

# Articles

## A New Methodology for the Preparation of Cationic Organoplatinum(II) Complexes with Hydrogen-Bonding Functionality

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A new methodology for the preparation of two series of cationic organoplatinum(II) complexes with hydrogen-bonding functionality is described. The mononuclear complexes of the type *trans*-[Pt( $\sigma$ -aryl)L(PPh<sub>3</sub>)<sub>2</sub>]OTf (L = nicotinic acid, aryl = C<sup>3</sup>-benzoic acid (**9**) or C<sup>4</sup>-benzoic acid (**10**); L = isonicotinic acid, aryl = C<sup>3</sup>-benzoic acid (**11**) or C<sup>4</sup>-benzoic acid (**12**); OTf = trifluoromethanesulfonate (triflate)) constitute the first series, and the dinuclear complexes of the type *trans*-[Pt( $\sigma$ -aryl)(PPh<sub>3</sub>)<sub>2</sub>( $\mu$ -L)Pt( $\sigma$ -aryl)(PPh<sub>3</sub>)<sub>2</sub>](OTf)<sub>2</sub> (L = 1,1-bis(4-pyridyl)ethene, aryl = C<sup>3</sup>-benzoic acid (**19**) or C<sup>4</sup>-benzoic acid (**20**); L = 4,7-phenanthroline, aryl = C<sup>3</sup>-benzoic acid (**21**) or C<sup>4</sup>-benzoic acid (**22**); L = 4,4'-bipyridine, aryl = C<sup>3</sup>-benzoic acid (**23**) or C<sup>4</sup>-benzoic acid (**24**)) constitute the second series. The methodology described here involves the protection of the carboxylic acid group of a 3- or 4-iodobenzoic acid precursor as the *tert*-butyldiphenylsilyl ester, followed by an oxidative addition reaction of the C–I bond with the Pt(0) species Pt(PPh<sub>3</sub>)<sub>4</sub> to yield the key ( $\sigma$ -aryl)iodoplatinum(II) intermediates **3** and **4**, the structures of which were determined by X-ray crystallography. Subsequent treatment of these products with AgOTf, followed by the addition of a suitable monodentate or bridging bidentate N-donor ligand and, finally, facile removal of the silyl protecting group(s) with HOTf affords the target complexes with hydrogen-bonding functionality in high yield. Variable-temperature <sup>1</sup>H NMR experiments with the silyl-protected complexes *trans*-[Pt( $\sigma$ -aryl)L(PPh<sub>3</sub>)<sub>2</sub>]OTf (aryl = C<sup>3</sup>-*tert*-butyldiphenylsilyl benzoate, L = nicotinic acid (**5**) or isonicotinic acid (**7**)) confirm that a dynamic intramolecular process involving the pyridyl ligand is occurring. The rotational barrier of a pyridyl ligand in an organoplatinum(II) complex is reported for the first time, where  $\Delta G^\ddagger = 48.3 \pm 0.9$  and  $45.7 \pm 0.9$  kJ mol<sup>-1</sup> for complexes **5** and **7**, respectively.

### Introduction

Although the coordinate-covalent bond is an efficient and versatile motif for the construction of molecular polygons and polyhedra,<sup>1</sup> its combination with the hydrogen bond is an alternative approach for the assembly of discrete macrocyclic entities containing transition metal centers. By using coordinate-covalent bonds to afford tectons<sup>2</sup> (building blocks) of appreciable size and the highly directional hydrogen bond as a

means of controlling the self-assembly process, hybrid molecular polygons are feasible.<sup>3,4</sup>

Recently, we have shown that dinuclear organoplatinum(II) tectons with hydrogen-bonding functionality can be programmed to self-assemble into dimeric and trimeric macrocycles in CD<sub>2</sub>Cl<sub>2</sub> solution at 298 K.<sup>4a</sup> The synthetic methodology that was employed in the preparation of the complexes consisted of a well-known double oxidative addition reaction of an aryl di-iodide to a platinum(0) species,<sup>5</sup> followed by triflate metathesis of the iodo ligands in the resulting diplatinum(II) product and, finally, the addition of a N-donor ligand containing the hydrogen-bonding functionality, e.g., nicotinic acid, to the diplatinum(II)-triflate species.<sup>4</sup> In principle, one

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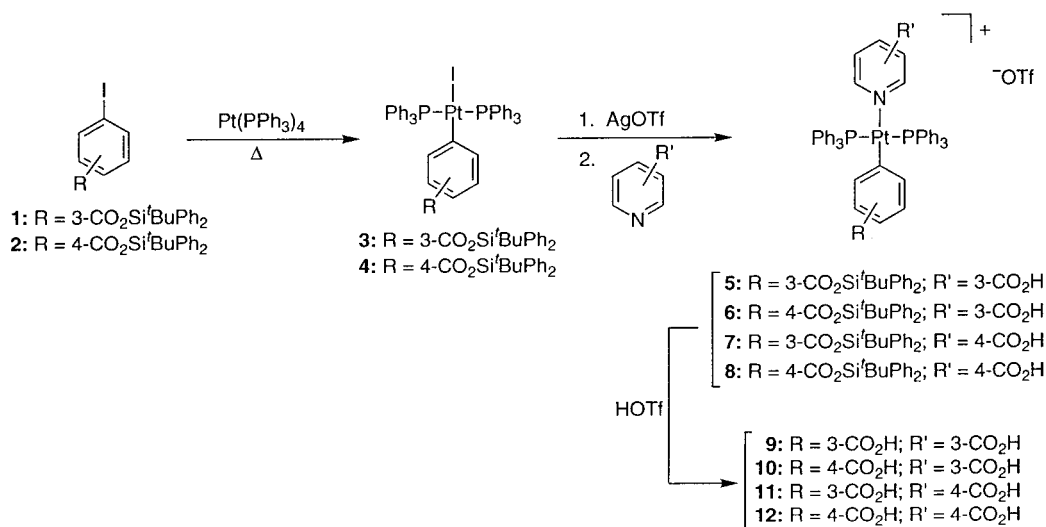
(2) (a) Ducharme, Y.; Wuest, J. D. *J. Org. Chem.* **1988**, *53*, 5787. (b) Gallant, M.; Viet, M. R. P.; Wuest, J. D. *J. Org. Chem.* **1991**, *56*, 2284.

(3) (a) Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1996**, *118*, 12467. (b) Sigel, R. K. O.; Freisinger, E.; Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1998**, *120*, 12000.

(4) (a) Gianneschi, N. C.; Tiekink, E. R. T.; Rendina, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 8474. (b) Crisp, M. G.; Pyke, S. M.; Rendina, L. M. *J. Organomet. Chem.* **2000**, *607*, 222.

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Scheme 1



could prepare platinum tectons that are isomeric to those described previously by employing an aryl iodide with hydrogen-bonding functionality in the oxidative addition reaction and by using a suitable N-donor ligand to bridge the two platinum(II) centers after triflate metathesis. However, this alternative synthetic method would present a formidable challenge. Several types of transition metal complexes in low oxidation states are known to react with the O–H bond of carboxylic acids,<sup>6</sup> and protection of the acidic functional group in the aryl iodide is a necessary step if the oxidative addition reaction involving platinum(0) is to proceed cleanly.

A protecting group that is sufficiently robust to withstand the reaction conditions throughout the synthetic pathway is required. In particular, it must be chemically stable at the elevated temperatures that are required for an oxidative addition reaction. Furthermore, the protecting group must be cleaved under mild conditions so that the integrity of the platinum coordination sphere is not compromised. Protecting the carboxylic acid as a silyl ester promises to satisfy both the stability and cleavage requirements. Silyl esters are particularly stable to nonaqueous environments, even when heated to high temperatures. In addition, they can be cleaved at room temperature by mildly acidic or basic hydrolysis or, more commonly, with fluoride salts.<sup>7</sup>

In this work, the wide applicability of a silyl ester protection/deprotection methodology will be demonstrated by the preparation of several types of cationic organoplatinum(II) complexes with carboxylic acid functionality from a platinum(0) precursor, some of which are isomeric with those reported previously.<sup>4a</sup> To the best of our knowledge, this approach has not been previously employed for an oxidative addition reaction in transition metal chemistry.

## Results and Discussion

The direct reaction of 3- or 4-iodobenzoic acid with Pt(PPh<sub>3</sub>)<sub>4</sub> in toluene solution resulted in the formation

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(7) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991.

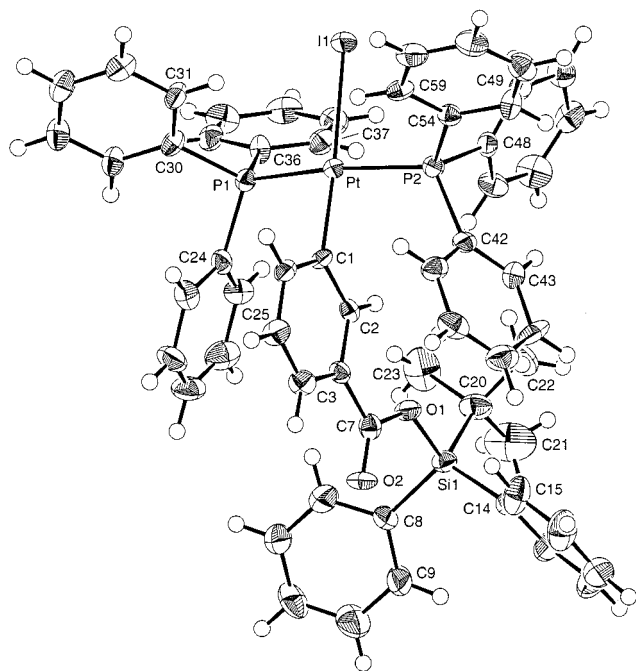
of an intractable mixture containing several unidentified products. After numerous attempts at obtaining a reproducible, high-yielding preparation of the desired organoplatinum(II) complexes with hydrogen-bonding functionality, an alternative approach employing the protection of the carboxylic acid group was investigated. 3- and 4-iodobenzoic acids were protected as the corresponding *tert*-butyldiphenylsilyl esters **1** and **2**, respectively.<sup>7</sup> Both products were obtained as colorless, crystalline solids in high yield.

**Preparation of the Iodoplatinum(II) Complexes 3 and 4.** The oxidative addition reaction of the aryl iodide derivatives **1** and **2** with Pt(PPh<sub>3</sub>)<sub>4</sub> successfully resulted in the formation of the corresponding iodoplatinum(II) complexes **3** and **4**, respectively, in high yield and purity (Scheme 1). Both products were isolated as air- and moisture-stable, colorless solids.

