

**Figure 2.** Infrared spectra of a  $\text{Mn}(\text{PEt}_3)\text{Br}_2$  film: (a) following initial preparation; (b) following exposure to 15 torr of  $\text{SO}_2$  for 15 min at 298 K and then brief evacuation; (c) following an evacuation cycle for 24 h at  $10^{-6}$  torr at 298 K; (d) following exposure to 50 torr of  $\text{SO}_2$  for 24 h at 298 K and then brief evacuation; (e) following evacuation for 24 h at  $10^{-6}$  torr at 298 K. Band positions for analogous  $\text{S}^{18}\text{O}_2$  complex spectra are given in parentheses.

are shown in parentheses. Again reversibility was observed as long as exposure time and pressure were minimized. It is clear that at least two types of  $\text{MnLBr}_2/\text{SO}_2$  complexes were formed in these experiments—one in which the  $\text{SO}_2$  bonds reversibly and one in which the  $\text{SO}_2$  is coordinated in an irreversible fashion. Comparison of the intensities of the 865-, 910-, and 970- $\text{cm}^{-1}$  bands in the spectra shown in Figure 2, parts d and e, reveals that the reversible complex can decompose to the irreversible one even during evacuation following high  $\text{SO}_2$  exposures.

Bulk samples of the two final irreversible  $\text{SO}_2$  complexes were prepared on a high-vacuum line in a manner completely analogous to the sample treatment conditions for the complex films. The bulk analyses of the two final irreversible  $\text{SO}_2$  complexes revealed that the stoichiometry for each was  $\text{MnLBr}_2 \cdot 1/2\text{SO}_2$ .<sup>5</sup> This data along with the observation of intense infrared bands in the 800–1075- $\text{cm}^{-1}$  regions of the spectra imply that the two forms of each complex contain  $\text{SO}_2$  bonded in a bridging mode,<sup>6</sup> with more than

one atom of  $\text{SO}_2$  involved in the bridge. Final structure determination must await X-ray crystallographic data.

It should be noted that McAuliffe and co-workers have reported recently the reaction of  $\text{SO}_2$  with several  $\text{MnLX}_2$  complexes in toluene solution and in toluene slurries.<sup>7</sup> They report a stoichiometry of  $\text{MnLX}_2 \cdot 2/3\text{SO}_2$  for their solution studies, and they were not able to observe reversibility. Furthermore, they report prominent infrared bands in the 1112–1140- $\text{cm}^{-1}$  region, which are not observed for the  $\text{MnPEt}_3\text{Br}_2/\text{SO}_2$  complex film. However, their experimental conditions (liquid phase, exposure to 760 torr of  $\text{SO}_2$  for 48 h) were markedly different than those used in this work; thus it is possible that a reversible complex was formed also in their work, but converted to an irreversible product before analysis.

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**Registry No.**  $\text{Mn}(\text{PPhMe}_2)\text{Br}_2$ , 71957-10-3;  $\text{Mn}(\text{PEt}_3)\text{Br}_2$ , 82758-64-3;  $\text{SO}_2$ , 7446-09-5.

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### Platinum(II) Trichlorostannate Complexes with Nitrogen Ligands. <sup>195</sup>Pt, <sup>119</sup>Sn, <sup>31</sup>P, and <sup>15</sup>N NMR Studies and the X-ray Crystallographic Structure of (*p*-Chloroaniline)-(triethylphosphine)chloro(trichlorostannato)platinum(II)

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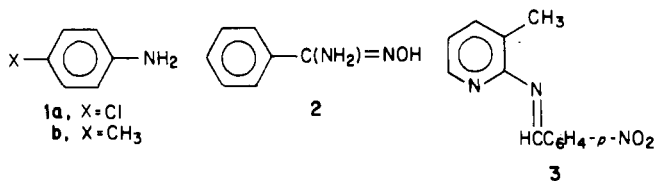
Although there are now many well-characterized  $\text{SnCl}_3$  complexes of platinum(II),<sup>1</sup> these frequently contain phosphorus, arsenic, carbonyl, or halogen ligands. We were interested in obtaining platinum(II) trichlorostannate complexes with nitrogen ligands since the latter are readily available with optically active carbon centers. As complexes of platinum(II) with  $\text{SnCl}_3$  ligands are active catalysts for the hydrogenation<sup>2</sup> and hydroformylation<sup>3</sup> reactions, introduction of an available optically active center might eventually afford a new optically active catalyst. Further, since there is little known concerning the trans influence of the  $\text{SnCl}_3$  it would be useful to have crystallographic and NMR measurements on a relatively simple system, for comparison purposes. We report here the preparation and characterization of the complexes  $[\text{PtCl}(\text{SnCl}_3)\text{L}(\text{PEt}_3)]$ ,  $\text{L} = 1-3$ , and the molecular structure for the complex with  $\text{L} = 1\mathbf{a}$  and suggest that all of these complexes have nitrogen coordinated to platinum.

