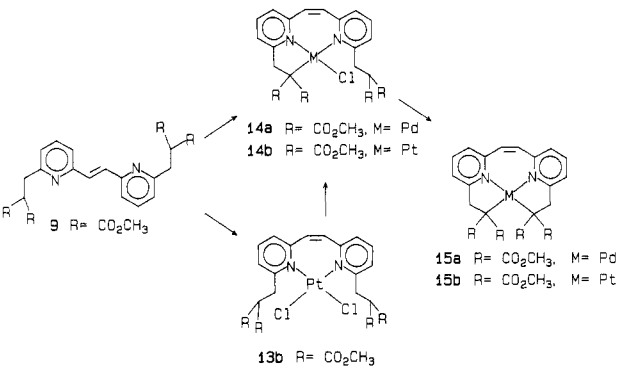
The 1,2-dipyridinylalkenes (**6**) can be easily generated via a facile process.[10a] When di-*N*-oxide **7**[10] was treated with excess *p*-toluenesulfonyl chloride under anhydrous conditions, the ditosyl salt was formed. The crude reaction mixture was then pyrolyzed, neat, at 90–100 °C to give (50%) the rearranged bis(chloromethyl) derivative **8**.[11] The downfield shift of the side-chain protons from δ 2.53 to 4.67 showed that the α-substitution occurred exclusively. In fact, no evidence for internal substitution could be found under any conditions. The vinyl protons were also shifted upfield 0.49 ppm (from δ 8.18 to 7.69).

Conversion of **8** to **9** was accomplished upon reaction with excess malonate in the presence of anhydrous K_2CO_3. The presence of the characteristic malonate couplings (doublet with a triplet further downfield) confirmed the transformation.

The effect of increased structural rigidity in **9** on the "bite" was of interest because it has been shown[2b] that, despite the increased size of the central ring, the Pd(II) complex was readily formed and exhibited unusual stability toward normally destructive conditions, such as alcoholysis or hydrolysis.[2b]

2. Palladium(II) Complex Formation. Reaction of ligand **5** with $PdCl_2$ in K_2CO_3/CH_3CN at 50–60 °C yielded the bis-metalated complex **12a**. The ^1H NMR spectrum of complex **12a** was typical for bis-metalation. The aromatic pattern remained symmetrical but shifted downfield between 0.20 and 0.35 ppm. The signal for the methylene side chain collapsed to a singlet and shifted 0.47 ppm. Unlike the non-cyclometalated analogue of this complex, **24**, where a rigid boat conformation created diastereotopic malonate esters apparent in both the ^1H and ^{13}C NMR spectra,[12] complex **12a** appeared to have sufficient thermal motion to cause the esters to be equivalent. Under these reaction conditions, no evidence for the monometalated species **11a** could be found. As has been previously documented,[2b] this is probably due to the "bite" of this ligand matching the geometry required by the palladium(II) dication.

Scheme IV



Complex **14a** can be prepared (50%) by photoisomerization of *trans*-**9** to *cis*-**9** in a CH_3CN solution containing $PdCl_2$ and K_2CO_3. The isomerization from the *trans*- to *cis*-alkene was a prerequisite to N,N′-coordination and can readily be substantiated by the vinyl proton shift from δ 7.61 to ca. δ 6.0. The aromatic pattern for **14a** was unsymmetrical, which is typical for mono-metalated complexes, and the presence of signals for both a free malonate ester and a mono-metalated (doublet with downfield triplet and a singlet, respectively) further supported the assignment. The aromatic region consisted of an unresolved multiplet for the pyridine H-3 plus H-4 of the pyridine on the non-metalated half of the molecule. Two signals for the different pyridine H-5's can be observed at δ 7.05 (non-metalated) and at δ 6.88 (metalated), whereas the H-4 signal for the metalated side occurred at δ 7.75. The signal for the methylene adjacent to the C–Pd shifted upfield by 0.11 ppm, which suggests that the seven-membered central ring relieves the strain normally associated with cyclometalation of Pd(II).[2a,b]

Subsequent bis-metalation to yield (90%) **15a** was achieved by the addition of $AgNO_3$ (1 equiv). The sym-

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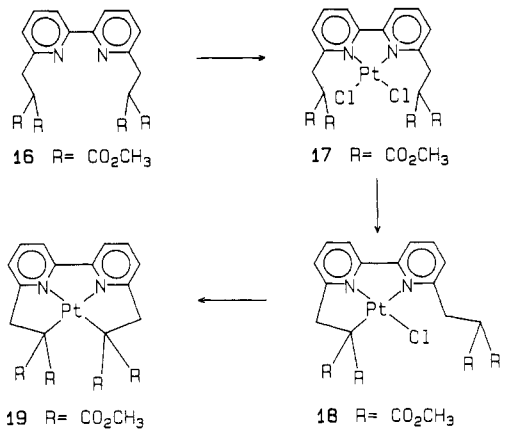
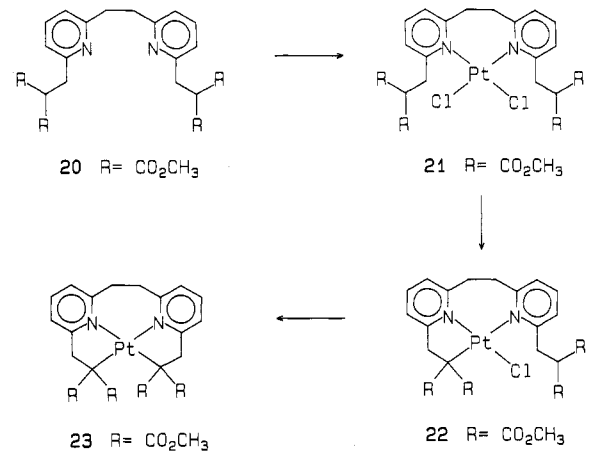
(11) (a) Matsumura, E. *J. Chem. Soc. Jpn.* **1953**, *74*, 363 (*Chem. Abstr.* **1954**, *48*, 6442b). (b) Matsumura, E.; Kirooka, T.; Imagawa, K. *Ibid.* **1961**, *82*, 616 (*Chem. Abstr.* **1962**, *57*, 12466f).

