

## Bromination of a Naphthalene Platinacycle

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Bromination of the four-membered Pt(II) metallacycle Pt(Et<sub>3</sub>P)<sub>2</sub>(1,8-naphthalendiyl) by Br<sub>2</sub> results in Pt–C bond cleavage and formation of *cis*-Pt(8-bromonaphthalen-1-yl)(Br)(PEt<sub>3</sub>)<sub>2</sub> (*cis*-2). Further Br<sub>2</sub> addition yields ionic *cis*-[Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>Br<sup>-</sup> (*cis*-3) in which the bromine atom of the bromonaphthalene is bonded to the six-coordinate Pt(IV) center. AgPF<sub>6</sub> and *cis*-3 give AgBr and *cis*-[Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (*cis*-4). All of the above complexes isomerize to more stable *trans*-complexes. Complex *cis*-3 slowly converts to neutral Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>3</sub>(PEt<sub>3</sub>) (*trans*-3) through displacement of a PEt<sub>3</sub> ligand by Br<sup>-</sup>. Photolysis of *trans*-3 yields naphthalene, Pt<sub>2</sub>Br<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>, Et<sub>3</sub>PBr<sub>2</sub>, and other products. Na/Hg reduction of *trans*-3 gives *trans*-2 and other unidentified products.

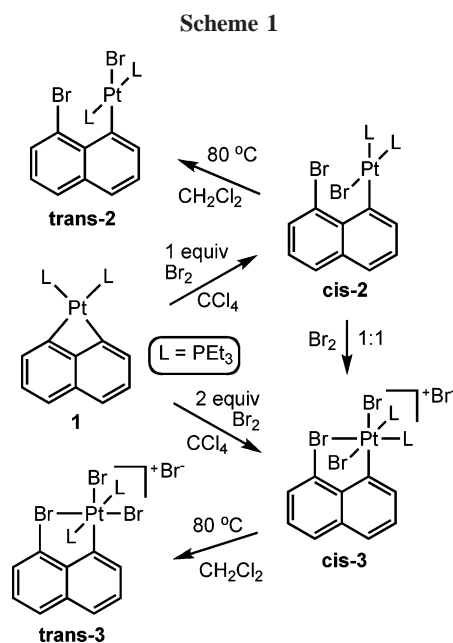
### Introduction

Metallacycles are an important class of organometallic complexes involved in a number of reactions.<sup>1</sup> We have been investigating an uncommon class of four- and five-membered metallacycles where the ring is fused to the edge of a polycyclic aromatic hydrocarbon<sup>2,3</sup> and recently reported the synthesis of Pt and Pd complexes and their novel colloidal metal-catalyzed alkyne coupling reactions.<sup>4,5</sup> In this paper we further characterize the reaction chemistry of the four-membered platinacycle Pt(Et<sub>3</sub>P)<sub>2</sub>(1,8-naphthalendiyl), describing its reactions with molecular bromine.

Reaction of organometallic complexes with molecular halogens or halogen sources is useful in the liberation of functionalized or coupled organic fragments from the metal center in both stoichiometric and catalytic processes.<sup>6</sup> With divalent organoplatinum complexes the reactions usually proceed through stable or transient Pt(IV) intermediates, which reductively eliminate the product of carbon–carbon or, more rarely, carbon–halogen coupling with the formation of a Pt(II) complex.<sup>7</sup> Although there have been a few examples of platinacycle bromination, these have been limited to five- and six-membered ring systems.<sup>8,9</sup> Oxidative addition of halogens to four-membered metallacycles followed by reductive elimination of halogenated or coupled organic compounds could enlarge the scope of polycyclic chemistry and lead to the development of new syntheses for polycyclic aromatic carbon compounds.

### Results

Dropwise addition of a CCl<sub>4</sub> solution of bromine to Pt(1,8-naphthalendiyl)(PEt<sub>3</sub>)<sub>2</sub> (**1**) in CCl<sub>4</sub> at room temperature gives a



brown precipitate at each drop, which dissolves as the reaction mixture is stirred. After the addition of 1 equiv of bromine a yellow homogeneous solution is obtained, from which yellow crystals of *cis*-2 can be isolated (Scheme 1). A crystal was subjected to X-ray analysis. Crystal data and data collection parameters and bond distances and angles are provided in Table 1. A drawing of the solid-state structure is shown in Figure 1.

The structure reveals the yellow product to be the Pt(II) complex *cis*-Pt(8-bromonaphthalen-1-yl)(Br)(PEt<sub>3</sub>)<sub>2</sub> (*cis*-2), not the anticipated oxidative addition product Pt(1,8-naphthalendiyl)(PEt<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>. The complex has a square-planar geometry about the Pt center with a *cis* orientation of the two phosphine ligands. The Pt plane is approximately perpendicular to the naphthalene ring plane. This arrangement places the *peri*-bromine atom (Br<sub>2</sub>) above the Pt coordination plane and in close proximity to the Pt center. A steric interaction between the Pt and Br centers is evident. The Pt1–Br<sub>2</sub> distance (3.196(1) Å) is much longer than the Pt1–Br<sub>1</sub> bonded distance of 2.508(1) Å and much longer than the distance between the *peri*-positions as defined by the C1–C9 distance of 2.55(1) Å. The long Pt–Br distance is

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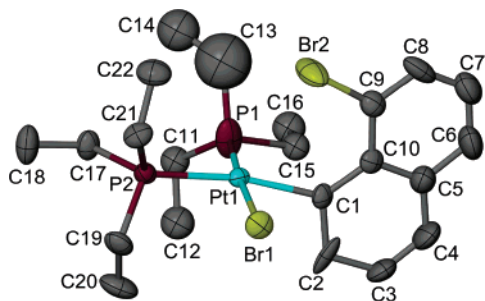
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**Figure 1.** Drawing of *cis*-Pt(8-bromonaphthalen-1-yl)(Br)(PEt<sub>3</sub>)<sub>2</sub> (*cis-2*). Only one orientation of the rotationally disordered phosphine ligand (P1) is shown. Atoms are drawn as 50% probability ellipsoids or spheres (C11–C16).