### Results

**1. X-ray Structure of  $[\text{PtCl}(\text{SnCl}_3)(1\mathbf{a})(\text{PEt}_3)]$ .** The complexes  $[\text{PtCl}(\text{SnCl}_3)\text{L}(\text{PEt}_3)]$  were prepared by reaction of 2 equiv of

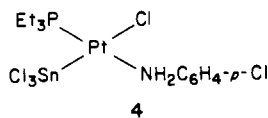
(5) Anal. Calcd (Atlantic Microlabs, Inc.) for  $\text{Mn}(\text{PPhMe}_2)\text{Br}_2 \cdot 1/2\text{SO}_2$ : C, 25.0; H, 2.9; Br, 41.5; S, 4.2. Found: C, 24.8; H, 3.0; Br, 41.4; S, 4.1. Anal. Calcd (Atlantic Microlabs, Inc.) for  $\text{Mn}(\text{PEt}_3)\text{Br}_2 \cdot 1/2\text{SO}_2$ : C, 19.7; H, 4.1; Br, 43.8; S, 4.4. Found: C, 19.7; H, 4.2; Br, 43.7; S, 4.4.

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L with the dimer  $[\text{PtCl}(\text{SnCl}_3)(\text{PET}_3)]_2$ .<sup>4</sup> Suitable crystals of  $[\text{PtCl}(\text{SnCl}_3)(\mathbf{1a})(\text{PET}_3)]$  were obtained by precipitating the complex from the mixture of chlorinated hydrocarbons used for the NMR measurements,  $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$  1:1, with ether/pentane 1:1.

The molecule shows slightly distorted square-planar geometry at platinum with the ligands arranged as shown in 4, and Figure 1 shows a view of the molecule. We attribute the large angles

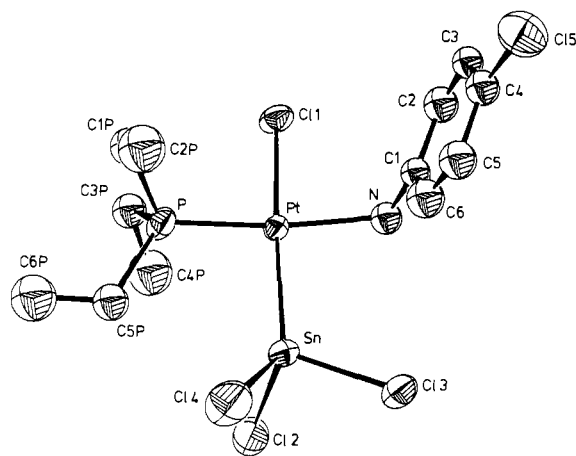


$\text{Sn-Pt-N}$ ,  $92.0(3)^\circ$ , and  $\text{Sn-Pt-P}$ ,  $95.0(1)^\circ$ , to steric repulsions between  $\text{SnCl}_3$  and its cis neighbors, so that the  $\text{Cl-Pt-P}$ ,  $88.0(1)^\circ$ , and  $\text{Cl-Pt-N}$ ,  $85.00(3)^\circ$ , angles are slightly less than  $90^\circ$ .