(12) Newkome, G. R.; Gupta, V. K.; Taylor, H. C. R.; Fronczek, F. R.; *Organometallics* **1984**, *3*, 1549.

Scheme V



Scheme VI



metrical nature of **15a** is shown in the ^1H NMR spectrum. The aromatic region collapsed to a well-resolved pattern: H-3, δ 7.32; H-4, δ 7.77; H-5, δ 6.87. The *cis*-vinyl and methylene protons collapsed to singlets at δ 6.00 and 3.34, respectively. The relative difficulty in forming complex **15a** versus the saturated bridge complex **25** indicated that the decrease in flexibility in the bridge hinders the approach of the second malonate anion necessary for formation of the second C–Pd bond. A similar effect has been previously noted for another rigid ligand, namely, the 2,9-phenanthroline derivative **26**;[2a] however, in that case, the second metalation could not be realized.

3. Platinum(II) Complexes. Formation of the corresponding Pt(II) complexes provided interesting insight into carbon–metal bond characteristics. Reaction of various Pt(II) salts and complexes with the ligands of this study under the standard Pd(II) conditions led to complex mixtures, which were comprised of mainly unreacted starting materials. Apparently, CH_3CN was too good of a ligand for Pt(II) and further reaction was inhibited. A change of solvents to either aqueous acetone or tetrahydrofuran gave satisfactory results. The synthesis of complex **17** was achieved by either of two methods.

The first consisted of refluxing a solution of K_2PtCl_4 and **16** in a 1:1 mixture of acetone and water, which yielded (80%) the desired N,N′-complex **17**. Alternatively, a soluion of $(Et_2S)_2PtCl_2$[13] and **16** in CH_2Cl_2 at 25 °C for 12 h gave (90%) **17**. In addition to the shifts normally observed upon N,N′-coordination, a characteristic of Pt(II) complexes is the appearance of ^{195}Pt–H coupling. For these complexes, five (5) bond coupling constants can be easily observed with H-4. Due to the poor solubility of most of the Pt(II) N,N′- and C,N,N′-coordinated complexes, good ^{13}C NMR spectra could not be obtained. A difference between these Pd(II) and Pt(II) complexes can readily be observed upon attempted cyclometalation. It has been shown[14] that a mono-metalated Pd(II) complex was formed when **16** and $PdCl_2$ were warmed (50–60 °C), in the absence of K_2CO_3, in MeCN! Addition of K_2CO_3 to the reaction mixture causes the exclusive formation of the bis-metalated complex. However, when the preformed Pt(II) N,N′-complex **17** was warmed (50–60 °C) in MeCN in the presence of K_2CO_3, only the mono-metalated complex **18** was formed in good (82%) yield.

As with complex **15a**, addition of $AgNO_3$ (1 equiv) was necessary to form the second C–Pt bond; thus, complex **1**, was smoothly converted (80%) to **19**. Comparison of the ^1H NMR spectra of the ligand **16** and the Pt(II) complex **19** showed downfield shifts of the 3,5-pyridinyl Hs, similar to those observed for the Pd(II) analogue;[2a] H-3 and H-5 were shifted to positions normal for a coordinated pyridine ring (δ 7.53 and 7.44, respectively, compared to δ 7.62 and 7.50 for Pd). These relatively large shifts, as opposed to those of the ligand **5** (0.4-0.6 ppm),[15] have been attributed to the change from a transoid to a cisoid geometry in addition to a shift due to the electronic effects of complexation. The shift of H-4 to δ 7.96 indicates that the Pt(II) is more tightly bound and hence exhibits a greater electronic effect than for complex **17** (δ 8.01). The methylene protons were also coupled with ^{195}Pt (^3J = 26.9 Hz) and are shifted downfield 0.46 ppm. This shift indicates that cyclization occurred with Pt(II); notably, for comparison, the Pd(II) complex exhibited a 0.52 ppm downfield shift. A feature of this synthetic procedure is the difficulty in forming all of the Pt(II) intermediates, in addition to the desired bis-metalated complex, when compared to Pd(II). This difficulty is observed throughout this ligand series. It should be noted that a variety of bases and solvents were utilized to form the bis-metalated complexes directly from these ligands and metal salt, but to no avail. The rationale for these difficulties is yet unclear.

Complex **12b** was synthesized (70% overall) in the same, stepwise manner via intermediate complexes **10b** and **11b**. The ^1H NMR spectrum of **12b** exhibited shifts similar to those outlined for **19**, in which the pyridine proton's signals shifted ±0.25 ppm from those of its Pd(II) analogue and with H-3 and H-5 shifting more upfield and H-4 more downfield. The ^{13}C NMR spectrum indicated that the six-membered central ring was amenable to Pt(II), since the shift of the methylene signal was significantly smaller than those observed for either Pd(II) or the 5.5.5-complex **20** (+4.8 ppm versus +13.1 and +14.2 ppm, respectively). The shift of this signal has been attributed mainly to ring strain.[2a,b]

Complex **13b** was synthesized in an analogous manner to **14a**. Analysis of the ^1H NMR spectrum of **13b** shows that, in addition to the previously observed shifts in the heteroaromatic region due to complexation, the vinyl protons were shifted slightly more upfield than for Pd(II) (δ 5.94 vs δ 6.00) and were coupled to ^{195}Pt ($^4J_{Pt,H}$ = 8.3 Hz). N,N′-Complex **13b** was subsequently converted to the C,C′,N,N-complex **15b** via the same reaction sequence as **10b** to **12b**. The Pd(II) fit appeared to be a good one, as indicated by the small (0.08 ppm) upfield shift of the methylene signal, whereas the Pt(II) coordination caused this signal to shift downfield 0.51 ppm, a shift more nor-

(13) Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1960**, *VI*, 211.
(14) Evans, D. W., unpublished results.
(15) Newkome, G. R.; Nayak, A.; Fronczek, F. R.; Kawato, T.; Taylor, H. C. R.; Meade, L.; Mattice, M. *J. Am. Chem. Soc.* **1979**, *101*, 4472.