**Table 1. Crystallographic and Data Collection Parameters for *cis-2* and **5**<sup>a</sup>**

	<i>cis-2</i>	<b>5</b>
formula	C <sub>22</sub> H <sub>36</sub> Br <sub>2</sub> P <sub>2</sub> Pt	C <sub>16</sub> H <sub>21</sub> Br <sub>4</sub> PPt
fw	717.36	759.03
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	8.3343(9)	14.251(3)
<i>b</i> , Å	18.2838(19)	10.554(2)
<i>c</i> , Å	16.5594(18)	13.122(3)
β, deg	97.411(2)	91.674(4)
<i>V</i> , Å <sup>3</sup>	2502.3(5)	1972.9(8)
<i>Z</i>	4	4
<i>d</i> <sub>calc.</sub> , g/cm <sup>3</sup>	2.23	2.56
μ, mm <sup>-1</sup>	8.94	15.29
R1, <sup>b</sup> wR2 <sup>c</sup>	0.0479, 0.1188	0.0342, 0.0799

<sup>a</sup> λ = 0.71070 Å (Mo), *T* = −100 °C. <sup>b</sup>R1 = (Σ||*F*<sub>o</sub> − |*F*<sub>c</sub>||)/Σ|*F*<sub>o</sub>. <sup>c</sup>wR2 = [(Σw(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>))/Σw(*F*<sub>c</sub><sup>2</sup>)]<sup>1/2</sup>.

achieved primarily by distortion around C1 and C9. A convenient measure of the distortion is the C4–C1–Pt angle (168.7°) and the C6–C9–Br2 angle (172.4°). In an undistorted system these angles would be 180°. Distortion is also evident in a “twist” of the Br2–naphthalene–Pt1 moiety such that Pt1 (0.373 Å) and Br2 (−0.287 Å) are displaced to opposite sides of the naphthalene plane (planar to ±0.07 Å). The twist is also indicated by the torsion angle Pt1–C1–C9–Br2 of 14.4°. Similar distortions have been observed in other 1,8-substituted naphthalenes<sup>10–12</sup> including the related Ni complex *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(Br)(8-bromonaphthalen-1-yl).<sup>13</sup>

NMR spectroscopic data for *cis-2* are characteristic of its structure and are identical to the data for the product obtained from oxidative addition of Pt(PEt<sub>3</sub>)<sub>4</sub> to 1,8-dibromonaphthalene. This product was apparently incorrectly assigned an ionic formula.<sup>5</sup> The <sup>31</sup>P NMR spectrum of *cis-2* shows two doublets at δ 5.06 and −3.50 with *J*<sub>P–P</sub> of 18 Hz, consistent with the *cis* arrangement of the two phosphine ligands. Each doublet displays satellites (*J*<sub>P–P</sub> = 1860 and 4370 Hz, respectively) with the smaller Pt–195 coupling indicative of a phosphine ligand *trans* to carbon and the larger coupling indicative of a phosphine ligand *trans* to bromine.<sup>14</sup> The <sup>1</sup>H NMR spectrum displays six proton signals in the aromatic region and signals for the phosphine ligands in the aliphatic region. Satellites are observed

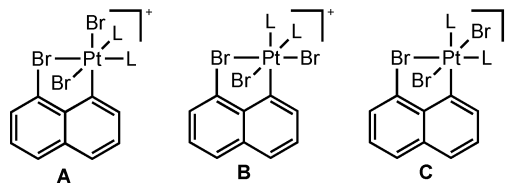
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**Figure 2.** Possible isomers of [Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*cis-3*).

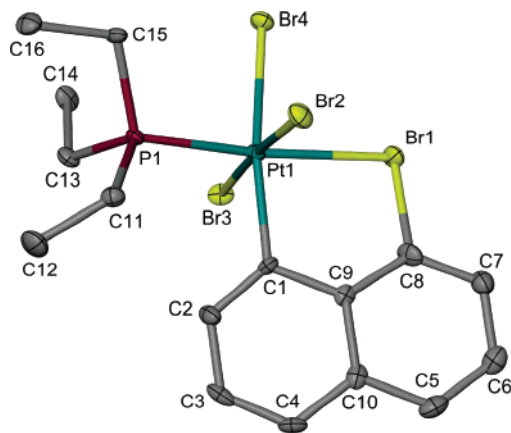
around the most downfield aromatic signal at 7.93 ppm and are assigned to coupling between the platinum and hydrogen atom attached to the C2 of the naphthalene ligand. Signals for the 10 different carbon atoms of the naphthalene ligand are observed in the <sup>13</sup>C NMR.

Complex *cis-2* slowly converts to the *trans* isomer, *trans-2* (Scheme 1), under prolonged heating at 80 °C in CH<sub>2</sub>Cl<sub>2</sub>. Due to the increase in symmetry, the <sup>31</sup>P NMR spectrum of *trans-2* shows a single resonance at 2.81 ppm with satellites (*J*<sub>Pt–P</sub> = 2898 Hz) for the phosphine ligands. The <sup>1</sup>H NMR spectrum shows the expected proton signals for the naphthalene ring in the aromatic region and the phosphine ligand in the aliphatic region.