The  $\text{Pt-Sn}$  bond distance of  $2.514(1) \text{ \AA}$  is short when compared with that of *trans*- $[\text{Pt}(\text{SnCl}_3)_2(\text{P}(\text{O}Ph)_3)_2]$ ,<sup>1c</sup>  $2.599(2) \text{ \AA}$ , but is comparable to those found for  $[\text{PtCl}(\text{SnCl}_3)(\text{PET}_3)]_2$ ,<sup>4</sup>  $2.481(4) \text{ \AA}$ , and  $[\text{PtCl}(\text{SnCl}_3)(\text{PhC}(\text{NH}_2)=\text{NOH})(\text{PET}_3)]$ <sup>5</sup> (oxime N coordinated),  $2.501(1) \text{ \AA}$ . The most interesting bond distance is that observed between platinum and chlorine,  $2.331(3) \text{ \AA}$ . This distance is a useful measure of the X-ray trans influence of the ligand opposite to Cl and thus provides the opportunity to evaluate the  $\text{SnCl}_3$  ligand relative to others. Typically, ligands with a large trans influence, e.g. hydride, alkyl, vinyl, or phosphine, show  $\text{Pt-Cl}$  distances in the range  $2.36\text{--}2.42 \text{ \AA}$  (see Table I), whereas the weaker trans-influence cases, e.g. Cl, N, and CO, have  $\text{Pt-Cl}$  distances of ca.  $2.29\text{--}2.32 \text{ \AA}$ . Clearly, our value of  $2.331(3) \text{ \AA}$  places the  $\text{SnCl}_3$  at the lower end of the scale, consistent with a picture of this ligand as exerting a weak-to-moderate trans influence similar to that of an olefin. The  $\text{Pt-P}$  bond distance of  $2.233(4) \text{ \AA}$  falls in the range expected for a phosphine trans to a ligand with a poor trans influence,<sup>6</sup> whereas the reverse is true for the observed  $\text{Pt-N}$  distance,  $2.152(11) \text{ \AA}$ , in keeping with P trans to N.<sup>7</sup>

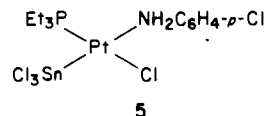
**2. NMR Solution Studies.** The solution studies on  $[\text{PtCl}(\text{SnCl}_3)(\text{NH}_2\text{C}_6\text{H}_4\text{-}p\text{-Cl})(\text{PET}_3)]$  required  $^{195}\text{Pt}$ ,  $^{119}\text{Sn}$ ,  $^{31}\text{P}$  and  $^{15}\text{N}$  NMR studies before structure 4 could be assigned with certainty.

The  $^{195}\text{P}\{^1\text{H}\}$  and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra for 4 confirm that the  $\text{SnCl}_3$  ligand is coordinated to platinum in that both NMR forms reveal ca.  $30\text{-kHz } ^1J(^{195}\text{Pt}, ^{119}\text{Sn})$  coupling constants, which values are now recognized<sup>1a-c,8</sup> as signifying a direct  $\text{Pt-Sn}$  bond.



**Figure 1.** ORTEP plot of the structure of complex **1a**. Bond lengths ( $\text{\AA}$ ) and angles ( $\text{deg}$ ):  $\text{Pt-Sn}$ ,  $2.514(1)$ ;  $\text{Pt-P}$ ,  $2.233(4)$ ;  $\text{Pt-Cl}(1)$ ,  $2.331(3)$ ;  $\text{Pt-N}$ ,  $2.152(11)$ ;  $\text{Sn-Pt-Cl}(1)$ ,  $174.3(1)$ ;  $\text{P-Pt-N}$ ,  $173.0(4)$ ;  $\text{Sn-Pt-N}$ ,  $92.0(3)$ ;  $\text{Sn-Pt-P}$ ,  $95.0(1)$ ;  $\text{Cl}(1)\text{-Pt-N}$ ,  $85.0(3)$ ;  $\text{Cl-Pt-P}$ ,  $88.0(1)$ .

The  $^{31}\text{P}$  NMR spectrum, via the value  $^2J(^{119}\text{Sn}, ^{31}\text{P})$ , places these two spins in a cis orientation,<sup>9</sup> and the magnitude of the coupling constant  $^1J(^{195}\text{Pt}, ^{31}\text{P})$  is consistent with a ligand trans to  $^{31}\text{P}$  that has a weak-to-moderate trans influence. Structure 5 was elim-