The <sup>1</sup>H NMR spectrum of **3** shows a broad multiplet between δ 7.17–7.74 due to the SiPh<sub>2</sub> and PPh<sub>3</sub> protons, which obscures the H<sup>2</sup> resonance of the *σ*-aryl group. The H<sup>4</sup> and H<sup>6</sup> protons appear as doublets at δ 7.03 and 7.08, respectively, each with three-bond coupling (<sup>3</sup>J<sub>HH</sub> = 7.8 Hz) to the adjacent H<sup>5</sup> proton which appears as a triplet at δ 6.28. 2D-COSY NMR experiments allowed the H<sup>4</sup>, H<sup>6</sup>, and H<sup>5</sup> protons to be assigned unambiguously. The symmetry of **4** simplifies its <sup>1</sup>H NMR spectrum, which shows only a broad multiplet between δ 7.22–7.72 due to the SiPh<sub>2</sub> and PPh<sub>3</sub> protons, a multiplet between δ 6.80–6.88 due to the AA'BB' spin system which is present in the *σ*-aryl ligand, and a singlet at δ 1.12 due to the CH<sub>3</sub> protons.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **3** and **4** display a singlet resonance that is flanked by <sup>195</sup>Pt (*I* = 1/2; abundance = 33.8%) satellite signals for the equivalent *trans*-PPh<sub>3</sub> ligands at δ 22.0 (<sup>1</sup>J<sub>Pt</sub> = 3024 Hz) and δ 21.4 (<sup>1</sup>J<sub>Pt</sub> = 3021 Hz), respectively. The chemical shifts of the resonances and the magnitude of the Pt–P coupling constants are comparable to those reported for other *σ*-arylplatinum(II) complexes with mutually *trans* PPh<sub>3</sub> ligands.<sup>4a,5,8</sup> The <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra of **3** and **4** show the expected triplet resonances at δ –4732 and –4700, respectively, with <sup>1</sup>J<sub>PtP</sub> within experimental error of those reported above.

(8) Pregosin, P. S.; Kunz, R. W. *<sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Complexes*; Springer-Verlag: Berlin, 1979.



**Figure 1.** Molecular structure and atomic numbering scheme for **3**.

**Table 1.** Selected Interatomic (Å, deg) Parameters for **3**

Pt–I	2.7071(8)	Pt–P(1)	2.309(2)
Pt–P(2)	2.302(2)	Pt–C(1)	2.015(6)
Si–O(1)	1.679(5)	C(7)–O(1)	1.346(9)
C(7)–O(2)	1.204(9)		
I–Pt–P(1)	94.42(5)	I–Pt–P(2)	88.39(5)
I–Pt–C(1)	171.5(2)	P(1)–Pt–P(2)	166.41(7)
P(1)–Pt–C(1)	88.1(2)	P(2)–Pt–C(1)	91.0(2)
Pt–C(1)–C(2)	122.8(5)	Pt–C(1)–C(6)	118.8(5)

**X-ray Structure of Complex 3.** The molecular structure of **3** was determined by X-ray crystallographic methods. The structure is shown in Figure 1, and selected geometric parameters are collected in Table 1. The platinum atom exists in the expected square planar geometry defined by a C, I, P<sub>2</sub> donor set. However, there are significant deviations from the ideal geometry, as seen in the respective deviations of the C(1), I, P(1), and P(2) atoms from their weighted least-squares plane of 0.0025(5), –0.042(2), –0.047(2), and 0.667(6) Å; the platinum atom lies 0.2172(3) Å above this plane. The aryl group, C(1)–C(6), is orthogonal to the ligand donor set, forming a dihedral angle of 83.9(2)°. The carboxylate residue is planar with the C(1)–C(6) ring, as evidenced by the O(1)/C(7)/C(3)/C(2) torsion angle of 1.7(9)°. Steric congestion in the structure is apparent from Figure 1, from which it can also be seen that two phosphorus-bound phenyl rings on each phosphorus atom are directed away from the platinum-bound aryl group. The dihedral angle of 22.9(4)° between C(1)–C(6) and C(24)–C(29), and 25.0(3)° between C(1)–C(6) and C(42)–C(47), indicates that there is no evidence for significant  $\pi \cdots \pi$  interactions between them, even though the respective distances between the ring centroids are 3.74 and 3.80 Å. The most significant intermolecular interaction in the lattice is of the type C–H $\cdots$  $\pi$ . The distance between C(33)–H(31) and the ring centroid of C(36)–C(41) is 2.75 Å, and the angle subtended at H(31) is 148.4°; symmetry operation: 0.5+x, –0.5–y, –1–z. The most

significant interaction involving the O(2) atom is manifested in the separation of 2.57 Å from a symmetry-related H(8) atom, symmetry operation: 0.5–x, –y, 0.5+z.

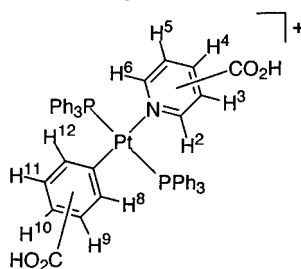
The molecular structure of **4** has also been determined. Although full details of the structure are not reported here owing to ambiguity associated with the solvent of crystallization, the molecular structure of the complex is unambiguous. Substitution at the 4-position of the  $\sigma$ -aryl ligand in **4** compared with that in **3** leads to a more “open” structure. Geometric parameters about the platinum center are experimentally equivalent to the comparable parameters in **3**, and the relative disposition of the phenyl rings also mirrors that in **3**.

**Preparation of Mononuclear Complexes with Hydrogen-Bonding Functionality.** Treatment of **3** or **4** with 1 equiv of AgOTf led to the formation of the corresponding triflate complexes in situ. The asymmetric, mononuclear complexes **5–8**, containing one free and one silyl-protected carboxylic acid group, were formed by the addition of nicotinic acid or isonicotinic acid to the solution containing the platinum(II)-triflate species. Facile removal of the silyl protecting group in **5–8** was effected by the addition of HOTf in CH<sub>2</sub>Cl<sub>2</sub> at room temperature to afford one series of target complexes **9–12** (Scheme 1), each containing two carboxylic acid groups that are available for hydrogen-bonding interactions.

Initially, Bu<sub>4</sub>NF was used for the deprotection of the carboxylic acid group in **5–8**. Although the silyl group appeared to be cleaved successfully by this method, the resulting product was found to be poorly soluble in common organic solvents, probably due to the fluoride acting as a counterion in the target cationic complexes **9–12**. To maintain the triflate counterion in these complexes, HOTf was used to hydrolyze the silyl ester. Interestingly, at no stage was electrophilic cleavage of the Pt–C bond observed, as reported for other organoplatinum(II) complexes where the reaction is thought to proceed by an oxidative addition mechanism involving protonation of the electron-rich, coordinatively unsaturated metal center to afford a hydridoplatinum(IV) intermediate.<sup>9</sup> The absence of Pt–C bond protonolysis in any of the complexes prepared in this work is most probably the result of the cationic nature of the silyl-protected complexes.

Selected <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectroscopic data for the isomeric dicarboxylic acid complexes **9–12** are presented in Table 2. The assignment of the pyridyl proton resonances was facilitated by 2D-COSY NMR experiments for **9** and **11**, whereby distinct cross-peaks were observed for all coupled protons of the pyridyl ring system. For the nicotinic acid complexes **9** and **10**, the H<sup>2</sup> proton appears as a singlet at  $\delta$  8.6 owing to its proximity to the pyridyl nitrogen atom. The H<sup>4</sup> and H<sup>6</sup> protons each appear as doublets at  $\delta$  7.85 and 8.5, respectively, with three-bond couplings to the adjacent H<sup>5</sup> proton. The H<sup>5</sup> proton in complex **9** appears as a doublet of doublets at  $\delta$  6.8, while the H<sup>5</sup> proton in **10** is masked by other aromatic signals. For the isonicotinic acid complexes **11** and **12**, the H<sup>2,6</sup> and H<sup>3,5</sup> protons appear as characteristic AA'XX' signals at  $\delta$  8.5 and 7.24, respectively, with cross-peaks to each



**Table 2.** Selected  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{195}\text{Pt}\{^1\text{H}\}$  NMR Spectroscopic Data for the Mononuclear Complexes **9–12**<sup>a</sup>

complex	$\delta$ ( $^1\text{H}$ )										$\delta$ ( $^{31}\text{P}$ ) <sup>b</sup>	$\delta$ ( $^{195}\text{Pt}$ ) <sup>b</sup>
	H <sup>2</sup>	H <sup>3</sup>	H <sup>4</sup>	H <sup>5</sup>	H <sup>6</sup>	H <sup>8</sup>	H <sup>9</sup>	H <sup>10</sup>	H <sup>11</sup>	H <sup>12</sup>		
<b>9</b>	8.58 (s)	<i>c</i>	7.85 (d, $^3J_{\text{HH}} = 7.8$ )	6.96 (dd, $^3J_{\text{HH}} = 7.8, ^3J_{\text{HH}} = 5.4$ )	8.51 (d, $^3J_{\text{HH}} = 5.4$ )	<i>d</i>	<i>c</i>	7.04 (d, $^3J_{\text{HH}} = 7.8$ )	6.39 (t, $^3J_{\text{HH}} = 7.8$ )	7.11 (d, $^3J_{\text{HH}} = 7.8$ )	22.6 (2995)	-4318 (3008)
<b>10</b>	8.58 (s)	<i>c</i>	7.84 (d, $^3J_{\text{HH}} = 7.5$ )	<i>d</i>	8.51 (d, $^3J_{\text{HH}} = 5.1$ )	6.90–6.98 (m, AA'BB')	<i>c</i>		<i>e</i>	<i>f</i>	22.2 (2993)	-4297 (2990)
<b>11</b>	8.47 (AA' portion)	7.24 (XX' portion)	<i>c</i>	<i>g</i>	<i>h</i>	<i>d</i>	<i>c</i>	6.95 (d, $^3J_{\text{HH}} = 7.5$ )	6.36 (t, $^3J_{\text{HH}} = 7.5$ )	7.10 (d, $^3J_{\text{HH}} = 7.5$ )	22.2 (2990)	-4309 (2993)
<b>12</b>	8.46 (AA' portion)	7.24 (XX' portion)	<i>c</i>	<i>g</i>	<i>h</i>	6.89 (m, AA'BB')	<i>c</i>		<i>e</i>	<i>f</i>	21.9 (2992)	-4288 (2984)