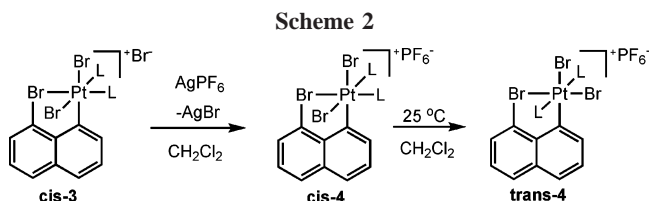
Addition of 1 equiv of bromine in CCl<sub>4</sub> to a CCl<sub>4</sub> solution of *cis-2* or addition of 2 equiv of bromine in CCl<sub>4</sub> to a CCl<sub>4</sub> solution of **1** yields a brown precipitate of *cis*-[Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*cis-3*) (Scheme 1). The <sup>31</sup>P NMR spectrum of *cis-3* in CD<sub>2</sub>Cl<sub>2</sub> shows two equal intensity doublets with Pt–195 satellites at δ 47.42 (*J*<sub>Pt–P</sub> = 2636 Hz) and 13.85 (*J*<sub>Pt–P</sub> = 2242 Hz) with *J*<sub>P–P</sub> of 4.1 Hz, indicating the presence of two inequivalent Pt-bonded phosphine ligands in a *cis* orientation. Six aromatic peaks (two overlapping) are observed in the <sup>1</sup>H NMR spectrum, indicating that the naphthalene moiety is intact and remains bonded to the Pt center. The lower *J*<sub>Pt–P</sub> values of *cis-3* in comparison to *cis-2* and the <sup>1</sup>H NMR data indicate Br<sub>2</sub> addition at the Pt center and the formation of an octahedral Pt(IV) complex. Simple oxidative addition of Br<sub>2</sub> with coordination of the two bromine atoms to the Pt center is unlikely given the steric hindrance that the naphthalene ring bromine atom would present. We therefore formulate the complex as ionic where one of the added bromines is present as an outer-sphere ion and the sixth coordination site is filled by the bromine atom bonded to the naphthalene ring. Three isomers are possible for the cationic portion and are shown in Figure 2. Both of the observed <sup>31</sup>P–<sup>195</sup>Pt coupling constants appear to be too large for a phosphine ligand *trans* to a strong donor carbon atom, eliminating isomers B and C, leaving isomer A as the assigned structure for *cis-3*. The <sup>31</sup>P NMR signal at 47.42 ppm is in an unusual region for a PEt<sub>3</sub> bonded to a Pt(IV) center, and we assign this signal to the PEt<sub>3</sub> ligand *trans* to the carbon-bonded bromine. This is also the signal with the largest <sup>31</sup>P–<sup>195</sup>Pt coupling (2636 Hz), consistent with the expected weak donor properties of this bromine atom.

Elemental analysis of the solid is consistent with the addition of Br<sub>2</sub> to *cis-2*. Brief heating in CH<sub>2</sub>Cl<sub>2</sub> converts *cis-3* to a new complex, which we assign as the *trans* isomer, *trans-3* (Scheme 1). This complex shows a single peak in its <sup>31</sup>P NMR spectrum with *J*<sub>Pt–P</sub> = 2047 Hz and was not isolated.

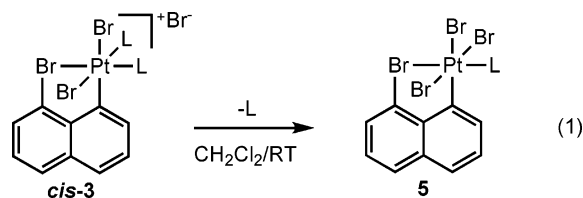
Treating *cis-3* with 1 equiv of AgPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> immediately produces a light brown precipitate of AgBr and *cis*-[Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (*cis-4*) (Scheme 2). NMR spectra of *cis-4* are almost identical to those of *cis-3*. Complex *cis-4* also shows a septet <sup>31</sup>P NMR signal in the area expected for the PF<sub>6</sub><sup>−</sup> anion (−143.86 ppm) with a *J*<sub>P–F</sub> value of 710.8



**Figure 3.** Drawing of Pt(8-bromonaphthalen-1-yl)(Br)<sub>3</sub>(PEt<sub>3</sub>) (**5**). Atoms are drawn as 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Hz.<sup>15</sup> These observations imply that the cationic portions of *cis-3* and *cis-4* are isostructural and that both complexes are ionic in nature with counteranions Br<sup>−</sup> and PF<sub>6</sub><sup>−</sup>, respectively. Complex *cis-4* is stable in the solid state, but in CH<sub>2</sub>Cl<sub>2</sub> solution it isomerizes to *trans-4*, the PF<sub>6</sub><sup>−</sup> analogue of *trans-3* (Scheme 2). As with *cis-4* and *cis-3*, NMR data for *trans-4* and *trans-3* are virtually identical (with the exception of the PF<sub>6</sub> signals for *trans-4*). Complex *trans-4* was not isolated.



While *cis-3* is stable in the solid state, in solution it undergoes displacement of one of the two coordinated phosphine ligands by its counteranion Br<sup>−</sup> to produce neutral Pt(η<sup>2</sup>-8-bromonaphthalen-1-yl)(Br)<sub>3</sub>(PEt<sub>3</sub>) (**5**) (eq 1). The formation of **5** is confirmed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, X-ray crystallography, and elemental analysis. The <sup>31</sup>P NMR spectrum of **5** shows a single resonance for the only phosphine ligand at 45.28 ppm with a *J*<sub>Pt–P</sub> value of 2720 Hz. Again, this is an unusual shift apparently associated with the phosphine ligand being *trans* to the carbon-bonded bromine atom (Br1). Six peaks are observed in the aromatic region of the <sup>1</sup>H NMR spectrum, in agreement with the lack of equivalent protons on the naphthalene ligand. <sup>195</sup>Pt satellites are observed around the lowest frequency aromatic signal at 7.24 ppm. Complex **5** is stable toward reductive elimination of dibromonaphthalene, and CH<sub>2</sub>Cl<sub>2</sub> solutions remain unchanged after 12 h at 80 °C.