inated for the two aniline complexes by using  $^{15}\text{N}$ -enriched compounds (Enrichment is not strictly necessary, and in one case we have obtained an  $^{15}\text{N}$  NMR spectrum in natural abundance.) The values of  $^2J(^{31}\text{P}, ^{15}\text{N})$  are known<sup>10</sup> to be dependent on the geometric orientation of these spins, and the observed values of  $37 \text{ Hz}$  for the  $\text{NH}_2\text{C}_6\text{H}_4\text{-}p\text{-Cl}$  and  $\text{NH}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$  compounds are consistent with 4 but not 5. The values for  $^1J(^{195}\text{Pt}, ^{15}\text{N})$  of  $107$  and  $114 \text{ Hz}$  are close to those found in *trans*- $[\text{PtCl}_2(^{15}\text{NH}_2\text{-(CH}_2)_5(\text{P-}n\text{-Bu}_3)]$ ,<sup>11</sup>  $138 \text{ Hz}$ , and  $[\text{Pt}(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Cl}(\text{PPh}_3)]$ ,<sup>12a</sup>  $122 \text{ Hz}$ , thereby further confirming nitrogen coordination to platinum. There is a  $9\text{--}10\text{-Hz}$  coupling observable between  $^{15}\text{N}$  and  $^{119}\text{Sn}$ . It is likely—but not proven—that a solution geometry analogous to 4 may be assigned to  $[\text{PtCl}(\text{SnCl}_3)(\mathbf{2})(\text{PET}_3)]$  and  $[\text{PtCl}(\text{SnCl}_3)(\mathbf{3})(\text{PET}_3)]$ , as the solid-state structure for the former shows  $\text{PET}_3$  trans to oxime nitrogen<sup>5</sup> and the  $^1J(^{195}\text{Pt}, ^{31}\text{P})$  values for both of these are identical within the experimental error. The decision for pyridine nitrogen coordination, with ligand 3, can be made via  $^1\text{H}$  NMR spectroscopy and these details will be discussed elsewhere. A summary of the NMR spectroscopic data is provided in Table II. It appears that the dimer  $[\text{PtCl}(\text{SnCl}_3)(\text{PET}_3)]_2$  is a good starting material for coordinating nitrogen to platinum when an  $\text{SnCl}_3$  ligand is present.

In view of the paucity of  $^{195}\text{Pt}$  NMR data for aniline complexes of  $\text{Pt}(\text{II})$  we have prepared the complexes *trans*- $[\text{PtCl}_2(^{15}\text{NH}_2\text{C}_6\text{H}_4\text{-}p\text{-X})(\text{C}_2\text{H}_4)]$  (6) for comparison purposes, and show NMR data for these in Table III. The observed value for  $\delta(^{195}\text{Pt})$  in *trans*- $[\text{PtCl}_2(^{15}\text{NH}_2\text{C}_6\text{H}_4\text{-}p\text{-Cl})(\text{C}_2\text{H}_4)]$ ,  $\delta = -3011$ , is in good agreement with that reported<sup>11</sup> earlier for the corresponding *n*-hexylamine complex,  $\delta = -3006$ , although the  $^1J(^{195}\text{Pt}, ^{15}\text{N})$  value for the aniline, at  $242 \text{ Hz}$ , is considerably smaller than that found for the alkylamine,  $284 \text{ Hz}$ , and also smaller than that observed for *trans*- $[\text{PtCl}_2(^{15}\text{NHMe}_2)(\text{C}_2\text{H}_4)]$ ,<sup>12b</sup>  $299 \text{ Hz}$ .

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Table I. Pt-Cl Bond Separations

compd	Pt-Cl, Å	ref
[PtHCl(PEtPh <sub>2</sub> ) <sub>2</sub> ]	2.422 (9)	16
[Pt(C(CO <sub>2</sub> Me)=C(Cl)COO)Cl(CO)] <sup>-</sup> (PPN) <sup>+</sup>	2.415 (3)	17
<i>trans</i> -[PtClPh(PPh <sub>3</sub> ) <sub>2</sub> ]	2.408 (5)	18
<i>trans</i> -[PtCl(CH <sub>2</sub> CN)(PPh <sub>3</sub> ) <sub>2</sub> ]	2.390 (3)	19
<i>cis</i> -[PtCl <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> ]	(2.376) <sub>av</sub> (9)	20
<i>cis</i> -[PtCl <sub>2</sub> (P- <i>t</i> -Bu <sub>3</sub> ) <sub>2</sub> ]	(2.358) <sub>av</sub> (6)	21
<i>cis</i> -[PtCl <sub>2</sub> (CO)(C(CO <sub>2</sub> Et)=CCl(CO <sub>2</sub> - <i>i</i> -Pr))] <sup>-</sup> (PPN) <sup>+</sup>	2.355 (7) <i>trans</i> to C=C	22
	2.297 (6) <i>trans</i> to CO	
K[PtCl <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )]	2.340 (2) <i>trans</i> to olefin	23
	2.302 (2) <i>trans</i> to Cl	
[PtCl(SnCl <sub>3</sub> )(NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Cl)(PEt <sub>3</sub> )]	2.331 (3)	this work
(Et <sub>4</sub> N)[PtCl <sub>3</sub> (CH <sub>3</sub> CH <sub>2</sub> OCH=CH <sub>2</sub> )]	2.324 (2) <i>trans</i> to olefin	24
	(2.301) <sub>av</sub> (2) <i>trans</i> to Cl	
(Bu <sub>4</sub> N)[PtCl <sub>3</sub> (CO)]	2.289 (3) <i>trans</i> to CO	25
	(2.292) <sub>av</sub> (4) <i>trans</i> to Cl	
<i>cis</i> -[PtCl <sub>2</sub> (py) <sub>2</sub> ]	(2.296) <sub>av</sub> (5)	26
<i>trans</i> -[PtCl <sub>2</sub> (py) <sub>2</sub> ]	(2.308) <sub>av</sub> (5)	26
<i>cis</i> -[PtCl <sub>2</sub> (NH <sub>3</sub> )(Me <sub>2</sub> SO)]	2.2978 (5) <i>trans</i> to N	27
	2.321 (5) <i>trans</i> to S	

