

A Family of Platinaoxetanes

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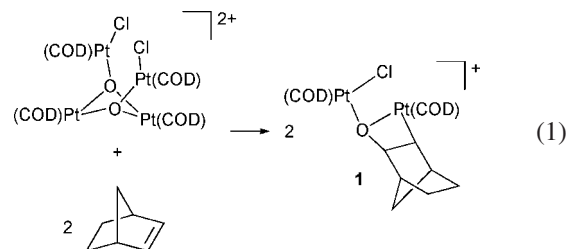
Treatment of the platinaoxetane $[\text{Pt}_2(\text{COD})_2(\text{OC}_7\text{H}_{10})\text{Cl}]\text{BF}_4$ (**1**), prepared from oxo complex $[\text{Pt}_4(\text{COD})_4(\text{O})_2(\text{Cl})_2](\text{BF}_4)_2$ and norbornene, with Cl^- yields platinaoxetane $\text{Pt}(\text{COD})(\text{OC}_7\text{H}_{10})$ (**2**) and $(\text{COD})\text{PtCl}_2$. Addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to **2** gives the BF_3 adduct $\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**3**). Treatment of **1** with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ also affords **3** along with $[\text{Pt}(\text{COD})(\mu\text{-Cl})_2(\text{BF}_4)_2]$. COD displacement from **1** by PEt_3 gives $\text{Pt}(\text{PEt}_3)_2(\text{OC}_7\text{H}_{10})$ (**5**) and $[\text{Pt}(\text{PEt}_3)_3(\text{Cl})]\text{BF}_4$. Complex **5** is also available from **2** and PEt_3 . Treatment of **5** with BF_3 gives $\text{Pt}(\text{PEt}_3)_2(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**6**). COD displacement from **3** by PPh_3 , bis(diphenylphosphino)ethane (dppe), 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy), or 4,4'-di-*tert*-butyl-2,2'-bipyridine ($\text{Bu}'_2\text{bpy}$) yields $\text{Pt}(\text{PPh}_3)_2(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**7**), $\text{Pt}(\text{dppe})(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**8**), $\text{Pt}(\text{Me}_2\text{bpy})(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**9**), and $\text{Pt}(\text{Bu}'_2\text{bpy})(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**10**), respectively. All new complexes have been fully characterized by ^1H , ^{13}C , DEPT, ^1H – ^1H COSY, ^1H – ^{13}C COSY (HMQC), and ^{195}Pt NMR spectroscopy and elemental analysis. Three complexes (**3**, **6**, **10**) were characterized by single-crystal X-ray crystallography.

Introduction

1-Metalla-2-oxacyclobutanes (metallaoxetanes)¹ have been of interest for a number of years as key species in alkene oxidation, metal-mediated epoxide reactions, and other transformations.^{2–5} Most recently, computational studies of the Wacker reaction have implicated a protonated palladium metallaoxetane.⁶ Despite this long-standing interest, relatively few metallaoxetanes have been prepared and studied.

The first metallaoxetanes are platinaoxetanes and are produced by Pt(0) insertion into the C–O bond of the activated epoxide tetracyanooxirane (2,2,3,3-tetracyanooxacyclop propane) with PtL_4 ($\text{L} = \text{AsPh}_3$, PPh_3).^{7–9} An analogous reaction with isobutylene oxide is reported to also give a platinaoxetane.¹⁰ Similarly, the Rh(I) complex $\text{Rh}(\text{PMe}_3)_3\text{Br}$ inserts into the C–O bond of isobutylene oxide to give a rhodaoxetane.^{11,12} Metallaoxetanes have also been obtained from the reaction of alkene complexes with dioxygen or

hydrogen peroxide,^{13–18} by ketone addition to a carbene complex,¹⁹ and by other less direct routes.^{11,12,20–22}



In 2003, we reported the first isolation of a metallaoxetane from the reaction of an oxo complex (eq 1).²³ This same oxo complex oxidizes ethylene to acetaldehyde and propylene to acetone presumably via analogous platinaoxetanes. More recently, an auroxetane has been obtained from the reaction of a gold(III) oxo complex with norbornene.²⁴

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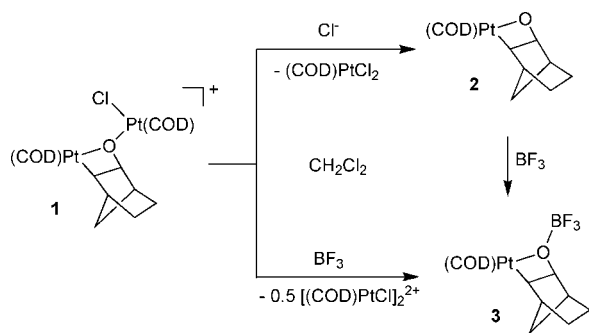
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Scheme 1



Platinaoxetane **1** displays unusual reactivity,²⁵ clearly indicating the need to further explore the chemistry of metallaoxetanes. Although a number of oxo complexes have been prepared previously in our group that could provide further examples of metallaoxetanes, they are generally found to be unreactive with alkenes.^{26–39} Fortunately, expectedly facile displacement of 1,5-COD by other ligands in **1** provides an excellent opportunity to easily prepare a family of platinaoxetanes that are unavailable by other means. In this paper we report new platinaoxetanes both by simple COD displacement and by removal and substitution of the Lewis acid fragment [(COD)Pt(Cl)]⁺ in **1**. The new complexes have been fully characterized by ¹H, ¹³C, DEPT, ¹H–¹H COSY, ¹H–¹³C COSY (HMQC), and ¹⁹⁵Pt NMR spectroscopy and elemental analysis. Three have been characterized by single-crystal X-ray crystallography.

Results and Discussion

Removal and Substitution of [(COD)Pt(Cl)]⁺ in **1.** Addition of an equimolar amount of Et₄NCl to a solution of **1** in CH₂Cl₂ gives a solution with a ¹⁹⁵Pt NMR spectrum showing complete loss of the peaks for **1** and two new peaks. One at –2908 ppm is due to new neutral platinaoxetane (COD)Pt(C₇H₁₀O) (**2**), and the other at –3338 ppm is due to (COD)PtCl₂, indicating the reaction stoichiometry shown in Scheme 1. The (COD)PtCl₂ is readily removed by precipitation with excess ether, leaving **2** in solution. Evaporation of the solvents gives white **2**, which is slightly soluble in hexane and soluble in ether, C₆H₆, and CH₂Cl₂.

Complex **2** was characterized by ¹H, ¹³C, DEPT, ¹H–¹H COSY, ¹H–¹³C COSY (HMQC), and ¹⁹⁵Pt NMR spectroscopy and elemental analysis. Crystals of **2** for X-ray analysis could not be obtained. Table 1 gives selected NMR data. ¹H NMR

spectra of **2** in CD₂Cl₂ and C₆D₆ display different patterns. The NB fragment exhibits resonances for all 10 protons (one overlapping with a COD peak) in C₆D₆. The most downfield peak, a broad singlet at 6.62 ppm with Pt satellites (*J*_{Pt–H} = 60 Hz), is assigned to the proton adjacent to the oxygen atom, H1 (see Table 1). The most upfield singlet at 0.84 ppm with *J*_{Pt–H} = 70 Hz is assigned to the Pt-bonded CH (H2). A singlet at 2.06 ppm with weaker coupling to ¹⁹⁵Pt (44 Hz) is assigned to H3, the bridgehead hydrogen atom adjacent to the Pt-bonded carbon atom. The COD olefinic protons *trans* to the carbon atom appear at 5.26 ppm with no satellites. The COD olefinic protons *trans* to the oxygen atom are found at 3.84 ppm with Pt satellites (*J*_{Pt–H} = 59 Hz). The COD methylene protons are in the range 1.89 to 1.33 ppm. ¹³C NMR spectra show 15 distinct carbon resonances. A peak at 8.6 ppm shows a large ¹³C–¹⁹⁵Pt coupling of 517 Hz and is assigned to a Pt-bonded norbornene carbon atom, C2. C1, the oxygen-bonded norbornene carbon, is found at 99.5 ppm with *J*_{Pt–C} = 128 Hz.

