dried in a stream of N_2. The yield was 50%. Anal. Calcd for $\mathbf{4}\cdot{}^1/_2CH_2Cl_2$, $C_{34.5}H_{35}Br_4ClMoP_3$: C, 41.8; H, 3.55; Br, 32.2; P, 9.37; Mo, 9.67. Found: C, 41.6; H, 3.62; Br, 33.0; P, 9.42; Mo, 9.52.

Hydrolysis Experiments. In separate experiments, the reaction of **1** with HBr in THF (assembled as described above) was stopped by removing volatiles in vacuo. To the residue were added CH_2Cl_2 (10 mL) and increments (ca. 3 mL) of water (25 mL total). Ammonia and hydrazine were analyzed for as described above. In those experiments carried out for less than 12 h, a mixture of **1A**(Br) and **1B**(Br) was prepared in the absence of solvent to which THF was added. The 12-h experiment was carried out by mixing **1**, HBr, and THF.

Instrumentation and Techniques. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 283 spectrophotometer. Solid samples were run as potassium bromide pellets. ^1H NMR spectra were recorded by using a Varian EM-390 (90 MHz) spectrometer or a Nicolet NMC 360 (361.06 MHz) spectrometer with a 1180E data processor. All ^{31}P NMR spectra were run on a Nicolet NMC 360 (146.17 MHz) spectrometer using a 12-mm tube and broadband decoupling of protons. About 10% by volume of the appropriate perdeuterated solvent was added for locking purposes. All spectra were recorded at ambient temperature unless otherwise stated. All chemical shifts are reported in ppm downfield from Me_4Si (^1H) or 85% H_3PO_4 (^{31}P) with positive values being to lower field.

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Syntheses, Structures, and Mechanism of Formation of *trans*-Chlorohydrobis(trimethylphosphine)platinum(II) and *trans*-Dihydrobis(trimethylphosphine)platinum(II). Energetics of Cis–Trans Isomerization

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The reaction between *cis*-$PtCl_2(PMe_3)_2$ (**1**) and Na(np) (np = naphthalene) under a H_2 atmosphere yields *trans*-$PtHCl(PMe_3)_2$ (**2**). Addition of a second 1 equiv of Na(np) produces *cis*- and *trans*-$PtH_2(PMe_3)_2$ (*cis*-**3** and *trans*-**3**). Complex **3** was crystallized in the presence of np to yield *trans*-**3**·np. Both the latter complex and **2** were characterized by X-ray diffraction at −145 °C. Crystals of **2** belong to the space group $P2_1/n$ with $Z = 4$, $a = 10.241$ (5) Å, $b = 19.012$ (11) Å, $c = 6.300$ (4) Å, $\beta = 96.36$ (1)°, and $V = 1227$ (1) Å^3. For the 1259 unique reflections that had $I_o > 3\sigma(I_o)$ the Patterson solution and least-squares refinement led to final $R = 0.063$ and $R_w = 0.082$. Crystals of *trans*-**3**·np belong to the space group $A2/m$ with $Z = 2$, $a = 6.146$ (2) Å, $b = 10.204$ (3) Å, $c = 14.925$ (4) Å, $\beta = 99.17$ (1)°, and $V = 936$ (1) Å^3. For the 864 unique reflections that had $I_o > 3\sigma(I_o)$ solution by direct methods and least-squares refinement led to final $R = 0.049$ and $R_w = 0.062$. Complex **2** adopts a square-planar geometry, P(1)–Pt–P(2) = 176.0 (2)°, with the Pt–Cl distance, 2.423 (6) Å, significantly lengthened because of the trans influence of hydride. The *trans*-**3**·np complex exhibits no interaction between *trans*-**3** and np, verifying the role of np as a crystallization agent. Electronic spectra of *trans*-**3**/np mixtures in *n*-hexane solvent did not provide evidence for a charge-transfer complex. Crystals of *trans*-**3**·np are extremely sensitive and lose H_2 under a N_2 atmosphere. They are stable under a H_2 atmosphere. In solution **3** exists as an equilibrium mixture of cis and trans isomers with the highest cis/trans ratios being observed in polar solvents (e.g. 3.3 in DMF). Study of the equilibrium ratios in acetone between −40 and −80 °C yielded $\Delta H = 0.3 \pm 0.1$ kcal/mol and $\Delta S = +3.7$ cal/(mol K) for the *trans*-**3** to *cis*-**3** equilibrium. The difference in reactivities and stabilities of the cis isomer between **3** and bulkier analogues is attributed to steric effects of the phosphine ligands. The source of hydride for the conversion **1** → **2** has been confirmed to be H_2 by deuterium-labeling studies. Analysis of organic products shows that Na(np) functions only as an electron-transfer agent for the **1** → **2** → **3** conversion. Addition of H_2 to dinuclear intermediates explains the sequential formation of **2** and **3**.

