

# Hydrogenation of Aryldiazenido Complexes. Synthesis and Structure of *trans*-Hyrido(acetone phenylhydrazone)bis(triphenylphosphine)platinum(II) Tetrafluoroborate

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**Abstract:** The compound formulated as  $\text{Pt}(\text{BF}_4)(\text{NNAr})(\text{PPh}_3)_2$ ,  $\text{Ar} = \text{C}_6\text{H}_5$ ,  $p\text{-FC}_6\text{H}_4$ , can be hydrogenated in a variety of solvents under mild conditions using no additional catalyst. In ethanol the hydrazine complex  $[\text{PtH}(\text{H}_2\text{NNHAr})(\text{PPh}_3)_2][\text{BF}_4]$  is formed, while in the presence of acetone the corresponding hydrazone complex results. The ready availability of a coordination site on the  $\text{Pt}(\text{NNAr})(\text{PPh}_3)_2$  unit must play a key role in the easy activation of molecular hydrogen which leads to these hydrazine derivatives. The hydrazone complex *trans*- $[\text{PtH}(\text{PhHNNC}_3\text{H}_6)(\text{PPh}_3)_2][\text{BF}_4] \cdot \text{C}_6\text{H}_6$  crystallizes in space group  $C_{2h}^5\text{-}P2_1/c$  with  $a = 13.403(4) \text{ \AA}$ ,  $b = 20.949(5) \text{ \AA}$ ,  $c = 16.535(4) \text{ \AA}$ ,  $\beta = 91.24(1)^\circ$ ,  $V = 4641 \text{ \AA}^3$ , and  $Z = 4$ . The structure has been determined from 5635 unique x-ray reflections and refined to a conventional  $R$  index of 0.046. The coordination geometry about the platinum atom is square planar with *trans* phosphine groups. The hydrazone group is bound to the platinum atom through the  $\text{sp}^2$  hybridized nitrogen atom.

The chemistry of aryldiazenido transition metal complexes is of current interest both because of the variety of coordination modes available to the ligand<sup>2</sup> and because such complexes have been proposed as simple models of nitrogen-fixing enzymes.<sup>3-5</sup> The recent preparation of diazenido complexes from dinitrogen compounds of Re, Mo, and W<sup>6,7</sup> increases the utility of diazenido complexes as models in nitrogen fixation reactions. Since natural systems need a source of electrons and protons (i.e., hydrogen) to metabolize dinitrogen, of particular interest is the hydrogenation of diazenides to derivatives such as arylhydrazine or ammonia and aniline.

Although in the last several years an appreciable number of aryldiazenido and related aryldiazeno complexes have been synthesized,<sup>8</sup> only a few studies of their interaction with molecular hydrogen have been reported.<sup>3,4,9-14</sup> Thus molecular hydrogen reacts in the presence of a heterogeneous catalyst such as Pd/C or Pd/BaSO<sub>4</sub> with *trans*-PtCl(NNAr)(PEt<sub>3</sub>)<sub>2</sub>,<sup>3</sup> *trans*-[PtCl(HNNAr)(PEt<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>],<sup>3</sup> or *trans*-[PtL(HNNAr)(PEt<sub>3</sub>)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> (L = NH<sub>3</sub>, Py, EtNC (Et = C<sub>2</sub>H<sub>5</sub>))<sup>13</sup> and with the orthometalated complex [Ir(CO)(HNNC<sub>6</sub>H<sub>3</sub>F)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sup>4</sup> to yield arylhydrazone derivatives. Yet with RhCl<sub>2</sub>(NNAr)(PPh<sub>3</sub>)<sub>2</sub>, RhCl<sub>3</sub>(HNNAr)(PPh<sub>3</sub>)<sub>2</sub>,<sup>9,11</sup> other systems based on aryldiazonium salts and RhH(PPh<sub>3</sub>)<sub>3</sub>, and "Pt(BF<sub>4</sub>)(NNAr)(PPh<sub>3</sub>)<sub>2</sub>"<sup>12</sup> (Ar = Ph = C<sub>6</sub>H<sub>5</sub>, Ia; Ar = *p*-FC<sub>6</sub>H<sub>4</sub>, Ib) the formation of arylhydrazine derivatives occurs under mild conditions even in the absence of an extra catalyst. Apparently the coordinating central metal atom is capable of promoting the activation of molecular hydrogen and of transferring it to the azo moiety.

We wish to report here on the facile hydrogenation of "Pt(BF<sub>4</sub>)(NNAr)(PPh<sub>3</sub>)<sub>2</sub>". When the hydrogenation is carried out in ethanol the compound *trans*-[PtH(H<sub>2</sub>NNHAr)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (Ar = Ph, IIa; Ar = *p*-FC<sub>6</sub>H<sub>4</sub>, IIb) is formed, whereas in acetone or ethanol-acetone the hydrazone complex *trans*-[PtH(ArHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (Ar = Ph, IIIa; Ar = *p*-FC<sub>6</sub>H<sub>4</sub>, IIIb) results. Because of recent interest in the bonding of the hydrazone ligand<sup>15-19</sup> and in order to characterize more fully the reaction products, we also report here on the x-ray structure of complex IIIa.

## Experimental Section

Unless otherwise noted, all reactions were performed at 16-17 °C

in the dark to prevent any possible photodecomposition.<sup>11</sup> The solvents were dried, deaerated, and distilled prior to use.

The compounds *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>20</sup> *trans*-PtHCl(PPh<sub>3</sub>)<sub>2</sub>,<sup>20</sup> Pt(PhC≡CPh)(PPh<sub>3</sub>)<sub>2</sub>,<sup>21</sup> Pt(HC≡CPh)(PPh<sub>3</sub>)<sub>2</sub>,<sup>21</sup> *trans*-[Pt(C≡CPh)(HN=NC<sub>6</sub>H<sub>4</sub>-*p*)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>],<sup>22</sup> acetone phenylhydrazone,<sup>23</sup> and diazonium tetrafluoroborates [ArN<sub>2</sub>][BF<sub>4</sub>]<sup>24</sup> were prepared according to literature methods.

The compound "Pt(BF<sub>4</sub>)(NNAr)(PPh<sub>3</sub>)<sub>2</sub>" (I) (Ar = C<sub>6</sub>H<sub>5</sub>, *p*-FC<sub>6</sub>H<sub>4</sub>) was prepared by the replacement of the acetylenic ligand in Pt(PhC≡CPh)(PPh<sub>3</sub>)<sub>2</sub> by ArN<sub>2</sub><sup>+</sup>, as described previously.<sup>12</sup> The Pt(PhC≡CPh)(PPh<sub>3</sub>)<sub>2</sub> complex is dissolved in benzene and an equimolar amount of [ArN<sub>2</sub>][BF<sub>4</sub>], dissolved either in ethanol or acetone, is added. From the benzene-acetone medium compound I precipitates as red-orange microcrystals with no solvate molecules; from the benzene-ethanol medium it precipitates as brick red microcrystals with variable amounts of ethanol of solvation, up to 0.5 mol of EtOH per Pt atom, as shown by <sup>1</sup>H NMR spectra. The complexes obtained from the above media show the same spectroscopic and chemical properties and the same conductivities.<sup>12</sup> Therefore, we believe that they are the same compound (see below) and we refer to them simply as Pt(BF<sub>4</sub>)(NNAr)(PPh<sub>3</sub>)<sub>2</sub>.

Infrared spectra were recorded from KBr pellets and Nujol mulls using a Perkin-Elmer 457 double-beam spectrometer, calibrated using a polystyrene film. The NMR spectra were recorded on a Bruker HFX-90 spectrometer at ambient temperature in CDCl<sub>3</sub> using Me<sub>4</sub>Si as an internal standard. GC analyses were performed using a Hewlett-Packard gas chromatograph Model 5830A equipped with a GC terminal Model 18850A, using a Carbowax 1500 20% Chr Gsi 6 ft long column at 80 °C, with He as carrier gas, rate flow 15 mL/min. Conductivities were measured in nitrobenzene at ca. 20-25 °C and 10<sup>-3</sup> M concentration using a LKB conductivity bridge Type 3216 B. Melting points were taken in air using a Kofler hot stage.