<sup>a</sup> Measured in CD<sub>3</sub>OD; coupling constants in hertz. Quoted multiplicities do not include  $^{195}\text{Pt}$  satellites. <sup>b</sup>  $^1J_{\text{PtP}}$  coupling constants (Hz) in parentheses. <sup>c</sup> Not applicable. <sup>d</sup> Resonance masked by other aromatic signals. <sup>e</sup> Equivalent to H<sup>9</sup>. <sup>f</sup> Equivalent to H<sup>8</sup>. <sup>g</sup> Equivalent to H<sup>3</sup>. <sup>h</sup> Equivalent to H<sup>2</sup>.

other in the 2D-COSY NMR spectrum. The proton resonances of the 3-substituted  $\sigma$ -aryl ligand in **9** and **11** were unambiguously assigned with the assistance of 2D-COSY NMR experiments. The H<sup>11</sup> proton appears as a triplet at ca.  $\delta$  6.4, with three-bond couplings to the H<sup>10</sup> and H<sup>12</sup> protons, which appear as doublets at ca.  $\delta$  7.0 and 7.1, respectively. All aromatic protons of the 4-substituted  $\sigma$ -aryl ligand in **10** and **12** appear as a multiplet due to the AA'BB' spin system that is present in the  $\sigma$ -aryl group. The H<sup>8,12</sup> and H<sup>9,11</sup> protons of **10** appear as a multiplet between  $\delta$  6.90–6.98, and the corresponding protons of **12** appear as a multiplet centered at  $\delta$  6.89.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **9–12** display a singlet resonance that is flanked by  $^{195}\text{Pt}$  satellite signals at ca.  $\delta$  22 ( $^1J_{\text{PtP}} \approx 3000$  Hz). The signal has shifted ca. 1 ppm downfield when compared to the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the silyl-protected complexes **5–8**. This small shift is mainly attributed to the change in solvent from CDCl<sub>3</sub> to CD<sub>3</sub>OD, which was necessary to maintain the solubility of the complexes.

The  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectra of **9–12** show the expected triplet resonance at ca.  $\delta$  -4300 and coupling constants ( $^1J_{\text{PtP}} \approx 3000$  Hz). As would be expected, essentially no shift in the  $^{195}\text{Pt}$  signal is observed after deprotection of the carboxylic acid group. Furthermore, a considerable downfield shift of ca. 400 ppm is observed in the  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectra upon substituting the less electronegative iodo ligand with a N-donor ligand.<sup>10</sup>

The complexes **9–12** were further analyzed by ESI mass spectrometry in the positive ion mode. Each of the complexes displayed a peak at  $m/z$  963 attributed to  $[\text{M} - \text{OTf}]^+$ . Furthermore, peaks at  $m/z$  840 and 719 were also detected, and they are most likely attributed to the loss of nicotinic acid followed by the loss of the  $\sigma$ -aryl

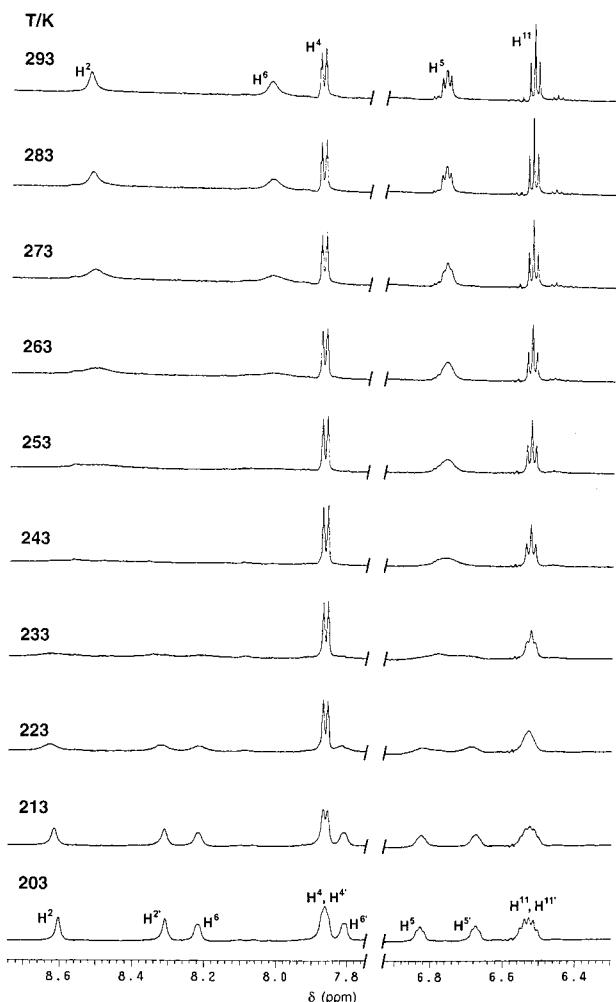
ligand from the parent platinum(II) species, a feature that has been reported previously for related complexes.<sup>4</sup>

**Dynamic Intramolecular Rearrangements of Complexes 5 and 7.** The  $^1\text{H}$  NMR spectra of **5** and **7** displayed the H<sup>2</sup> and H<sup>6</sup> protons as broad peaks at room temperature. To further investigate this phenomenon, variable-temperature (VT)  $^1\text{H}$  NMR spectroscopy experiments were performed with **5** (Figure 2) and **7** in CD<sub>2</sub>Cl<sub>2</sub> solution.

The VT  $^1\text{H}$  NMR spectroscopy experiments support a nondegenerate intramolecular rearrangement between the *syn* (**5a**) and *anti* (**5b**) isomers of complex **5** (Scheme 2). Free rotation about the Pt–C(aryl) bond is not possible as a consequence of the considerable steric interactions between the bulky PPh<sub>3</sub> ligands and the 3-substituted *tert*-butyldiphenylsilyl ester group. This proposal is supported by the X-ray structure of the precursor complex **3** (Figure 1), which shows that the silyl group is effectively locked between the mutually *trans* PPh<sub>3</sub> ligands. Furthermore, the 4-substituted isomers **6** and **8** do not exhibit related dynamic NMR behavior, consistent with free rotation about the Pt–C(aryl) bond in these complexes. The rotation of the pyridyl ligand about the Pt–N bond in **5** is not significantly hindered, however, even though it would possess partial double-bond character owing to the back-bonding of the filled metal d-orbitals with appropriate symmetry into the unoccupied  $\pi^*$ -orbitals of the pyridyl ligand.<sup>11,12</sup> As a result, both the *syn* and *anti* rotamers of **5** are readily observed by  $^1\text{H}$  NMR spectroscopy at low temperatures. As the populations of the two rotamers are almost equal in CD<sub>2</sub>Cl<sub>2</sub> solution, the difference in free energies for the ground-state molecular structures of **5**

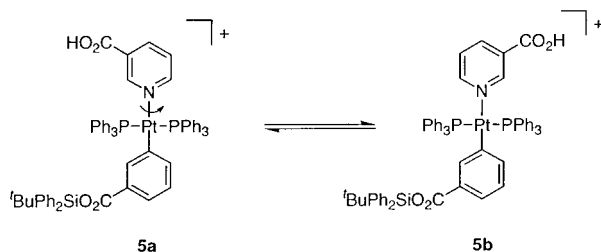
(11) Tomasik, P.; Ratajewicz, Z. *Pyridine-Metal Complexes*; John Wiley & Sons: New York, 1985; Vol. 14, Part 6B.

(12) Note that the cationic charge of complex **5** is expected to diminish the degree of back-bonding.



**Figure 2.** VT  $^1\text{H}$  NMR spectra of the pyridyl ( $\text{H}^2$ ,  $\text{H}^4$ ,  $\text{H}^5$ , and  $\text{H}^6$ ) and  $\sigma$ -aryl ( $\text{H}^{11}$ ) protons of **5** in  $\text{CD}_2\text{Cl}_2$  solution.

**Scheme 2**



must be negligible in this solvent.<sup>13</sup> Furthermore, one can reasonably assume that the free energies of activation ( $\Delta G^\ddagger$ ) for the forward and reverse processes are almost equal, and a value for  $\Delta G^\ddagger$  can thus be derived from the coalescence temperature ( $T_c$ ) by means of a modified Eyring equation.<sup>14</sup> For example,  $T_c = 243$  K and  $\Delta G^\ddagger_{243} = 48.3 \pm 0.9$  kJ mol<sup>-1</sup> for the  $\text{H}^5$  and  $\text{H}^{5'}$  signals.<sup>15</sup> To our knowledge, this is the first time the rotational barrier of a pyridyl ligand in an organoplati-

(13) We were unable to observe any significant increase in the intensity of one or more of the signals when  $\text{CD}_3\text{OD}$  was used as the solvent.

(14) Günther, H. *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1995; p 335.

(15) Alternatively,  $\Delta G^\ddagger$  for the rotation process can also be calculated from the  $T_c$  (240 K) of resonances  $\text{H}^6/\text{H}^{6'}$  and  $\text{H}^2/\text{H}^{2'}$ . In both cases,  $\Delta G^\ddagger_{240} = 46.1 \pm 1.0$  kJ mol<sup>-1</sup>. A more detailed study of this phenomenon based on line shape analysis of the spectra is planned.

num(II) complex has been determined. Its value is comparable to that determined for the rotation of the 3-picoline ligands about the Pt–N bond in the cationic coordination complex  $[\text{Pt}(\text{R}^-(+)\text{-BINAP})(3\text{-picoline})_2](\text{OTf})_2$  (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) in  $\text{CD}_3\text{OD}$  solution ( $58.5 \pm 2.1$  kJ mol<sup>-1</sup>).<sup>16</sup>

In the case of the isonicotinic acid derivative **7**, a dynamic process related to **5** was observed by means of VT  $^1\text{H}$  NMR spectroscopy experiments in  $\text{CD}_2\text{Cl}_2$  solution. In contrast to **5**, however, complex **7** displays degenerate intramolecular behavior, where the ground-state free energies of the rotamers are identical. Once again, a value for  $\Delta G^\ddagger$  can be derived from  $T_c$  (238 K) of the  $\text{H}^{2,6}$  protons, and in this case  $\Delta G^\ddagger_{238} = 45.7 \pm 0.9$  kJ mol<sup>-1</sup>.