Introduction

Dihydrobis(phosphine)platinum(II) complexes exhibit a rich chemistry,[2-16] and have been postulated as intermediates in the catalysis of olefin hydrogenation[17] and the water gas shift reaction.[18] Previous experimental studies have been limited to sterically hindered compounds. Several theoretical investigations of unhindered $PtH_2(PH_3)_2$ and $PtH_2(PMe_3)_2$ systems have examined the mechanism of oxidative addition of hydrogen to the platinum center.[19-24] Important concerns are the facility of

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cis–trans isomerization in sterically unhindered complexes and the relative stability of these isomers. Dihydride complexes that are sterically unhindered should be much more reactive than those containing bulky or chelating phosphine ligands.

Previous attempts to isolate sterically unhindered platinum dihydrides were hampered because of the instability and reactivity[2–6,17,25] of these complexes. The complex *trans*-$PtH_2(PEt_3)_2$ was prepared and isolated[26,27] by bubbling hydrogen through a solution of the photochemically generated ethylene complex (eq 1). The less hindered complex $PtH_2(PMe_3)_2$ could not be prepared cleanly by this method because of the low solubility of the precursor oxalate complex in inert solvents.[27] We report here the synthesis of the unhindered dihydrides *cis*- and *trans*-$PtH_2(PMe_3)_2$ from the reaction between *cis*-$PtCl_2(PMe_3)_2$ (**1**) and sodium naphthalide under hydrogen. Thermally sensitive *trans*-$PtH_2(PMe_3)_2{\cdot}C_{10}H_8$ has been characterized by low-temperature X-ray crystallography. Variable-temperature NMR studies of this complex provide the first experimental data for the energetics of cis–trans isomerization of platinum dihydrides to be compared with theoretical predictions. We also report the synthesis and molecular structure of *trans*-$PtHCl(PMe_3)_2$ (**2**) and its role as an intermediate in the reaction of **1** with naphthalide to form $PtH_2(PMe_3)_2$ (**3**).

$$C_2H_4 + Pt(C_2O_4)L_2 \xrightarrow[CH_3CN]{h\nu} Pt(C_2H_4)L_2 + 2CO_2 \xrightarrow[n\text{-}C_6H_{14}]{H_2} PtH_2L_2 + C_2H_4 \quad (1)$$

Experimental Section

General Procedures. Reactions were carried out by using standard Schlenk techniques under an atmosphere of prepurified nitrogen or hydrogen. Reactions monitored by NMR spectroscopy were conducted in 10-mm NMR tubes sealed with septum caps and flushed with hydrogen. Unless otherwise noted, all procedures were carried out at ambient temperature.

Materials. Hydrogen (99.999%) was obtained from Liquid Carbonics. Tetrahydrofuran (Aldrich, Gold Label) and ether were dried over sodium benzophenone ketyl and distilled under nitrogen. *n*-Hexane (Aldrich, 99%) was distilled from lithium aluminum hydride. The following deuterated solvents were obtained from Merck and were used as received: acetone-d_6, toluene-d_8, cyclohexane-d_{12}. Naphthalene (Aldrich, Gold Label), sodium (Cerac), sodium bis(trimethylsilyl)amide (Aldrich), and trimethylphosphine (Strem) were used without further purification.

Physical Measurements. Solution IR spectra were recorded with a Perkin-Elmer 1320 IR spectrometer in 0.1-mm CaF_2 cells that were flushed with hydrogen before use. UV–vis spectra were recorded with an IBM Instruments, Inc., Model 9420 spectrophotometer in a 1-mm quartz cell fitted with a stopcock and 14/20 joint and flushed with hydrogen before use. Fourier transform NMR spectra were recorded with a Nicolet 200 (^{31}P, 80.99 MHz) NMR spectrometer, or a JW 360-MHz ^1H NMR spectrometer[28] fabricated at the UCSD Chemistry Department's NMR facility. The notation $\{^1H\}$ denotes broad-band noise decoupling of the hydrogen nuclei. All chemical shifts are positive in the direction of increasing frequency. Proton chemical shifts were measured relative to Me_4Si at 0.0 ppm and ^{31}P NMR chemical shifts were measured relative to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so that the resonance from a capillary of 85% H_3PO_4, centered in a 10-mm NMR tube containing the deuterated solvent, appeared at 0 ppm at 20 °C. No chemical shift corrections were made for spectra recorded at other temperatures.