**Hydrogenation of Pt(BF<sub>4</sub>)(NNPh)(PPh<sub>3</sub>)<sub>2</sub> (Ia) in Acetone-Ethanol.** Complex Ia was dissolved in acetone under a hydrogen atmosphere (455 mg = 0.5 mmol, 60 mL) and then 20 mL of ethanol was added. Hydrogen was allowed to bubble through the initial reddish brown solution at such a rate as to reduce the initial volume to ca. 10 mL; colorless crystals precipitated. The suspension was kept at -3 °C for 10 h and then *n*-heptane (ca. 5 mL) was slowly added dropwise. After 1 day at -20 °C, the precipitate was dried and identified as the acetone phenylhydrazone complex *trans*-[PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (IIIa), mp 176-181 °C dec (350 mg, yield 73%). Crystallization from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> gave colorless crystals, suitable for x-ray diffraction studies, of *trans*-[PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub>, mp 142-145 °C dec.

**Hydrogenation of Pt(BF<sub>4</sub>)(NNC<sub>6</sub>H<sub>4</sub>F-*p*)(PPh<sub>3</sub>)<sub>2</sub> (Ib).<sup>25</sup> (a) In Acetone.** Complex Ib, obtained from a benzene-acetone medium, was

Table I. Analytical and Spectroscopic Data

Compound	C	H	N	Mp, °C	A. Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	
<i>trans</i> -[PtH(H <sub>2</sub> NNHPh)(PPh <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ], 11a	55.30 (55.09) <sup>a</sup>	4.37 (4.29)	2.80 (3.06)	170–172 dec	22.5	
<i>trans</i> -[PtH(H <sub>2</sub> NNHC <sub>6</sub> H <sub>4</sub> F- <i>p</i> )(PPh <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ], 11b	53.86 (54.03)	4.20 (4.10)	2.86 (3.00)	173–178 dec	22.4	
<i>trans</i> -[PtH(PhHNNC <sub>3</sub> H <sub>6</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]-C <sub>6</sub> H <sub>6</sub> , 111a	59.03 (59.25)	4.78 (4.78)	2.60 (2.71)	142–145 dec	22.8	
<i>trans</i> -[PtH( <i>p</i> -FC <sub>6</sub> H <sub>4</sub> HNNC <sub>3</sub> H <sub>6</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]-C <sub>6</sub> H <sub>6</sub> , 111b	58.15 (58.24)	4.34 (4.60)	2.44 (2.66)	150–152 dec	22.8	
	$\nu_{N-H}$ , cm <sup>-1</sup>	$\nu_{Pt-H}$ , cm <sup>-1</sup>	$\tau_{Pt-H}$ , ppm	$J_{Pt-H}$ , Hz	$J_{P-H}$ , Hz	$\tau_{CH_3}$ , ppm
	3550 m, 3290 m, 3220 w <sup>b</sup>	2210 m <sup>b</sup>	26.68	1077	13	
	3340 m, 3285 m, 3215 w <sup>c</sup>	2210 m <sup>c</sup>	26.67	1075	13.5	
	3320 m <sup>b</sup>	2220 m <sup>b</sup>	27.36	1041	13.5	8.18
	3310 m <sup>c</sup>	2220 m <sup>c</sup>	27.38	1036	13.5	8.26

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Nujol mulls. <sup>c</sup> KBr pellets.

dissolved in acetone under a hydrogen atmosphere at 12–14 °C (185 mg = 0.2 mmol; 20 mL). Hydrogen gas was bubbled through the initially reddish brown solution at such a rate as to remove all the solvent in ca. 20 h. The residue was crystallized from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub>, affording 30 mg of pure complex 111b as the C<sub>6</sub>H<sub>6</sub> solvate (yield 14%).

(b) **In Ethanol.** Hydrogen was allowed to bubble through an ethanol suspension of the complex (40 mL, 190 mg = 0.2 mmol) for 20 h. The initial reddish brown suspension changed to a yellow solution. *n*-Octane was added dropwise until some precipitate formed. The suspension was kept at 3 °C for 4 h, at –5 °C for 4 h, and at –20 °C for 20 h. Finally it was filtered. The precipitate was identified as *trans*-[PtH(H<sub>2</sub>NNHC<sub>6</sub>H<sub>4</sub>F-*p*)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (11b) (140 mg, yield 74%).

(c) **In Benzene–Acetone.** This experiment was carried out directly in the preparative reaction mixture of complex 1b, i.e., in the presence of PhC≡CPh. To a benzene solution of Pt(PhC≡CPh)(PPh<sub>3</sub>)<sub>2</sub> (20 mL, 290 mg = 0.3 mmol), previously saturated with nitrogen, an acetone solution of the diazonium salt [*p*-FC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>][BF<sub>4</sub>] (20 mL, 70 mg = 0.3 mmol), previously saturated with hydrogen, was added dropwise in ca. 1 min while hydrogen was bubbled through at 1 atm pressure. Hydrogen bubbling was continued for 20 h, during the course of which the initial reddish brown color dissipated and the volume was reduced to ca. 10 mL with the formation of a crystalline product. The suspension was held at 3 °C for 20 h, and then filtered. After drying the precipitate (50 mg), crystallization from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> gave the pure product identified as *trans*-[PtH(*p*-FC<sub>6</sub>H<sub>4</sub>HNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]-C<sub>6</sub>H<sub>6</sub> (111b) (30 mg, yield 9%).

In a similar experiment in a benzene–acetone medium but using Pt(HC≡CPh)(PPh<sub>3</sub>)<sub>2</sub> in place of Pt(PhC≡CPh)(PPh<sub>3</sub>)<sub>2</sub>, the initial reddish brown solution lightened in color as hydrogen was bubbled through the solution for 1 day. To the resulting yellowish solution, *n*-heptane was slowly added dropwise until a precipitate formed. The suspension was kept at 12 °C for 5 h, at 3 °C for 5 h, and at –3 °C for 5 h, and then filtered. The product (50 mg) was crystallized from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> yielding 20 mg of pure *trans*-[PtH(*p*-FC<sub>6</sub>H<sub>4</sub>HNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]-C<sub>6</sub>H<sub>6</sub> (111b) as colorless crystals (yield 6%).

An analogous experiment was performed starting from [*p*-FC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>][BF<sub>4</sub>] in ethanol and Pt(HC≡CPh)(PPh<sub>3</sub>)<sub>2</sub> (in place of Pt(PhC≡CPh)(PPh<sub>3</sub>)<sub>2</sub>) in benzene, under the above conditions. The main product was identified as *trans*-[Pt(C≡CPh)(HN=NC<sub>6</sub>H<sub>4</sub>F-*p*)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (1V) (150 mg, yield 48%) and no hydrazine derivative could be detected.

In another experiment complex 1b was treated with HC≡CPh in ethanol under hydrogen for 20 h. Again the main product was identified as *trans*-[Pt(C≡CPh)(HN=NC<sub>6</sub>H<sub>4</sub>F-*p*)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]. In a different experiment an attempt to hydrogenate an ethanol solution of this complex was unsuccessful, and the complex was recovered unreacted after precipitation with *n*-heptane.