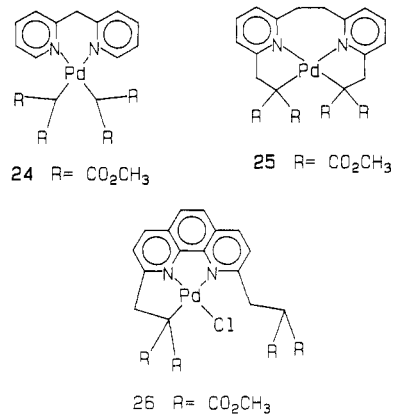


Figure 1.

mally observed with cyclometalation. Another indication of strain due to cyclometalation is seen in the further shifting of the vinyl protons to δ 5.92. Unfortunately, the unsaturated 5.7.5-complexes of both Pd(II) and Pt(II) were too insoluble to obtain good ^{13}C NMR data for further insight into the strains involved in this system.

The 5.75-ligand with a saturated ethylene bridge (**20**) is more amenable to both N,N′-coordination and subsequent C–Pt bond formations due to the flexibility of the bridge. As seen with **15b**, this ring system is not as well suited for Pt(II) as Pd(II), though the differences are smaller than for its unsaturated bridge analogue. The aromatic protons of **23** all shift downfield (0.10–0.35 ppm), with H-3 and H-4 shifting more than for **25**. The increased ring strain can also been seen from a comparison of the side-chain methylene for **23**, **22**, and **25**. For Pd(II) complex **25**, bis-cyclometalation causes a 0.09 ppm downfield shift, while for **22**, mono-metalation causes a 0.02 ppm downfield shift. However, subsequent metalation to give **23** causes this signal to shift 0.19 ppm downfield, indicative of the strain due to formation of the second C–Pt bond.

Experimental Section

All melting points were taken in capillary tubes on a Thomas-Hoover Uni-melt apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined on either an IBM NR/80 or an IBM AF/100 spectrometer using $CDCl_3$, as solvent, with TMS, as internal standard. For the unsymmetrical monometalated complexes, primed positions indicate the metalated side of the molecule. Mass spectral (MS) data (70 eV) were determined by Mr. H. Land on a Hewlett-Packard HP5895 GC/mass spectrometer and are herein reported as (relative intensity, assignment). Preparative thick-layer chromatography (ThLC) was performed on 20 × 40 cm glass plates coated with a 2-mm layer of Brinkmann silica gel PF-254-366. "Dry-Column" flash chromatography (FC) was performed by using the technique of Harwood[16] with TLC grade silica gel. IR spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer.

Solvents. Anhydrous *N,N*-dimethylformamide (DMF) was purified to remove traces of HCN, which formed by photolytic decomposition upon standing.[17] Anhydrous acetonitrile was prepared by distillation from P_2O_5, after preliminary drying over $CaCl_2$ and stored over molecular sieves.

Reagents. 2-Bromo-6-methylpyridine (**1**),[18] 1,2-bis(6-methylpyridin-2-yl)ethylene (**6**),[10] dimethyl α,α′-bis(methoxycarbonyl)[2,2′-bipyridine]-6,6′-dipropanoate (**16**),[2a] and 1,2-bis-[6-[2,2-bis(methoxycarbonyl)ethyl]pyridin-2-yl]ethane (**20**)[2b] were prepared by literature methods.

Bis(6-methylpyridin-2-yl)acetonitrile (2). Method A. A slurry of 50% NaH (1.20 g, 25 mmol) and anhyrous MeCN (1.3 mL, 1.02 g, 25 mmol) in dry DMF (25 mL) was warmed to 90 ± 10 °C. After 5 min, 2-bromo-6-methylpyridine (**1**) (1.9 mL, 3.16 g, 18 mmol) was added and the resultant solution maintained at ca. 90 °C for at least 6 h. After the solution was cooled in an ice bath, a saturated solution of aqueous NH_4Cl (25 mL) was added, which yielded an orange precipitate. The solvents were evaporated in vacuo, and the residue was dissolved in water. The resulting aqueous solution was extracted (3 × 50 mL) with $CHCl_3$, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give crude **2**, as a brown residue. Purification was achieved via column chromatography (silica gel; $CHCl_3$) to give (32%) pure **2**, as orange needles: 650 mg; mp 287–289 °C; ^1H NMR δ 2.45 (s, CH_3, 3 H), 6.26 (d, 5-py*H*, *J* = 7.5 Hz, 1 H), 7.14 (d, 3-py*H*, *J* = 7.5 Hz, 1 H), 7.60 (t, 4-py*H*, *J* 7.5 Hz, 1 H); ^{13}C NMR δ 21.4 (*C*H_3), 67.0 (*C*C≡N), 111.9 (5-py*C*), 116.7 (3-py*C*), 121.7 (*C*≡N), 136.9 (4-py*C*), 148.6 (6-py*C*), 155.6 (2-py*C*); MS, *m/e* (relative intensity) 223 (92, M^+), 222 (100, M^+ – H), 197 (45, M^+ – CN). Anal. Calcd for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82. Found: C, 75.08; H, 5.92; N, 18.94.

Method B. A solution of (6-methylpyridin-2-yl)acetonitrile[10] (1.65 g, 12.5 mmol) in dry DMF (10 mL) was added dropwise to a stirred slurry of 50% NaH (600 mg, 12.5 mmol) in DMF (80 mL) at 25 °C under argon. After H_2 evolution ceased, a solution of **1** (500 μL, 860 mg, 5 mmol) in DMF (10 mL) was added and the resulting mixture warmed to 90 ± 10 °C for 20 h. Workup as above gave (96%) **2**, 1.07 g.