Upon cleavage of the silyl ester by treatment of **5** or **7** with HOTf, the  $\sigma$ -aryl ligand is able to rotate freely about the Pt–C(aryl) bond, and consequently, no broad aromatic signals are observed in the room-temperature  $^1\text{H}$  NMR spectra of the deprotected complexes **9** and **11**. This observation further supports the proposed dynamic intramolecular rearrangement of complexes **5** and **7**.

**Preparation of Dinuclear Complexes with Hydrogen-Bonding Functionality.** A second series of organoplatinum(II) complexes was synthesized by the same methodology as the first series except that a bridging bidentate N-donor ligand such as 4,4'-bipyridine was added to 2 equiv of the platinum(II)-triflate species derived from the corresponding iodo complex **3** or **4**. Removal of the silyl protecting groups in **13–18** with HOTf yielded the symmetrical, dinuclear organoplatinum(II) complexes with hydrogen-bonding functionality, **19–24** (Scheme 3).

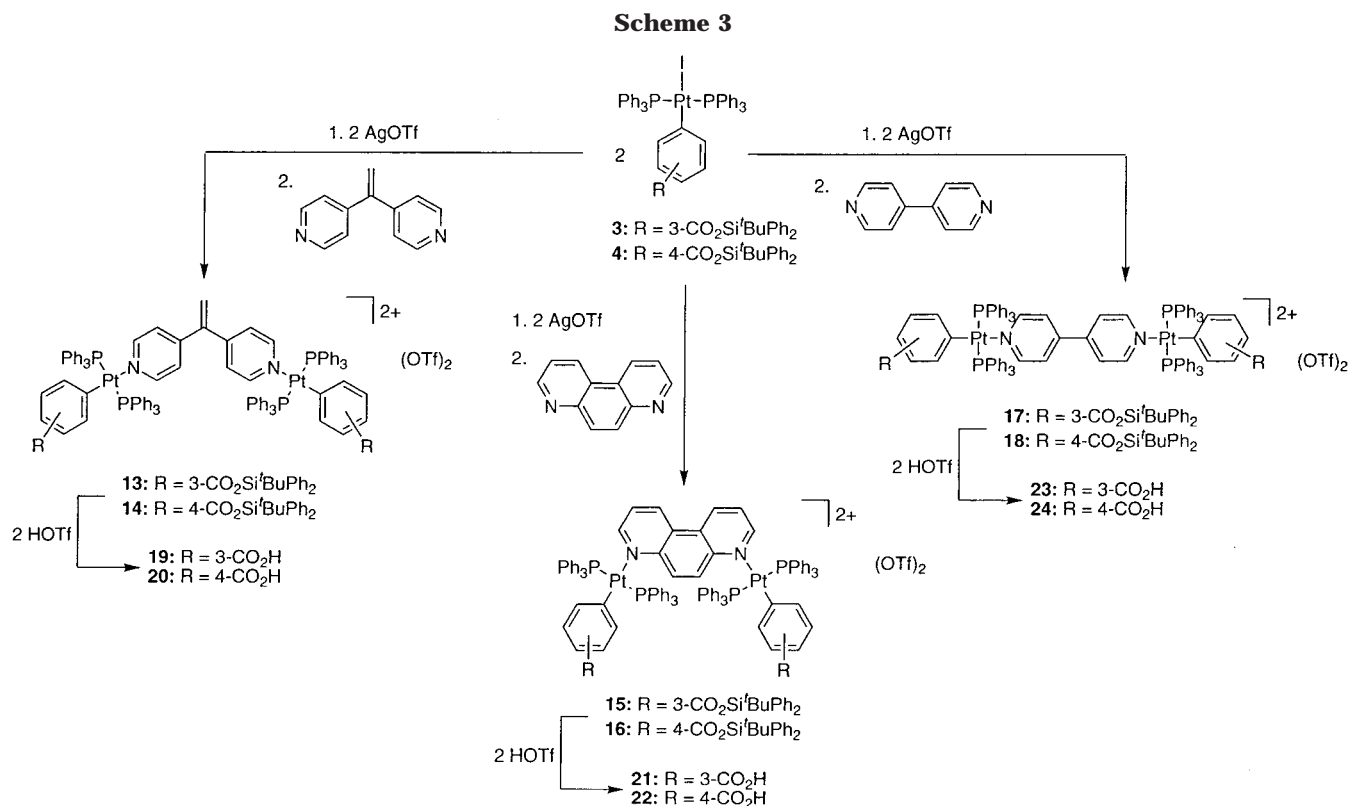
Selected  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectroscopic data for the deprotected species **19**, **20**, **23**, and **24** are presented in Table 3. The broad aromatic signals that are observed in the room-temperature  $^1\text{H}$  NMR spectra of the 4,7-phenanthroline complexes **21** and **22** (and their precursors **15** and **16**) are most probably the result of a dynamic intramolecular process related to that described earlier for the mononuclear species **5** and **7**, the details of which require further investigation. As expected, the  $^{31}\text{P}\{^1\text{H}\}$  and  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectra of **19–24** are almost identical to those observed for the corresponding silyl-protected species, and furthermore, the signals lie in the same chemical shift range as those of the mononuclear species **9–12**.

Complexes **19–24** were analyzed by ESI mass spectrometry in the positive ion mode. The base peaks in the MS of the complexes were observed at  $m/z$  1022, 1020, and 996 for the 1,1-bis(4-pyridyl)ethene, 4,7-phenanthroline, and 4,4'-bipyridine derivatives, respectively, and each is attributed to the species  $[\text{M} - 2\text{OTf} - [\text{Pt}(\text{PPh}_3)_2\text{C}_6\text{H}_4(\text{CO}_2\text{H})]^\ddagger]^+$ . No evidence was obtained for an intact, doubly charged species. The facile loss of the N-donor ligand is probably facilitated by the strong *trans* effect of the  $\sigma$ -aryl group.

## Conclusions

The facile protection and deprotection steps employed in this work extend the utility of the oxidative addition

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**Table 3. Selected  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{195}\text{Pt}\{^1\text{H}\}$  NMR Spectroscopic Data for the Dinuclear Species 19, 20, 23, and 24<sup>a</sup>**

complex	$\delta$ ( $^1\text{H}$ )							$\delta$ ( $^{31}\text{P}$ ) <sup>b</sup>	$\delta$ ( $^{195}\text{Pt}$ ) <sup>b</sup>
	H <sup>3,5</sup>	H <sup>2,6</sup>	H <sup>8</sup>	H <sup>9</sup>	H <sup>10</sup>	H <sup>11</sup>	H <sup>12</sup>		
<b>19</b>	6.38 (XX' portion)	8.29 (AA' portion)	<i>c</i>	<i>d</i>	6.96 (d, <sup>3</sup> J <sub>HH</sub> = 7.5)	6.37 (t, <sup>3</sup> J <sub>HH</sub> = 7.5)	7.12 (d, <sup>3</sup> J <sub>HH</sub> = 7.5)	22.4 (3002)	-4310 (2992)
<b>20</b>	6.36 (XX' portion)	8.28 (AA' portion)	6.90 (m, AA'BB')		<i>d</i>	<i>e</i>	<i>f</i>	22.1 (3000)	-4288 (3016)
<b>23</b>	6.84 (XX' portion)	8.39 (AA' portion)	<i>c</i>	<i>d</i>	6.96 (d, <sup>3</sup> J <sub>HH</sub> = 7.8)	6.38 (t, <sup>3</sup> J <sub>HH</sub> = 7.8)	7.11 (d, <sup>3</sup> J <sub>HH</sub> = 7.8)	22.2 (2985)	-4310 (3009)
<b>24</b>	6.83 (XX' portion)	8.36 (AA' portion)	6.90 (m, AA'BB')		<i>d</i>	<i>e</i>	<i>f</i>	21.9 (2990)	-4288 (2979)

<sup>a</sup> Measured on CD<sub>3</sub>OD; coupling constants in hertz. Quoted multiplicities do not include  $^{195}\text{Pt}$  satellites. <sup>b</sup>  $^1J_{\text{PtP}}$  coupling constants (Hz) in parentheses. <sup>c</sup> Resonance masked by other aromatic signals. <sup>d</sup> Not applicable. <sup>e</sup> Equivalent to H<sup>9</sup>. <sup>f</sup> Equivalent to H<sup>8</sup>.

reaction in inorganic synthesis when reactive organic functionalities need to be incorporated into the desired product. The wide applicability of the new methodology is demonstrated by the preparation of two series of cationic organoplatinum(II) complexes with hydrogen-bonding functionality. It greatly expands the avenues available for the synthesis of the subunits that are required in the construction of hybrid supramolecular entities, for which the combination of both the coordination and hydrogen-bonding motifs vastly increases the versatility of self-assembly as a tool for supramolecular

architecture. Studies of the self-association characteristics of selected complexes in low-polarity solvents are planned.

### Experimental Section

**General Methods.** All procedures were performed under an inert atmosphere of high-purity N<sub>2</sub> using standard Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub> and THF were distilled from CaH<sub>2</sub> and sodium metal, respectively. Toluene was predried over CaSO<sub>4</sub>, followed by distillation from sodium metal. 3- and 4-iodobenzoic acid were purified by recrystallization from toluene and ethanol, respectively, and dried in a desiccator over P<sub>2</sub>O<sub>5</sub>. All



1D NMR spectra were recorded at 298 K by means of a Varian Gemini 2000 NMR spectrometer ( $^1\text{H}$  at 300.10 MHz,  $^{31}\text{P}$  at 121.50 MHz, and  $^{195}\text{Pt}$  at 64.38 MHz). 2D and VT  $^1\text{H}$  NMR spectroscopy experiments were performed on a Varian Unity INOVA 600 MHz NMR instrument.  $^1\text{H}$  chemical shifts are reported in ppm relative to TMS.  $^{31}\text{P}\{^1\text{H}\}$  and  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectra were referenced to a sealed external standard of 85%  $\text{H}_3\text{PO}_4$  and  $\text{Na}_2[\text{PtCl}_6]$  in  $\text{D}_2\text{O}$ , respectively. Electrospray mass spectra were obtained using a Finnegan LCQ mass spectrometer, in the positive ion mode, using HPLC grade methanol as the solvent. Melting points were determined using a Kofler hot-stage apparatus under a Reichert microscope, and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1920x spectrophotometer. Elemental analyses were determined by Chemical and Micro Analytical Services, Pty. Ltd., Victoria (Australia). Tetrakis(triphenylphosphine)platinum(0)<sup>17</sup> and 1,1-bis(4-pyridyl)ethene<sup>18</sup> were prepared according to the literature procedures.