A drawing of the solid-state structure of **5** is given in Figure 3. An abbreviated summary of the crystal data and data collection and processing is given in Table 1. Selected bond distances and angles are listed in Table 3. The structure shows

**Table 2.** Selected Distances and Angles for *cis-2*

Pt1–C1	2.063(9)	C1–C2	1.498(15)
Pt1–P1	2.237(3)	Br2–C9	1.885(10)
Pt1–P2	2.330(2)	C9–C8	1.375(13)
Pt1–Br1	2.5077(10)	C9–C10	1.457(13)
C1–C10	1.428(12)		
C1–Pt1–P1	89.1(2)	C10–C1–C2	120.0(8)
C1–Pt1–P2	168.5(2)	C10–C1–Pt1	129.7(7)
P1–Pt1–P2	100.07(10)	C2–C1–Pt1	110.2(6)
C1–Pt1–Br1	85.7(2)	C8–C9–C10	122.2(10)
P1–Pt1–Br1	174.80(9)	C8–C9–Br2	114.8(8)
P2–Pt1–Br1	84.94(6)	C10–C9–Br2	123.0(7)

**Table 3.** Selected Distances and Angles for **5**

Pt1–C1	2.062(6)	Pt1–Br4	2.5683(8)
Pt1–P1	2.3000(17)	Pt1–Br1	2.5782(8)
Pt1–Br3	2.4733(8)	Br1–C8	1.925(7)
Pt1–Br2	2.4742(8)		
C1–Pt1–P1	97.63(18)	Br1–Pt1–Br3	91.91(3)
C1–Pt1–Br1	85.45(18)	Br1–Pt1–Br4	84.67(3)
C1–Pt1–Br2	91.15(18)	Br2–Pt1–Br3	175.40(2)
C1–Pt1–Br3	84.32(18)	Br2–Pt1–Br4	94.10(3)
C1–Pt1–Br4	168.53(18)	Br3–Pt1–Br4	90.20(3)
P1–Pt1–Br1	170.21(5)	C8–Br1–Pt1	92.8(2)
P1–Pt1–Br2	83.81(5)	C2–C1–C9	118.0(6)
P1–Pt1–Br3	97.63(5)	C2–C1–Pt1	125.0(5)
P1–Pt1–Br4	93.07(5)	C9–C1–Pt1	116.9(5)
Br1–Pt1–Br2	86.85(3)		

the platinum atom in a distorted octahedral environment with the three bromine ligands in a *mer* orientation. The central bromine atom (Br4) is *trans* to the naphthalene carbon atom (C1). The carbon-bonded bromine atom (Br1) is *trans* to the phosphine ligand with a Pt–Br1 distance of 2.5782(8) Å. This is ca. 0.1 Å longer than the Pt distances to the mutually *trans* terminal bromine atoms Br2 (2.4742(8) Å) and Br3 (2.4733(8) Å) and only slightly longer than the Pt–Br4 distance (2.5683(8) Å) *trans* to the carbon. The Pt1–Br1 bond has eliminated some of the naphthalene unit distortion present in the structure of *cis-2*. The C4–C1–Pt1 angle (177.08°) is closer to linearity. (A similar change from nonbonding to bonding of a methoxy group has been reported in the I<sub>2</sub> oxidation of a Pt(II) 8-methoxynaphthalen-1-yl complex.<sup>10</sup>) However, the C5–C8–Br1 angle (171.30°) is still distorted, but the distortion is now due primarily to an out-of-naphthalene-plane positioning of Br1 (0.40 Å) resulting from a rotation (17.3°) of the Pt octahedron about the Pt–carbon bond. The rotation appears to be driven by steric interactions between the PEt<sub>3</sub> ligand, the *cis* bromine atom (Br4), and the naphthalene ligand.

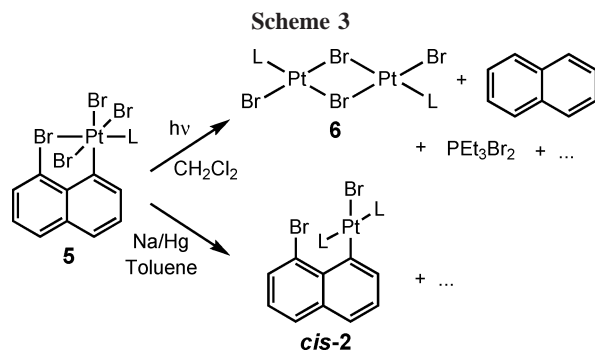
**Photolysis of 5.** Recent work in our group has shown that Pt(IV) aromatic complexes undergo interesting photochemistry involving photoreduction of the Pt(IV) center and aromatic ring bromination.<sup>16</sup> To check for similar chemistry, **5** was irradiated with a 500 W halogen lamp with the UV filter removed. The orange solution slowly became pale yellow. After ~15 h, <sup>31</sup>P NMR spectroscopy revealed two new singlets at 10.92 and 2.27 ppm with <sup>195</sup>Pt satellites (*J*<sub>Pt–P</sub> value of 3696 and 3594 Hz), respectively. With continued irradiation (~40 h), the peak at 2.27 ppm disappeared with a concomitant increase in the peak at 10.92 ppm and the formation of a new broad peak at ~90.0 ppm presumably due to the formation of Et<sub>3</sub>PBr<sub>2</sub>.<sup>17</sup> <sup>1</sup>H NMR spectroscopy revealed the formation of peaks associated with free naphthalene in nearly quantitative yield. Concentration of