**Quantitative Hydrogen Absorption Experiments.** These experiments were performed using 1b (310 mg = 0.33 mmol) dissolved in ca. 35

mL of ethanol–acetone (ca. 1.2:1 by volume) at 1 atm total pressure and 16 °C. Hydrogen absorption (8.5 mL, ca. 0.3 mmol) was completed in 3 h. (At 16 °C the partial pressure of hydrogen was estimated to be ca. 650 mmHg.) In the solution after 1 day ca. 0.3 mmol of acetaldehyde was formed, as identified by GC analysis. Initially, the ethanol that was used for the experiment showed only traces (ca. 0.005%) of acetaldehyde. Note that acetaldehyde also forms when pure complex 111 is dissolved in ethanol–acetone.

**Preparation of *trans*-[PtH(H<sub>2</sub>NNHPh)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (11a).** The compound was prepared following a method already reported in the literature for other hydridic complexes of Pt(II).<sup>26</sup> A CH<sub>2</sub>Cl<sub>2</sub> solution of *trans*-PtHCl(PPh<sub>3</sub>)<sub>2</sub> (20 mL, 380 mg = 0.5 mmol) and PhHNNH<sub>2</sub> (ca. 200 mg) was shaken with a saturated aqueous solution of NaBF<sub>4</sub> for 1 h. The CH<sub>2</sub>Cl<sub>2</sub> layer was then reduced in volume and Et<sub>2</sub>O was added dropwise. The whitish powder (350 mg, yield = 76%) was crystallized from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> yielding the pure complex as colorless crystals.

**Preparation of *trans*-[PtH(H<sub>2</sub>NNHC<sub>6</sub>H<sub>4</sub>F-*p*)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (11b).** This compound was prepared by the same procedure as above, using *p*-FC<sub>6</sub>H<sub>4</sub>HNNH<sub>2</sub> in place of PhHNNH<sub>2</sub>. The same yield resulted.

**Preparation of *trans*-[PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (111a).** (a) The complex 11a (90 mg, 0.1 mmol) was dissolved in 5 mL of acetone.<sup>27</sup> The solvent was then allowed to evaporate to dryness at room temperature. The resulting brownish tar was crystallized from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub>, yielding the pure complex as a benzene solvate (40 mg, yield = 38%). (b) To a THF solution of *trans*-PtHCl(PPh<sub>3</sub>)<sub>2</sub> (30 mL, 380 mg = 0.5 mmol) an equimolar amount of AgBF<sub>4</sub> was added with stirring.<sup>28</sup> Precipitation of a brownish material (AgCl) occurred immediately. The suspension was stirred for ca. 10 min and then filtered. The solution was treated with an equimolar amount of acetone phenylhydrazine. After a few minutes Et<sub>2</sub>O was added dropwise until a white powder began to precipitate. After keeping the suspension at –5 °C for several hours, the suspension was filtered and the precipitate identified as *trans*-[PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (111a) (250 mg, yield = 52%), mp 177–180 °C. Crystallization from CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> gave the pure crystalline product as the benzene solvate.

**Preparation of *trans*-[PtH(*p*-FC<sub>6</sub>H<sub>4</sub>HNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (111b).** The procedure was the same as method (a) above, using the corresponding fluoro derivative. The same yield was obtained.

**Characterization of Complexes II and III.** The nature of compound 111a has been established from a crystal structure analysis. The results are in agreement with those deduced from spectroscopic data. The IR spectra of complexes II and III show  $\nu_{N-H}$  and  $\nu_{Pt-H}$  where these vibrations usually occur in other related complexes<sup>8,27,29</sup> (see Table I). In the 1600-cm<sup>-1</sup> region, where other acetone phenylhydrazine complexes of Pd(II)<sup>27</sup> and Pt(II)<sup>30</sup> show  $\nu_{C=N}$  bands, only one of the hydrazine complexes reported here, *trans*-[PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>], shows a strong band (1595 cm<sup>-1</sup>). The acetone *p*-fluorophenylhydrazine complex, *trans*-[PtH(*p*-FC<sub>6</sub>H<sub>4</sub>HNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>], shows only bands of weak intensity in this region, and a strong band at 1505 cm<sup>-1</sup>. Moreover, note that both aryl hydrazine complexes (II) show bands of strong intensity at ca. 1600

**Table II.** Summary of Crystallographic and Data Collection Information

Compound	[PtH((C <sub>6</sub> H <sub>5</sub> )HNNC <sub>3</sub> H <sub>6</sub> )(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ] $\cdot$ C <sub>6</sub> H <sub>6</sub>
Formula	C <sub>51</sub> H <sub>49</sub> BF <sub>4</sub> N <sub>2</sub> P <sub>2</sub> Pt
Mol wt	1033.81 amu
Space group	C <sub>2h</sub> <sup>5</sup> -P2 <sub>1</sub> /c
Unit cell (22°)	<i>a</i> = 13.403 (4), <i>b</i> = 20.949 (5), <i>c</i> = 16.535 (4) Å; $\beta$ = 91.24 (1)°; <i>V</i> = 4641 Å <sup>3</sup> ; <i>Z</i> = 4
Density	$\rho_{\text{calcd}}$ = 1.479, $\rho_{\text{obsd}}$ = 1.47 (1) g/cm <sup>3</sup>
$\mu$	67.9 cm <sup>-1</sup>
Transmission factors	0.162–0.413
Morphology	Crystal exhibits faces of the forms {011}, {010}, {111}, {1 $\bar{1}$ 1}, and {100}.
Crystal dimensions along crystallographic axes	0.39 $\times$ 0.33 $\times$ 0.34 mm
Radiation	Cu K $\alpha$ <sub>1</sub> ( $\lambda$ 1.540 562 Å)
Scan rate	2°/min
Receiving aperture	3.5 $\times$ 3.5 mm, 32 cm from the crystal
Data collection limits	5.0° < 2 $\theta$ < 119.0°; + <i>h</i> , - <i>k</i> , $\pm$ l
Scan range	0.9° below K $\alpha$ <sub>1</sub> to 0.9° above K $\alpha$ <sub>2</sub>
Backgrounds	10 s, measd at each end of scan range
Attenuators	Cu foil attenuators inserted if intensity exceeded 7000 counts/s
Standards	6 every 100 reflections
No. of data	7348 collected, 5635 unique with $F_o^2 > 3\sigma(F_o^2)$

and 1500 cm<sup>-1</sup>. Thus the  $\nu_{\text{C=N}}$  bands have not been unambiguously assigned.

The <sup>1</sup>H NMR spectrum of complexes II and III shows the hydrido ligand as three 1:2:1 triplets in the ratio 1:4:1 owing to coupling of the mutually *trans* <sup>31</sup>P nuclei and to further coupling to <sup>195</sup>Pt (*I* = 1/2, 34% natural abundance). Complex III shows two singlets at ca.  $\tau$  8.20 from room temperature up to 50 °C for the nonequivalent CH<sub>3</sub> protons of the hydrazone ligand. Such nonequivalence, which arises from the lack of free rotation around the C=N double bond, is also found in the uncoordinated molecule (two methyl signals at  $\tau$  7.93 and 8.12). Thus the nature of the molecule is not markedly influenced by coordination to the metal. Note that the hydrazone complex derived from Zeise's salt, *trans*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(PhHNNC<sub>3</sub>H<sub>6</sub>), shows the two nonequivalent groups at  $\tau$  7.13 and 7.62 with satellites of 11 and 6 Hz arising from the coupling with the platinum atom.<sup>30</sup> Here the magnetic environment is very different from that in free hydrazone ( $\Delta\tau$  = 0.19) or in complex III ( $\Delta\tau$  = 0.06 or 0.08). In this case no Pt–H coupling could be unambiguously detected.

Two broad signals in the intensity ratio 2:1, centered at ca.  $\tau$  5.5 and 5.2 in complex II, disappeared upon D<sub>2</sub>O exchange; they may be attributed to the nitrogen-bonded protons of the hydrazine ligand.