**tert-Butyldiphenylsilyl-3-iodobenzoate (1).** A solution of *N*-methylmorpholine (0.44 mL, 4.04 mmol) and *tert*-butylchlorodiphenylsilane (1.05 mL, 4.04 mmol) in THF (5 mL) was added dropwise to a stirred solution of 3-iodobenzoic acid (1.00 g, 4.03 mmol) in THF (10 mL). The resulting solution was stirred at room temperature for 20 h, during which time a white precipitate had formed. The mixture was filtered off, the solvent was removed in vacuo, and the residual oil was eluted through a plug of silica gel (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ , 2:1). The solvent was removed in vacuo to afford **1** as a white solid (1.92 g, 98%). An analytical sample was recrystallized from  $\text{CH}_2\text{Cl}_2$ /ethanol to yield colorless crystals: mp 70–72 °C; IR (KBr) 3075, 3048, 3033  $\nu(\text{Ar}-\text{H})$ , 2958, 2930, 2893, 2858  $\nu(\text{C}-\text{H})$ , 1707  $\nu(\text{C}=\text{O})$ , 1588, 1568, 1558, 1472, 1461, 1428  $\nu(\text{C}=\text{C})$   $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.47 (t, 1H,  $^3J_{\text{HH}} = 1.5$  Hz,  $\text{H}^2$ ), 8.10 (dt, 1H,  $^3J_{\text{HH}} = 7.9$  Hz,  $^4J_{\text{HH}} = 1.5$  Hz,  $\text{H}^6$ ), 7.92 (dt, 1H,  $^3J_{\text{HH}} = 7.9$  Hz,  $^4J_{\text{HH}} = 1.5$  Hz,  $\text{H}^4$ ), 7.22 (t, 1H,  $^3J_{\text{HH}} = 7.9$  Hz,  $\text{H}^5$ ), 7.74–7.70 (m, 4H, SiPh), 7.48–7.37 (m, 6H, SiPh), 1.19 (s, 9H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{IO}_2\text{Si}$ : C, 56.79; H, 4.77. Found: C, 56.61; H, 4.87.

**tert-Butyldiphenylsilyl-4-iodobenzoate (2).** Following a procedure similar to that described for **1**, 4-iodobenzoic acid (1.00 g, 4.03 mmol) in THF solution was reacted with *N*-methylmorpholine (0.44 mL, 4.04 mmol) and *tert*-butylchlorodiphenylsilane (1.05 mL, 4.04 mmol) to give **2** as a white solid (1.69 g, 86%): mp 119–120 °C; IR (KBr) 3091, 3072, 3031  $\nu(\text{C}-\text{H})$ , 2952, 2934, 2893, 2857  $\nu(\text{C}-\text{H})$ , 1702  $\nu(\text{C}=\text{O})$ , 1583, 1479, 1472, 1463, 1428  $\nu(\text{C}=\text{C})$   $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.89 (s, 4H, ArH), 7.82–7.75 (m, 4H, SiPh), 7.53–7.41 (m, 6H, SiPh), 1.23 (s, 9H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{IO}_2\text{Si}$ : C, 56.79; H, 4.77. Found: C, 56.89; H, 4.87.

**trans-Iodo(tert-butyl)diphenylsilyl benzoate-C<sup>3</sup>bis(triphenylphosphine)platinum(II) (3).** *tert*-Butyldiphenylsilyl-3-iodobenzoate (0.67 g, 1.40 mmol) in toluene (60 mL) was added to  $\text{Pt}(\text{PPh}_3)_4$  (1.50 g, 1.25 mmol). The resulting mixture was stirred at 75 °C for 14 h. After allowing the solution to cool to room temperature, the solvent was reduced in vacuo to ca. 15 mL, and *n*-hexane (50 mL) was added to precipitate the product as an off-white solid. The product was filtered off, washed with *n*-hexane, and dried in vacuo (1.43 g, 98%). An analytical sample was recrystallized from  $\text{CH}_2\text{Cl}_2$ /*n*-hexane to yield colorless crystals: mp 248–249 °C; IR (KBr) 3073, 3054  $\nu(\text{Ar}-\text{H})$ , 2954, 2930, 2856  $\nu(\text{C}-\text{H})$ , 1699  $\nu(\text{C}=\text{O})$ , 1560, 1480, 1464, 1434  $\nu(\text{C}=\text{C})$   $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.74–7.17 (m, 41H,  $\text{PPh}_3$ , SiPh,  $\text{H}^2$ ), 7.08 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^6$ ), 7.03 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^4$ ), 6.28 (t, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^5$ ), 1.13 (s, 9H,  $\text{CH}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  22.0 (s,  $^1J_{\text{PPt}} = 3024$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4732 (t,  $^1J_{\text{PtP}} = 3024$  Hz). Anal. Calcd for  $\text{C}_{59}\text{H}_{53}\text{IO}_2\text{P}_2\text{PtSi}$ : C, 58.76; H, 4.43. Found: C, 58.75; H, 4.47.

**trans-Iodo(tert-butyl)diphenylsilyl benzoate-C<sup>3</sup>bis(triphenylphosphine)platinum(II) (4).** Following a procedure similar to that described for **3**, *tert*-butyldiphenylsilyl-4-iodobenzoate (0.99 g, 2.04 mmol) in toluene was reacted with  $\text{Pt}(\text{PPh}_3)_4$  (2.03 g, 1.70 mmol) to give **4** as an off-white solid (1.97 g, 96%): mp 127–129 °C; IR (KBr) 3051  $\nu(\text{C}-\text{H})$ , 2929, 2892  $\nu(\text{C}-\text{H})$ , 1695  $\nu(\text{C}=\text{O})$ , 1577, 1480, 1434  $\nu(\text{C}=\text{C})$   $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.72–7.22 (m, 40H,  $\text{PPh}_3$ , SiPh), 6.88–6.80 (m, 4H, AA'BB', ArH),  $\delta$  1.12 (s, 9H,  $\text{CH}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.4 (s,  $^1J_{\text{PPt}} = 3021$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4700 (t,  $^1J_{\text{PtP}} = 3027$  Hz). Anal. Calcd for  $\text{C}_{59}\text{H}_{53}\text{IO}_2\text{P}_2\text{PtSi}$ : C, 58.66; H, 4.59. Found: C, 58.76; H, 4.43.

**trans-(Nicotinic acid)(tert-butyl)diphenylsilyl benzoate-C<sup>3</sup>bis(triphenylphosphine)platinum(II) Triflate (5).** To a stirred solution of **3** (0.250 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added AgOTf (0.053 g, 0.21 mmol), and the mixture was stirred at room temperature for 16 h in the absence of light. AgI was filtered off using Celite filter-aid, and the solvent was reduced in vacuo to ca. 5 mL. Nicotinic acid (0.023 g, 0.19 mmol) was added, and the mixture was stirred at room temperature for 17 h. The solvent was removed in vacuo to afford **5** as a white solid (0.239 g, 86%). An analytical sample was recrystallized from  $\text{CH}_2\text{Cl}_2$ /diethyl ether: IR (Nujol) 3394  $\nu(\text{O}-\text{H})$ , 1729, 1709  $\nu(\text{C}=\text{O})$ , 1607, 1587, 1562, 1434  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$  1252, 1220, 1187, 1158, 1039 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.48 (bs, 1H,  $\text{H}^2$ ), 8.13 (d, 1H,  $^3J_{\text{HH}} = 5.4$  Hz,  $\text{H}^6$ ), 7.87 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^4$ ), 7.65–7.19 (m, 42H,  $\text{PPh}_3$ , SiPh,  $\text{H}^8$ ,  $\text{H}^{12}$ ), 7.05 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{10}$ ), 6.82 (dd, 1H,  $^3J_{\text{HH}} = 5.4$  Hz, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^5$ ), 6.49 (t, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ ), 1.16 (s, 9H,  $\text{CH}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.2 (s,  $^1J_{\text{PPt}} = 2976$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4325 (t,  $^1J_{\text{PtP}} = 2971$  Hz). Anal. Calcd for  $\text{C}_{66}\text{H}_{58}\text{F}_3\text{NO}_7\text{P}_2\text{PtSSi}$ : C, 58.66; H, 4.33; N, 1.04. Found: C, 58.64; H, 4.49; N, 0.99.

**trans-(Nicotinic acid)(tert-butyl)diphenylsilyl benzoate-C<sup>3</sup>bis(triphenylphosphine)platinum(II) Triflate (6).** Following a procedure similar to that described for **5**, complex **4** (0.250 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (0.053 g, 0.21 mmol), followed by nicotinic acid (0.023 g, 0.19 mmol), to give **6** as a white solid (0.228 g, 83%): IR (Nujol) 3457  $\nu(\text{O}-\text{H})$ , 1729, 1699  $\nu(\text{C}=\text{O})$ , 1608, 1581, 1435  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1280, 1261, 1224, 1176, 1159, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.52 (s, 1H,  $\text{H}^2$ ), 8.22 (d, 1H,  $^3J_{\text{HH}} = 4.7$  Hz,  $\text{H}^6$ ), 7.85 (d, 1H,  $^3J_{\text{HH}} = 8.0$  Hz,  $\text{H}^4$ ), 7.70–7.67 (m, 4H, SiPh), 7.47–7.24 (m, 36H,  $\text{PPh}_3$ , SiPh), 7.08 (2H, AA' portion of AA'XX',  $\text{H}^{8,12}$ ), 6.90 (2H, XX' portion of AA'XX',  $\text{H}^{9,11}$ ), 6.84 (dd, 1H,  $^3J_{\text{HH}} = 4.7$  Hz,  $^3J_{\text{HH}} = 8.0$  Hz,  $\text{H}^5$ ), 1.14 (s, 9H,  $\text{CH}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.8 (s,  $^1J_{\text{PPt}} = 2985$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4299 (t,  $^1J_{\text{PtP}} = 2974$  Hz). Anal. Calcd for  $\text{C}_{66}\text{H}_{58}\text{F}_3\text{NO}_7\text{P}_2\text{PtSSi}$ : C, 58.66; H, 4.33; N, 1.04. Found: C, 58.42; H, 4.37; N, 0.97.