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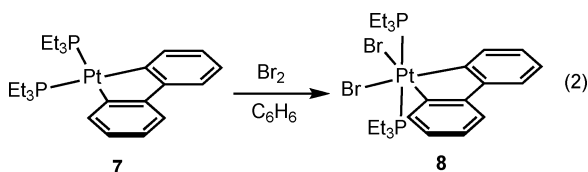


the solution followed by cooling of the concentrate to  $-20\text{ }^\circ\text{C}$  gave deep yellow crystals, which proved, by X-ray crystallography, to be  $\text{Pt}_2\text{Br}_4(\text{PEt}_3)_2$  (**6**) (Scheme 3). Unit cell parameters and  $^{31}\text{P}$  NMR and  $^1\text{H}$  NMR spectra of the crystals match the literature values.<sup>18</sup>

**Na-Amalgam Reduction of 5.** In an effort to identify the intermediate complexes in the photochemical reaction of **5**, **5** was reduced with sodium amalgam in toluene (Scheme 3). The initially orange solution turned light yellow in  $\sim 30$  min and showed a sharp  $^{31}\text{P}$  signal at 2.81 ppm with  $^{195}\text{Pt}$  satellites ( $J_{\text{Pt-P}} = 2898$  Hz), suggesting the presence of *trans*-**2**. The yellow solution was filtered and the solvent removed to obtain a yellow solid. A  $^1\text{H}$  NMR spectrum of the solid confirmed the formation of *trans*-**2** but also showed a number of unidentified peaks in the aromatic region.

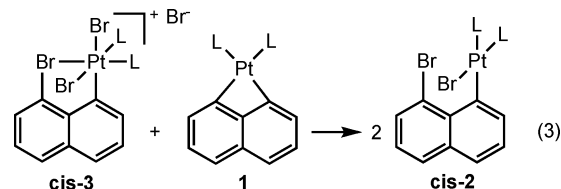
## Discussion

Our results on bromine addition to four-membered platinacycle **1** contrast with those for the larger five-membered platinacycle  $\text{Pt}(2,2'\text{-biphenyl})(\text{PEt}_3)_2$  (**7**, eq 2).<sup>8</sup> Platinacycle **7** and bromine give the Pt(IV) complex **8**, where both Pt–C bonds of the platinacycle remain intact. It is possible that a similar reaction occurs with platinacycle **1** to give an analogue of **8**, but the strain from the smaller four-membered ring results in facile reductive elimination with formation of the C–Br bond in *cis*-**2**. However, we did not detect any intermediates (see below) in the formation of *cis*-**2**, so a direct addition across a Pt–C bond without formation of a Pt(IV) intermediate is also possible.



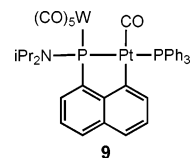
There is the formation of a brown precipitate in the bromine reaction of **1** (see Results), which could be an intermediate in the formation of *cis*-**2**. However, we believe the brown precipitate is due to formation of the second bromine addition product *cis*-**3** by a rapid reaction of *cis*-**2** with a locally high concentration of bromine. The disappearance of the precipitate of *cis*-**3** as the mixture stirs is explained by a reaction between *cis*-**3** and **1** yielding 2 equiv of *cis*-**2**. This reaction has been confirmed by mixing a solution of **1** with solid *cis*-**3**, with the resulting disappearance of solid *cis*-**3** and the formation of a solution of *cis*-**2** (eq 3).

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The second bromination of *cis*-**2** in  $\text{CCl}_4$  does result in oxidation of the Pt(II) center and formation of the cationic octahedral Pt(IV) species *cis*-**3**. Although, the proposed structure of *cis*-**3** could not be confirmed by X-ray analysis, spectroscopic data are diagnostic and consistent with the structures for its derivatives *trans*-**3**, *cis*-**4**, *trans*-**4**, and **5**. Most notable in *cis*-**3**, *cis*-**4**, and **5**, the latter of which has been characterized by X-ray analysis, is the coordination of the carbon-bonded bromine of the bromonaphthalenyl ligand. Halocarbon coordination through a halogen has been known for some time, but such complexes are still relatively rare.<sup>19</sup> In fact, **5** appears to be the first well characterized example for Pt(IV).<sup>20</sup>

In *cis*-**3**, *cis*-**4**, and **5** an unusually large shift is observed for the  $\text{PEt}_3$  ligand *trans* to the carbon-bonded bromine. It is tempting to attribute this to the  $\text{PEt}_3$  ligand's position *trans* to the halocarbon bond. However, the better explanation appears to be associated with the  $\text{PEt}_3$  ligand being near and in the plane of the naphthalene ring. In this position the naphthalene ring current deshields the  $^{31}\text{P}$  nucleus. An unusually large shift (75.2 ppm) is observed for the  $\text{PPh}_3$  ligand in structurally related **9** for the same reason.<sup>21</sup>



## Conclusions and Summary

In contrast to the more usual oxidative addition product for Pt(II) complexes, bromine addition to the four-membered platinacycle **1** results in cleavage of one of the Pt–C bonds. The failure of **1** to produce a Pt(IV) product is attributed to ring strain associated with the four-membered platinacycle ring. Further bromination does yield a Pt(IV) complex, *cis*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*cis*-**3**). The carbon-bonded bromine atom of the naphthalene ring fills one of the six coordination sites of *cis*-**3**. The analogous PF<sub>6</sub><sup>−</sup> salt is readily prepared from Ag<sup>+</sup> precipitation of AgBr. The complexes isomerize in solution to more stable *trans*-isomers. Complex *cis*-**3** slowly reacts with its bromide anion to produce neutral Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>3</sub>(PEt<sub>3</sub>) (**5**). Photolysis of **5** yields bromo-bridged [Pt<sup>II</sup><sub>2</sub>Br<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] (**6**), free naphthalene, and unidentified products. Na-amalgam reduction gives *trans*-**2** along with unidentified products.