Changing the NMR solvent to CD₂Cl₂ alters the appearance of the ¹H NMR spectrum of **2**. Instead of a broad singlet, proton H1 appears as a doublet and is shifted upfield to 5.99 ppm with *J*_{H–H} = 5 Hz and *J*_{Pt–H} = 60 Hz. Other NB fragment protons are similarly shifted upfield, but the olefinic protons *trans* to the oxygen atom are shifted downfield to 4.19 ppm with somewhat stronger coupling to ¹⁹⁵Pt (75 Hz). The COD methylene protons are shifted downfield to between 2.53 and 2.05 ppm. The ¹⁹⁵Pt NMR resonance for **2** is –2892 (C₆D₆) or –2908 ppm (CD₂Cl₂).

Addition of BF₃·Et₂O to an equimolar amount of **2**, followed by removal of the volatiles gives white platinaoxetane (COD)Pt(C₇H₁₀OBF₃) (**3**) (Scheme 1). Complex **3** is also obtained by reaction of BF₃·Et₂O with **1**, followed by removal of [(COD)Pt(Cl)]₂(BF₄)₂ (Scheme 1). Crystals of **3** are readily obtained, and one was subjected to X-ray analysis, confirming the formulation. A drawing of the solid-state structure of **3** is given in Figure 1. Crystallographic data are summarized in Table 2. Selected bond distances and bond angles are given in Table 3. A discussion of the structure may be found below.

NMR spectra are similar to those for **2**. Selected data are given in Table 1. The ¹H NMR spectrum of **3** in CD₂Cl₂ shows the COD olefinic protons *trans* to oxygen at 4.68 and 4.50 ppm flanked with satellites (*J*_{Pt–H} = 68 Hz). Although not equivalent, the remaining COD olefinic protons are found as a single multiplet peak at 5.79 ppm with satellites (*J*_{Pt–H} = 38 Hz). The H1 resonance is a doublet with satellites at 6.08 ppm with *J*_{H–H} = 5.7 Hz and *J*_{Pt–H} = 33 Hz. The resonance of H2 is a doublet of doublets at 1.41 ppm due to coupling to H1 and H3. The two protons on C7 are found at 2.56 and 1.23 ppm. The other protons of the NB fragment are indistinct because of overlap with other peaks. In the spectrum in C₆D₆ all 10 NB fragment protons are resolved. The H1 proton appears as a doublet shifted downfield compared to CD₂Cl₂ to 6.42 ppm, but the H2 proton is shifted upfield to 0.76 ppm. The two COD olefinic protons *trans* to oxygen overlap and appear upfield from those in CD₂Cl₂ at 3.63 ppm with satellites (*J*_{Pt–H} = 80 Hz). The ¹⁹⁵Pt NMR resonance for **3** (–3103 ppm in C₆D₆, –3116 ppm in CD₂Cl₂) is at a lower frequency than for **2** (–2891 ppm in C₆D₆).

COD Ligand Substitution. PEt₃ addition to **1** or **2** results in rapid substitution of the COD ligand with two PEt₃ ligands and, in the case of **1**, displacement of the [(COD)Pt(Cl)]⁺ fragment as [Pt(PEt₃)₃(Cl)]⁺ (Scheme 2). The platinaoxetane product (PEt₃)₂Pt(OC₇H₁₀) (**5**) is readily isolated as a white solid soluble in hydrocarbon solvents. The ³¹P NMR spectrum of **5** shows two doublets flanked by ¹⁹⁵Pt satellites. The inequivalence

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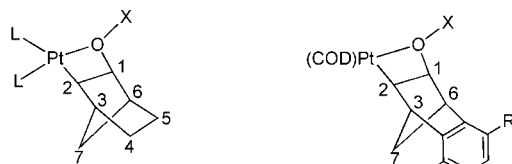
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Table 1. Selected NMR Data and Numbering Scheme ^a

- 1, L₂ = COD, X = (COD)PtCl⁺
 2, L₂ = COD, X = none
 3, L₂ = COD, X = BF₃
 5, L = PET₃, X = none
 6, L = PET₃, X = BF₃
 7, L = PPh₃, X = BF₃
 8, L₂ = dppe, X = BF₃
 9, L₂ = Me₂bpy, X = BF₃
 10, L₂ = Bu^tbpy, X = BF₃
 R = OC(O)CH₃
 4, X = BF₃
 11, X = (COD)PtCl⁺

	δ H1	δ H2	δ C1	δ C2	δ Pt
1 ^{b,e}	6.23 (<i>J</i> _{Pt-H} = 32)	1.36 (dd, <i>J</i> _{H-H} = 5.5, 2.2)	110.3	19.9	−2965, −3099
11 ^{b,e}	6.21 (<i>J</i> _{Pt-H} = 34)	1.44 (d, <i>J</i> _{H-H} = 5.5, <i>J</i> _{Pt-H} = 56)	107.7 ^d	16.6 ^d	−3054, −3110
2 ^b	5.99 (<i>J</i> _{PtH} = 60)	0.69 (br s, <i>J</i> _{PtH} = 66)	98.7	8.8	−2908
2 ^c	6.62 (<i>J</i> _{PtH} = 60)	0.84 (br s, <i>J</i> _{PtH} = 70)	99.5	8.6	−2891
3 ^b	6.08 (<i>J</i> _{PtH} = 33)	0.89 (m) ^f	101.2	18.6	−3117
3 ^c	6.42 (<i>J</i> _{PtH} = 33)	0.76 (dd, <i>J</i> _{H-H} = 5.7, 2.1)			−3103
4 ^{b,e}	5.93	1.36 (d, <i>J</i> _{H-H} = 5.4, <i>J</i> _{PtH} = 58)	98.5	16.7	−3204
5 ^c	6.92 (<i>J</i> _{PtH} = 40)	0.77 (m, <i>J</i> _{PtH} = 40.5)	100.1	8.2	−3883
6 ^c	6.65	~0.66 ^f	100.4	8.1	−4008
7 ^b	5.97	0.47 (d, <i>J</i> _{H-H} = 5.5)	98.6	23.4	−4049
8 ^b	6.16	0.77 (m)	100.9	24.1	−4148
9 ^b	5.92	1.66 (dd, <i>J</i> _{H-H} = 6, 2.5)			−4045
10 ^b	5.92	1.66 (dd, <i>J</i> _{H-H} = 5.5, 2)	102.0	3.8	−4042

^a Shifts in ppm, coupling constants in Hz. ^b In CD₂Cl₂. ^c In C₆D₆. ^d In CD₃NO₂. ^e From ref 23 and 25. ^f Overlapping with another peak.

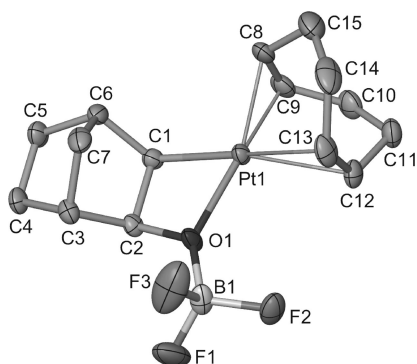


Figure 1. Drawing of the solid-state structure of **3** (50% probability ellipsoids, hydrogen atoms omitted for clarity).