Preparation of *cis*-Dichlorobis(trimethylphosphine)platinum(II), *cis*-$PtCl_2(PMe_3)_2$ (1). Trimethylphosphine (1.6 mL, 16 mmol) was added drop by drop under nitrogen to a stirred solution of *cis*-$PtCl_2(SEt_2)_2$[29,30] (3.2 g, 7.2 mmol) dissolved in a minimum amount of CH_2Cl_2. A white solid precipitated from the yellow solution. The solvent was removed in vacuo, and the solid was washed with Et_2O and dried under vacuum to remove excess PMe_3. Recrystallization by dissolving the crude material in hot EtOH and then adding Et_2O yielded 2.1 g of *cis*-$PtCl_2(PMe_3)_2$ (70%) whose spectral parameters were identical with those reported[30] in different syntheses. IR (KBr): 2970 (w), 2918 (w), 950 (s) cm^{-1}. ^1H NMR ($CDCl_3$, −32 °C): δ 1.76 (d, $^2J(P\text{–}H) = 10.7$ Hz, $^3J(Pt\text{–}H) = 35$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, −32 °C): δ −24.8 ($^1J(Pt\text{–}P) = 3479$ Hz).

Preparation of *trans*-Chlorohydrobis(trimethylphosphine)platinum(II), *trans*-$PtHCl(PMe_3)_2$ (*trans*-2). A 25-mL Schlenk flask, charged with a stir bar and **1** (0.2 g, 0.48 mmol), was flushed with nitrogen. After addition of 5 mL of dry, deoxygenated THF, the resulting suspension was cooled to 0 °C. A stream of hydrogen gas was bubbled through the suspension for 5 min. One equivalent of sodium naphthalide (0.48 mmol, 1.9 mL of a 0.25 M THF solution) was added drop by drop with vigorous stirring, and the H_2 purge was maintained during addition. Flushing the resulting colorless to yellow solution with nitrogen decomposed traces of $PtH_2(PMe_3)_2$ that may have formed. Filtration through activated charcoal and Celite yielded a colorless solution. The filtrate was concentrated to 1 mL under vacuum, and 5 mL of pentane was layered on top. After the solution was cooled to −20 °C for 10 h, well-formed colorless crystals separated. The supernatant was removed by cannula filtration to yield 0.12 g (65%) of *trans*-$PtHCl(PMe_3)_2$.

Preparation of *trans*-Dihydrobis(trimethylphosphine)platinum(II), *trans*-$PtH_2(PMe_3)_2{\cdot}C_{10}H_8$ (*trans*-3·np). In a typical preparation 0.2 g of **1** (0.48 mmol) was suspended in 8 mL of THF at 0 °C under a nitrogen atmosphere in a Schlenk flask equipped with a stir bar. Hydrogen was bubbled rapidly through the suspension for 5 min, and bubbling was continued as sodium naphthalide (4.41 mL of a 0.25 M THF solution) was added drop by drop with stirring. When the cloudy solution became clear (except for a small amount of NaCl precipitate), the solution was filtered through a Schlenk frit under a hydrogen atmosphere, the volume was reduced to about 1 mL by rapid purging with H_2, and 3 mL of *n*-hexane was layered over the solution. Cooling to −30 °C (under hydrogen) for 10 h produced white crystals of the title complex that contain one naphthalene of crystallization per platinum. The yellow solution was cannulated away, and the crystals were dried under a stream of H_2; yield 0.09 g (39%). The yield could be increased to 66% by adding 0.15 g (2.5 equiv) of naphthalene to the filtered THF solution before reducing the volume. Since the complex decomposes in the absence of H_2, it was not possible to obtain elemental analyses.

Reaction between *trans*-$PtHCl(PMe_3)_2$ and Sodium Naphthalide. A solution of **2** (0.058 g, 0.152 mM) in 5 mL of THF under hydrogen was treated dropwise with 0.31 mL of sodium naphthalide (0.50 M in THF solution) while hydrogen was rapidly bubbled through the solution. The volume was reduced to 1 mL with a vigorous hydrogen purge, and 1 mL of acetone-d_6 was added for the NMR lock. The ^{31}P NMR spectrum of the reaction mixture, obtained at −30 °C, contained the characteristic resonances of *cis*- and *trans*-**3** as the only major (>90%) products.