## Experimental Section

**General Procedures.** Pt(1,8-naphthalendiyl)(PEt<sub>3</sub>)<sub>2</sub> (**1**) was prepared by the reported procedures.<sup>5</sup> Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox or on a Schlenk line with dried and degassed solvents

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stored under dinitrogen over 4 Å molecular sieves or sodium metal. NMR spectra were recorded on a Bruker AMX-250, -300, or -500 spectrometer at ambient probe temperatures except as noted. Shifts are given in ppm with positive values downfield of TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ), external  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ), or external  $\text{K}_2\text{PtCl}_4(\text{aq})$  ( $^{195}\text{Pt}$ , -1630 ppm).  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were recorded in proton-decoupled mode. Desert Analytics performed the microanalyses (inert atmosphere).

**Synthesis. *cis*-Pt(8-bromonaphthalen-1-yl)(Br)(PEt<sub>3</sub>)<sub>2</sub> (*cis*-2).** A carbon tetrachloride solution (2 mL) of bromine (4.6  $\mu\text{L}$ , 14.3 mg, 0.0895 mmol) was added dropwise to a carbon tetrachloride solution (10 mL) of Pt(1,8-naphthalendiyl)(PEt<sub>3</sub>)<sub>2</sub> (**1**) (50.0 mg, 0.0897 mmol). After each drop a brown precipitate that quickly dissolved was observed. After complete addition the mixture was stirred for ca. 10 min and then filtered to give a yellow solution. The solution was concentrated to ~5 mL and stored at -30 °C to give yellow crystals of *cis*-2, which were isolated by filtration, washed with cold carbon tetrachloride, and dried in vacuo. Yield: 56.0 mg (87%). Spectroscopic data matched that previously reported for the compound reported as [Pt( $\eta^2$ -8-bromonaphthalen-1-yl)-(PEt<sub>3</sub>)<sub>2</sub>Br] $\cdot$ 5 Br.<sup>5</sup> Anal. Calc (found) for C<sub>22</sub>H<sub>36</sub>Br<sub>2</sub>Pt: C, 36.83 (37.39); H, 5.06 (4.94).

$^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.93 (t with satellites,  $J_{\text{HH}} = 6.0$  Hz,  $J_{\text{PH}} = 18.0$  Hz, 1H), 7.79 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 7.73 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.41 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.20 (t,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.16 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 2.07 (m, CH<sub>2</sub>, 6H), 1.62 (m, CH<sub>2</sub>, 6H), 1.20 (m, CH<sub>3</sub>, 9H), 0.97 (m, CH<sub>3</sub>, 9H).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 5.06 (d with satellites,  $J_{\text{P-P}}$  of 18 Hz,  $J_{\text{PP}} = 1860$  Hz, 1P, P *trans* to C), -3.50 (d with satellites,  $J_{\text{P-P}}$  of 18 Hz,  $J_{\text{PP}} = 4370$  Hz, 1P, P *trans* to Br).  $^{13}\text{C}$  NMR (125.75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 156.87 (d,  $J_{\text{CP}} = 114$  Hz), 137.78 (d,  $J_{\text{CP}} = 5.2$  Hz), 137.54 (s), 136.42 (s), 130.78 (s), 129.70 (s), 126.54 (d,  $J_{\text{CP}} = 25$  Hz), 125.70 (d,  $J_{\text{CP}} = 25$  Hz), 124.71 (s), 123.90 (s), 18.56 (d,  $J_{\text{CP}} = 155$  Hz), 16.0 (d,  $J_{\text{CP}} = 115$  Hz), 8.51 (d,  $J_{\text{CP}} = 25$  Hz), 8.35 (d,  $J_{\text{CP}} = 10$  Hz).

***trans*-Pt(8-bromonaphthalen-1-yl)(Br)(PEt<sub>3</sub>)<sub>2</sub> (*trans*-2).** Complex *cis*-2 was heated at 80 °C in CH<sub>2</sub>Cl<sub>2</sub> to give a solution of *trans*-2.  $^1\text{H}$  NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.98 (d,  $J_{\text{HH}} = 7.0$  Hz, 1H), 7.80 (d,  $J_{\text{HH}} = 7.0$  Hz, 1H), 7.71 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.39 (d,  $J_{\text{HH}} = 7.8$  Hz, 1H), 7.14 (t,  $J_{\text{HH}} = 7.8$  Hz, 1H), 7.08 (t,  $J_{\text{HH}} = 7.2$  Hz, 1H), 1.59 (m, CH<sub>2</sub>, 12H), 0.97 (m, CH<sub>3</sub>, 18H).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 2.81 (s with satellites,  $J_{\text{PP}} = 2898$  Hz, 2P).