Table II. NMR Data<sup>a</sup> for the Complexes

no.	complex	δ( <sup>31</sup> P)	<sup>1</sup> J(Pt,P)	<sup>2</sup> J(Sn,P) <sup>b</sup>	δ( <sup>119</sup> Sn)	<sup>1</sup> J(Pt,Sn) <sup>c</sup>	δ( <sup>195</sup> Pt)
1a	NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Cl <sup>d</sup>	3.7	3042	278	-243	31348	-4452
1b	NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub> <sup>e</sup>	3.0	3018	280	-248	31570	-4444
2	C <sub>6</sub> H <sub>5</sub> C(NH <sub>2</sub> )=NOH	-0.3	3043	269	-299	32769	-4279
		-0.1	3044	258	-269	31193	-4295
3	Pt <sub>2</sub> (μ-Cl) <sub>2</sub> (SnCl <sub>3</sub> ) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	12.2	3480	238	-383	35309	-4320

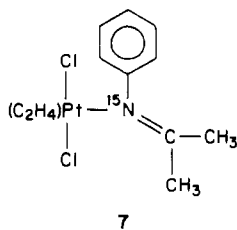
<sup>a</sup> Chemical shifts are relative to external H<sub>3</sub>PO<sub>4</sub>, Me<sub>4</sub>Sn and Na<sub>2</sub>PtCl<sub>6</sub>, respectively; *J* values are given in hertz (CH<sub>2</sub>CH<sub>2</sub>/CDCl<sub>3</sub> solution). <sup>b</sup> Average of <sup>117</sup>Sn and <sup>119</sup>Sn coupling. <sup>c</sup> <sup>1</sup>J(<sup>195</sup>Pt,<sup>119</sup>Sn). <sup>d</sup> 253 K, δ(<sup>15</sup>N) = -344.1 (CH<sub>3</sub>NO<sub>2</sub>), <sup>1</sup>J(Pt,<sup>15</sup>N) = 107 Hz, <sup>2</sup>J(P,<sup>15</sup>N) = 37 Hz, <sup>2</sup>J(Sn,<sup>15</sup>N) = ca. 9 Hz. <sup>e</sup> <sup>31</sup>P and <sup>195</sup>Pt data measured at 273 K. <sup>f</sup> 253 K, δ(<sup>15</sup>N) = -344.7, <sup>1</sup>J(Pt,<sup>15</sup>N) = 114 Hz, <sup>2</sup>J(P,<sup>15</sup>N) = 37 Hz, <sup>2</sup>J(Sn,<sup>15</sup>N) = ca. 10 Hz. <sup>31</sup>P and <sup>195</sup>Pt data measured at 273 K.