2,2-Bis(6-methylpyridin-2-yl)propionitrile (3). A slurry of **2** (500 mg, 2.2 mmol), CH_3I (155 μL, 350 mg, 2.5 mmol), and anhydrous K_2CO_3 (930 mg, 6.7 mmol) in dry DMF (25 mL) was stirred at 25 °C for 24 h. The DMF was evaporated in vacuo and the residue taken up in H_2O and extracted (3 × 25 mL) with $CHCl_3$. The combined organic layers were dried over anhydrous K_2CO_3, concentrated, and column chromatographed (silica; $CHCl_3$) to give (75%) **3**, as a pale yellow solid: 400 mg; mp 183–184 °C; ^1H NMR δ 2.20 (s, C*C*H_3, 3 H), 2.53 (s, py*C*H_3, 6 H), 7.05 (d, 5-py*H*, *J* = 6.7 Hz, 2 H), 7.21 (d, 3-py*H*, *J* = 6.7 Hz, 2H), 7.52 (t, 4-py*H*, *J* = 6.7 Hz, 2 H); ^{13}C NMR δ 23.9 (py*C*H_3), 25.1 (*C*CH_3), 50.6 (*C*C≡N), 120.1 (5-py*C*), 120.2 (*C*≡N), 122.1 (3-py*C*), 136.9 (4-py*C*), 157.1 (6-py*C*), 158.1 (2-py*C*); MS, *m/e* (relative intensity) 237 (13, M^+), 222 (100, M^+ – CH_3), 211 (22, M^+ – CN). Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.86; H, 6.20; N, 17.83.

2,2-Bis[6-(bromomethyl)pyridin-2-yl]propionitrile (4). A stirred slurry of **3** (400 mg, 1.7 mmol), freshly recrystallized *N*-bromosuccinimide[19] (600 mg, 3.4 mmol), and a small amount of AIBN in CH_2Cl_2 (25 mL) was irradiated with a 150-W bulb under an argon atmosphere for 18 h. The resulting yellow-brown solution was extracted (2 × 25 mL) with 2 N NaOH, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude mixture was purified via flash chromatography (FC; SiO_2; CH_2Cl_2) to give (67%) **4**, as a pale yellow oil: 450 mg; bp 110 °C (1 mm); ^1H NMR δ 2.21 (s, C*C*H_3, 3 H), 4.52 (s, *C*H_2Br, 4 H), 7.04–7.88 (m, 3,4,5-py*H*, 6 H); MS, *m/e* (relative intensity) 397 (5, M^+), 395 (11, M^+), 393 (4, M^+), 315 (100, M^+ – Br). Anal. Calcd for $C_{15}H_{13}N_3Br_2$: C, 45.60; H, 3.32; N, 10.64. Found: C, 45.37; H, 3.25, N, 10.43.

1,2-Bis(6-methylpyridin-2-yl)ethene Di-*N*-oxide (7). A solution of **6** (1.81 g, 8.6 mmol) and 85% *m*-chloroperbenzoic acid (3.72 g, 21.5 mmol) in $CHCl_3$ (250 mL) was stirred at 25 °C for 3 h. (Note: a more concentrated solution causes precipitation of the crude product, which hinders an otherwise facile workup.) The reaction mixture was washed (2 × 50 mL) with 10% aqueous Na_2CO_3, dried anhydrous Na_2CO_3, and concentrated in vacuo to give the crude product, which was recrystallized from EtOH/C_6H_6 to give (81%) **7**, as bright, pale yellow crystals: 1.81 g; mp 246–247 °C dec (lit.[10b] mp 247–249 °C dec); ^1H NMR δ 2.53 (s, CH_3, 6 H), 7.18 (d, 5-py*H*, *J* = 7.1 Hz, 2 H), 7.22 (d, 3-py*H*, *J* = 7.1 Hz, 2 H), 7.71 (t, 4-py*H*, *J* = 7.1 Hz, 2 H), 8.18 (s, C*H*=C*H*, 2 H).

1,2-Bis[6-(chloromethyl)-2-pyridin-2-yl]ethene (8). A modification of the procedure of Matsumura[11] was used. A solution of 7 [dried (24 h) at 50–60 °C (1 mm) for at least 24 h; 1.21

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(20) Observed as specified multiplicity with ^{195}Pt satellites.

g, 5.0 mmol] and freshly recrystallized ($CHCl_3$) *p*-toluenesulfonyl chloride (2.48 g, 13.0 mmol) in anhydrous $CHCl_3$ (50 mL) was refluxed under argon for 20 h. The solvent was removed in vacuo to give a bright yellow solid, which was pyrolyzed at 100 °C under argon for 6 h. The pyrolysate was treated with H_2O (50 mL) and then filtered to remove excess *p*-toluenesulfonyl chloride. The yellow-brown filtrate was made basic with 10% aqueous Na_2CO_3 and extracted (4 × 25 mL) with CH_2Cl_2. The combined organic layers were dried (anhydrous Na_2CO_3) and concentrated to give crude **8**. Purification by FC (SiO_2; MeOH (2%)/CH_2Cl_2) gave (50%) pure **8**, as a white crystalline solid: 690 mg; mp 153–154 °C ($CHCl_3/C_6H_{12}$); ^1H NMR δ 4.67 (s, CH_2Cl, 2 H), 7.29 (d, 5-py*H*, J = 7.6 Hz, 1 H), 7.38 (d, 3-py*H*, J = 7.6 Hz, 1 H), 7.69 (s, *trans*-C*H*=C*H*, 1 H), 7.72 (t, 4-py*H*, J = 7.6 Hz, 1 H); IR (KBr) 1590 cm^{-1} (CH=CH); MS, m/e (relative intensity) 280 (58, M^+), 278 (100, M^+), 243 (37, $M^+ - Cl$), 208 (46, $M^+ - 2Cl$). Anal. Calcd for $C_{14}H_{12}N_2Cl_2$: C, 60.23; H, 4.33; N, 10.04. Found: C, 60.38; H, 4.22; N, 10.27.

General Preparation of Ligands 5 and 9. A mixture of the bis(halomethyl) compound (1 equiv), dimethyl malonate (3 equiv), and anhydrous K_2CO_3 (5 equiv) in dry DMF was stirred at 25 °C for 24 h. The mixture was filtered and concentrated in vacuo to give an off-white solid, which was crystallized from C_6H_{12} to afford the desired white crystalline solid.