***cis*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*cis*-3).** A carbon tetrachloride solution (2 mL) of bromine (3.5  $\mu\text{L}$ , 11.2 mg, 0.0701 mmol) was added dropwise to a carbon tetrachloride solution (15 mL) of Pt(8-bromonaphthalen-1-yl)(Br)(PEt<sub>3</sub>)<sub>2</sub> (*cis*-2) (50.0 mg, 0.0697 mmol). A brown precipitate was produced. To ensure completion of the reaction, a second CCl<sub>4</sub> solution of Br<sub>2</sub> was added dropwise until no further precipitate formed (2–3 drops). The solid was isolated by filtration, washed with cold carbon tetrachloride, and dried in vacuo. Yield: 56.2 mg (92%). Anal. Calc (found) for C<sub>22</sub>H<sub>36</sub>Br<sub>4</sub>P<sub>2</sub>Pt $\cdot$ CCl<sub>4</sub>: C, 26.79 (26.97, 26.77); H, 3.52 (3.86, 3.50). The presence of CCl<sub>4</sub> could not be confirmed by  $^{13}\text{C}$  NMR spectroscopy, but the signal is expected to be weak.

$^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.89 (d,  $J = 8.0$  Hz, 1H), 7.82–7.76 (m, 2H), 7.74 (dd,  $J = 7.5$  Hz, 1H), 7.68 (dd,  $J = 7.5$  Hz, 1H), 7.53 (t,  $J = 7.5$  Hz, 1H), 3.21–3.12 (m, 3H), 2.87–2.79 (m, 3H), 2.65–2.54 (m, 3H), 2.51–2.35 (m, 3H), 1.58–1.46 (m, 9H), 1.02–0.89 (m, 9H).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 47.42 (d with satellites,  $J_{\text{PP}} = 4.1$  Hz,  $J_{\text{PP}} = 2636$  Hz, 1P), 13.85 (d with satellites,  $J_{\text{PP}} = 4.1$  Hz,  $J_{\text{PP}} = 2242$  Hz, 1P).  $^{13}\text{C}$  NMR (125.75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 137.92 (s), 137.60 (s), 134.06 (s), 130.19 (s), 129.27 (s), 128.36 (d,  $J_{\text{CP}} = 20.5$  Hz), 127.69 (s), 127.46 (s), 126.84 (d,  $J_{\text{CP}} = 6.1$  Hz), 126.50 (s), 17.60 (d,  $J_{\text{CP}} = 5.1$  Hz), 16.92 (d,  $J_{\text{CP}} = 31.0$  Hz), 9.02 (d,  $J_{\text{CP}} = 7.5$  Hz), 8.15 (d,  $J_{\text{CP}} = 6.1$  Hz).

***trans*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*trans*-3).** Complex *cis*-3 was briefly heated at 80 °C in CH<sub>2</sub>Cl<sub>2</sub> to give a

solution of *trans*-3.  $^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 8.33 (d with satellites,  $J_{\text{HH}} = 8.0$  Hz,  $J_{\text{PH}} = 17.5$  Hz, 1H), 7.85 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.72 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.67 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.51 (t,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.48 (t,  $J_{\text{HH}} = 8.0$  Hz, 1H), 2.20 (m, 12H), 1.29 (m, 18H).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 9.78 (s with satellites,  $J_{\text{PP}} = 2047$  Hz, 2P).

***cis*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>) (*cis*-4).** AgPF<sub>6</sub> (5.8 mg, 0.0228 mmol) was added to 2 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was agitated until most all of the solid had dissolved. The solution was filtered and added to a dichloromethane solution (5 mL) of *cis*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*cis*-3) (20.0 mg, 0.0228 mmol). A light brown precipitate of AgBr was immediately observed. To ensure completion of the reaction, a second CH<sub>2</sub>Cl<sub>2</sub> solution of AgPF<sub>6</sub> was added dropwise until no further precipitate formed (2–3 drops). The precipitate was removed by filtration through diatomaceous earth, and the clear filtrate was then concentrated to ~2 mL. Addition of pentane gave deep brown solid *cis*-4, which was isolated by decantation, washed with cold pentane, and dried in vacuo. Yield: 18.7 mg (87%). Anal. Calc (found) for C<sub>22</sub>H<sub>36</sub>Br<sub>3</sub>F<sub>6</sub>P<sub>3</sub>Pt: C, 28.04 (27.98); H, 3.85 (3.75).

$^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.89 (d,  $J = 8.0$  Hz, 1H), 7.79 (t,  $J = 8.0$  Hz, 2H), 7.61 (t,  $J = 8.0$  Hz, 1H), 7.51 (dd, with satellites,  $J_{\text{HH}} = 7.5$  Hz,  $J_{\text{PH}} = 24.0$  Hz, 1H), 3.07–2.99 (m, 3H), 2.78–2.71 (m, 3H), 2.55–2.48 (m, 3H), 2.38–2.29 (m, 3H), 1.52–1.41 (m, 9H), 0.95–0.87 (m, 9H).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 46.49 (s with satellites,  $J_{\text{PP}} = 2639$  Hz, 1P), 13.14 (s with satellites,  $J_{\text{PP}} = 2237$  Hz, 1P), -143.86 (sept,  $J_{\text{PF}} = 710.8$  Hz, 1P).  $^{13}\text{C}$  NMR (125.75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 139.56 (s), 138.05 (s), 134.64 (d,  $J_{\text{CP}} = 15.0$  Hz), 130.26 (s), 129.33 (s), 128.89 (d,  $J_{\text{CP}} = 20.0$  Hz), 128.42 (s), 128.23 (d,  $J_{\text{CP}} = 5.0$  Hz), 127.91 (s), 127.38 (s), 34.49 (s), 23.68 (d,  $J_{\text{CP}} = 150.0$  Hz), 22.71 (s), 21.60 (d,  $J_{\text{CP}} = 150.0$  Hz), 19.45 (s), 19.15 (s), 14.18 (s), 10.96 (d,  $J_{\text{CP}} = 30.0$  Hz), 9.79 (d,  $J_{\text{CP}} = 25.0$  Hz), 8.76 (d,  $J_{\text{CP}} = 25.0$  Hz), 7.97 (s), 5.08 (s).