Table III. NMR Data<sup>a</sup> for the Ethylene Complexes

L	δ( <sup>195</sup> Pt)	<sup>1</sup> J( <sup>195</sup> Pt, <sup>15</sup> N)
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <sup>15</sup> NH <sub>2</sub> <sup>b</sup>	-3011	242
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>15</sup> NH <sub>2</sub> <sup>c</sup>	-3013	244
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <sup>15</sup> N=C(CH <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	-2904	396
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>15</sup> N=C(CH <sub>3</sub> ) <sub>2</sub> <sup>e</sup>	-2899	400

<sup>a</sup> Coupling constants in hertz, CDCl<sub>3</sub> solution. <sup>b</sup> δ(CH<sub>2</sub>=CH<sub>2</sub>) = 74.90, <sup>1</sup>J(<sup>195</sup>Pt,<sup>13</sup>C) = 192 Hz; δ(CH<sub>2</sub>=CH<sub>2</sub>) = 4.67, <sup>2</sup>J(<sup>195</sup>Pt,<sup>1</sup>H) = 65 Hz. <sup>15</sup>N shift at -30 °C. <sup>195</sup>Pt shift at -20 °C. δ(<sup>15</sup>N) = -343; Δ(<sup>15</sup>N) = -18.6. <sup>c</sup> δ(CH<sub>2</sub>=CH<sub>2</sub>) = 74.75. 0 °C. <sup>d</sup> δ(<sup>1</sup>H) (CD<sub>2</sub>Cl<sub>2</sub>) = 4.65 (C<sub>2</sub>H<sub>4</sub>), <sup>1</sup>J(<sup>195</sup>Pt,<sup>1</sup>H) = 62 Hz; δ(<sup>1</sup>H) = 2.94 (CH<sub>3</sub>), <sup>1</sup>J(<sup>15</sup>N,<sup>1</sup>H) = 4 Hz; δ(<sup>1</sup>H) = 2.06 (CH<sub>3</sub>), <sup>1</sup>J(<sup>15</sup>N,<sup>1</sup>H) = 2.9 Hz; δ(<sup>195</sup>Pt) (CDCl<sub>3</sub>) measured at -20 °C. <sup>e</sup> <sup>195</sup>Pt spectrum measured at 0 °C.

During the attempted preparation of **6** from K[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)] in acetone we observed the metal-mediated condensation of the aniline to the Schiff base complex, **7**, and details for these are also provided.



7

### Experimental Section

The complexes were prepared by adding 2 equiv of the nitrogen ligand to [PtCl(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>]<sup>4</sup> dissolved in either CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. Stirring for 30 min was followed by filtration. The complexes can be crystallized by the addition of 1:1 ether/pentane and storage at -20 °C. Simple removal of the chlorocarbon solvent gives powders, which (after drying) give good microanalytical data and show NMR properties corresponding

to the products. Anal. for L = <sup>15</sup>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Cl. Calcd for C<sub>12</sub>H<sub>11</sub><sup>15</sup>NCl<sub>3</sub>PPtSn: C, 20.53; H, 3.01; <sup>15</sup>N, 2.14; Cl, 25.25. Found: C, 20.44; H, 2.93; <sup>15</sup>N, 2.34; Cl 25.71.

The ethylene complexes may be prepared as follows: A solution of Zeise's salt (0.171 g, 0.464 mmol) in 5 mL of methanol was added dropwise to a solution of <sup>15</sup>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Cl (0.060 g, 0.464 mmol) in methylene chloride at 0 °C. After the mixture was stirred for 30 min at 0 °C, the solvent was removed in vacuo and the yellow solid that remained extracted with 10 mL of ether. Addition of pentane results in crystallization of the product (0.134 g, 68%). Anal. Calcd for C<sub>8</sub>H<sub>10</sub>NCl<sub>3</sub>Pt: C, 22.80; H, 2.39; N, 3.32. Found: C, 22.66; H, 2.34; N, 3.57. The *p*-toluidine complex was prepared in an identical fashion (yield 67%). Anal. Calcd for C<sub>9</sub>H<sub>13</sub>NCl<sub>3</sub>Pt: C, 26.95; H, 3.27; N, 3.49; Cl, 17.68. Found: C, 27.19; H, 3.31; N, 3.74; Cl, 17.73.

The Schiff base complex was prepared by addition of Zeise's salt (0.226 g, 0.600 mmol) dissolved in 3 mL of acetone to <sup>15</sup>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Cl (0.079 g, 0.600 mmol). Stirring for 15 min is followed by filtration, to remove KCl. Concentration of the solvent was followed by extraction with ether. Storage at -20 °C gave the product as an orange crystalline compound (0.237 g, 85%). Anal. Calcd for C<sub>17</sub>H<sub>14</sub><sup>15</sup>NCl<sub>3</sub>Pt: C, 28.56; H, 3.05; <sup>15</sup>N, 3.24; Cl, 22.99. Found: C, 28.50; H, 3.97; <sup>15</sup>N, 3.09; Cl, 23.09. The <sup>15</sup>N aniline compounds were prepared according to the literature.