**trans-(Isonicotinic acid)(tert-butyl)diphenylsilyl benzoate-C<sup>3</sup>bis(triphenylphosphine)platinum(II) Triflate (7).** Following a procedure similar to that described for **5**, complex **3** (0.250 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (0.053 g, 0.21 mmol), followed by isonicotinic acid (0.023 g, 0.19 mmol), to give **7** as a white solid (0.238 g, 86%): IR (Nujol) 3384  $\nu(\text{O}-\text{H})$ , 1728, 1698  $\nu(\text{C}=\text{O})$ , 1617, 1588, 1560, 1438  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1279, 1254, 1224, 1164, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.12 (2H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.64–7.12 (m, 44H,  $\text{PPh}_3$ , SiPh,  $\text{H}^{3,5}$ ,  $\text{H}^8$ ,  $\text{H}^{12}$ ), 7.07 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{10}$ ), 6.47 (t, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ ), 1.15 (s, 9H,  $\text{CH}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.0 (s,  $^1J_{\text{PPt}} = 2985$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4314 (t,  $^1J_{\text{PtP}} = 2985$  Hz). Anal. Calcd for  $\text{C}_{66}\text{H}_{58}\text{F}_3\text{NO}_7\text{P}_2\text{PtSSi}$ : C, 58.66; H, 4.33; N, 1.04. Found: C, 58.49; H, 4.46; N, 0.98.

**trans-(Isonicotinic acid)(tert-butyl)diphenylsilyl benzoate-C<sup>3</sup>bis(triphenylphosphine)platinum(II) Triflate (8).** Following a procedure similar to that described for **5**, complex **4** (0.250 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (2.03 g, 1.70 mmol), followed by isonicotinic acid (0.023 g, 0.19 mmol), to give **8** as a white solid (0.226 g, 82%): IR

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(Nujol) 3501  $\nu(\text{O-H})$ , 1708, 1687  $\nu(\text{C=O})$ , 1616, 1582, 1438  $\nu(\text{C=C, C=N})$ , 1293, 1237, 1177, 1160, 1025 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.26 (2H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.70–7.67 (m, 4H, SiPh), 7.47–7.26 (m, 38H, PPh<sub>3</sub>, SiPh,  $\text{H}^{3,5}$ ), 7.03 (2H, AA' portion of AA'XX',  $\text{H}^{8,12}$ ), 6.90 (2H, XX' portion of AA'XX',  $\text{H}^{9,11}$ ), 1.14 (s, 9H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.7 (s,  $^1J_{\text{PtP}} = 2989$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4286 (t,  $^1J_{\text{PtP}} = 2993$  Hz). Anal. Calcd for  $\text{C}_{66}\text{H}_{58}\text{F}_3\text{NO}_7\text{P}_2\text{PtSi}$ : C, 58.66; H, 4.33; N, 1.04. Found: C, 58.56; H, 4.42; N, 1.02.

**trans-(Benzoic acid-*C*<sup>3</sup>)(nicotinic acid)bis(triphenylphosphine)platinum(II) Triflate (9).** To a stirred solution of complex **5** (0.120 g, 0.089 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added HOTf (0.85 mL of 0.109 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.093 mmol). The mixture was then stirred at room temperature for 2 h. Diethyl ether was added to precipitate **9** as a white solid, which was filtered off, washed with diethyl ether, and dried in vacuo (0.074 g, 75%). An analytical sample was recrystallized from  $\text{CH}_2\text{Cl}_2$ /diethyl ether: IR (Nujol) 3425  $\nu(\text{O-H})$ , 1726, 1684  $\nu(\text{C=O})$ , 1608, 1585, 1560, 1439, 1435  $\nu(\text{C=C, C=N})$ , 1287, 1263, 1225, 1167, 1027 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.58 (s, 1H,  $\text{H}^2$ ), 8.51 (d, 1H,  $^3J_{\text{HH}} = 5.4$  Hz,  $\text{H}^6$ ), 7.85 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^4$ ), 7.49–7.27 (m, 31H, PPh<sub>3</sub>,  $\text{H}^8$ ), 7.11 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{12}$ ), 7.04 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{10}$ ), 6.96 (dd, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $^3J_{\text{HH}} = 5.4$  Hz,  $\text{H}^9$ ), 6.39 (d, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  22.6 (s,  $^1J_{\text{PtP}} = 2995$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4318 (t,  $^1J_{\text{PtP}} = 3008$  Hz); ES-MS ( $m/z$ ) 963 [M - OTf]<sup>+</sup>, 840 [M - OTf - C<sub>4</sub>H<sub>4</sub>N(CO<sub>2</sub>H)]<sup>+</sup>, 719 [M - OTf - C<sub>5</sub>H<sub>4</sub>N(CO<sub>2</sub>H) - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]. Anal. Calcd for  $\text{C}_{50}\text{H}_{40}\text{F}_3\text{NO}_7\text{P}_2\text{PtS}$ : C, 53.96; H, 3.62; N, 1.26. Found: C, 53.79; H, 3.75; N, 1.35.

**trans-(Benzoic acid-*C*<sup>4</sup>)(nicotinic acid)bis(triphenylphosphine)platinum(II) Triflate (10).** Following a procedure similar to that described for **9**, complex **6** (0.110 g, 0.081 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (0.55 mL of 0.164 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.090 mmol) to give **10** as a white solid (0.070 g, 77%): IR (Nujol) 3427 (O-H), 1710  $\nu(\text{C=O})$ , 1610, 1584, 1439  $\nu(\text{C=C, C=N})$ , 1284, 1254, 1225, 1168, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.55 (s, 1H,  $\text{H}^2$ ), 8.51 (d, 1H,  $^3J_{\text{HH}} = 5.1$  Hz,  $\text{H}^6$ ), 7.84 (d, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{H}^4$ ), 7.46–7.26 (m, 30H, Ph), 6.98–6.90 (m, 5H,  $\text{H}^{8,12}$ ,  $\text{H}^{9,11}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  22.2 (s,  $^1J_{\text{PtP}} = 2993$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4297 (t,  $^1J_{\text{PtP}} = 2990$  Hz); ES-MS ( $m/z$ ) 963 [M - OTf]<sup>+</sup>, 840 [M - OTf - C<sub>4</sub>H<sub>4</sub>N(CO<sub>2</sub>H)]<sup>+</sup>, 719 [M - OTf - C<sub>5</sub>H<sub>4</sub>N(CO<sub>2</sub>H) - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]. Anal. Calcd for  $\text{C}_{50}\text{H}_{40}\text{F}_3\text{NO}_7\text{P}_2\text{PtS}$ : C, 53.96; H, 3.62; N, 1.26. Found: C, 53.80; H, 3.86; N, 1.24.

**trans-(Benzoic acid-*C*<sup>3</sup>)(isonicotinic acid)bis(triphenylphosphine)platinum(II) Triflate (11).** Following a procedure similar to that described for **9**, complex **7** (0.160 g, 0.12 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (1.2 mL of 0.107 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.13 mmol) to give **11** as a white solid (0.086 g, 65%): IR (Nujol) 3436  $\nu(\text{O-H})$ , 1732, 1679  $\nu(\text{C=O})$ , 1583, 1564, 1438, 1435  $\nu(\text{C=C, C=N})$ , 1294, 1265, 1230, 1176, 1025 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.47 (2H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.53–7.23 (m, 31H, PPh<sub>3</sub>,  $\text{H}^8$ ), 7.24 (2H, XX' portion of AA'XX',  $\text{H}^{3,5}$ ), 7.10 (d, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{H}^{12}$ ), 6.95 (d, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{H}^{10}$ ), 6.36 (t, 1H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  22.2 (s,  $^1J_{\text{PtP}} = 2990$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4309 (t,  $^1J_{\text{PtP}} = 2993$  Hz). ES-MS ( $m/z$ ): 963 [M - OTf]<sup>+</sup>, 840 [M - OTf - C<sub>4</sub>H<sub>4</sub>N(CO<sub>2</sub>H)]<sup>+</sup>, 719 [M - OTf - C<sub>5</sub>H<sub>4</sub>N(CO<sub>2</sub>H) - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]. Anal. Calcd for  $\text{C}_{50}\text{H}_{40}\text{F}_3\text{NO}_7\text{P}_2\text{PtS}$ : C, 53.96; H, 3.62; N, 1.26. Found: C, 53.65; H, 3.25; N, 1.27.

**trans-(Benzoic acid-*C*<sup>4</sup>)(isonicotinic acid)bis(triphenylphosphine)platinum(II) Triflate (12).** Following a procedure similar to that described for **9**, complex **8** (0.060 g, 0.044 mmol) in  $\text{CH}_2\text{Cl}_2$  was reacted with HOTf (0.45 mL of 0.107 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.048 mmol) to give **12** as a white solid (0.036 g, 73%): IR (Nujol) 3407  $\nu(\text{O-H})$ , 1702  $\nu(\text{C=O})$ , 1583, 1438  $\nu(\text{C=C, C=N})$ , 1282, 1225, 1183, 1154, 1032 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.46 (2H, AA' portion of AA'XX',

$\text{H}^{2,6}$ ), 7.47–7.30 (m, 30H, PPh<sub>3</sub>), 7.24 (2H, XX' portion of AA'XX',  $\text{H}^{3,5}$ ), 6.89 (m, 4H, AA'BB',  $\text{H}^{8,12}$ ,  $\text{H}^{9,11}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  21.9 (s,  $^1J_{\text{PtP}} = 2992$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4288 (t,  $^1J_{\text{PtP}} = 2984$  Hz); ES-MS ( $m/z$ ) 963 [M - OTf]<sup>+</sup>, 840 [M - OTf - C<sub>4</sub>H<sub>4</sub>N(CO<sub>2</sub>H)]<sup>+</sup>, 719 [M - OTf - C<sub>5</sub>H<sub>4</sub>N(CO<sub>2</sub>H) - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]. Anal. Calcd for  $\text{C}_{50}\text{H}_{40}\text{F}_3\text{NO}_7\text{P}_2\text{PtS}$ : C, 53.96; H, 3.62; N, 1.26. Found: C, 54.08; H, 3.54; N, 1.37.