***trans*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>) (*trans*-4).** Compound *cis*-4 is stable in the solid state but converts (2 to 3 h) at room temperature in CH<sub>2</sub>Cl<sub>2</sub> to *trans*-4.  $^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 8.32 (d with satellites,  $J_{\text{HH}} = 9.0$  Hz,  $J_{\text{PH}} = 17.0$  Hz, 1H), 7.86 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.68 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.59 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.56–7.49 (m, 2H), 2.21–2.15 (m, 6H), 1.29–1.22 (m, 9H).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 9.76 (s with satellites,  $J_{\text{PP}} = 2049$  Hz, 2P), -143.90 (sept,  $J_{\text{PF}} = 710.5$  Hz, 1P).

**Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>3</sub>(PEt<sub>3</sub>) (**5**).** *cis*-[Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]Br (*cis*-3) (50 mg, 0.0570 mmol) was dissolved in 5 mL of dichloromethane and kept for recrystallization by solvent evaporation at room temperature. After 2 days, the solvent was nearly gone and orange crystalline solid **5** had formed. The crystals were washed with cold diethyl ether and dried in vacuo. Yield: 41.1 mg (95%). Anal. Calc (found) for C<sub>16</sub>H<sub>21</sub>Br<sub>4</sub>Pt: C, 25.32 (25.41); H, 2.79 (2.85).

$^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.80 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.71 (dd,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.58 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.48 (t,  $J_{\text{HH}} = 8.0$  Hz, 1H), 7.39 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.24 (dd with satellites,  $J_{\text{HH}} = 7.5$  Hz,  $J_{\text{PH}} = 17.5$  Hz, 1H), 2.84 (m, 6H, CH<sub>2</sub>), 1.43 (m, 9H, CH<sub>3</sub>).  $^{31}\text{P}$  NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 45.28 (s with satellites,  $J_{\text{PP}} = 2720$  Hz).  $^{13}\text{C}$  NMR (75.47 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 139.56 (s), 138.37 (s), 137.37 (s), 134.64 (d,  $J_{\text{CP}} = 12.0$  Hz), 134.37 (s), 129.32 (s), 128.52 (s), 128.25 (d,  $J_{\text{CP}} = 10.0$  Hz), 127.37 (d,  $J_{\text{CP}} = 12.0$  Hz), 125.59 (s), 21.60 (d with satellites,  $J_{\text{CP}} = 156.0$  Hz,  $J_{\text{CPt}} = 57.0$  Hz), 9.80 (d with satellites,  $J_{\text{CP}} = 24.0$  Hz,  $J_{\text{CPt}} = 30.0$  Hz).

**Reaction of **5** with Na/Hg.** Pt( $\eta^2$ -8-bromonaphthalen-1-yl)(Br)<sub>3</sub>(PEt<sub>3</sub>) (**5**) (25 mg, 0.0329 mmol) was stirred with excess 0.5% Na/Hg in toluene. After 30 min stirring, a yellow solution was obtained, which was filtered through diatomaceous earth. The solvent was then removed under vacuum, which gave a yellow solid. The solid was then dissolved in CD<sub>2</sub>Cl<sub>2</sub> and a  $^{31}\text{P}$  NMR spectrum was recorded, which showed a sharp peak at 2.78 ppm with satellites

( $J_{\text{PtP}} = 2898$  Hz), attributed to *trans*-**2**, and a broad peak at  $\sim 90$  ppm due to  $\text{Et}_3\text{PBr}_2$ .<sup>17</sup> A  $^1\text{H}$  NMR spectrum of the solution also indicated the presence of another naphthalene-containing complex apart from *trans*-**2**, but attempts to isolate the complex were unsuccessful.

**Photochemical Decomposition of 5.** A dichloromethane solution (0.70 mL) of complex **5** (10.0 mg, 0.0132 mmol) was placed in a quartz NMR tube. The sample was irradiated with a 500 W halogen lamp. The reaction was followed by  $^{31}\text{P}$  NMR spectroscopy. During the reaction, two distinct peaks at 10.92 and 2.27 ppm with  $^{195}\text{Pt}$  satellites and one broad peak at  $\sim 90.0$  without  $^{195}\text{Pt}$  satellites were observed. The broad peak at  $\sim 90.0$  ppm is assigned to  $\text{Et}_3\text{PBr}_2$ .<sup>17</sup> The peak at 10.92 ppm (s,  $J_{\text{Pt-P}} = 3700$  Hz) is assigned to  $\text{Pt}_2(\text{PEt}_3)_2\text{Br}_4$  **6**, but characterization of the complex giving the peak at 2.27 ppm (s,  $J_{\text{Pt-P}} = 3560$  Hz) was not successful. At the end of reaction ( $\sim 40$  h), the peak at 2.27 ppm disappeared with concomitant formation of **6**. Concentration of the product solution followed by cooling to  $-30$  °C gave deep yellow crystals that were isolated

by decantation, washed with cold hexane, and dried in vacuo. These were shown to be **6** by comparison to the literature values of the unit cell parameters and the NMR data.<sup>18</sup> The volatiles were removed from the mother liquor in vacuo, and the resulting solid was dissolved in  $\text{CD}_2\text{Cl}_2$ . A  $^1\text{H}$  NMR spectrum showed only free naphthalene.

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**Supporting Information Available:** Full X-ray data (cif files) for *cis*-**2** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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