Their precise detection is rather uncertain because of the relatively low solubility of complex II in CDCl<sub>3</sub> (ca. 30 mg in 0.5 mL). However, the presence of the N–H bonds is unambiguous from the IR spectrum (see Table I). Moreover, the fact that (i) complex II obtained by hydrogenation of I in EtOH alone is identical with that obtained from *trans*-PtHCl(PPh<sub>3</sub>)<sub>2</sub> by displacement of the Cl<sup>-</sup> ligand by *p*-FC<sub>6</sub>H<sub>4</sub>HNH<sub>2</sub> in the presence of NaBF<sub>4</sub> and that (ii) complex II reacts with acetone, yielding the arylhydrazone complex III, prove the presence of the arylhydrazone ligand in complex II. The nitrogen-bonded proton in the hydrazone complexes III could not be detected, probably because of overlap with the phenyl protons. The presence of an N–H bond, however, is clear from the IR spectrum (see Table I).

**X-Ray Data Collection.** Initial film examination of the [PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] $\cdot$ C<sub>6</sub>H<sub>6</sub> crystals (IIa) indicated that they belong to the monoclinic system. The systematic extinctions (*h*0*l*, *l* odd; 0*k*0, *k* odd) uniquely determine the space group as C<sub>2h</sub><sup>5</sup>-P2<sub>1</sub>/c. After examination of a number of crystals, one of acceptable mosaicity was found. The shape of this crystal as well as the pertinent details of data collection are given in Table II. The cell constants were determined from the setting angles of 15 high-angle reflections which were hand-centered on a Picker FACS-I computer-controlled diffractometer. No trends were observed in the intensities of the six standard reflections which were measured periodically during the course of data collection. The recorded reflections were processed in the usual way,<sup>31</sup> resulting in 5635 unique, observed ( $F_o^2 \geq 3\sigma(F_o^2)$ ) reflections which were used in further calculations.

**Structure Refinement.** A Patterson synthesis revealed the position of the platinum atom.<sup>32</sup> Subsequent cycles of refinement and difference syntheses resulted in the location of all nonhydrogen atoms.<sup>33</sup> Anomalous dispersion terms were included in  $F_c$ <sup>34</sup> for the platinum and phosphorus atoms. During these and later refinements, all phenyl rings were treated as rigid groups with *D*<sub>6h</sub> symmetry and a C–C bond length of 1.397 Å. After correction of the data for absorption, one more cycle of refinement was run during which the nongroup atoms were allowed to vibrate anisotropically. This resulted in *R* indices of *R* = 0.055 and *R*<sub>w</sub> = 0.091.<sup>35</sup> From the difference Fourier map the methyl hydrogen atoms of the hydrazone ligand could easily be found. We could not determine, however, in which of the two possible positions the amine hydrogen atom was located. The position of the hydrido ligand was also in doubt. The hydrogen positions were idealized assuming tetrahedral geometry for the methyl group, trigonal planar geometry for the phenyl carbon atoms, and C–H distances of 1.0 Å throughout. The hydrido ligand was placed 1.65 Å from the Pt atom with the N–Pt–H angle of 180°. The scattering for all hydrogen atoms (except the amine hydrogen atom) was added as a fixed contribution. Two more cycles of full-matrix least-squares refinement resulted in values for *R* and *R*<sub>w</sub> of 0.046 and 0.063, respectively. The largest peak in the final difference synthesis is of height 1.0 e/Å<sup>3</sup> and is located in the vicinity of the BF<sub>4</sub> anion.

A listing of final positional and thermal parameters for the atoms and groups appears in Tables III and IV. Table V gives the derived hydrogen parameters and the root-mean-square amplitudes of vi-

**Table III.** Positional and Thermal Parameters for the Nongroup Atoms of [PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] $\cdot$ C<sub>6</sub>H<sub>6</sub>

ATOM	<i>x</i> <sup>A</sup>	<i>y</i>	<i>z</i>	B <sub>11</sub> <sup>B</sup>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Pt	-0.260367(22)	0.044076(14)	0.196474(16)	61.96(23)	22.01(9)	31.30(14)	3.70(10)	5.64(11)	2.28(8)
P(1)	-0.30709(15)	0.03010(9)	0.32771(11)	68.4(13)	23.5(5)	33.2(7)	3.4(6)	6.2(7)	2.6(4)
P(2)	-0.24359(14)	0.08463(9)	0.06861(11)	59.8(12)	24.1(5)	32.9(7)	4.8(6)	3.9(7)	2.7(4)
N(1)	-0.2422(4)	-0.05535(26)	0.1640(4)	56.(4)	24.5(15)	37.4(24)	5.2(19)	1.0(24)	0.3(15)
N(2)	-0.1496(5)	-0.0850(3)	0.1794(4)	57.(4)	28.4(20)	51.(3)	8.2(23)	-9.4(28)	-5.3(19)
C(1)	-0.2892(8)	-0.1539(4)	0.0971(7)	110.(8)	30.0(27)	92.(6)	0.(4)	-23.(5)	-16.(3)
C(2)	-0.3080(6)	-0.0884(4)	0.1262(5)	57.(5)	24.0(19)	50.(4)	0.7(26)	0.(4)	3.4(21)
C(3)	-0.4096(6)	-0.0610(4)	0.1112(5)	59.(5)	30.8(24)	67.(4)	-5.3(27)	-10.(4)	1.2(25)
F(1)	0.1198(4)	0.27722(20)	0.2790(4)	166.(5)	24.5(11)	87.(3)	7.4(19)	-16.(3)	1.0(15)
F(2)	0.1698(6)	0.2119(3)	0.3757(4)	230.(8)	55.6(23)	64.9(27)	13.(4)	-32.(4)	16.8(20)
F(3)	0.1964(7)	0.1911(5)	0.2460(5)	356.(10)	113.(4)	114.(5)	153.(6)	38.(6)	-13.(4)
F(4)	0.0616(12)	0.1830(6)	0.2882(8)	414.(19)	39.(7)	165.(9)	-117.(10)	-21.(11)	10.(6)
B	0.1501(10)	0.2193(5)	0.2969(7)	167.(11)	16.9(26)	64.(6)	2.(4)	-10.(6)	-10.(3)

<sup>a</sup> Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. <sup>b</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ . The quantities given in the table are the thermal coefficients  $\times 10^4$ .

Table IV. Derived Parameters for the Rigid Group Atoms of [PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub>