### Determination and Refinement of the Structure

Yellow crystals of compound **4** are stable in air and are obtained as described above; a suitable crystal, chosen for the data collection, was mounted on a glass fiber. An Enraf-Nonius CAD4 diffractometer was used both for the lattice parameters determination and for the data collection (room temperature): space group *P2<sub>1</sub>/n* with *a* = 10.631 (6) Å, *b* = 9.214 (4) Å, *c* = 21.576 (4) Å, β = 90.77 (3)°, *V* = 2113.3 Å<sup>3</sup>, and *Z* = 4. See Table S2 (supplementary material) for additional crystal data. An empirical absorption correction<sup>13</sup> was applied by using azim-

- (13) Programs used included the absorption and data reduction programs from the Enraf-Nonius SDP structure determination package and local versions of the structure factor, Fourier and least-squares calculations. The drawing was made by using the program ORTEP II (Johnson, C. K. *Oak Ridge Natl. Lab. [Rep.], ORNL(U.S.) 1976, ORNL-5138*).

muthal ( $\Psi$ ) scans of five reflections ( $00\bar{4}$ ;  $00\bar{8}$ ;  $0,0,\bar{12}$ ;  $0,0,\bar{18}$ ;  $0,0,\bar{22}$ ) at high  $\chi$  angles ( $85.90^\circ$ ). Transmission factors were in the range 0.997-0.579. Structure factors were calculated in the usual way ( $Lp$  corrections applied, no extinction correction), and the standard deviations on the intensities were calculated in terms of statistics alone. Reflections having  $|F_o| \geq 3\sigma|F_c|$  were considered as observed. The structure was solved by Patterson and Fourier methods<sup>13</sup> and refined by a block-diagonal least-squares procedure (the function minimized is  $\sum_w(|F_o| - \frac{1}{2}|F_c|)^2$ ) with weights obtained from a Cruickshank scheme.<sup>14</sup> The refined parameters included anisotropic thermal factors for Pt, Sn, Cl, and P atoms, isotropic for the others. During the final least-squares cycles the contribution of the hydrogen atoms in their calculated positions ( $C-H = 1.00 \text{ \AA}$ ;  $B = 5.0 \text{ \AA}^2$ ) was taken into account but not refined.<sup>15</sup>

**Registry No.** 4, 99148-35-3; [PtCl(SnCl<sub>3</sub>)(1b)(PEt<sub>3</sub>)], 99148-37-5; [PtCl(SnCl<sub>3</sub>)(2)(PEt<sub>3</sub>)], 79453-27-3; [PtCl(SnCl<sub>3</sub>)(3)(PEt<sub>3</sub>)], 99148-36-4; *trans*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(*p*-ClC<sub>6</sub>H<sub>4</sub><sup>15</sup>NH<sub>2</sub>), 99148-38-6; *trans*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>15</sup>NH<sub>2</sub>), 99148-39-7; *trans*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(*p*-ClC<sub>6</sub>H<sub>4</sub><sup>15</sup>N=C(CH<sub>3</sub>)<sub>2</sub>), 99148-40-0; *trans*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>15</sup>N=C(CH<sub>3</sub>)<sub>2</sub>), 99148-41-1; [PtCl(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>], 83719-68-0; <sup>15</sup>NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Cl, 24176-54-3; Pt, 7440-06-4; Sn, 7440-31-5; Zeise's salt, 16405-35-9; *p*-toluidine, 106-49-0.

**Supplementary Material Available:** Tables of bond distances and angles, crystal data and intensity collection parameters, positional and thermal parameters, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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## Reexamination of the Deuteration of Phenol Catalyzed by an Ortho-Metalated Ruthenium Complex