Reaction between *trans*-$PtHCl(PMe_3)_2$ and Sodium Bis(trimethylsilyl)amide. Sodium bis(trimethylsilyl)amide (0.028 g, 0.15 mmol) was slowly added from a solid addition tube to a stirred solution of **2** (0.058 g, 0.15 mmol) in 5 mL of THF under a hydrogen atmosphere. The volume was reduced to 1 mL with a rapid hydrogen purge, and 1 mL of acetone-d_6 was added for the NMR lock. The ^{31}P NMR spectrum of the reaction mixture, obtained at −30 °C, contained the characteristic resonances of *cis*- and *trans*-**3** as the only major (>90%) products.

Equilibrium Studies. Solutions of *trans*-**3** (0.07 M) were prepared under H_2 in a 10-mm NMR tube by dissolving the crystalline compound at room temperature. The amounts of trans and cis isomers were determined by $^{31}P\{^1H\}$ NMR spectroscopy. The sample was placed in the NMR probe at the desired temperature and allowed to equilibrate for 15 min. The temperature of the sample in the probe was checked by inserting a thermocouple into a 10-mm NMR tube containing the reaction solvent, allowing it to equilibrate in the probe 15 min, and then measuring the temperature. The solvent temperature was within 1 °C of the temperature probe of the variable-temperature unit. Relative

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Table I. Atomic Positional Parameters

atom	x	y	z
	trans-$PtH_2(PMe_3)_2 \cdot C_{10}H_8$		
Pt	0.0000	0.0000	0.0000
P	0.1066 (5)	0.0000	−0.1380 (2)
C(1)	−0.113 (3)	0.0000	−0.236 (1)
C(2)	0.273 (2)	−0.139 (1)	−0.1590 (7)
C(3)	0.184 (2)	−0.3627 (9)	0.0478 (6)
C(4)	0.0000	−0.431 (1)	0.0000
C(5)	0.361 (2)	−0.431 (1)	0.0926 (6)
H(1)	0.3924	−0.1309	−0.1276
H(2)	0.3344	−0.1331	−0.2125
H(3)	0.1884	−0.2210	−0.1533
H(4)	−0.2210	0.0660	−0.2291
H(5)	−0.0309	−0.0003	−0.2916
H(6)	−0.1787	−0.2709	−0.0446
H(7)	0.5138	−0.3917	0.1215
	trans-$PtHCl(PMe_3)_2$		
Pt	−0.1526 (1)	0.1204 (1)	0.0525 (1)
P(1)	−0.0504 (5)	0.2114 (3)	0.2393 (9)
P(2)	−0.2408 (5)	0.0260 (3)	−0.1354 (8)
C(1)	0.120 (2)	0.233 (1)	0.184 (4)
C(2)	−0.039 (2)	0.198 (2)	0.525 (4)
C(3)	−0.134 (2)	0.296 (1)	0.189 (5)
C(4)	−0.258 (2)	−0.051 (1)	0.040 (4)
C(5)	−0.154 (2)	−0.009 (1)	−0.355 (3)
C(6)	−0.411 (2)	0.041 (1)	−0.252 (3)
Cl	−0.3499 (5)	0.1351 (3)	0.2277 (9)

concentrations of trans and cis isomers were determined by integrating the platinum satellites (that were better separated then the central lines) in the ^{31}P NMR spectra. The equilibrium constant, $K = [cis]/[trans]$, varied reproducibly with temperature between −40 and −80 °C, and a plot of ln K vs. $1/T$ was a straight line that yielded ΔH.

Collection and Reduction of X-ray Data for *trans*-$PtH_2(PMe_3)_2 \cdot C_{10}H_8$ and *trans*-$PtHCl(PMe_3)_2$. Under an atmosphere of hydrogen a crystal of *trans*-$PtH_2(PMe_3)_2 \cdot C_{10}H_8$ was coated with epoxy, mounted on a glass fiber, and immediately placed in a −145 °C stream of N_2 gas.[31] The positions of 16 reflections were then automatically determined on a locally automated Picker diffractometer equipped with a graphite-monochromatized Mo source. These positions were used in the determination of the lattice and orientation parameters. Intensities were extracted from the profile analysis of θ–2θ scans.[32] Crystal and instrument stability were monitored with a set of three standard reflections measured every 100 reflections; no significant variation was found. The mirror plane observed in an axial photograph and the systematic absence $k + l = 2n + 1$ are consistent with the space groups $A2/m$ and $A2$. The structure was successfully solved and refined in the centrosymmetric space group $A2/m$.