ATOM	X	Y	Z	B <sub>u</sub> A <sup>2</sup>	ATOM	X	Y	Z	B <sub>u</sub> A <sup>2</sup>
R1C(1)	-0.0799(4)	-0.05352(23)	0.23075(28)	4.39(13)	R5C(1)	-0.1296(3)	0.12865(23)	0.05145(28)	4.57(14)
R1C(2)	-0.0348(4)	0.00314(24)	0.20601(27)	5.25(17)	R5C(2)	-0.0933(4)	0.13418(24)	-0.02681(24)	5.45(15)
R1C(3)	0.0361(4)	0.03304(23)	0.2562(4)	6.82(23)	R5C(3)	-0.0122(4)	0.17410(28)	-0.04166(25)	6.41(18)
R1C(4)	0.0620(4)	0.0063(3)	0.3312(4)	7.61(25)	R5C(4)	0.0325(4)	0.20850(27)	0.0218(4)	6.78(24)
R1C(5)	0.0169(5)	-0.0504(3)	0.35593(27)	7.88(23)	R5C(5)	-0.0038(4)	0.20298(27)	0.1000(3)	6.37(21)
R1C(6)	-0.0541(4)	-0.08027(22)	0.3057(3)	5.44(17)	R5C(6)	-0.0848(4)	0.16305(27)	0.11488(22)	5.35(17)
R2C(1)	-0.2918(4)	-0.04843(20)	0.3719(3)	4.63(14)	R6C(1)	-0.2507(4)	0.02657(22)	-0.01266(26)	4.03(14)
R2C(2)	-0.2327(4)	-0.05849(24)	0.4414(3)	5.96(19)	R6C(2)	-0.1746(3)	-0.01882(26)	-0.0174(3)	5.55(16)
R2C(3)	-0.2185(5)	-0.1203(3)	0.4712(3)	7.06(23)	R6C(3)	-0.1797(4)	-0.06636(24)	-0.0766(4)	6.69(22)
R2C(4)	-0.2634(5)	-0.17207(21)	0.4315(4)	7.68(23)	R6C(4)	-0.2608(5)	-0.06852(25)	-0.1310(3)	6.50(20)
R2C(5)	-0.3225(5)	-0.16200(22)	0.3620(4)	7.52(23)	R6C(5)	-0.3366(4)	-0.02314(28)	-0.1263(3)	6.64(21)
R2C(6)	-0.3367(4)	-0.10018(27)	0.33223(28)	5.98(19)	R6C(6)	-0.3318(3)	0.02441(23)	-0.0671(3)	5.22(15)
R3C(1)	-0.4393(3)	0.04967(25)	0.3362(3)	4.56(15)	R7C(1)	-0.3428(3)	0.14108(22)	0.0437(3)	4.21(13)
R3C(2)	-0.5078(4)	0.00897(22)	0.3724(4)	6.47(18)	R7C(2)	-0.3309(3)	0.18787(26)	-0.0155(3)	6.05(19)
R3C(3)	-0.6073(4)	0.0277(3)	0.3791(4)	8.64(25)	R7C(3)	-0.4070(4)	0.23201(23)	-0.0311(3)	6.78(20)
R3C(4)	-0.6384(3)	0.0871(3)	0.3495(4)	7.71(23)	R7C(4)	-0.4950(4)	0.22935(24)	0.0125(4)	6.21(18)
R3C(5)	-0.5699(4)	0.12776(23)	0.3132(4)	6.53(21)	R7C(5)	-0.5069(3)	0.19256(28)	0.0717(3)	6.16(20)
R3C(6)	-0.4704(4)	0.10906(23)	0.3066(3)	5.65(18)	R7C(6)	-0.4308(4)	0.13843(24)	0.08735(28)	5.44(17)
R4C(1)	-0.2485(4)	0.08401(25)	0.3984(3)	4.85(16)	BNZC(1)	-0.3787(6)	0.3057(6)	0.2378(6)	13.7(5)
R4C(2)	-0.1542(4)	0.1085(3)	0.3816(3)	6.40(21)	BNZC(2)	-0.3041(10)	0.2597(4)	0.2485(7)	13.7(4)
R4C(3)	-0.1088(4)	0.1498(3)	0.4365(4)	7.81(26)	BNZC(3)	-0.2052(8)	0.2784(5)	0.2620(6)	12.8(5)
R4C(4)	-0.1536(5)	0.1666(3)	0.5081(4)	8.07(24)	BNZC(4)	-0.1807(6)	0.3432(6)	0.2647(6)	11.3(4)
R4C(5)	-0.2478(5)	0.1421(3)	0.5249(3)	7.02(23)	BNZC(5)	-0.2553(9)	0.3893(4)	0.2540(6)	10.7(3)
R4C(6)	-0.2953(3)	0.10078(29)	0.4700(3)	5.98(19)	BNZC(6)	-0.3543(7)	0.3705(5)	0.2405(6)	11.8(5)

## RIGID GROUP PARAMETERS

GROUP	X <sub>C</sub> <sup>A</sup>	Y <sub>C</sub>	Z <sub>C</sub>	DELTA <sup>B</sup>	EPSILON	ETA
R1	-0.00898(27)	-0.02362(18)	0.28097(23)	2.995(5)	-2.389(3)	2.224(5)
R2	-0.27761(27)	-0.11025(19)	6.40170(23)	2.131(5)	2.318(4)	2.682(5)
R3	-0.5388(3)	0.06836(19)	0.34283(22)	-0.235(4)	2.670(4)	3.030(4)
R4	-0.2010(3)	0.12530(19)	0.45324(25)	1.656(5)	-2.472(4)	0.955(5)
R5	-0.04853(27)	0.16858(18)	0.03661(22)	-0.186(12)	-1.828(3)	-0.858(12)
R6	-0.25573(27)	-0.02098(17)	-0.07185(21)	1.165(4)	2.815(3)	-2.311(4)
R7	-0.41891(27)	0.18522(17)	0.02812(21)	2.229(4)	-2.346(4)	-0.244(4)
BNZ	-0.2797(5)	0.3245(4)	0.2512(3)	0.282(7)	3.093(7)	0.140(6)

<sup>a</sup> x<sub>C</sub>, y<sub>C</sub>, and z<sub>C</sub> are the fractional coordinates of the origin of the rigid group. <sup>b</sup> The rigid group orientation angles delta, epsilon, and eta (radians) have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

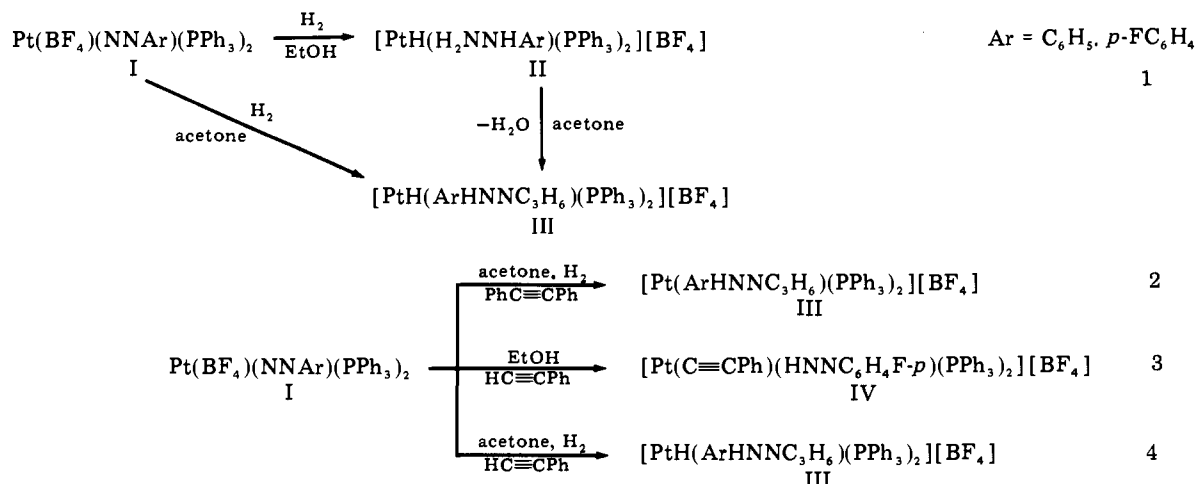
bration.<sup>36</sup> The observed and calculated structure amplitudes are tabulated in Table VI.<sup>36</sup>

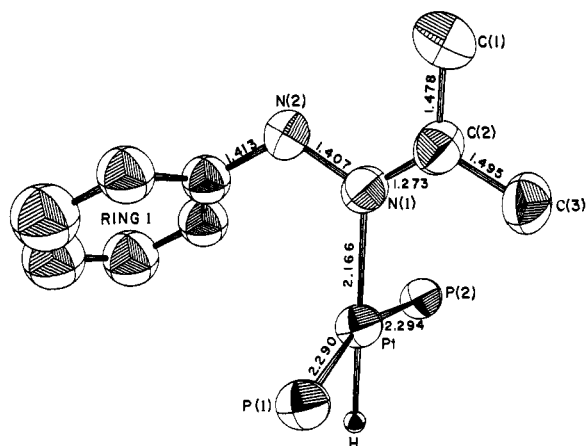
## Results and Discussion

When molecular hydrogen is passed through an ethanol suspension of complex Ib<sup>12</sup> for several hours in the absence of any heterogeneous hydrogenation catalyst, the initially reddish brown suspension becomes yellow and complex IIb may be

precipitated as a whitish powder upon addition of *n*-octane. This hydrazine complex will react with acetone forming complex IIIb. If the initial hydrogenation of complex Ib is carried out in an ethanol-acetone or acetone medium, complex IIIb is formed directly (Scheme I). A third method of synthesis involves the displacement of the Cl<sup>-</sup> anion from *trans*-PtHCl(PPh<sub>3</sub>)<sub>2</sub> by acetone phenylhydrazine. Complex II can also be made in this way when an arylhydrazine is the replacing agent (see Experimental Section).