Table 2. Crystal Data and Structure Refinement Details for **3**, **6**, and **10**^a

	3	6	10
formula	C ₁₅ H ₂₂ BF ₃ OPt	C ₁₉ H ₄₀ BF ₃ OP ₂ Pt · C ₆ H ₆	C ₂₅ H ₃₄ BF ₃ N ₂ OPt · 1.125(C ₇ H ₈)
fw	481.23	687.46	745.09
space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> , Å	13.6535(6)	9.8764(11)	30.3734(12)
<i>b</i> , Å	11.6850(5)	21.340(2)	10.4959(4)
<i>c</i> , Å	18.6671(8)	13.5382(14)	23.0024(9)
α, deg	90	90	90
β, deg	90	93.188(2)	97.1150(10)
γ, deg	90	90	90
<i>V</i> , Å ³	2978.2(2)	2849.0(5)	7276.6(5)
<i>Z</i>	8	4	8
<i>d</i> _{calc} , g/cm ³	2.147	1.603	1.360
μ, mm ^{−1}	9.450	5.073	3.896
<i>R</i> ¹ , w <i>R</i> ² ^c	0.0287, 0.0614	0.0219, 0.0436	0.0350, 0.0823
Gof	1.038	1.017	0.996

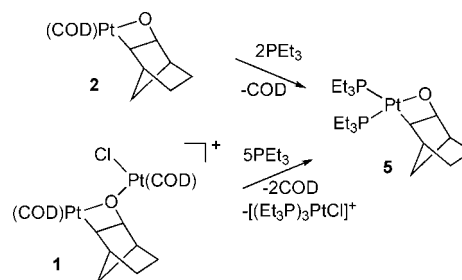
^a λ = 0.71070 Å (Mo), *T* = −100 °C. ^b *R*¹ = (Σ||*F*_o| − |*F*_c||)/Σ|*F*_o|. ^c w*R*² = [(Σw(|*F*_o| − |*F*_c||)²)/Σw*F*_o²]^{1/2}; w = 4*F*_o²/(Σ*F*_o²)².

of the phosphine ligands and the small P–P coupling of 5 Hz indicate a *cis*-phosphine geometry at the Pt center. In C₆D₆ the upfield doublet at −0.04 ppm shows much larger Pt–P coupling

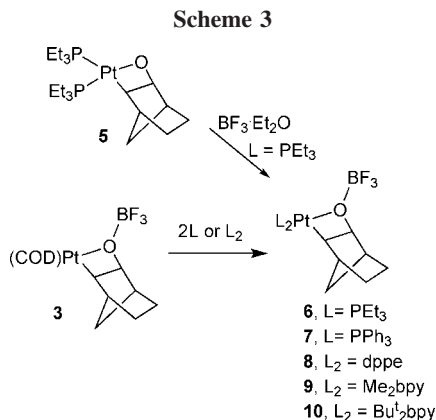
Table 3. Selected Distances (Å) and Angles (deg) for **3**, **6**, and **10**

	3	6	10
Pt1–O1	2.038(3)	2.1459(18)	2.055(3)
Pt1–C1	2.052(5)	2.071(3)	2.023(4)
O1–C2	1.466(6)	1.471(3)	1.467(5)
C1–C2	1.551(7)	1.540(4)	1.525(6)
O1–B1	1.484(7)	1.486(4)	1.484(6)
Pt1–C8	2.126(5)		
Pt1–C9	2.126(5)		
Pt1–C12	2.321(5)		
Pt1–C13	2.301(5)		
Pt1–P1		2.2027(7)	
Pt1–P2		2.3532(8)	
Pt1–N1			2.117(3)
Pt1–N2			1.973(3)
O1–Pt1–C1	68.93(16)	68.31(9)	69.20(14)
C2–O1–Pt1	97.1(3)	93.37(13)	94.9(2)
B1–O1–Pt1	136.0(3)	127.92(18)	127.5(3)
C2–O1–B1	126.4(4)	116.0(2)	117.9(3)
C2–C1–Pt1	93.8(3)	94.31(16)	94.4(3)
C1–C2–O1	100.2(4)	103.7(2)	101.4(3)

Scheme 2



(*J*_{P–Pt} = 3485 Hz) than the downfield doublet at 14.42 ppm (*J*_{P–Pt} = 1566 Hz) and is assigned to the P atom *trans* to the more weakly donating oxygen atom.^{40,41} The downfield doublet is then assigned to the P atom *trans* to the more strongly donating carbon atom of the platinaoxetane ring. In CD₂Cl₂ the shifts and coupling constants are similar to those in C₆D₆ except for the Pt–P coupling *trans* to the oxygen atom. This increases



from 3485 to 3600 Hz, suggesting some alteration in the Pt–O bonding as the solvent polarity increases. This effect is also observed for the other phosphine complexes discussed below.

A comparison of the ^{195}Pt coupling constants of **5** with known $\text{Pt}(\text{PEt}_3)_2(\text{OMe})(\text{Me})$ ⁴² would be useful for evaluating the donor properties of the oxetane ring. Unfortunately, $\text{Pt}(\text{PEt}_3)_2(\text{OMe})(\text{Me})$ has a *trans* geometry. Platinacyclobutane complex $\text{Pt}(\text{Et}_3\text{P})_2(\text{CH}_2)_4$ has a coupling constant (1782 Hz)⁴³ that is ca. 100 Hz greater than the smallest for **5**, suggesting that the carbon atom of **5** is a better donor. The Pt–P coupling *trans* to the O atom is similar to that of $[(\text{Et}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2]^{2+}$ (3475 Hz),^{44,45} suggesting that the O atom of **5** is a weaker donor than might be expected for an alkoxo-type ligand. The ^{195}Pt NMR spectrum of **5** in C_6D_6 shows a doublet of doublets at –3883 ppm, further confirming coupling between the Pt center and two different phosphine ligands.

^1H NMR spectra of **5** show all 10 proton peaks for the norbornene fragment in addition to resonances for the phosphine ligands. None of the norbornene peaks display coupling to the ^{31}P nuclei of the phosphine ligands. The most downfield signal at 6.92 ppm is assigned to H1 and the most upfield signal at 0.77 ppm is assigned to H2 (Table 1). Both display similar coupling to ^{195}Pt (~40 Hz), which is ~20 Hz (H1) or ~30 Hz (H2) less than that of **2**. H3 show similar coupling to that of **2**. Signals for the seven different carbons atoms of the norbornene fragment are observed in the ^{13}C NMR spectrum with the signal for the Pt-bonded carbon atom at 8.2 ppm. As in the ^1H NMR, the norbornene fragment peaks do not show coupling to the ^{31}P nuclei.

Addition of an equimolar amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to **5** immediately affords the white BF_3 adduct $(\text{Et}_3\text{P})_2\text{Pt}(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**6**) in high yield (Scheme 3). Complex **6** is also available by COD ligand displacement via addition of 2 molar equiv of PEt_3 to **3** (Scheme 3). Complex **6** has been characterized by ^1H , ^{13}C , DEPT, ^1H – ^1H COSY, ^1H – ^{13}C COSY (HMQC), and ^{195}Pt NMR spectroscopy, elemental analysis, and X-ray crystallography. A drawing of the solid-state structure of **6** is shown in Figure 2. Crystallographic data and data collection parameters are summarized in Table 2. Selected distances and angles are

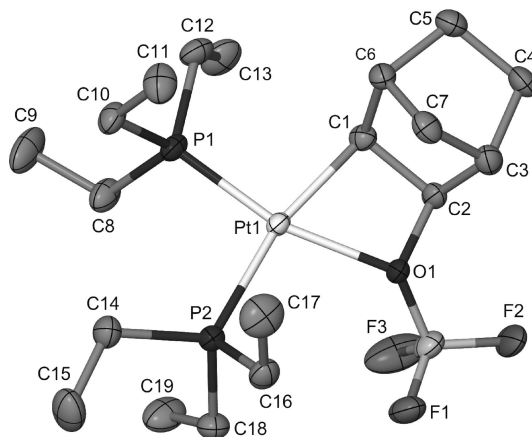


Figure 2. Drawing of the solid-state structure of **6** (50% probability ellipsoids, hydrogen atoms omitted for clarity).

given in Table 3. Details of the structure are discussed below. ^{31}P NMR spectra in C_6D_6 show two doublets at 20.62 and 0.56 ppm flanked by ^{195}Pt satellites, which are shifted downfield compared to those of **5**. The largest ^{195}Pt coupling constant for the P atom *trans* to the oxygen atom is 4570 Hz in C_6D_6 but increases to 4730 Hz in CD_2Cl_2 . The effect on the coupling constant for the P atom *trans* to the carbon atom is much smaller, where the constant changes only slightly from 1644 Hz in C_6D_6 to 1659 Hz in CD_2Cl_2 . In comparison to **5** in C_6D_6 , the coupling constant for the P atom *trans* to the oxygen atom has increased by almost 1100 Hz. This is attributed to the coordination of the Lewis acid BF_3 to the oxygen atom, strongly reducing its donating ability.^{40,41} The coupling constant (1644 Hz) for the P atom *trans* to the C atom is slightly greater than that (1566 Hz) of precursor **5**. The P–Pt coupling constants for **6** can be compared to the protonated methoxo complex *cis*- $[\text{Pt}(\text{PEt}_3)_2(\text{HOMe})(\text{Me})]^+$.⁴⁶ Although unstable with respect to the *trans* isomer, this complex has been generated and characterized in solution and displays ^{195}Pt coupling constants of 4344 (*trans* to O) and 1829 (*trans* to C) Hz, again suggesting a relatively weak O atom donor and a relatively strong C atom donor for the platinaoxetane. The six-membered ring complex $[\text{Pt}(\text{PEt}_3)_2(\text{CHCF}_3\text{CCF}_3=\text{CMeOMe})]^+$, where the ether group coordinates to the Pt center, also shows similar coupling for the P atom *trans* to the oxygen atom (4530 Hz).⁴⁷ The ^{195}Pt NMR resonance of **6** in C_6D_6 is found as a doublet of doublets at –4008 ppm, shifted upfield by about 120 ppm from that of **5**. ^1H and ^{13}C NMR spectra show similar patterns to those of **5**, but ^{195}Pt coupling with H1 and H2 is not observed.