2,2-Bis[6-[2,2-bis(methoxycarbonyl)ethyl]pyridin-2-yl]-propionitrile (5): 92%; mp 181–182 °C; ^1H NMR δ 2.22 (s, CCH_3, 3 H), 3.43 (d, $pyCH_2$, J = 12.4 Hz, 4 H), 3.75 (s, CO_2CH_3, 12 H), 4.22 (t, C*H*, J = 12.4 Hz, 2 H), 6.91 (t, 5-py*H*, J = 7.0 Hz, 2 H), 7.05 (d, 3-py*H*, J = 7.0 Hz, 2 H), 7.42 (t, 4-py*H*, J = 7.0 Hz, 2 H); ^{13}C NMR δ 25.3 (CCH_3), 34.9 (CH_2), 49.8 (*C*H), 50.8 (*C*C≡N), 50.6 (OCH_3), 119.8 (5-py*C*), 120.5 (*C*≡N), 121.7 (3-py*C*), 136.9 (4-py*C*), 157.1 (6-py*C*), 158.1 (2-py*C*), 169.5 (*C*=O); MS, m/e (relative intensity) 497 (23, M^+), 466 (20, $M^+ - OCH_3$), 438 (100, $M^+ - CO_2CH_3$). Anal. Calcd for $C_{25}H_{27}N_2O_8$: C, 60.35; H, 5.47; N, 8.45. Found: C, 60.17; H, 5.72; N, 8.52.

1,2-Bis[6-[2,2-bis(methoxycarbonyl)ethyl]pyridin-2-yl]-ethene (9): 87%; mp 172–173 °C; ^1H NMR δ 3.42 (d, $pyCH_2$, J = 12.6 Hz, 2 H), 3.71 (s, OCH_3, 6 H), 4.24 (t, $CHCH_2$, J = 12.6 Hz, 1 H), 7.05 (d, 5-py*H*, J = 8.0 Hz, 1 H), 7.20 (d, 3-py*H*, J = 8.0 Hz, 1 H), 7.61 (s, C*H*=C*H*, 1 H), 7.67 (t, 4-py*H*, J = 8.0 Hz, 1 H); MS, m/e (relative intensity) 470 (12, M^+), 439 ($M^+ - OCH_3$), 411 (100, $M^+ - CO_2CH_3$). Anal. Calcd for $C_{24}H_{26}N_2O_8$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.48; H, 5.25; N, 6.17.

General Preparation of Carbon–Palladium Complexes. A stirred slurry of $PdCl_2$ (1.1 equiv) in anhydrous MeCN (25 mL) was warmed to 55 ± 10 °C until the metal salt dissolved. A solution of ligand (1 equiv) in anhydrous MeCN (10 mL) was then added in one portion. After 15 min, anhydrous K_2CO_3 (3.0 equiv) was added and the resulting yellow heterogeneous mixture was stirred at ca. 55 °C for 18 h. The reaction mixture was filtered, concentrated in vacuo, and chromatographed (SiO_2; CH_2Cl_2/MeOAc). The complex was then recrystallized from the stipulated solvent.

[[(1-Cyanoethylidene)bis(6,2-pyridinediyl)bis[1,1-bis-(methoxycarbonyl)-2,1-ethanediyl]]-*C,C',N,N'*]palladium(II) (12a): orange-yellow crystals from CH_2Cl_2/C_6H_{12}; 70%; mp 195–196 °C; ^1H NMR δ 2.41 (s, CCH_3, 3 H), 3.71 (s, OCH_3, 12 H), 3.90 (s, CH_2, 4 H), 7.22 (d, 5-py*H*, J = 7.4 Hz, 2 H), 7.31 (3-py*H*, J = 7.4 Hz, 2 H), 7.63 (t, 4-py*H*, J = 7.4 Hz, 2 H); ^{13}C NMR δ 25.9 (CCH_3), 46.6 (*C*Pd), 48.0 (CH_2), 50.2 (*C*C≡N), 51.2 (OCH_3), 120.1 (5-pyC), 121.0 (C≡N), 121.5 (3-py*C*), 138.7 (4-py*C*), 154.6 (2-py*C*), 170.3 (6-py*C*), 172.3 (*C*=O). Anal. Calcd for $C_{25}H_{25}N_3O_8Pd$: C, 49.89; H, 4.19; N, 6.98. Found: C, 49.82; H, 4.37; N, 7.03.

Chloro[[2-[6-[2-[6-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]pyridin-2-yl]ethenyl]pyridin-2-yl]-1,1-bis(methoxycarbonyl)ethyl]-*C,N,N'*]palladium(II) (14a) was prepared by the above procedure except with the addition of irradiation (150-W bulb) under an argon atmosphere for 20 h. Workup as above and crystallization from acetone yielded (50%) **14a**, as deep orange crystals: mp 227–228 °C dec; ^1H NMR δ 3.31 (s, CH_2CPd, 2 H), 3.47 (d, CH_2CH, J = 6.9 Hz, 2 H), 3.71 [s, $CH(CO_2CH_3)$, 6 H], 3.75 [s, $PdC(CO_2CH_3)$, 6 H], 3.94 (t, $CHCH_2$, J = 6.9 Hz, 1 H), 5.9–6.1 (m, *cis*-C*H*=C*H*, 2 H), 6.88 (d, 5-py*H*, J = 8.3 Hz, 1 H), 7.05 (d, 2'-py*H*, J = 7.5 Hz, 1 H), 7.20–7.7 (m, 3,3',4-py*H*, 3 H), 7.75 (t, 4'-py*H*, J = 7.5 Hz, 1 H). Anal. Calcd for $C_{24}H_{25}N_2O_8PdCl$: C, 47.15; H, 4.12; N, 4.58. Found: C, 46.89; H, 4.01; N, 4.31.