The structure was solved[32] with the direct-methods program MULTAN, whereby all non-hydrogen atoms were located. Refinement utilized full-matrix least-squares procedures[33] with the atomic scattering factors taken from ref 34. After all non-hydrogen atoms were refined anisotropically, the phosphino methyl and naphthalene hydrogens were located and included in subsequent structure factor calculations. Final atomic positional parameters and their standard deviations are given in Table I. Crystallographic data are summarized in Table II.

A crystal of *trans*-$PtHCl(PMe_3)_2$ was mounted on a glass fiber under nitrogen, and the same crystal centering, data collection, and processing procedure described above were followed. From the observed $2/m$ Laue symmetry and the systematic absences of $0k0$ reflections for $k = 2n + 1$ and $h0l$ reflections for $h + l = 2n + 1$ the space group was assigned as $P2_1/n$. The position of the platinum atom was determined from a three-dimensional Patterson synthesis. Three Fourier syntheses yielded the positions of all non-hydrogen atoms. Refinement was carried out as described above. Atomic positional parameters and crystal data are provided in Tables I and II.

Table II. Crystal and Intensity Collection Data

	trans-PtH_2-$(PMe_3)_2 \cdot C_{10}H_8$	*trans*-PtHCl-$(PMe_3)_2$
fw	466.3	383.7
a/Å	6.146 (2)	10.241 (5)
b/Å	10.204 (3)	19.012 (11)
c/Å	14.925 (4)	6.300 (4)
β/deg	99.17 (1)	96.36 (1)
V/Å^3	936 (1)	1227 (1)
Z	2	4
ρ(calcd)/g cm^{-3}	1.71	2.09
space group	$A2/m$	$P2_1/n$
cryst size/mm^3	0.075 15	0.025 12
indices of faces	$\{\bar{3}02\}, \{135\}, \{02\bar{1}\}$[a]	$\{010\}, \{100\}, \{122\}$[b]
temp/°C	−145	−145
radiatn source (λ/Å)	Mo$K\alpha$ (0.7107)	Mo$K\alpha$ (0.7107)
abs coeff μ/cm^{-1}	78.32	120.60
transmissn factors	0.0443–0.1525	0.0292–0.2200
scan rate/deg min^{-1}	9	4.5
scan range: deg below $K\alpha_1$; deg below $K\alpha_2$	1; 1	1; 1
2θ limits/deg	0–50	0–45
observns	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of obsd unique data ($I_o > 3\sigma(I_o)$)	864	1259
final no. of variables	156	91
goodness of fit[c]	3.08	3.08
R	0.049	0.063
R_w	0.062	0.082

[a] Distances between parallel faces are 0.0405, 0.0297, and 0.0567 cm, respectively. [b] Distances between parallel faces are 0.0135, 0.0405, and 0.0405 cm, respectively. [c] GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where $w = 1/\sigma(|F_o|)^2$.

Results and Discussion

Synthesis and Spectra of $PtH_2(PMe_3)_2$. The photochemical synthesis[26,27] of PtH_2L_2 (eq 1) proved inconvenient when $L = PMe_3$ because of the low solubility of the oxalate complex in CH_3CN; the reaction was not clean, and the yield of product was low. The dihydride $PtH_2(PMe_3)_2$ can be prepared thermally according to eq 2. The reaction between **1** and 2 equiv of sodium naphthalide

$$\underset{\mathbf{1}}{cis\text{-}PtCl_2L_2} + H_2 \xrightarrow[\text{THF, 0 °C}]{2NaC_{10}H_8} \underset{\mathbf{3}}{trans\text{-}PtH_2L_2C_{10}\cdot H_8} + 2NaCl + C_{10}H_8 \quad (2)$$

in THF, under a hydrogen atmosphere, produces the dihydride in quantitative yield (determined by IR and ^{31}P NMR spectra). Concentration of this solution under hydrogen, addition of *n*-hexane, and cooling to −30 °C produces white crystals of ***trans*-3** as a naphthalene inclusion complex in 39% yield. This yield can be increased to 66% by addition of naphthalene to the reaction mixture to precipitate more of the dihydride from solution as the inclusion complex. Complex **3** also forms in the absence of hydrogen, as seen by IR spectroscopy; however, the reaction is not clean, and attempts were not made to isolate the product.