Treatment of **3** with PPh_3 affords the PPh_3 analogue of **6**, $\text{Pt}(\text{Ph}_3\text{P})_2(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**7**) (Scheme 3). The ^{31}P NMR spectrum of **7** shows the expected pair of doublets with satellites. As observed for **6**, the ^{31}P – ^{195}Pt coupling constants are solvent dependent. In CD_2Cl_2 , a large value of 5122 Hz is observed for the P atom *trans* to the O atom, while in C_6D_6 the observed value is 4980 Hz. As observed for **6**, the ^{195}Pt spectrum of **7** exhibits a doublet of doublets at –4049 ppm.

Addition of 1 equiv of dppe to a solution of **3** results in rapid formation of $\text{Pt}(\text{dppe})(\text{C}_7\text{H}_{10}\text{OBF}_3)$ (**8**) as a white precipitate (Scheme 3). The ^{31}P NMR spectrum in CD_2Cl_2 shows two singlets with ^{195}Pt satellites. The large difference in ^{195}Pt coupling constants (3030 Hz) of the two P atoms is similar to

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that in **6** (3070 Hz) and **7** (3054 Hz) and consistent with the formation of a five-membered chelate ring with one P atom *trans* to the carbon atom and one *trans* to the O atom of the platinaoxetane ring. The chemical shifts of 48.4 and 30.7 ppm are also consistent with dppe chelation.⁴⁸ The coupling constant (4730 Hz) of the P atom *trans* to the weakly donating oxygen atom in CD₂Cl₂ is identical to that of **6** (4730 Hz) and is comparable to that of the P atom *trans* to the triflate oxygen atom of Pt(dppe)(R)OTf (R = *n*-C₃F₇, 4651 Hz;⁴⁹ R = Me, 4646 Hz⁵⁰), indicating that the O atom of **8** is a comparable donor to the triflate anion. As observed for the other phosphine complexes (see above), the P–Pt coupling decreases in C₆D₆, in this case by 146 to 4584 Hz. The ¹⁹⁵Pt resonance of **8** is found as a doublet of doublets at –4148 ppm. The poor solubility of **8** in common organic solvent precluded recording a strong ¹³C NMR spectrum, but inequivalence of the two dppe methylene carbons is observed (29.5 and 25.1 ppm). Both display a doublet of doublets pattern due to coupling to the two inequivalent P atoms.

COD substitution by diimines is much slower than COD substitution by phosphines and reveals reaction rate differences between platinaoxetane **2** and **3**. Addition of 4,4′-di-*tert*-butyl-2,2′-bipyridine (Bu′₂bpy) to (COD)Pt(C₇H₁₀O) (**2**) in C₆D₆ shows no observable change after 1 day at room temperature. Heating the mixture at 54 °C for 5 days and then 75 °C for 2 days still shows mostly **2**. Complex **2** is mostly consumed after the mixture is heated at 110 °C for another day, resulting in a brown precipitate and a dark red solution. The ¹H NMR spectrum of the precipitate in CD₂Cl₂ suggests the presence of two complexes. Attempts to purify the material were unsuccessful.

In contrast to **2**, addition of Bu′₂bpy to (COD)Pt(C₇H₁₀OBf₃) (**3**) in C₆D₆ results in the formation of a bright yellow solution after 2 days at room temperature (Scheme 3). Once free COD is removed from the mixture, pure **10** is readily obtained as a yellow solid, slightly soluble in toluene and benzene and soluble in methylene chloride. The much less soluble 4,4′-di-*tert*-butyl-2,2′-bipyridine (Me₂bpy) analogue of **10**, (Me₂bpy)Pt(C₇H₁₀OBf₃) (**9**), is similarly prepared by addition of Me₂bpy to **3** in CH₂Cl₂ (Scheme 3). Precipitation of white **9** is complete after ca. 24 h. Complex **9** is sparsely soluble in common organic solvents including DMSO. The difference in COD substitution rates for **2** and **3** may be attributed to the lower electron density on the Pt center in **3** as a result of BF₃ bonding to the O atom of **3**. The Pt center is more electrophilic for the incoming diimine, and there is reduced back-bonding to the COD ligand, allowing more facile COD substitution.

¹H NMR spectra for diimine complexes **9** and **10** are very similar. Both exhibit, in addition to the methyl protons, six distinct peaks in the aromatic region for the bipyridine ring protons and 10 peaks for the NB fragment's protons, consistent with the absence of symmetry in the complexes. Chemical shifts for H1 (in CD₂Cl₂) are found at 5.92 ppm in both complexes with no ¹⁹⁵Pt satellites and are comparable to those of the phosphine and COD platinaoxetanes (Table 1). The Pt–CH (H2) resonances are found as doublets of doublets at 1.68 ppm (for **10**) and 1.66 ppm (for **9**) with *J*_{Pt–H} ≈ 54 Hz. The most upfield signals (3.8 ppm) in the ¹³C spectra of **10** is assigned to the Pt σ-bonded carbon. ¹³C NMR spectra of **9** are not available

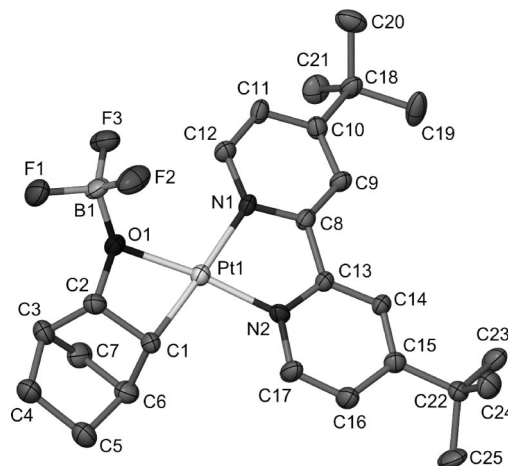


Figure 3. Drawing of the solid-state structure of **10** (50% probability ellipsoids, hydrogen atoms omitted for clarity).

because of its poor solubility in common organic solvents. ¹⁹⁵Pt resonances are found at –4045 ppm (**9**) and –4042 ppm (**10**). Complex **10** has been characterized by X-ray crystallography. A drawing of the structure is shown in Figure 3. Crystallographic data and data collection parameters are summarized in Table 2. Selected distances and angles are given in Table 3.

Structures. We will begin this section by comparing the structures of **3**, **6**, and **10**. These complexes differ only by the identity of the ancillary ligand set *trans* to the platinaoxetane ring, and the overall structures are correspondingly very similar. In keeping with the *trans* influence trend N-donor < alkene < phosphine,⁵¹ the Pt–C distances increase in the order **10** < **3** < **6**. The Pt–O distance in **6** is also the longest, but the order of **10** and **3** is inverted such that the Pt–O distance of **3** is the shortest. While the difference between the two values is small and may not be significant, other factors indicate an anomaly in **3**. The B–O–Pt angles for **10** and **6** are nearly identical at 128°, while that for **3** is nearly 10° larger at 136°. The other angles around the O atoms are also larger for **3** but nearly identical for **6** and **10**, indicating a more planar O atom for **3**. The planarity of the O atom is evident from the deviation of the boron atom, B1, from the essentially planar platinaoxetane ring. The boron atom of **3** is only 0.13 Å out of the Pt1, O1, C1, and C2 least-squares plane (largest deviation 0.008 Å). In contrast, B1 of **6** and **10** are 0.85 and 0.83 Å, respectively, out of their least-squares planes (largest deviation 0.039 Å (**6**) and 0.028 Å (**10**)). Electronic factors in this difference can be eliminated by the fact that the closely related platinaoxetane **4** (see Table 1), previously reported by our group, more closely matches the structures of **6** and **10** with the boron atom 0.93 Å out of the platinaoxetane ring plane (largest deviation 0.007 Å).²⁵ Thus, it seems likely that the deviation of **3** is due to crystal-packing forces.