## Scheme I





**Figure 1.** A view of the coordination sphere and hydrazone ligand of *trans*-[PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] $\cdot$ C<sub>6</sub>H<sub>6</sub>. The thermal ellipsoids have been drawn at the 50% probability level except for the hydride ligand which is drawn on an arbitrary scale at its calculated position for a Pt-H bond of 1.65 Å and an N(1)-Pt-H angle of 180°.

As an aid to understanding the reaction chemistry and because of current interest<sup>15-19</sup> in the bonding of hydrazones to transition metals, the crystal structure of compound IIIa was determined, and the results are reported in the next section.

**Description of the Structure.** The structure of [PtH(PhHNNC<sub>3</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] $\cdot$ C<sub>6</sub>H<sub>6</sub> (IIIa) was found to consist of discrete anion, cation, and solvate benzene species occupying general positions in space group *P2*<sub>1</sub>/*c*. Figure 1 shows the platinum coordination sphere and the hydrazone ligand, with a labeling scheme. A stereoscopic view of the unit cell is shown in Figure 2.

Two short nonbonded contacts occur in the structure. Both are calculated from idealized, hydrogen-atom positions. The F(1)-N(2)H distance of 2.1 Å is slightly longer than that expected for a strong H $\cdots$ F interaction (1.9 Å).<sup>37</sup> The N-H $\cdots$ F angle is 146°. A modest contact of 2.2 Å also occurs between the hydrido ligand and the H2 atom of the solvate benzene molecule.

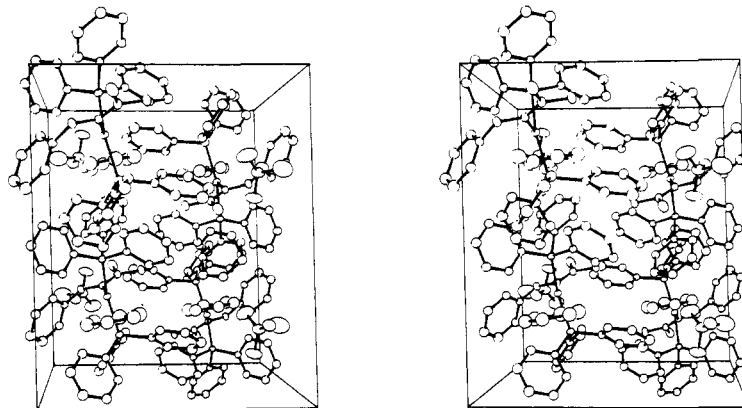
Although the hydrido ligand could not be unambiguously located from an electron density map, examination of the observed bond lengths and angles (Table VII) shows that it does occupy a definite coordination position. The IR and NMR data also unequivocally prove the existence of the hydrido ligand. The P(1)-Pt-P(2) angle is normal for a hydride complex.<sup>38</sup> Consideration of the least-squares plane data (Table VIII) shows that the Pt atom coordination approaches the expected square-planar geometry.

The Pt-P bond distances found here are equal to each other

**Table VII.** Selected Bond Distances and Angles

Bond	Distance (Å)	Bond	Distance (Å)
Pt-P(1)	2.290 (2)	N(1)-N(2)	1.407 (8)
Pt-P(2)	2.294 (2)	N(2)-R1C(1)	1.413 (8)
Pt-N(1)	2.166 (6)	B-F(1)	1.302 (12)
C(2)-C(1)	1.478 (11)	B-F(2)	1.334 (12)
C(2)-C(3)	1.495 (11)	B-F(3)	1.216 (13)
N(1)-C(2)	1.273 (9)	B-F(4)	1.419 (14)
Bond angle	Angle (deg)	Bond angle	Angle (deg)
P(1)-Pt-P(2)	162.71 (7)	N(1)-N(2)-R1C(1)	118.2 (5)
P(1)-Pt-N(1)	98.4 (2)	F(1)-B-F(2)	113.0 (9)
P(2)-Pt-N(1)	96.5 (2)	F(1)-B-F(3)	117 (1)
C(1)-C(2)-C(3)	117.6 (7)	F(1)-B-F(4)	103 (1)
C(1)-C(2)-N(1)	123.0 (8)	F(2)-B-F(3)	121 (1)
C(3)-C(2)-N(1)	119.4 (7)	F(2)-B-F(4)	100 (1)
C(2)-N(1)-N(2)	116.6 (6)	F(3)-B-F(4)	96 (1)
Torsion Angles (deg)			
C(2)-N(1)-N(2)-R1C(1)	-171.2 (6)	C(2)-N(1)-Pt-P(1)	97.9 (6)
Pt-N(1)-N(2)-R1C(1)	13.5 (8)	C(2)-N(1)-Pt-P(2)	-73.4 (6)
C(1)-C(2)-N(1)-N(2)	-1.9 (11)		

and are in line with those found in other Pt(II) complexes.<sup>39,40</sup> The Pt-N bond length is long compared with that in several other platinum compounds<sup>15-17,41,42</sup> (Table IX). This can be attributed to the strong trans influence of the hydrido ligand. The trans influence of the hydrazone moiety is expected to be rather weak, based on spectroscopic evidence. A comparison of  $\nu_{\text{Pt-H}}$ ,  $\tau_{\text{Pt-H}}$ ,  $J_{\text{Pt-H}}$ , and  $J_{\text{P-H}}$  for the complexes reported in Table I shows that the sp<sup>3</sup> and sp<sup>2</sup> nitrogen-coordinated ligands of complex II and III, respectively, exert a comparable trans influence on the Pt-H  $\sigma$  bond.<sup>29</sup> A recent study has indicated that the hydrazine ligand in *trans*-[PtCl(H<sub>2</sub>NNHC<sub>6</sub>H<sub>4</sub>F-*p*)(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (which is obviously closely related to complex II) has little trans influence.<sup>41</sup> This is also true for the hydrazone complex *trans*-PtCl<sub>2</sub>(PhMeNNC<sub>3</sub>H<sub>6</sub>)<sub>2</sub>, where the sp<sup>2</sup> hybridized Pt-N distance of 2.047 (12) Å (Table IX) is in line with the value found in simple amine complexes.<sup>15</sup> The Ru-N bond length at 2.17 (1) Å in *trans*-[Ru(H<sub>2</sub>NNC<sub>3</sub>-H<sub>6</sub>)<sub>2</sub>(P(OMe)<sub>3</sub>)<sub>4</sub>][BPh<sub>4</sub>]<sub>2</sub>, where the hydrazone is bound through the aminic nitrogen atom, is, however, anomalously long.<sup>16</sup>



**Figure 2.** A stereoscopic view of the unit cell. The x axis goes to the right, the y axis goes up, and the z axis comes out of the page. Hydrogen atoms have been removed to improve visibility. The ellipsoids have been drawn at the 20% probability level.