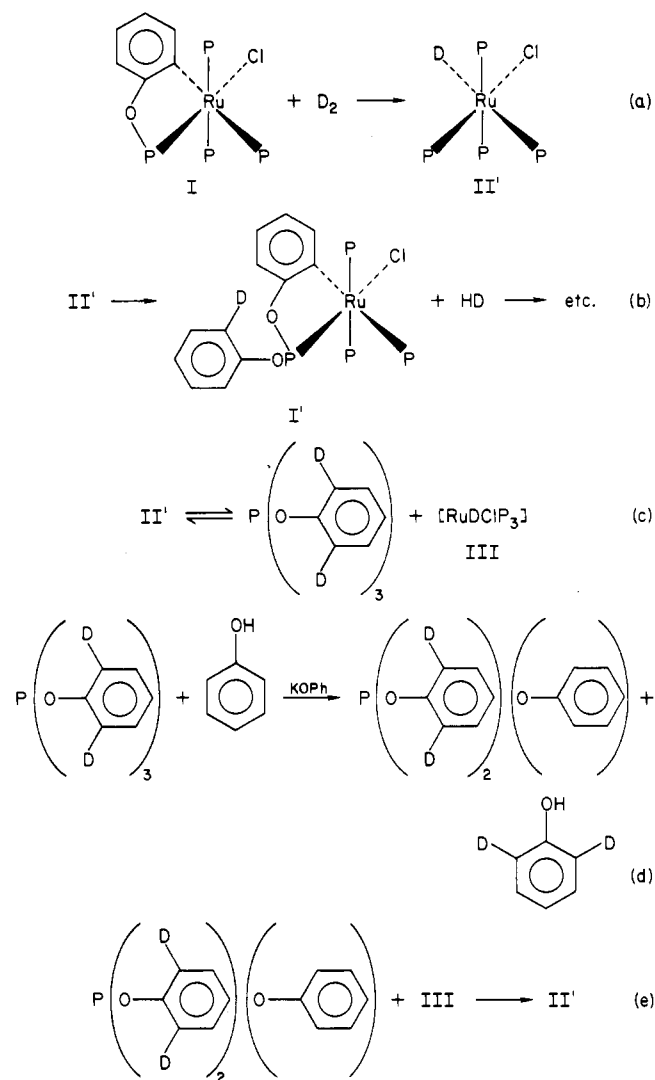
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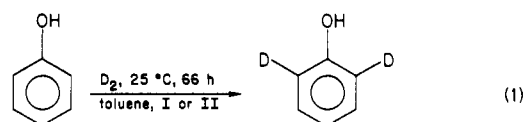
The synthesis of I was reported in 1969<sup>1</sup> (see Scheme I). Complex I reacted with H<sub>2</sub> to produce II (or II' with D<sub>2</sub>, see Scheme I), in which the ortho-metalated bond is broken.<sup>1</sup> The reaction of I with D<sub>2</sub> results in the deuterated analogue of II. In addition, all the ortho positions of the triphenyl phosphite ligands were deuterated.<sup>1</sup>

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## Scheme I



Complexes I and II were reported to catalyze the ortho deuteration of phenol with D<sub>2</sub>, eq 1.<sup>1</sup>



While work in this laboratory confirmed that the reaction of D<sub>2</sub> with I resulted in selective ortho deuteration of the phosphite ligands on I, the reaction of eq 1 did not proceed as reported. Deuterium incorporation into phenol was found to be extremely slow when phenol was reacted with I and D<sub>2</sub>. Phenol ortho deuteration with D<sub>2</sub> catalyzed by I was only accomplished by using a transesterification cocatalyst, the details of which reactions are presented here.

## Experimental Section

The syntheses of ruthenium complexes<sup>1</sup> were carried out in an argon-filled Vacuum Atmospheres drybox or by utilizing standard Schlenk techniques. Toluene and THF were distilled from purple solutions of sodium benzophenone ketyl. Chloroform was vacuum-transferred from P<sub>4</sub>O<sub>10</sub>. Mass spectra of gas samples were recorded on a Varian MAT 731 instrument. GCMS were recorded by using a Varian 311A instrument. <sup>13</sup>C (20 MHz) and <sup>31</sup>P (32.203 MHz) NMR spectra were recorded on a Varian FT-80 NMR spectrometer.

**Attempted Phenol Deuteration in Toluene (Eq 1). Run a.** Phenol (0.0792 g, 0.84 mmol) and I (0.084 g, 0.061 mmol) were combined in 13 mL of toluene and placed in a 90-mL Fischer-Porter bottle under argon. The mixture was subjected to three freeze/degas/thaw cycles. D<sub>2</sub> was added (860 mm, 3.57 mmol) and the contents stirred at ambient temperature for 72 h. The noncondensable gases were analyzed by mass