Other features in the platinaoxetane rings of **3**, **6**, and **10** are essentially identical. The C2–O1 bond distances are equal at 1.47 Å, as are the B1–O1 distances at 1.48 Å. There is some variation in the C1–C2 distances but within the experimental error. Similarly, there is little variation in the angles within the ring other than those around O1, as already discussed.

In comparing the structures of **3**, **6**, and **10** to other metallaioxetanes, a noticeable feature is that **3**, **6**, and **10** (and the other members of this class, **1** and **4**)²⁵ contain planar rings,

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whereas most other metallaoxetanes contain “puckered” rings, including the closely related Pt(II) complexes Pt(AsPh₃)₂(C₂(CN)₄O)⁷ and Pt(PPh₃)₂(C(CN)₂CH(CN)O).⁸ Only three other metallaoxetanes are planar. One of these is the Au(III) d⁸ complex [Au(6-Me-bpy)(C₇H₁₀O)]⁺,²⁴ a close relative of **10** but without a BF₃ bonded to the ring O atom. The other two are the Rh(III) d⁶ octahedral complexes Rh(PMe₃)₃(Br)(CH₂-CMe₂O)^{11,12} and [Rh(MeTPA)(CH₂CMe₂O)]⁺ (MeTPA = *N*-[(6-methyl-2-pyridyl)methyl]-*N,N*-di(2-pyridylmethyl)amine).¹⁶ No trend is evident in this set, suggesting that planar versus puckered rings is a subtle feature of metallaoxetanes.

The Pt–C and Pt–O distances of **6** are best compared with Pt(AsPh₃)₂(C₂(CN)₄O) and Pt(PPh₃)₂(C(CN)₂CH(CN)O).^{7,8} The Pt–C distances of 2.103(7) and 2.13(2) Å appear marginally longer than those in **6** probably as a result of the CN substituents. The Pt–O distances of 2.050(5) and 2.06(2) Å are substantially shorter than that of **6** (2.1459(18) Å). This may be attributed to the BF₃ coordination to the O atom, which should lengthen the Pt–O bond in **6**, as suggested by the large ³¹P–¹⁹⁵Pt coupling constant for the P atoms *trans* to the ring O atom (see above). In fact, this is the longest observed M–O distance in any reported metallaoxetane but is comparable to the ether complex [Pt(PEt₃)₂(CHCF₃CCF₃=CMeOMe)]⁺, where the Pt–O distance is 2.144(9) Å and the *trans* to O atom ³¹P–¹⁹⁵Pt coupling constant is similar to that of **6** (see above).⁴⁷ Similarly, the Pt–O bond distance of the tethered ether complex [Pt(Ph₂-PCH₂CH₂OMe)₂Cl]⁺ is 2.192(7) Å.⁵²

M–atom distances in **10** are comparable to those in [Au(6-Me-bpy)(C₇H₁₀O)]⁺ with recognition of the difference in metal ionic radii.²⁴ The Au–C and Au–N distances of [Au(6-Me-bpy)(C₇H₁₀O)]⁺ are larger than the corresponding ones for **10** by 0.032, 0.068, and 0.051 Å, consistent with the larger ionic radius of Au(III). (A difference of 0.08 Å is found in a listing of ionic radii.) In contrast, the Au–O distance is smaller by 0.088 Å, suggesting that there is an elongation of the Pt–O bond of 0.12 Å (0.088 + 0.032) to 0.16 Å (0.088 + 0.068) upon coordination of the BF₃ group. This puts the expected Pt–O bond distance of the BF₃-free complex **5** at 1.99 to 2.02 Å, a Pt–O distance in the range observed for Pt(dppe)(OMe)₂ (2.041(7), 2.037(7) Å) and Pt(dppe)(OMe)Me (1.99(1) Å).⁵³

As noted above, the C–O distances in **3**, **6**, and **10** are all similar at 1.47 Å. This lies at the upper end of the range of 1.36 to 1.45 Å for all but one of the reported metallaoxetanes. The one exception is [Ir(P₃O₉)(C₈H₁₂O)]²⁻, which has a C–O distance of 1.858 Å. Such an exceptionally long distance must be considered with caution. The C–C ring distances of **3**, **6**, and **10** vary somewhat more but fall within the range (1.43–1.58 Å) of the other metallaoxetanes.

Conclusions

In conclusion, the platinaoxetane ring of **1** survives displacement and substitution with BF₃ of the oxygen-coordinated [Pt(COD)Cl]⁺ fragment and substitution of the COD ligand with phosphines and bipyridine ligands, giving access to a family of platinaoxetanes. Spectroscopic and structural parameters of the complexes are consistent with the expected *trans* influence of the ligands and with the BF₃ bonding to the platinaoxetane ring oxygen atom. ³¹P NMR data suggest that the O atom of the platinaoxetane is a weaker donor than comparable acyclic or

larger ring complexes. The effect of the ligands and BF₃ and other Lewis acids on the reactivity and stability of the platinaoxetanes is now under study in our laboratories and will be reported shortly.

Experimental Section

General Procedures. Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmosphere Corporation drybox. Solvents were dried by standard techniques and stored under dinitrogen over 4 Å molecular sieves or sodium metal. Alkenes were purchased from Acros or Aldrich. PEt₃ (10 wt % in hexane) was obtained from Strem. BF₃·Et₂O, PPh₃, and bis(diphenylphosphino)ethane (dppe) were obtained from Acros, and 4,4′-dimethyl-2,2′-bipyridine (Me₂bpy) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (Bu₂bpy) were purchased from Aldrich. All commercial chemicals were used as received except where noted. Complex **1** was synthesized by literature procedures.²³ NMR spectra were recorded on Bruker AMX-250, -300, or -500 spectrometers at ambient probe temperatures. Data are given in ppm relative to solvent signals referenced to TMS for ¹H and ¹³C spectra or relative to external standards for ¹⁹⁵Pt (K₂PtCl₄/D₂O at -1624 ppm), ³¹P (85% H₃PO₄ at 0.0 ppm), and ¹⁹F (CFCl₃ at 0.0 ppm). Atom numbering for the peak assignments is given in Table 1 and below. Desert Analytics, Inc. performed the elemental analyses (inert atmosphere).