**trans- $\mu$ -1,1-Bis(4-pyridyl)ethenebis[(*tert*-butyldiphenylsilyl benzoate-*C*<sup>3</sup>)bis(triphenylphosphine)platinum(II) Bis(triflate) (13).** Following a procedure similar to that described for **5**, complex **3** (0.210 g, 0.17 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (0.045 g, 0.17 mmol) and stirred with 1,1-bis(4-pyridyl)ethene (0.014 g, 0.078 mmol) for 1 h to give **13** as a white solid (0.202 g, 88%): IR (Nujol) 1695  $\nu(\text{C=O})$ , 1611, 1561  $\nu(\text{C=C, C=N})$ , 1276, 1260, 1222, 1150, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.14 (4H, AA' portion of AA'XX',  $\text{H}^{3,5}$ ), 7.61–7.19 (m, 64H, PPh<sub>3</sub>, SiPh,  $\text{H}^8$ ,  $\text{H}^{12}$ ), 6.96 (d, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{10}$ ), 6.43 (t, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ ), 6.42 (4H, XX' portion of AA'XX',  $\text{H}^{2,6}$ ), 5.47 (s, 2H, CH<sub>2</sub>), 1.14 (s, 18H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.6 (s,  $^1J_{\text{PtP}} = 2989$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4282 (t,  $^1J_{\text{PtP}} = 3010$  Hz). Anal. Calcd for  $\text{C}_{132}\text{H}_{116}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2\text{Si}_2$ : C, 60.08; H, 4.43; N, 1.06. Found: C, 59.90; H, 4.72; N, 1.03.

**trans- $\mu$ -1,1-Bis(4-pyridyl)ethenebis[(*tert*-butyldiphenylsilyl benzoate-*C*<sup>4</sup>)bis(triphenylphosphine)platinum(II) Bis(triflate) (14).** Following a procedure similar to that described for **5**, complex **4** (0.300 g, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (0.064 g, 0.25 mmol) and stirred with 1,1-bis(4-pyridyl)ethene (0.020 g, 0.11 mmol) for 1 h to give **14** as a white solid (0.296 g, 88%): IR (Nujol) 1699  $\nu(\text{C=O})$ , 1611, 1581, 1439  $\nu(\text{C=C, C=N})$ , 1277, 1261, 1223, 1176, 1151, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.20 (4H, AA' portion of AA'XX',  $\text{H}^{3,5}$ ), 7.70–7.67 (m, 8H, SiPh), 7.43–7.25 (m, 72H, PPh<sub>3</sub>, SiPh), 7.03 (4H, AA' portion of AA'XX',  $\text{H}^{8,12}$ ), 6.82 (4H, XX' portion of AA'XX',  $\text{H}^{9,11}$ ), 6.40 (4H, XX' portion of AA'XX',  $\text{H}^{2,6}$ ), 5.45 (s, 2H, CH<sub>2</sub>), 1.14 (s, 9H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.2 (s,  $^1J_{\text{PtP}} = 2999$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4282 (t,  $^1J_{\text{PtP}} = 3010$  Hz). Anal. Calcd for  $\text{C}_{132}\text{H}_{116}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2\text{Si}_2$ : C, 60.08; H, 4.43; N, 1.06. Found: C, 59.85; H, 4.50; N, 0.99.

**trans- $\mu$ -4,7-Phenanthrolinebis[(*tert*-butyldiphenylsilyl benzoate-*C*<sup>3</sup>)bis(triphenylphosphine)platinum(II) Bis(triflate) (15).** Following a procedure similar to that described for **5**, complex **3** (0.250 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (0.053 g, 0.21 mmol) and stirred with 4,7-phenanthroline (0.017 g, 0.094 mmol) for 1 h to give **15** as a white solid (0.245 g, 89%): IR (Nujol) 1698  $\nu(\text{C=O})$ , 1587, 1563, 1439, 1435  $\nu(\text{C=C, C=N})$ , 1277, 1260, 1223, 1153, 1031 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  9.82 (s, 2H,  $\text{H}^{5,6}$ ), 9.15 (d, 2H,  $^3J_{\text{HH}} = 4.2$  Hz,  $\text{H}^{3,8}$ ), 9.00 (d, 2H,  $^3J_{\text{HH}} = 8.4$  Hz,  $\text{H}^{1,10}$ ), 7.76–7.10 (m, 88H, PPh<sub>3</sub>, SiPh,  $\text{H}^{2,9}$ ,  $\text{H}^{12}$ ,  $\text{H}^{14}$ ,  $\text{H}^{16}$ ), 6.40 (bs, 2H,  $\text{H}^{15}$ ), 1.14 (s, 18H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.9 (s,  $^1J_{\text{PtP}} = 3029$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4267 (t,  $^1J_{\text{PtP}} = 2974$  Hz). Anal. Calcd for  $\text{C}_{132}\text{H}_{114}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2\text{Si}_2$ : C, 60.13; H, 4.36; N, 1.06. Found: C, 59.99; H, 4.58; N, 1.06.

**trans- $\mu$ -4,7-Phenanthrolinebis[(*tert*-butyldiphenylsilyl benzoate-*C*<sup>4</sup>)bis(triphenylphosphine)platinum(II) Bis(triflate) (16).** Following a procedure similar to that described for **5**, complex **4** (0.300 g, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with AgOTf (0.064 g, 0.25 mmol) and stirred with 4,7-phenanthroline (0.020 g, 0.11 mmol) for 1 h to give **16** as a white solid (0.289 g, 88%): IR (Nujol) 1700  $\nu(\text{C=O})$ , 1582, 1439  $\nu(\text{C=C, C=N})$ , 1279, 1262, 1223, 1180, 1153, 1031 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  9.83 (s, 2H,  $\text{H}^{5,6}$ ), 9.12 (d, 2H,  $^3J_{\text{HH}} = 5.1$  Hz,  $\text{H}^{3,8}$ ), 9.03 (d, 2H,  $^3J_{\text{HH}} = 8.7$  Hz,  $\text{H}^{1,10}$ ), 7.73–7.17 (m, 82H, PPh<sub>3</sub>, SiPh,  $\text{H}^{2,9}$ ), 6.94 (bs, 8H,  $\text{H}^{12,16}$ ,  $\text{H}^{13,15}$ ), 1.12 (s, 18H, CH<sub>3</sub>);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.95 (s, 2H,  $\text{H}^{5,6}$ ), 8.96 (d, 2H,  $^3J_{\text{HH}} = 8.4$  Hz,  $\text{H}^{1,10}$ ), 8.70 (d, 2H,  $^3J_{\text{HH}} = 5.4$  Hz,  $\text{H}^{3,8}$ ), 7.69–7.66 (m, 8H, SiPh), 7.50–7.13 (m, 82H, PPh<sub>3</sub>, SiPh,  $\text{H}^{2,9}$ ,  $\text{H}^{12,16}$ ,  $\text{H}^{13,15}$ ), 1.14 (s, 18H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.9 (s,  $^1J_{\text{PtP}} = 3026$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.7 (s,  $^1J_{\text{PtP}} = 3007$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



$\delta$  -4237 (t,  $^1J_{\text{PtP}} = 3035$  Hz). Anal. Calcd for  $\text{C}_{132}\text{H}_{114}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{-Pt}_2\text{S}_2\text{Si}_2$ : C, 60.13; H, 4.36; N, 1.06. Found: C, 59.92; H, 4.52; N, 0.97.

**trans- $\mu$ -4,4'-Bipyridinebis(tert-butylidiphenylsilyl benzoate- $\text{C}^3$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (17).** Following a procedure similar to that described for **5**, complex **3** (0.250 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with  $\text{AgOTf}$  (0.053 g, 0.21 mmol) and stirred with 4,4'-bipyridine (0.015 g, 0.093 mmol) for 1 h to give **17** as a white solid (0.240 g, 88%): IR (Nujol) 1699  $\nu(\text{C}=\text{O})$ , 1611, 1559, 1439  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1276, 1262, 1223, 1151, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.17 (4H, AA' portion of AA'XX',  $\text{H}^{3,5}$ ), 7.64–7.19 (m, 64H, PPh<sub>3</sub>, SiPh,  $\text{H}^8$   $\text{H}^{12}$ ), 7.09 (4H, XX' portion of AA'XX',  $\text{H}^{2,6}$ ), 6.94 (d, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{10}$ ), 6.45 (t, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ ), 1.15 (s, 18H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.1 (s,  $^1J_{\text{Ppt}} = 2981$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4311 (t,  $^1J_{\text{PtP}} = 2980$  Hz). Anal. Calcd for  $\text{C}_{130}\text{H}_{114}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2\text{-Si}_2$ : C, 59.76; H, 4.40; N, 1.07. Found: C, 59.58; H, 4.47; N, 1.10.

**trans- $\mu$ -4,4'-Bipyridinebis(tert-butylidiphenylsilyl benzoate- $\text{C}^4$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (18).** Following a procedure similar to that described for **5**, complex **4** (0.300 g, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with  $\text{AgOTf}$  (0.064 g, 0.25 mmol) and stirred with 4,4'-bipyridine (0.018 g, 0.11 mmol) for 1 h to give **18** as a white solid (0.276 g, 85%): IR (Nujol) 1699  $\nu(\text{C}=\text{O})$ , 1609, 1581  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1278, 1260, 1224, 1176, 1152, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.21 (4H, AA' portion of AA'XX',  $\text{H}^{3,5}$ ), 7.70–7.67 (m, 8H, SiPh), 7.47–7.25 (m, 72H, PPh<sub>3</sub>, SiPh), 7.08 (4H, XX' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.06 (4H, AA' portion of AA'XX',  $\text{H}^{8,12}$ ), 6.82 (4H, XX' portion of AA'XX',  $\text{H}^{9,11}$ ), 1.14 (s, 18H, CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.7 (s,  $^1J_{\text{Ppt}} = 2971$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4284 (t,  $^1J_{\text{PtP}} = 2986$  Hz). Anal. Calcd for  $\text{C}_{130}\text{H}_{114}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2\text{-Si}_2$ : C, 59.76; H, 4.40; N, 1.07. Found: C, 59.64; H, 4.50; N, 0.95.

**trans- $\mu$ -1,1-Bis(4-pyridyl)ethenebis(benzoic acid- $\text{C}^3$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (19).** Following a procedure similar to that described for **9**, complex **13** (0.090 g, 0.034 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (0.70 mL of 0.104 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.073 mmol) to give **19** as a white solid (0.053 g, 72%): IR (Nujol) 3406  $\nu(\text{O}-\text{H})$ , 1700  $\nu(\text{C}=\text{O})$ , 1612, 1561, 1480, 1439, 1435  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1277, 1260, 1224, 1159, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.29 (4H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.49–7.30 (m, 60H, PPh<sub>3</sub>), 7.12 (d, 2H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{H}^{12}$ ), 6.96 (d, 2H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{H}^{10}$ ), 6.38 (4H, XX' portion of AA'XX',  $\text{H}^{3,5}$ ), 6.37 (t, 2H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{H}^{11}$ ), 5.59 (s, 2H, CH<sub>2</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  22.4 (s,  $^1J_{\text{Ppt}} = 3002$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4310 (t,  $^1J_{\text{PtP}} = 2992$  Hz); ES-MS ( $m/z$ ) 1022 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]<sup>+</sup>, 840 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>]<sup>+</sup>, 719 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>10</sub>N<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>. Anal. Calcd for  $\text{C}_{100}\text{H}_{80}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2$ : C, 55.56; H, 3.73; N, 1.30. Found: C, 55.47; H, 3.89; N, 1.33.