**Table VIII.** Deviations ( $\text{\AA} \times 10^3$ ) from and Equations of Least-Squares Planes

Atom	Deviations		Atom	Plane 2
	Plane 1			
Pt	108 (1)		N(1)	20 (2)
P(1)	-47 (2)		N(2)	-18 (2)
P(2)	-47 (2)		C(1)	3 (2)
N(1)	-13 (2)		C(2)	10 (2)
			C(3)	-15 (2)

Plane	Equations of the Planes $Ax + By + Cz = D$			
	A	B	C	D
1	12.914	2.379	3.665	-2.646
2	4.496	7.827	-14.416	-3.906
Ring 1	9.844	-11.037	-7.334	-1.888

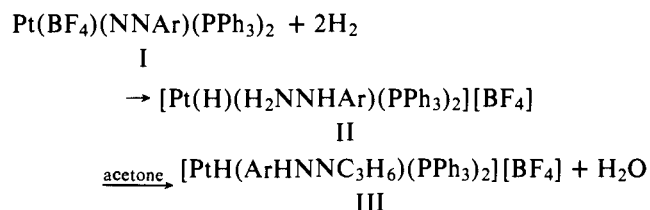
Plane A	Plane B	Dihedral Angles		Plane A	Plane B	Angle (deg)
		Angle (deg)	Plane			
1	2	81.0	2	Ring 1		65.2
1	Ring 1	57.0				

The hydrazone ligand in the complex studied here meets proposed requirements for orthometalation<sup>43</sup> and has a proper orientation for the interaction between the platinum atom and the ortho C-H bond of the phenyl ring of the hydrazone ligand. However, a metallocycle is not obtained. Previous work has shown that only an ortho-C atom on the aromatic ring of the ketone portion can give rise to orthometalation with formation of a five-membered ring containing two conjugated double bonds.<sup>27</sup> This type of conjugated system is not possible in a metallocycle having the phenyl ring bonded to atom N(2). This inability to gain the extra stability probably prevents orthometalation in this complex.

As seen in Table VIII the plane of the hydrazone ligand makes an angle of  $81.0^\circ$  with the plane of the platinum-atom coordination sphere. This nearly perpendicular arrangement is typical of complexes where the hydrazone is attached via an  $sp^2$  nitrogen atom. The determining forces are probably steric in nature. Although in this orientation there is the possibility of overlap between the metal orbitals and the  $\pi$  orbitals of the hydrazone ligand, there is no evidence that this type of interaction takes place. As stated before, the hydrazone ligands of compounds II and III have similar, most probably small, trans influences. Therefore, no multiple M-N bonding takes place. Indeed, comparison of the observed structural parameters with those calculated from van der Waals' radii (Table IX) indicates, as did the NMR data (vide supra), that little change occurs to the hydrazone ligand upon coordination.

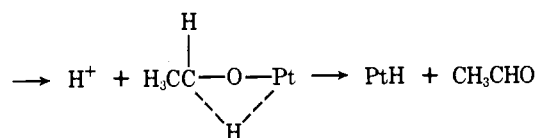
**Hydrogenation of  $\text{Pt}(\text{BF}_4)(\text{NNAr})(\text{PPh}_3)_2$ .** Since complex III can be prepared by reaction of the phenylhydrazine com-

plex II with acetone, as has been reported for the preparation of hydrazone derivatives of Pd(II),<sup>27</sup> we suggest that II is a possible intermediate in the formation of III in acetone, as shown by



Hydrogen absorption experiments show that the formation of complex III in an acetone-ethanol medium (ca. 1:1.2 by volume) from I occurs with the uptake of ca. 1 mol of hydrogen per mole of I to produce ca. 1 mol of acetaldehyde. This suggests that ethanol acts as an  $\alpha$ -hydridic agent<sup>44</sup> at some stage of the reaction shown below.

$\text{CH}_3\text{CH}_2\text{OH} + \text{Pt complex (derived from I)}$



Since (i) acetaldehyde also forms when pure complex III is dissolved in an ethanol-acetone medium (ca. 1 mol of aldehyde per mole of complex III) and (ii) complex III also forms when acetone alone is used as solvent, the above hydrogenation absorption experiments do not prove that ethanol supplies half the amount of hydrogen necessary in the formation of III. Thus the hydrogen absorption results may involve partial decomposition of complex I with nitrogen evolution before reaction with molecular hydrogen. Indeed, under an inert atmosphere complex I decomposes yielding a product whose elemental analysis does not show the presence of nitrogen and corresponds to " $\text{Pt}(\text{BF}_4)(\text{Ar})(\text{PPh}_3)_2$ ".

It is reasonable to assume that the facile hydrogenation of complex I is related to the catalytic homogeneous hydrogenation of olefins and acetylenes in the presence of transition metal complexes. Here it has been generally accepted that the formation of the metal-hydride bond and its reaction with unsaturated compounds are the key steps in the overall reaction.<sup>45,46</sup> Some olefins undergo insertion into the Pt-H bonds of  $\text{PtHX}(\text{PR}_3)_2$  complexes, in most cases under rather vigorous conditions.<sup>44</sup> However, easy insertion under ambient conditions is achieved when X is a readily displaced ligand, such as a molecule of solvent or a nitrate group.<sup>28,47,48</sup> For the arylidiazenido complex I the unsaturated ligand  $\text{ArNN}^-$  is already coordinated to the platinum atom and its hydrogenation can occur after activation of molecular hydrogen on the metal atom.

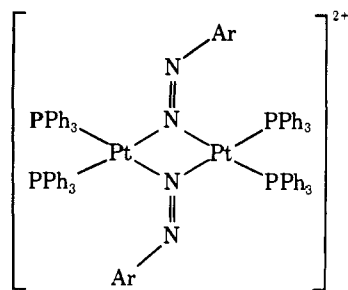
Compared with other related complexes of Pt(II), such

**Table IX.** Comparison of Bond Lengths ( $\text{\AA}$ )

	Pt-N	N=C	N-N	C-N
<i>trans</i> - $[\text{PtH}(\text{PhHNNC}_3\text{H}_6)(\text{PPh}_3)_2][\text{BF}_4] \cdot \text{C}_6\text{H}_6^a$	2.166 (6)	1.273 (9)	1.407 (8)	1.413 (8)
<i>trans</i> - $\text{PtCl}_2(\text{PhMeNNC}_3\text{H}_6)(\text{H}_2\text{CCH}_2)^b$	2.05 (2)	1.34 (3)	1.41 (3)	1.43 (3)
<i>trans</i> - $\text{PtCl}_2(\text{MeHCNNMe}_2)(\text{H}_2\text{CCH}_2)^b$	2.047 (12)	1.43 (5)	1.41 (5)	
<i>trans</i> - $[\text{Ru}(\text{H}_2\text{NNC}_3\text{H}_6)_2(\text{P}(\text{OMe})_3)_4][\text{BPh}_4]_2^c$	2.17 (1)	1.28 (1)	1.46 (1)	
<i>trans</i> - $\text{PdCl}_2(\text{PhMeNNC}_3\text{H}_6)_2^d$	2.047 (12)	1.288 (21)	1.398 (19)	1.464 (20)
<i>trans</i> - $[\text{PtCl}(\text{H}_2\text{NNHC}_6\text{H}_4\text{F}-p)(\text{PEt}_3)_2][\text{BF}_4]^e$	2.081 (7)		1.436 (11)	1.408 (11)
$\text{Me}_2\text{CNHC}_6\text{H}_4\text{NO}_2\text{-}p^f$		1.304 (13)	1.424 (6)	1.350 (6)
Calcd <sup>g</sup>		1.29 (2)	1.44 (2)	1.45 (2)

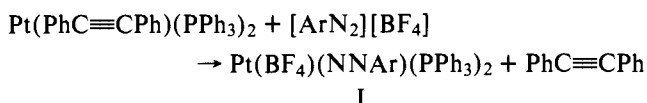
<sup>a</sup> Present study. <sup>b</sup> Reference 17. <sup>c</sup> Reference 16. <sup>d</sup> Reference 15. <sup>e</sup> Reference 41. <sup>f</sup> G. Mencil, G. Samay, and K. Simon, *Acta Chim. Acad. Sci. Hung.*, **72**, 441 (1972). <sup>g</sup> L. Pauling, "The Nature of the Chemical Bond", Third ed, Cornell University Press, Ithaca, N.Y., 1960.