(COD)Pt(OC₇H₁₀) (2). A solution of Et₄NCl (39 mg, 0.238 mmol) in 1 mL of CH₂Cl₂ was added dropwise to an agitated solution of platinaoxetane **1** (200 mg, 0.238 mmol) in 2 mL of CH₂Cl₂. After 20 min, ether was added dropwise until precipitate formation ceased. The (COD)PtCl₂ precipitate was removed by filtration, and the filtrate was evaporated to dryness in vacuo. The residue was redissolved in ~0.5 mL of CH₂Cl₂ and excess ether was added. The resulting small amount of precipitate was removed by filtration. Evaporation of the filtrate gave white product **2**, which was dried in vacuo. Yield: 74.6 mg, 76%. Anal. Calcd (found) for C₁₅H₂₂O₂Pt·0.25CH₂Cl₂: C, 42.16 (42.45); H, 5.07 (5.22). ¹H NMR (500 MHz, CD₂Cl₂): 5.99 (d with satellites, *J*_{H–H} = 5 Hz, *J*_{Pt–H} = 60 Hz, 1H, H1), 5.55 (br s with satellites, *J*_{Pt–H} ≈ 70 Hz, 1H, COD CH), ~5.28 (m, overlapping with solvent residue peak, 1H, COD CH), 2.41 (overlapping with COD CH₂, 1H, H4), 2.39 (br, s, 1H, H6), 2.06 (s, 1H, H3), 2.35 (overlapping with H4) and 2.06 (m's, 8H, COD CH₂), 1.45 (m, 1H, H5), 1.35 (m, 1H, H7), 1.01 (d, *J*_{H–H} = 9 Hz, 1H, H4'), 0.90 (br m, 1H, H7'), 0.79 (m, 1H, H5'), 0.69 (br s with satellites, *J*_{Pt–H} = 66 Hz, 1H, H2). ¹H NMR (500 MHz, C₆D₆): 6.62 (m with satellites, *J*_{Pt–H} = 60 Hz, 1H, H1), 5.26 (m, 2H, COD CH), 3.84 (m with satellites, *J*_{Pt–H} ≈ 59 Hz, 2H, COD CH), 2.81(s, br, 1H, H4), 2.39 (s, br, 1H, H6), 2.06 (s with satellites, *J*_{Pt–H} = 43.5 Hz, 1H, H3), 1.89, 1.74, 1.66, 1.56 and 1.33 (m's, 8H total, COD CH₂), 1.57 (s, 1H overlapping with COD CH₂ at 1.56, H7), 1.47 (m, 1H, H5), 1.20 (d, *J*_{H–H} = 9 Hz, 1H, H4'), 1.05 (br m, 1H, H7'), 0.97 (br m, 1H, H5'), 0.84 (br s with satellites, *J*_{Pt–H} = 70 Hz, 1H, H2). ¹³C{¹H} NMR (75 MHz, C₆D₆): 111.4 (COD CH), 111.3 (COD CH), 99.5 (*J*_{Pt–C} = 128.3, C1), 73.2 (*J*_{Pt–C} = 182.6, COD CH), 72.9 (*J*_{Pt–C} = 197.0 (COD CH), 43.8 (C6), 40.3 (C3), 36.7 (C4), 32.2 (C7), 31.8 (COD CH₂), 31.5 (COD CH₂), 27.5 (COD CH₂), 27.2 (COD CH₂), 23.3 (C5), 8.6 (*J*_{Pt–C} = 517.6, C2). ¹⁹⁵Pt NMR (64 MHz, C₆D₆): -2891.

(COD)Pt(C₇H₁₀OBF₃) (3). From **2**. BF₃·Et₂O (2.6 μL, 0.022 mmol) was added to an agitated solution of platinaoxetane **2** (9.0 mg, 0.022 mmol) in 1 mL of CH₂Cl₂. The solvent was evaporated to give pure product **3**. Yield: 10.2 mg, 95%.

From 1. This procedure is similar to that reported previously but with an improved workup giving higher yields. BF₃·Et₂O (18 μL, 0.14 mmol) was added to an agitated solution of platinaoxetane **1** (118 mg, 0.14 mmol) in 2 mL of CH₂Cl₂. After 4 min the resulting precipitate was removed by filtration. Excess ether was added to the filtrate, and the resulting small amount of precipitate was removed. The clear solution was evaporated to dryness and

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redissolved in minimum CH_2Cl_2 . Excess hexane was added, and the mixture was kept at -30°C for 1 day. The resulting white precipitate was collected, washed with cold hexane, and dried in vacuo. Colorless single crystals for the X-ray analysis were grown from CH_2Cl_2 /hexane. Yield: 52 mg, 78%. Anal. Calcd (found) for $\text{C}_{15}\text{H}_{22}\text{OBF}_3\text{Pt}$: C, 37.43 (36.86); H, 4.58 (4.43). NMR data in CD_2Cl_2 have been previously reported.²⁵ ^1H NMR (300 MHz, C_6D_6): 6.42 (d with satellites, $J_{\text{H-H}} = 5.7$ Hz, $J_{\text{Pt-H}} = 33$ Hz, 1H, H1), 5.78 (m, 1H, COD CH), 5.78 (m, 1H, COD CH), 3.63 (m with satellites, $J_{\text{Pt-H}} \approx 80$ Hz, 2H, COD CH), 2.85 (br s, 1H, H4), 2.43 (d, $J_{\text{H-H}} = 9.9$ Hz, 1H, H6), 1.61 (s, 1H, H3), 1.48, 1.27, 1.19, 1.09, and 0.86 (m's, 8H total, COD CH_2), 1.35 (s, 1H, H7), 1.22 (m, 1H, H5), 1.07 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, H4), 0.76 (dd, $J_{\text{H2-H1}} = 5.7$ Hz, $J_{\text{H2-H3}} = 2.1$ Hz, 1H, H2), 0.68 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, H7), 0.65 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, H5). ^{195}Pt NMR (C_6D_6 , 64 MHz): -3103 (s).

(PEt_3)₂Pt(OC_7H_{10}) (5). From **2**. PEt_3 in hexane (45 μL of a 10% solution, 0.026 mmol) was added dropwise to an agitated solution of **2** (5.4 mg, 0.013 mmol) in 0.5 mL of C_6D_6 . After 5 min, the volatiles were removed in vacuo. The resulting oily residue was redissolved in toluene, and the mixture was evaporated to dryness and left in vacuo for 2 h. This procedure was repeated for two or three times until residual COD and PEt_3 were eliminated and a solid residue was obtained. The residue was washed with hexane and dried in vacuo to give white solid **5**. Yield: 6.8 mg, 98%.

From 1. PEt_3 in hexane (82 μL of a 10% solution, 0.047 mmol) was added to a solution of **1** (8.0 mg, 0.0095 mmol) in 0.4 mL of CH_2Cl_2 . After 10 min, excess hexane was added and a white precipitate of $[(\text{PEt}_3)_3\text{Pt}(\text{Cl})]\text{BF}_4$ formed. The clear solution was decanted off the precipitate and evaporated in vacuo to give white solid **5**. Yield: 4.2 mg, 81%. Anal. Calcd (found) for $\text{C}_{19}\text{H}_{40}\text{OP}_2\text{Pt}$: C, 42.14 (41.78); H, 7.38 (6.93). ^1H NMR (500 MHz, C_6D_6): 6.92 (m with satellites, $J_{\text{Pt-H}} = 40$ Hz, 1H, H1), 3.24 (d, $J_{\text{H-H}} = 5.1$ Hz, 1H, H7), 2.65 (br s, 1H, H6), 2.54 (s, $J_{\text{Pt-H}} = 39$ Hz, 1H, H3), 2.01 (m, 1H, H4), 1.71 (m, 1H, H5), 1.59 (m, 6H, PCH_2Me), 1.51 (d, $J_{\text{H-H}} = 8$ Hz, 1H, H4'), 1.48 (t, $J_{\text{H-H}} = 9.6$ Hz, 6H, PCH_2Me), 1.44 (br m, 1H, H7'), 1.30 (br m, 1H, H5'), 1.08 (m, 9H, CH_3), 1.00 (m, 9H, C H_3), 0.77 (m with satellites, $J_{\text{Pt-H}} = 40.5$ Hz, 1H, H2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 100.1 (C1), 46.0 (C6), 41.6 (C3), 36.7 (C7), 34.3 (C4 or C5), 34.2 (C4 or C5), 17.78 (dd, $^1J_{\text{P-C}} = 20.4$ Hz, $^3J_{\text{P-C}} = 3.8$ Hz, PCH_2Me), 14.9 (d, $J_{\text{P-C}} = 21.9$ Hz, PCH_2Me), 8.2 (C2), 8.3 (PCH_2CH_3), 8.1 (PCH_2CH_3). ^{31}P NMR (101 MHz, C_6D_6): 14.42 (d with satellites, $J_{\text{Pt-P}} = 1566$ Hz, $J_{\text{P-P}} = 5$ Hz), -0.04 (d with satellites, $J_{\text{Pt-P}} = 3485$ Hz, $J_{\text{P-P}} = 5$ Hz). ^{31}P NMR (101 MHz, CD_2Cl_2): 13.92 (br s with satellites, $J_{\text{Pt-P}} = 1575$ Hz), -0.40 (d with satellites, $J_{\text{Pt-P}} = 3600$ Hz, $J_{\text{P-P}} = 6$ Hz). ^{195}Pt NMR (64 MHz, C_6D_6): -3883 (dd, $J_{\text{Pt-P1}} = 1594$ Hz, $J_{\text{Pt-P2}} = 3542$ Hz).