We investigated other methods of synthesizing **3**. The reaction between **1** and sodium amalgam in THF under a hydrogen atmosphere or with NaK and a catalytic amount of naphthalene under hydrogen produces the dihydride, as observed in the IR spectrum. These reducing agents yield large quantities of platinum metal and presumably $Pt(PMe_3)_4$; consequently the yield of product is low.

In the solid state, **3** exists as off-white crystals containing one molecule of naphthalene per molecule of platinum complex. The complex is pyrophoric, decomposes slowly under vacuum, and

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(32) The UCLA Crystallographic Computing package includes modified versions of the following: CARESS (Broach; includes the program PROFILE (Coppens, Becker, and Blessing)), peak profile analysis and Lorentz and polarization corrections; MULTAN (Main), package of programs, including direct methods, structure factor normalization, Fourier transform, and peak search; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix, least-squares refinement; ORFFE (Busing, Martin, and Levy), distance, angle, and error calculations; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculation; ORTEP (Johnson), figure plotting; HYDROGEN (Trubeblood), calculation of hydrogen atom positions.

(33) All least-squares refinements computed the agreement factors R and R_w according to $R = (\sum||F_o| - |F_c||/\sum|F_o|)$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $w = 1/\sigma^2(F_o)$.

(34) Scattering factors and corrections for anomalous dispersion were taken from: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

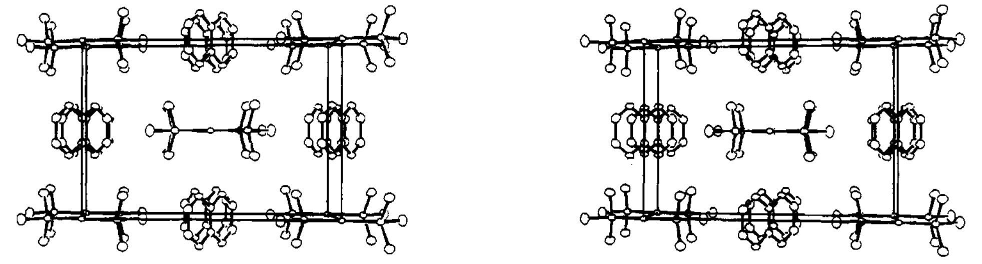

Figure 1. Packing diagram of *trans*-$PtH_2(PMe_3)_2{\cdot}C_{10}H_8$ viewed down the *a* axis with the *c* axis to the right.

Table III. Variation of K = [*cis*-3]/[*trans*-3] with Solvent at −53 °C

solvent	ϵ^a	K	solvent	ϵ^a	K
toluene	2.4	0.24	acetone	20.7	2.9
THF	7.3	0.96	DMF	36.7	3.3

[a] Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972.

Table IV. Selected Interatomic Distances (Å)

	trans-$PtH_2(PMe_3)_2{\cdot}C_{10}H_8$		
Pt–P	2.259 (3)	C(2)–H(1)	0.81 (1)
P–C(1)	1.83 (1)	C(2)–H(2)	0.94 (1)
P–C(2)	1.80 (1)	C(2)–H(3)	1.00 (1)
C(4)–C(4)	1.41 (3)	C(1)–H(4)	0.96 (1)
C(4)–C(3)	1.42 (1)	C(1)–H(5)	1.04 (2)
C(3)–C(5)	1.38 (1)	C(3)–H(6)	0.94 (1)
C(5)–C(5)	1.40 (2)	C(5)–H(7)	1.05 (1)
	trans-$PtHCl(PMe_3)_2$		
Pt–P(1)	2.280 (6)	P(1)–C(3)	1.84 (3)
Pt–P(2)	2.281 (6)	P(2)–C(4)	1.85 (2)
Pt–Cl	2.423 (6)	P(2)–C(5)	1.85 (2)
P(1)–C(1)	1.87 (2)	P(2)–C(6)	1.84 (2)
P(1)–C(2)	1.81 (3)		

begins to eliminate hydrogen irreversibly within minutes under a nitrogen glovebox atmosphere. Thus it is much more reactive than the triethylphosphine analogue *trans*-$PtH_2(PEt_3)_2$, which can be handled under nitrogen and briefly in air.[26]