**trans- $\mu$ -1,1-Bis(4-pyridyl)ethenebis(benzoic acid- $\text{C}^4$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (20).** Following a procedure similar to that described for **9**, complex **14** (0.090 g, 0.044 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (0.65 mL of 0.107 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.070 mmol) to give **20** as a white solid (0.069 g, 93%): IR (Nujol) 3419  $\nu(\text{O}-\text{H})$ , 1700  $\nu(\text{C}=\text{O})$ , 1612, 1583, 1439  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1279, 1260, 1224, 1159, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.28 (4H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.49–7.31 (m, 60H, PPh<sub>3</sub>), 6.90 (m, 8H, AA'BB',  $\text{H}^{8,12}$   $\text{H}^{9,11}$ ), 6.36 (4H, XX' portion of AA'XX',  $\text{H}^{3,5}$ ), 5.58 (s, 2H, CH<sub>2</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  22.1 (s,  $^1J_{\text{Ppt}} = 3000$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4288 (t,  $^1J_{\text{PtP}} = 3016$  Hz); ES-MS ( $m/z$ ) 1022 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]<sup>+</sup>, 840 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>]<sup>+</sup>, 719 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>10</sub>N<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>. Anal. Calcd for  $\text{C}_{100}\text{H}_{80}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2$ : C, 55.56; H, 3.73; N, 1.30. Found: C, 55.47; H, 4.09; N, 1.27.

**trans- $\mu$ -4,7-Phenanthrolinebis(benzoic acid- $\text{C}^3$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (21).** Following a procedure similar to that described for **9**, complex **15** (0.090 g, 0.034 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (0.45 mL of 0.164 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.074 mmol) to give **21** as a white solid (0.058 g, 79%): IR (Nujol) 3399  $\nu(\text{O}-\text{H})$ , 1699  $\nu(\text{C}=\text{O})$ , 1585, 1562, 1493, 1439, 1435  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1281, 1267, 1225, 1156, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  9.94 (s, 2H,  $\text{H}^{5,6}$ ), 9.16 (d, 2H,  $^3J_{\text{HH}} = 4.5$  Hz,  $\text{H}^{3,8}$ ), 9.02 (d, 2H,  $^3J_{\text{HH}} = 8.4$  Hz,  $\text{H}^{1,10}$ ), 7.41–7.16 (m, 66H, PPh<sub>3</sub>,  $\text{H}^{2,9}$   $\text{H}^{12}$   $\text{H}^{16}$ ), 7.04 (d, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{14}$ ), 6.28 (bs, 2H,  $\text{H}^{15}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  21.1 (s,  $^1J_{\text{Ppt}} = 2989$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4274 (t,  $^1J_{\text{PtP}} = 2961$  Hz); ES-MS ( $m/z$ ) 1020 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]<sup>+</sup>, 840 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup>, 719 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>. Anal. Calcd for  $\text{C}_{100}\text{H}_{78}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2$ : C, 55.61; H, 3.64; N, 1.30. Found: C, 55.62; H, 3.55; N, 1.32.

**trans- $\mu$ -4,7-Phenanthrolinebis(benzoic acid- $\text{C}^4$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (22).** Following a procedure similar to that described for **9**, complex **16** (0.160 g, 0.061 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (0.75 mL of 0.164 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.12 mmol) to give **22** as a white solid (0.112 g, 85%): IR (Nujol) 3427  $\nu(\text{O}-\text{H})$ , 1688  $\nu(\text{C}=\text{O})$ , 1584, 1490, 1481, 1439  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1276, 1265, 1224, 1180, 1155, 1032 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  9.86 (s, 2H,  $\text{H}^{5,6}$ ), 9.10 (d, 2H,  $^3J_{\text{HH}} = 4.8$  Hz,  $\text{H}^{3,8}$ ), 8.99 (d, 2H,  $^3J_{\text{HH}} = 9.0$  Hz,  $\text{H}^{1,10}$ ), 7.42–7.16 (m, 62H, PPh<sub>3</sub>,  $\text{H}^{2,9}$ ), 6.86 (bs, 8H, AA'BB',  $\text{H}^{12,16}$   $\text{H}^{13,15}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  21.0 (s,  $^1J_{\text{Ppt}} = 2978$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4252 (t,  $^1J_{\text{PtP}} = 2990$  Hz); ES-MS ( $m/z$ ) 1020 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]<sup>+</sup>, 840 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup>, 719 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>. Anal. Calcd for  $\text{C}_{100}\text{H}_{78}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2$ : C, 55.61; H, 3.64; N, 1.30. Found: C, 55.64; H, 3.55; N, 1.40.

**trans- $\mu$ -4,4'-Bipyridinebis(benzoic acid- $\text{C}^3$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (23).** Following a procedure similar to that described for **9**, complex **17** (0.150 g, 0.057 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (1.1 mL of 0.109 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.12 mmol) to give **23** as a white solid (0.101 g, 82%): IR (Nujol) 3398  $\nu(\text{O}-\text{H})$ , 1700  $\nu(\text{C}=\text{O})$ , 1611, 1559, 1439, 1435  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1279, 1258, 1224, 1166, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.39 (4H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.47–7.27 (m, 61H, PPh<sub>3</sub>,  $\text{H}^8$ ), 7.11 (d, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{12}$ ), 6.96 (d, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{10}$ ), 6.84 (4H, XX' portion of AA'XX',  $\text{H}^{3,5}$ ), 6.38 (t, 2H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{H}^{11}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  22.2 (s,  $^1J_{\text{Ppt}} = 2985$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4310 (t,  $^1J_{\text{PtP}} = 3009$  Hz); ES-MS ( $m/z$ ) 996 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]<sup>+</sup>, 840 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup>, 719 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>. Anal. Calcd for  $\text{C}_{98}\text{H}_{78}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2$ : C, 55.11; H, 3.68; N, 1.31. Found: C, 54.84; H, 3.90; N, 1.26.

**trans- $\mu$ -4,4'-Bipyridinebis(benzoic acid- $\text{C}^4$ )bis(triphenylphosphine)platinum(II) Bis(triflate) (24).** Following a procedure similar to that described for **9**, complex **18** (0.130 g, 0.050 mmol) in  $\text{CH}_2\text{Cl}_2$  was treated with HOTf (0.95 mL of 0.107 M solution in  $\text{CH}_2\text{Cl}_2$ , 0.10 mmol) to give **24** as a white solid (0.105 g, 99%): IR (Nujol) 3413  $\nu(\text{O}-\text{H})$ , 1700  $\nu(\text{C}=\text{O})$ , 1611, 1583, 1439, 1435  $\nu(\text{C}=\text{C}, \text{C}=\text{N})$ , 1282, 1260, 1225, 1176, 1030 (OTf)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  8.36 (4H, AA' portion of AA'XX',  $\text{H}^{2,6}$ ), 7.46–7.30 (m, 60H, PPh<sub>3</sub>), 6.90 (m, 8H, AA'BB',  $\text{H}^{8,12}$   $\text{H}^{9,11}$ ), 6.83 (4H, XX' portion of AA'XX',  $\text{H}^{3,5}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  21.9 (s,  $^1J_{\text{Ppt}} = 2990$  Hz);  $^{195}\text{Pt}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  -4288 (t,  $^1J_{\text{PtP}} = 2979$  Hz); ES-MS ( $m/z$ ) 996 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>]<sup>+</sup>, 840 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup>, 719 [M - 2OTf - [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup> - C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)]<sup>+</sup>. Anal. Calcd for  $\text{C}_{98}\text{H}_{78}\text{F}_6\text{N}_2\text{O}_{10}\text{P}_4\text{Pt}_2\text{S}_2\cdot\text{CH}_2\text{Cl}_2$ : C, 53.54; H, 3.63; N, 1.26. Found: C, 53.71; H, 3.81; N, 1.50.

**X-ray Crystallography.** Suitable crystals of complex **3** were grown from  $\text{CH}_2\text{Cl}_2/n$ -hexane by means of diffusion layering techniques. Data for a colorless crystal of **3** ( $11 \times 0.15 \times 0.40$  mm) were collected at 173 K employing graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Rigaku AFC7R diffractometer. Corrections were made for Lorentz and polarization effects<sup>19</sup> and for absorption using an empirical procedure.<sup>20</sup>

**Crystal data for 3:**  $\text{C}_{59}\text{H}_{53}\text{I}_2\text{O}_2\text{P}_2\text{PtSi}$ ,  $M = 1206.1$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.014(4)$  Å,  $b = 36.823(8)$  Å,  $c = 11.614(4)$  Å,  $V = 5138(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.559$  g cm<sup>-3</sup>,  $T = 173$  K,  $\mu(\text{Mo } K\alpha) = 34.49$  cm<sup>-1</sup>, 12 249 reflections measured,  $\theta_{\text{max}} = 27.5^\circ$ , 9051 unique, 5031 with  $I \geq 2.0\sigma(I)$ .

The structure was solved by heavy-atom methods<sup>21</sup> and refined by a full-matrix least-squares procedure based on  $F$ .<sup>19</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters, and H atoms were included in the model in their calculated positions (C–H 0.95 Å). The refinement was continued until convergence with the application of a weighting scheme of the form  $w = 1/[\sigma^2(F_o) + 0.00001|F_o|^2]$  when  $R = 0.030$  and  $R_w = 0.029$ . The absolute structure was deter-

mined by comparing the refinements for both hands. The structure reported herein had a significantly reduced value of  $R_w$ . Figure 1 shows a diagram of the molecule that was drawn with ORTEP<sup>22</sup> at the 50% probability level. PLATON<sup>23</sup> was also used in the analysis of crystal structure.

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**Supporting Information Available:** X-ray crystallographic data file for **3**, including atomic coordinates, bond distances and angles, and thermal parameters, is available in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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