(PEt_3)₂Pt($\text{C}_7\text{H}_{10}\text{OBF}_3$) (6). From **3**. PEt_3 in hexane (50 μL of a 10% solution, 0.029 mmol) was added dropwise to an agitated solution of **3** (7.0 mg, 0.014 mmol) in 0.5 mL of C_6D_6 . After 5 min, the mixture was evaporated in vacuo. The resulting oily residue was redissolved in toluene and the mixture evaporated to dryness and left in vacuo for 2 h. This procedure was repeated for two or three times until residual COD and PEt_3 were eliminated and a solid residue was obtained. The residue was washed with hexane and dried in vacuo to give white solid **6**. Yield: 8.4 mg, 95%. Colorless single crystals for X-ray analysis were grown from a C_6H_6 solution layered with hexane.

From 5. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.5 μL , 0.013 mmol) was added to a solution of **5** (6.8 mg, 0.013 mmol) in 1 mL of CH_2Cl_2 . All volatiles were removed in vacuo to give **6**. Yield: 7.2 mg, 94%. Anal. Calcd (found) for $\text{C}_{19}\text{H}_{40}\text{OBF}_3\text{P}_2\text{Pt}$: C, 37.45 (37.47); H, 6.56 (6.11). ^1H NMR (500 MHz, C_6D_6): 6.65 (br s, 1H, H1), 2.94 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, H7), 2.77 (d, 1H, H6), 2.14 (s, $J_{\text{Pt-H}} \approx 29$ Hz, 1H, H3), 1.80 (m, 1H, H4), 1.72 (m, 6H, PCH_2Me), 1.52 (m, 1H, H5), 1.35

(m, 1H, H7'), 1.20 (m, 6H, PCH_2Me), 0.98 (m, 1H, H4'), 0.96 (br m, 1H, H5'), 0.88 (m, 9H, $-\text{CH}_3$), 0.70 (m, 9H, $-\text{CH}_3$), ~ 0.66 (overlapping with $-\text{CH}_3$ peak at 0.88, H2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): 100.5 (C1), 44.1 (C6), 42.4 (C3), 36.1 (C7), 32.4 (C4), 22.7 (C5), 17.4 (dd, $^1J_{\text{P-C}} = 40.3$ Hz, $^3J_{\text{P-C}} = 3.8$ Hz, PCH_2Me), 15.4 (d, $J_{\text{P-C}} = 27.7$ Hz, PCH_2Me), 8.59 (PCH_2CH_3), 8.57 (PCH_2CH_3), 8.31 (C2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 100.4 (C1), 44.4 (C6), 42.5 (C3), 36.1 (C7), 32.6 (C4), 22.8 (C5), 16.5 (dd, $^1J_{\text{P-C}} = 40.3$ Hz, $^3J_{\text{P-C}} = 7.5$ Hz, PCH_2Me) and 14.9 (dd, $^1J_{\text{P-C}} = 17.6$ Hz, $^3J_{\text{P-C}} = 5.0$ Hz, PCH_2Me), 8.2 (PCH_2CH_3), 8.1 (PCH_2CH_3), 8.1 (C2). ^{31}P NMR (101 MHz, C_6D_6): 20.6 (d with satellites, $J_{\text{Pt-P}} = 1644$ Hz, $J_{\text{P-P}} = 9.7$), 0.6 (br s with satellites, $J_{\text{Pt-P}} = 4570$). ^{31}P NMR (101 MHz, CD_2Cl_2): 20.8 (d with satellites, $J_{\text{Pt-P}} = 1659$ Hz, $J_{\text{P-P}} = 9.8$ Hz), 1.6 (br s with satellites, $J_{\text{Pt-P}} = 4730$ Hz). ^{195}Pt NMR (64 MHz, C_6D_6 or CD_2Cl_2): -4008 (dd, $J_{\text{Pt-P1}} = 1690$ Hz, $J_{\text{Pt-P2}} = 4807$ Hz). ^{19}F NMR (235 MHz, C_6D_6): -148.6 (br s). ^{19}F NMR (235 MHz, CD_2Cl_2): -149.2 (m).

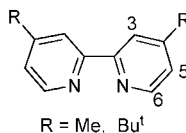
(PPh_3)₂Pt($\text{C}_7\text{H}_{10}\text{OBF}_3$) (7). A solution of PPh_3 (4.3 mg, 0.017 mmol) in 0.3 mL of C_6D_6 was added to an agitated solution of **3** (4.0 mg, 0.0083 mmol) in 0.2 mL of C_6D_6 . After 1 h, the mixture was evaporated to dryness and the residue was dissolved in minimum CH_2Cl_2 . Excess hexane was added to precipitate white solid **7**. The solution was carefully decanted off the product, which was washed with hexane and dried in vacuo. Yield: 6.6 mg, 88%. Anal. Calcd (found) for $\text{C}_{44}\text{H}_{43}\text{OBF}_3\text{P}_2\text{Pt} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 55.92 (56.00); H, 4.71 (5.30). ^1H NMR (500 MHz, CD_2Cl_2): 7.56 (m, 6H, Ph), 7.30 (m, 18H, Ph), 7.15 (m, 6H, Ph), 5.97 (br s, 1H, H1), 2.77 (d, $J_{\text{H-H}} = 9.5$ Hz, 1H, H7), 2.39 (br s, 1H, H6), 1.65 (br s, 1H, H3), 1.26 (s, 1H, H5), 1.16 (d, $J_{\text{H-H}} = 7.5$ Hz, 1H, H7'), 0.87 (m, 1H, H4), 0.69 (br m, 1H, H5'), 0.47 (d, $J_{\text{H-H}} = 5.5$ Hz, 1H, H2), 0.21 (t, $J_{\text{H-H}} = 9.9$ Hz, 1H, H4'). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): 133.71 (d, $J_{\text{P-C}} = 11.3$ Hz), 133.11 (d, $J_{\text{P-C}} = 10.6$ Hz), 129.97 (s), 128.87 (s), 127.15 (d, $J_{\text{P-C}} = 11.3$ Hz), 126.71 (d, $J_{\text{P-C}} = 9.8$ Hz), 98.6 (s, C1), 42.8 (C6), 39.8 (C3), 34.7 (C7), 30.1 (C4), 23.4 (C2), 21.0 (C5). ^{31}P NMR (101 MHz, CD_2Cl_2): 27.66 (d with satellites, $J_{\text{Pt-P}} = 1671$ Hz, $J_{\text{P-P}} = 8.9$ Hz), 11.49 (br s with satellites, $J_{\text{Pt-P}} = 5122$ Hz). ^{31}P NMR (101 MHz, C_6D_6): 27.77 (d with satellites, $J_{\text{Pt-P}} = 1836$ Hz, $J_{\text{P-P}} = 8.6$ Hz), 12.67 (br s with satellites, $J_{\text{Pt-P}} = 4890$ Hz). ^{195}Pt NMR (64 MHz, C_6D_6 or CD_2Cl_2): -4049 (dd, $J_{\text{Pt-P}} = 1697$ Hz, 5181 Hz). ^{19}F NMR (235 MHz, C_6D_6 or CD_2Cl_2): -149.2 .