Complex **3** is soluble in most organic solvents at room temperature, though it reacts with protic and chlorinated solvents to evolve hydrogen gas.[26-28] Solutions are stable under 1 atm of hydrogen at ambient temperature for long periods (days) but decompose above 32 °C. The dihydride is readily identified by its solution IR spectrum, which exhibits a strong band at 1715 cm^{-1} attributable to the overlapping platinum–hydrogen stretches from the cis and trans isomers (see below). Like its triethylphosphine analogue, *trans*-**3** exists in equilibrium with *cis*-**3**, when dissolved in a variety of solvents. The relative concentrations of *trans*-**3** and *cis*-**3** depend on solvent polarity; the polar cis isomer predominates in more polar solvents. Table III shows the variation of K = [cis]/[trans] with solvent dielectric constant at −53 °C. It was previously determined[26] for $PtH_2(PEt_3)_2$ that the cis geometry was favored in polar solvents, with 10% cis isomer being observed in an acetone solution of $PtH_2(PEt_3)_2$. For **3** the equilibrium constant K = [cis]/[trans] increases markedly with solvent dielectric constant. This is expected, as the cis isomer has a dipole moment and should be better solvated in polar media than the nonpolar trans isomer. In the polar solvent DMF (ϵ = 36.7) at −53 °C, K = 3.3. This marks the greatest amount of cis isomer ever observed in a platinum dihydride where the geometry is not constrained by chelating phosphine ligands.

The ^1H NMR spectrum of *trans*-**3** exhibits a hydride resonance at −2.7 ppm (acetone-d_6, −80 °C) that is a 1:2:1 triplet ($^2J(P\text{–}H)^{cis}$ = 20 Hz) arising from coupling to two phosphorus atoms cis to a hydride and is flanked by ^{195}Pt (34% abundance) satellites with $^1J(Pt\text{–}H)$ = 807 Hz. The signal for *cis*-**3** is a second-order doublet of doublets at −3.7 ppm, arising from coupling of each hydride to a cis and trans phosphorus: $^1J(Pt\text{–}H)$ = 1028 Hz; $^2J(P\text{–}H)^{cis}$ = 24 Hz; $^2J(P\text{–}H)^{trans}$ = 179 Hz. The $^{31}P\{^1H\}$ NMR spectrum of *trans*-**3** is a singlet at −19.4 ppm with the usual ^{195}Pt satellites (acetone-d_6, −80 °C, $^1J(Pt\text{–}P)$ = 2594 Hz), while *cis*-**3** shows a singlet at −20.0 ppm ($^1J(Pt\text{–}P)$ = 1875 Hz).

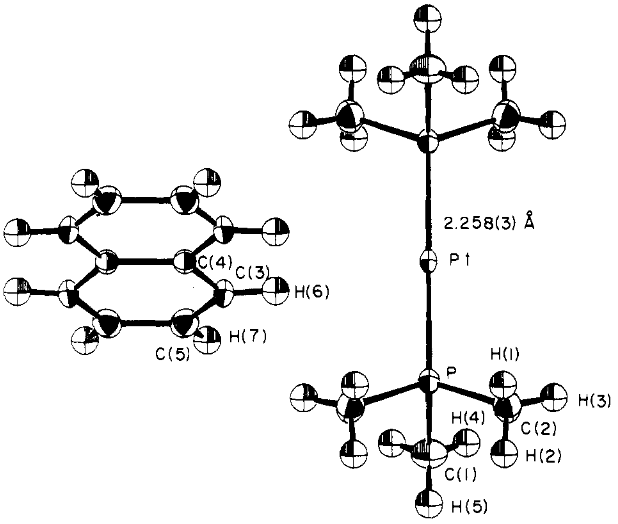

Figure 2. ORTEP diagram of *trans*-$PtH_2(PMe_3)_2{\cdot}C_{10}H_8$; ellipsoids at 50% probability.