as *trans*-PtCl(NNAr)(PEt<sub>3</sub>)<sub>2</sub>,<sup>3</sup> *trans*-[PtCl(HNNAr)-(PEt<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>],<sup>3</sup> *trans*-[Pt(HNNAr)(PEt<sub>3</sub>)<sub>2</sub>L][ClO<sub>4</sub>]<sub>2</sub> (L = NH<sub>3</sub>, Py, EtNC),<sup>13</sup> and [Pt(NNAr)(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>],<sup>10</sup> complex I is the only one capable of undergoing facile hydrogenation to hydrazine derivatives.<sup>49</sup> Presumably these other Pt(II) complexes are not hydrogenated in the absence of extra heterogeneous hydrogenation catalysts because they do not present an easily available coordination site in the plane of the [Pt(NNAr)L<sub>2</sub>] unit. It is known that all four ligands in the above examples are not easily displaced from the metal atom. This peculiar property of complex I suggests the presence of an easily available coordination site in the [Pt(PPh<sub>3</sub>)<sub>2</sub>(NNAr)] plane capable of activating a molecule of hydrogen and transferring it to the azo function. We have suggested<sup>12</sup> that in the solid or in solution complex I might be a dimeric species.



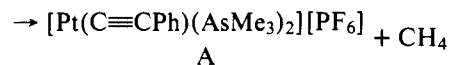
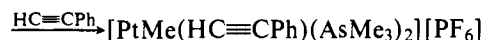
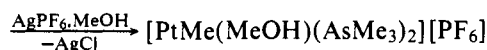
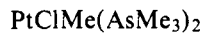
Such an arrangement has been established by an x-ray diffraction study on [Mn(NNPh)(CO)<sub>4</sub>]<sub>2</sub>,<sup>50</sup> and on the closely related [Pt(NNH)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>2+</sup> cation.<sup>51</sup> Interestingly, this cation also undergoes easy hydrogenation to hydrazine derivatives.<sup>51</sup> At least in solution the supposed dimeric species of complex I may be in equilibrium with a monomeric, active species in which the fourth coordination site of the [Pt(NNAr)(PPh<sub>3</sub>)<sub>2</sub>] unit is occupied by the weakly coordinated BF<sub>4</sub><sup>-</sup> group or by a molecule of solvent.<sup>12</sup>

If an empty coordination site is important in the hydrogenation reactions, blocking the site should slow the reaction. When complex I is allowed to react with molecular hydrogen in its preparative reaction mixture (i.e., in the presence of PhC≡CPh, Scheme I) in a benzene-acetone medium, formation of complex III quickly occurs. In this case the acetylene ligand PhC≡CPh is not able to coordinate firmly to the fourth coordination site of complex I, as proved by the very reaction which results in the formation of I:<sup>12</sup>



However, no formation of hydrazine derivatives occurs when complex I is dissolved in ethanol under a hydrogen atmosphere in the presence of HC≡CPh (reaction 3, Scheme I). The main reaction product is the four-coordinated aryldiazenephenylacetylideplatinum(II) complex (IV), which cannot be hydrogenated, as shown also by unsuccessful hydrogenation experiments on separately prepared samples of complex IV. Nelson et al.<sup>52</sup> have noted that terminal and nonterminal acetylenes behave differently toward Pd(0). These facts suggest that the hydrogen molecule competes with HC≡CPh for the available coordination site of the active species of complex I and that the acetylenic C—H bond, though coordination of the C≡C triple bond<sup>22,42</sup> is more easily activated than the H—H one, with consequent formation of complex IV in place of complex II.

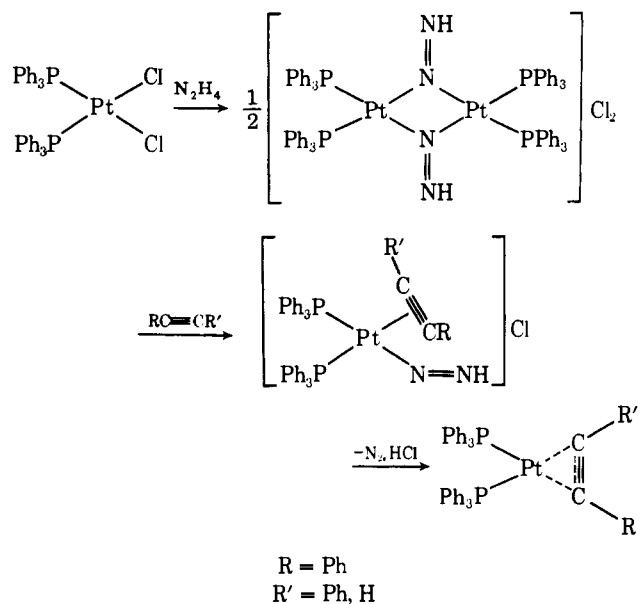
Note that reaction 3 may be related to the one that leads to the phenylacetylide complex of Pt(II), [Pt(C≡CPh)(AsMe<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>].<sup>42</sup>



This reaction can occur only if the acetylene molecule occupies the fourth coordination site (initially occupied by Cl<sup>-</sup>) in the plane of the PtMe(AsMe<sub>3</sub>)<sub>2</sub> unit to form the cationic acetylenic platinum(II) intermediate (A). The main difference between reaction 3 and this reaction is that here upon attack by the acetylenic proton the methyl ligand evolves as methane while in reaction 3 the ArNN<sup>-</sup> ligand is protonated to an aryldiazene ligand which is stabilized by coordination to the platinum atom.<sup>22</sup>

That a readily available coordination site on complex I plays a key role in the easy hydrogenation to complexes II and III is suggested also by the following facts: (i) The IR spectrum of the products obtained by reacting Pt(HC≡CPh)(PPh<sub>3</sub>)<sub>2</sub> dissolved in benzene with the diazonium salt [*p*-FC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> dissolved in acetone under a nitrogen atmosphere shows a very weak band at ca. 2100 cm<sup>-1</sup> from ν<sub>C≡C</sub> of the PtC≡CPh linkage,<sup>22</sup> but the elemental analysis shows only traces of nitrogen and a significantly lower amount of carbon (54.5%) than that required by complex IV (58%). Thus with the use of acetone in place of ethanol the formation of complex IV is not favored and nitrogen evolution probably occurs from I before acetylenic C—H activation. (ii) In an analogous experiment in a hydrogen atmosphere complex III can be isolated, even though in low yield. While the solvent medium does not favor the formation of complex IV the fourth coordination site in the plane of the [Pt(NNAr)(PPh<sub>3</sub>)<sub>2</sub>] unit is still available for the activation of a molecule of hydrogen, which occurs before nitrogen is completely lost and complex III forms. Similar solvent effects on hydrido vs. acetylide formation are observed<sup>52</sup> in Pd(0) chemistry.

Also, note that reactions 2 and 3 may be closely related to those leading to acetyleneplatinum(0) complexes by reduction of *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with hydrazine in the presence of the



acetylene.<sup>53</sup> Here the N<sub>2</sub>H<sup>-</sup> ligand forms by dehydrogenation of the hydrazine molecule and is displaced by the acetylene molecule, evolving as molecular nitrogen with formation of the acetyleneplatinum(0) complex. In reactions 2 and 3 the acet-

ylene is not able to displace the  $\text{ArNN}^-$  ligand which is hydrogenated (reaction 2) to a hydrazine derivative. Thus reaction 2 substantially reverses the above mechanism. In reaction 3 the acetylene interacts with the active species of complex I with formation of the aryldiazenephenylacetyldeplatinum(II) complex IV.

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**Supplementary Material Available:** Table V, containing the derived hydrogen positions and the root-mean-square amplitudes of vibration, and Table VI, a listing of the structure amplitudes (41 pages). Ordering information is given on any current masthead page.

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