(dppe)Pt($\text{C}_7\text{H}_{10}\text{OBF}_3$) (8). A solution of dppe (5.0 mg, 0.012 mmol) in minimum CH_2Cl_2 was added to an agitated solution of **3** (6.0 mg, 0.012 mmol) in 0.2 mL of CD_2Cl_2 . A white precipitate of **8** formed immediately. After 2 h the clear solution was carefully decanted off the solid. The solid was washed with minimum C_6H_6 and dried in vacuo. Yield: 8.8 mg, 91%. Anal. Calcd (found) for $\text{C}_{33}\text{H}_{34}\text{BF}_3\text{OP}_2\text{Pt}$: C, 51.38 (51.53); H, 4.51 (4.44). ^1H NMR (500 MHz, CD_2Cl_2): 7.79 (m, 4H, Ph), 7.71 (m, 4H, Ph), 7.52 (m, 10H, Ph), 7.36 (m, 1H, Ph), 7.32 (m, 1H, Ph), 6.16 (s, 1H, H1), 2.45 (br s, 1H, H7), 2.42 (s, 1H, H6), 2.31 (m, 2H, PCH_2), 2.10 (m, 1H, PCH_2), 1.83 (m, 1H, PCH_2), 1.62 (s, H3), 1.32 (m, 1H, H4), 1.28 (m, 1H, H5), 1.06 (m, 1H, H7'), 0.79 (m, 1H, H4'), 0.77 (m, 1H, H2), 0.65 (t, $J_{\text{H-H}} = 6.6$ Hz, 1H, H5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): 133.6 (s, Ph), 133.5 (s, Ph), 133.4 (s, Ph), 133.3 (s, Ph), 133.1 (s, Ph), 132.4 (s, Ph), 132.3 (s, Ph), 131.9 (d, $J_{\text{P-C}} = 2.3$ Hz, Ph), 131.6 (d, $J_{\text{P-C}} = 3.0$ Hz, Ph), 130.8 (t, $J_{\text{P-C}} = 2.3$ Hz, Ph), 129.0 (s, Ph), 129.9 (s, Ph), 128.8 (t, $J_{\text{P-C}} = 2.3$ Hz, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 128.4 (s, Ph), 100.9 (s, C1), 43.3 (s, C6), 40.3 (s, C3), 36.1 (s, C7), 31.9 (s, C4), 29.5 (dd, $^1J_{\text{P-C}} = 43.0$ Hz, $^3J_{\text{P-C}} = 17.4$ Hz, CH_2PPh_2), 25.1 (dd, $^1J_{\text{P-C}} = 34.0$ Hz, $^3J_{\text{P-C}} = 6$ Hz, CH_2PPh_2), 24.1 (s, C2), 22.3 (s, C5). ^{195}Pt NMR (64 MHz, CD_2Cl_2): -4148 (dd, $J_{\text{Pt-P}} = 1729$ Hz, 4684 Hz). ^{31}P NMR (101 MHz, CD_2Cl_2): 48.35 (s, $J_{\text{Pt-P}} = 1697$ Hz), 30.68 (s with satellites, $J_{\text{Pt-P}}$

= 4730 Hz). ^{31}P NMR (101 MHz, C_6D_6): 47.36 (s, $J_{\text{Pt-P}} = 1676$ Hz), 30.99 (s, $J_{\text{Pt-P}} = 4584$ Hz). ^{19}F NMR (235 MHz, CD_2Cl_2): -153.1 (s).

(Me₂bpy)Pt(C₇H₁₀OBF₃) (9). A solution of 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) (2 mg, 0.01 mmol) in 0.3 mL of CD_2Cl_2 was added to an agitated solution of **3** (5.0 mg, 0.010 mmol) in 0.2 mL of CD_2Cl_2 . After about 10 min, a white precipitate of **9** began to form. After 1 day at room temperature the solvent volume was reduced to ~0.2 mL and the solution was carefully decanted off the product. The solid was washed with 0.2 mL of CH_2Cl_2 and dried *in vacuo*. Yield: 6.3 mg, 94%. Anal. Calcd (found) for $\text{C}_{19}\text{H}_{22}\text{BF}_3\text{ON}_2\text{Pt}$: C, 40.89 (40.28); H, 3.98 (3.83). ^1H NMR (500 MHz, CD_2Cl_2): 9.10 (m, 1H, bpy H6 or H6'), 8.66 (d, $J_{\text{H-H}} = 6$ Hz, 1H, bpy H6 or H6'), 7.82 (s, 1H, bpy H3 or H3'), 7.76 (s, 1H, bpy H3 or H3'), 7.45 (d, $J_{\text{H-H}} = 5.5$ Hz, 1H, bpy H5 or H5'), 7.18 (d, $J_{\text{H-H}} = 5.5$ Hz, 1H, bpy H5 or H5'), 5.92 (d, $J_{\text{H-H}} = 6$ Hz, 1H, H1), 2.67 (d, $J_{\text{H-H}} = 9.5$ Hz, 1H, H7, or H7'), 2.49 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 2.28 (d, $J_{\text{H-H}} = 4.5$ Hz, 1H, H6), 2.24 (br s, 1H, H3), 1.66 (dd, $J_{\text{H2-H1}} = 6$ Hz, $J_{\text{H2-H3}} = 2.5$ Hz, H2), 1.52 (m, 1H, H4), 1.42 (s, 1H, H5), 1.26 (d, $J_{\text{H-H}} = 3$ Hz, 1H, H4'), 1.15 (m, 1H, H7'), 0.90 (br, m, 1H, H5'). ^{195}Pt NMR (64 MHz, CD_2Cl_2): -4045 (s). ^{19}F NMR (235 MHz, CD_2Cl_2): -150.4.

NMR numbering for the bipyridine ligands



(Bu^t₂bpy)Pt(C₇H₁₀OBF₃) (10). A solution of **3** (5.6 mg, 0.012 mmol) in 0.4 mL of C_6D_6 was added to an agitated solution of 4,4'-di-*tert*-butyl-2,2'-bipyridine (Bu^t₂bpy) (3.1 mg, 0.012 mmol) in minimum CH_2Cl_2 . After 2 days, the volatiles were removed *in vacuo*. The resulting oily residue was redissolved in toluene/ CH_2Cl_2 , and the volatiles were removed *in vacuo*, after which the residue was left *in vacuo* for 2 h. This procedure was repeated for two or three times until residual COD was removed. The remaining solid

was washed with a small amount of benzene and dried *in vacuo* to give yellow solid **10**. Yield: 6.6 mg, 88%. Anal. Calcd (found) for $\text{C}_{25}\text{H}_{34}\text{BF}_3\text{ON}_2\text{Pt}$: C, 46.70 (46.12); H, 5.34 (5.04). ^1H NMR (500 MHz, CD_2Cl_2): 9.17 (m, 1H, bpy H6 or H6'), 8.74 (d, $J_{\text{Pt-H}} \approx 55$ Hz, $J_{\text{H-H}} = 6$ Hz, 1H, bpy H6 or H6'), 7.94 (d, $J_{\text{H-H}} = 2$ Hz, 1H, bpy H3 or H3'), 7.87 (d, $J_{\text{H-H}} = 2$ Hz, 1H, bpy H3 or H3'), 7.66 (dd, $J_{\text{H-H}} = 6$ Hz, 2 Hz, 1H, bpy H5 or H5'), 7.37 (dd, $J_{\text{H-H}} = 6$ Hz, $J_{\text{H-H}} = 2$ Hz, 1H, bpy H5 or H5'), 5.92 (d, $J_{\text{H-H}} = 6$ Hz, 1H, H1), 2.67 (d, $J_{\text{H-H}} = 9.5$ Hz, 1H, H7), 2.28 (d, $J_{\text{H-H}} = 4$ Hz, 1H, H6), 2.26 (br s, 1H, H3), 1.68 (dd, $J_{\text{Pt-H}} \approx 54$ Hz, $J_{\text{H2-H1}} = 6$ Hz, $J_{\text{H2-H3}} = 2$ Hz, H2), 1.51 (m, 2H, H4 and H4'), 1.44 (s, 1H, H5), 1.42 (s, 9H, CH₃), 1.41 (s, 9H, CH₃), 1.15 (m, 1H, H7'), 0.91 (br m, 1H, H5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): 163.9 (s, bpy), 163.2 (s, bpy), 157.6 (s, bpy), 153.3 (s, bpy), 151.8 (s, bpy), 150.8 (s, bpy), 125.5 (s, bpy), 124.9 (s, bpy), 119.8 (s, bpy), 118.7 (s, bpy), 102.0 (s, C1), 43.2 (s, C6), 40.9 (s, C3), 36.2 (s, C7), 36.1 (s, CMe₃), 35.9 (s, CMe₃), 30.3 (s, CH₃), 30.1 (s, CH₃), 29.9 (s, C4), 22.8 (s, C5), 3.8 (s, C2). ^{195}Pt NMR (64 MHz, CD_2Cl_2): -4042 (s). ^{19}F NMR (235 MHz, CD_2Cl_2): -150.3 (s).

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Supporting Information Available: Details of crystal structure determination (cif files). This materials is available free of charge via the Internet at <http://pubs.acs.org>.

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