[[1,2-Ethylenediylbis(6,2-pyridinediyl)bis[1,1-bis(methoxycarbonyl)-2,1-ethanediyl]]-*C,C',N,N'*]palladium(II) (15a) was prepared (90%) by the above procedure from **14a** with the addition of $AgNO_3$ (1.0 equiv): mp 164–165 °C dec; ^1H NMR δ 3.34 (s, CH_2, 2 H), 3.75 (s, OCH_3, 6 H), 6.00 (s, *cis*-C*H*=C*H*, 1 H), 6.87 (d, 5-py*H*, J = 8.0 Hz, 1 H), 7.32 (d, 3-py*H*, J = 8.0 Hz, 1 H), 7.77 (t, 4-py*H*, J = 8.0 Hz, 1 H). Anal. Calcd for $C_{24}H_{24}N_2O_8Pd$: C, 50.14; H, 4.21; N, 4.87. Found: C, 50.07; H, 4.35; N, 4.79.

General Preparation of Platinum Complexes. Method A. An aqueous solution of K_2PtCl_4 (1.1 equiv, 10 mL) was added to a solution of ligand (1.0 equiv) in acetone (15 mL). The resulting mixture was then refluxed for 6 h. The acetone was evaporated in vacuo and the aqueous solution extracted (2 × 25 mL) with CH_2Cl_2. The crude complex was then purified by either a short column (SiO_2; MeOAc) for FC under the same conditions, depending on the scale.

Method B. A solution of ligand (1.0 equiv) and $(Et_2S)_2PtCl_2$ (1.1 equiv) in CH_2Cl_2 (25 mL) was stirred for 24 h at 25 °C. The solution was then concentrated in vacuo and worked up as described above.

Dichloro[2,2-bis[6-[2,2-bis(methoxycarbonyl)ethyl]-pyridin-2-yl]propionitrile]platinum(II) (10b) was prepared (80%) by method B, as a yellow crystalline solid: mp 201–202 °C dec; ^1H NMR δ 2.45 (s, CCH_3, 3 H), 3.75 (s, OCH_3, 12 H), 4.01 (d, CH_2, J = 8.3 Hz, 4 H), 4.38 (t, C*H*, J = 8.3 Hz, 2 H), 6.95 (d, 5-pyH, J = 7.5 Hz, 2 H), 7.02 (d, 3-py*H*, J = 7.5 Hz, 2 H), 7.70 (t,[20] 4-py*H*, J = 7.5 Hz, $^5J_{Pt-H}$ = 6.5 Hz, 2 H). Anal. Calcd for $C_{25}H_{27}N_3O_8PtCl_2$: C, 39.33; H, 3.57; N, 5.50. Found: C, 39.06; H, 3.23; N, 5.42.

Chloro[[2-[6-[1-cyano-2-[6-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]pyridin-2-yl]ethylidene]pyridin-2-yl]-1,1-bis(methoxycarbonyl)ethyl]-*C,N,N'*]platinum(II) (11b). A stirred suspension of **10b** (19.1 mg, 25 μmol) and anhydrous K_2CO_3 (17.1 mg, 124 μmol) in MeCN (25 mL) was warmed to 50–60 °C. After 20 h, the solution was concentrated in vacuo and the crude mixture purified by FC (SiO_2; MeOAc (20%)/CH_2Cl_2) to give (70%) **11b**, as orange crystals: 12.7 mg; mp 217–218 °C dec; ^1H NMR δ 2.47 (s, CCH_3, 3 H), 3.75 [s, $CH(CO_2CH_3)$, 6 H], 3.77 [s, $PtC(CO_2CH_3)$, 6 H], 3.99 (d, CH_2CH, J = 8.1 Hz, 2 H), 4.05 (s,[20] CH_2CPt, $^3J_{Pt-H}$ = 24.1 Hz, 2 H), 4.40 (t, C*H*, J = 8.1 Hz, 1 H), 6.9–7.2 (m, 3,3',5,5'-py*H*, 4 H), 7.67 (t,[20] 4'-py*H*, J = 7.8 Hz, $^5J_{Pt-H}$ = 6.9 Hz, 1 H), 7.82 (t,[20] 4-py*H*, J = 8.0 Hz, $^5J_{Pt-H}$ = 7.0 Hz, 1H). Anal. Calcd for $C_{25}H_{26}N_3O_8PtCl$: C, 41.30; H, 3.61; N, 5.78. Found: C, 41.10; H, 3.44; N, 5.46.

[[(1-Cyanoethylidene)bis(6,2-pyridinediyl)bis[1,1-bis-(methoxycarbonyl)-2,1-ethanediyl]]-*C,C,N,N'*]platinum(II) (12b). A stirred solution of **11b** (18.1 mg, 25 μmol), $AgNO_3$ (4.7 mg, 27.5 μmol), and anhydrous K_2CO_3 (17.1 mg, 124 μmol) in MeCN (25 mL) was warmed to 50–60 °C for 3 h. Purification by FC [SiO_2; MeOAc (5%)/CH_2Cl_2] gave (85%) **12b**, as orange crystals: 14.6 mg; mp 185–187 °C dec; ^1H NMR δ 2.46 (s, CCH_3, 3 H), 3.77 (s, OCH_3, 12 H), 4.05 (s,[20] $(CH_2$, $^3J_{Pt-H}$ = 26.5 Hz, 4 H), 6.97 (d, 5-py*H*, J = 8.1 Hz, 2 H), 7.05 (d, 3-py*H*, J = 8.1 Hz, 2 H), 7.83 (t,[20] 4-py*H*, J = 8.1 Hz, $^5J_{Pt-H}$ = 7.1 Hz, 2 H); ^{13}C NMR δ 26.8 (CCH_3), 39.7 (CH_2), 48.2 (*C*Pt), 50.9 (OCH_3), 120.0 (5-py*C*), 120.9 (*C*≡N), 120.4 (3-py*C*), 137.8 (4-py*C*). Anal. Calcd for $C_{25}H_{25}N_3O_8Pt$: C, 43.48; H, 3.65; N, 6.08. Found: C, 43.32; H, 3.44; N, 5.97.

Dichloro[1,2-bis[6-[2,2-bis(methoxycarbonyl)ethyl]-pyridin-2-yl]ethylene]platinum(II) (13b) was prepared by method B with irradiation (150-W bulb) under an argon atmosphere for 20 h. Workup as above gave (50%) **13b**, as pale yellow crystals: mp >240 °C dec; ^1H NMR δ 3.75 (s, OCH_3, 6 H), 3.85 (d, CH_2CH, J = 9.2 Hz, 2 H), 4.40 (t, C*H*, J = 9.2 Hz, 1 H), 5.94 (s,[20] C*H*=C*H*, $^5J_{Pt-H}$ = 8.3 Hz, 1 H), 7.08 (d, 5-py*H*, J = 7.7 Hz, 1 H), 7.13 (d, 3-py*H*, J = 7.7 Hz, 1 H), 8.03 (t,[20] 4-py*H*, J = 7.7 Hz, $^5J_{Pt-H}$ = 6.5 Hz, 1 H). Anal. Calcd for $C_{24}H_{26}N_2O_8PtCl_2$: C, 39.14; H, 3.56; N, 3.80. Found: C, 38.83, H, 3.28; N, 3.67.

Chloro[[2-[6-[2-[6-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]pyridin-2-yl]ethenyl]pyridin-2-yl]-1,1-bis(methoxycarbonyl)ethyl]-*C,N,N'*]platinum(II) (14b). A stirred slurry of **13b** (74 mg, 100 μmol) and anhydrous K_2CO_3 (41 mg, 300 μmol) in MeCN (15 mL) was warmed to 50–60 °C for 6 h.

Purification by FC (SiO_2; MeOAc (50%)/CH_2Cl_2) gave (70%) **14b**, as a deep orange crystalline solid: 49 mg; mp 233–234 °C dec; ^{1}H NMR δ 3.74 (s, CO_2CH_3, 6 H), 3.76 (s, $PtCCO_2CH_3$, 6 H), 3.87 (d, CH_2CH, J = 8.7 Hz, 2 H), 3.93 (s,[20] CH_2CPt, $^3J_{Pt-H}$ = 26.3 Hz, 2 H), 4.41 (t, $CHCH_2$, J = 8.7 Hz, 1 H), 5.9–6.0 (m, CH=CH, 2 H), 7.07–7.2 (m, 3,5,5′-py$H$, 3 H), 7.35 (d, 3′-py$H$, J = 7.2 Hz, 1 H), 7.91 (t,[20] 4′-py$H$, J = 7.0 Hz, $^5J_{Pt-H}$ = 6.7 Hz, 1 H). Anal. Calcd for $C_{24}H_{25}N_2O_8PtCl$: C, 41.18; H, 3.60; N, 4.00. Found: C, 41.07; H, 3.35; N, 3.88.

[[1,2-Ethylenediylbis(6,2-pyridinediyl)bis[1,1-bis(methoxycarbonyl)-2,1-ethanediyl]]-*C,C′,N,N′*]platinum(II) (15b) was prepared (87%) by the same procedure as **14b** except with added $AgNO_3$ (1.0 equiv): mp 181–182 °C dec; ^{1}H NMR δ 3.76 (s,[20] OCH_3, $^5J_{Pt-H}$ = 2.8 Hz, 6 H), 3.93 (s,[20] CH_2, $^3J_{Pt-H}$ = 26.6 Hz, 2 H), 5.92 (s,[20] CH=CH, $^5J_{Pt-H}$ = 9.0 Hz, 1 H), 7.16 (d, 5-py$H$, J = 7.8 Hz, 1 H), 7.35 (d, 3-py$H$, J = 7.8 Hz, 1 H), 7.91 (t,[20] 4-py$H$, J = 7.8 Hz, $^5J_{Pt-H}$ = 8.0 Hz, 1 H). Anal. Calcd for $C_{24}H_{24}N_2O_8Pt$: C, 43.44; H, 3.65; N, 4.22. Found: C, 43.38; H, 3.55; N, 4.17.

Dichloro[2,2′-bipyridine-6,6′-diylbis[1,1-bis(methoxycarbonyl)-2,1-ethanediyl]]platinum(II) (17) was prepared by both methods, as a yellow crystalline solid: method A, 65%; method B, 91%; mp 208–209 °C dec; ^{1}H NMR δ 3.75 (s, OCH_3, 12 H), 4.20 (d, CH_2CH, J = 8.0 Hz, 4 H), 4.57 (t, CH, J = 8.0 Hz, 2 H), 7.21 (d, 5-py$H$, J = 7.1 Hz, 2 H), 8.01 (t,[20] 4-py$H$, J = 7.1 Hz, $^2J_{Pt-H}$ = 7.0 Hz, 2 H), 8.19 (d, 3-py$H$, J = 7.1 Hz, 2 H). Anal. Calcd for $C_{22}H_{24}N_2O_8PtCl_2$: C, 37.19; H, 3.40, N, 3.94. Found: C, 36.95; H, 3.28; N, 3.77.

Chloro[[2-[6′-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]-2,2′-bipyridin-6-yl]-1,1-bis(methoxycarbonyl)ethyl]-*C,N,N′*]platinum(II) (18). A stirred heterogenous mixture of **17** (36 mg, 50 μmol) and anhydrous K_2CO_3 (21 mg, 150 μmol) in MeCN (15 mL) was warmed to 50–60 °C for 18 h. Purification by FC (SiO_2; MeOAc (10%)/CH_2Cl_2 gave (82%) **18**, as orange crystals: 28 mg; mp 212–213 °C dec; ^{1}H NMR δ 3.75 [s, $CH(CO_2CH_3)$, 6 H], 3.77 [s,[20] $PtC(CO_2CH_3)$, $^5J_{Pt-H}$ = 2.6 Hz, 6 H], 4.00 (s,[20] CH_2CPt, $^3J_{Pt-H}$ = 25.3 Hz, 2 H), 4.18 (d, CH_2CH, J = 7.9 Hz, 2 H), 4.60 (t, $CHCH_2$, J = 7.9 Hz, 1 H), 7.1–7.7 (m, 3,4,5,5′-py$H$, 4 H), 8.0–8.2 (m, 3′,4′-py$H$, 2 H). Anal. Calcd for $C_{22}H_{23}N_2O_8PtCl$: C, 39.20; H, 3.44; N, 4.16. Found: C, 39.03; H, 3.22; N, 3.97.

[[2,2′-Bipyridine-6,6′-diylbis[1,1-bis(methoxycarbonyl)-2,1-ethanediyl]]-*C,C′,N,N′*]platinum(II) (19) was prepared (80%) by the same procedure as **18** except with added $AgNO_3$ (1.0 equiv): mp 157–159 °C dec; ^{1}H NMR δ 3.77 (s,[20] CO_2CH_3, $^5J_{Pt-H}$ = 2.6 Hz, 6 H), 4.00 (s,[20] CH_2, $^3J_{Pt-H}$ = 26.9 Hz, 2 H), 7.44 (dd, 5-py$H$, J = 7.7, 1.0 Hz, 1 H), 7.53 (dd, 3-py$H$, J = 7.7, 1.0 Hz, 1 H), 7.96 (t,[20] 4-py$H$, J = 7.7 Hz, $^5J_{Pt-H}$ = 7.0 Hz, 1 H); ^{13}C NMR δ 49.0 (CPt), 50.0 (CH_2), 51.5 (OCH_3), 119.2 (5-py$C$), 123.9 (3-py$C$), 137.6 (4-py$C$). Anal. Calcd for $C_{22}H_{22}N_2O_8Pt$: C, 41.45; H, 3.48; N, 4.40. Found: C, 41.27; H, 3.55; N, 4.67.

Dichloro[1,2-bis[6-[2,2-bis(methoxycarbonyl)ethyl]-pyridin-2-yl]ethane]platinum(II) (21) was prepared (95%) by method B, as pale yellow crystals: mp 237–238 °C dec; ^{1}H NMR δ 3.16 (s, CH_2, 2 H), 3.40 (d, CH_2, J = 8.4 Hz, 2 H), 3.71 (s, OCH_3, 6 H), 4.17 (t, CH, J = 8.4 Hz, 1 H), 6.86 (d, 5-py$H$, J = 7.9 Hz, 1 H), 6.95 (d, 3-py$H$, J = 7.9 Hz, 1 H), 7.75 (t,[20] 4-py$H$, J = 7.9 Hz, $^5J_{Pt-H}$ = 6.8 Hz, 1 H). Anal. Calcd for $C_{24}H_{28}N_2O_8PtCl_2$: C, 39.03; H, 3.82; N, 3.79. Found: C, 38.85; H, 3.55; N, 3.64.

Chloro[[2-[6-[2-[6-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]pyridin-2-yl]ethyl]pyridin-2-yl]-1,1-bis(methoxycarbonyl)ethyl]-*C,N,N′*]platinum(II) (22) was prepared (72%) by the same procedure as **18**: mp 205–206 °C dec; ^{1}H NMR δ 3.06, 3.12 [2d, py(′)CH_2CH_2, J = 8.2 Hz, 2 H], 3.38 (d, CH_2CH, J = 7.5 Hz, 2 H), 3.41 (s,[20] CH_2CPt, $^3J_{Pt-H}$ = 24.6 Hz, 2 H), 3.61 [s,[20] $PtC(CO_2CH_3)$, $^5J_{Pt-H}$ = 2.4 Hz, 6 H], 3.72 [s, $CH(CO_2CH_3)$, 6 H], 4.16 (t, CH, J = 7.5 Hz, 1 H), 6.8–7.1 (m, 3,3′,5,5′-py$H$, 4 H), 7.34 (t,[20] 4-py$H$, J = 7.5 Hz, $^5J_{Pt-H}$ = 6.8 Hz, 1 H), 7.68 (t,[20] 4′-py$H$, J = 7.4 Hz, $^5J_{Pt-H}$ = 7.0 Hz, 1 H). Anal. Calcd for $C_{24}H_{27}N_2O_8PtCl$: C, 41.06; H, 3.88; N, 3.99. Found: C, 40.83; H, 3.70; N, 4.06.

[[1,2-Ethanediylbis(6,2-pyridinediyl)bis[1,1-bis(methoxycarbonyl)-2,1-ethanediyl]]-*C,C′,N,N′*]platinum(II) (23) was prepared (93%) by the same procedure as **19**: mp 173–174 °C dec; ^{1}H NMR δ 3.12 (s, CH_2CH_2, 2 H), 3.42 (s,[20] CH_2, $^3J_{Pt-H}$ = 17.9 Hz, 2 H), 3.62 (s,[20] OCH_3, $^5J_{Pt-H}$ = 2.5 Hz, 6 H), 7.00 (d, 5-py$H$, J = 7.7 Hz, 1 H), 7.28 (d, 3-py$H$, J = 7.7 Hz, 1 H), 7.68 (t,[20] 4-py$H$, J = 7.7 Hz, $^kJ_{Pt-H}$ = 7.0 Hz, 1 H); ^{13}C NMR δ 41.5 (CH_2CH_2), 44.7 (CH_2), 49.3 (CPt), 51.3 (OCH_3), 119.7 (5-py$C$), 120.4 (3-py$C$), 137.5 (4-py$C$). Anal. Calcd for $C_{24}H_{26}N_2O_8Pt$: C, 43.31; H, 3.94; N, 4.21. Found: C, 43.39; H, 3.66; N, 4.43.

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Registry No. **1**, 5315-25-3; **2**, 117162-55-7; **3**, 117162-56-8; **4**, 117162-57-9; **5**, 117162-58-0; **6**, 16552-23-1; **7**, 117162-59-1; **8**, 117162-60-4; **9**, 117162-61-5; **10b**, 117183-75-2; **11b**, 117183-76-3; **12a**, 117183-77-4; **12b**, 117183-86-5; **13b**, 117183-78-5; **14a**, 117183-79-6; **14b**, 117183-87-6; **15a**, 117183-80-9; **15b**, 117183-88-7; **16**, 87518-62-5; **17**, 117183-81-0; **18**, 117183-82-1; **19**, 117183-83-2; **20**, 99765-48-7; **21**, 117183-84-3; **22**, 117183-85-4; **23**, 117201-60-2; MeCN, 75-05-8; $PdCl_2$, 7647-10-1; K_2P+Cl_4, 10025-99-7; $(Et_2S)_2PtCl_2$, 14873-92-8; (6-methylpyridin-2-yl)acetonitrile, 14993-80-7.