Table V. Selected Interatomic Angles (deg)

trans-$PtH_2(PMe_3)_2{\cdot}C_{10}H_{18}$		*trans*-$PtHCl(PMe_3)_2$	
P–Pt–P	180.00	P(1)–Pt–P(2)	176.0 (2)
C(1)–P–Pt	116.5 (5)	C(1)–P(1)–Pt	117.2 (8)
C(2)–P–Pt	114.5 (3)	C(1)–P(1)–Pt	117.2 (8)
C(1)–P–C(2)	103.2 (5)	C(2)–P(1)–Pt	112.7 (9)
C(2)–P–C(2)	103.4 (7)	C(3)–P(1)–Pt	113.4 (8)
H(4)–C(1)–P	110.4 (10)	C(4)–P(2)–Pt	111.6 (7)
H(5)–C(1)–P	104.4 (10)	C(5)–P(2)–Pt	118.5 (8)
H(1)–C(2)–P	108.2 (10)	C(6)–P(2)–Pt	113.2 (8)
H(2)–C(2)–P	114.8 (9)	C(1)–P(1)–C(2)	104.7 (11)
H(3)–C(2)–P	109.1 (8)	C(1)–P(1)–C(3)	101.7 (12)
H(4)–C(1)–H(4)	88.9 (13)	C(2)–P(1)–C(3)	105.7 (13)
H(4)–C(1)–H(5)	121.3 (10)	C(4)–P(2)–C(5)	104.1 (11)
H(1)–C(2)–H(2)	92.2 (10)	C(4)–P(2)–C(6)	102.1 (10)
H(1)–C(2)–H(3)	117.9 (12)	C(5)–P(2)–C(6)	105.6 (11)
H(2)–C(2)–H(3)	114.0 (11)		
C(4)–C(3)–C(5)	120.0 (9)		
C(3)–C(4)–C(4)	119.4 (6)		
C(3)–C(5)–C(5)	120.6 (6)		
C(3)–C(4)–C(3)	121.2 (12)		
C(4)–C(3)–H(6)	116.5 (10)		
C(5)–C(3)–H(6)	123.4 (10)		
C(3)–C(5)–H(7)	148.4 (8)		
C(5)–C(5)–H(7)	112.6 (6)		

Structure of *trans*-$PtH_2(PMe_3)_2{\cdot}C_{10}H_8$. Since trimethylphosphine is the smallest phosphine to have a coordination chemistry, *cis*- and *trans*-**3** represent the "ultimate" sterically unhindered platinum dihydrides. They are also the most reactive platinum dihydrides known. No unhindered dihydrides of platinum have been characterized previously by X-ray diffraction. Only one other platinum dihydride has had its structure reported; $PtH_2(PCy_3)_2$, which assumes the trans geometry to accommodate the bulky phosphine ligands.[6]

A crystal-packing diagram of *trans*-**3** viewed down the *a* axis is depicted in Figure 1. The unit cell contains two platinum complexes as well as two naphthalene molecules of crystallization. The lack of coordinative interaction between the naphthalene molecules and platinum centers is demonstrated by their nonbonding intermolecular approach of 3.00 Å (H(1)–Pt).

The molecular structure and numbering scheme for the atoms of *trans*-**3** are depicted in Figure 2. Selected interatomic distances and angles are presented in Tables IV and V, respectively. The platinum atom lies on a special position with crystallographically imposed C_{2h} symmetry; therefore, only one-fourth of the complex and naphthalene are symmetry unique. Symmetrical constraints require the phosphines to be disposed in a 180° trans conformation. The Pt–P distance of 2.258 (3) Å matches those (2.26 (1) and 2.25 (1) Å) determined[6] for $PtH_2[P(C_6H_{11})_3]_2$ and implies similar bonding interactions between phosphorus and platinum atoms in the two complexes. The greater reactivity of the trimethylphosphine derivative must be primarily the result of steric effects.

The hydrides could not be located due to their close proximity to the platinum atom. Packing considerations place them in the crystallographic *ab* plane.

We considered the possibility that the structure represented a charge-transfer complex of naphthalene. Several donor–acceptor complexes between naphthalene and organic molecules have been characterized[35-37] by X-ray diffraction. As is typical of charge-transfer complexes in the solid phase,[38] the stoichiometry in these compounds is 1:1 and the structures consist of infinite stacks (Figure 1) of donor and acceptor molecules. Arguing against the charge-transfer assignment is the close naphthalene–Pt contact (Figure 2) that involves the naphthalene hydrogens rather than the naphthalene π system. The UV–vis spectrum of *trans*-**3**-$C_{10}H_8$ in *n*-hexane solution does not show an absorption band characteristic of a charge-transfer complex. The only features present in the absorption spectrum are those attributable to naphthalene at 215, 260, 273, and 285 nm (not shifted from their normal positions in *n*-hexane) and a weak band at 335 nm. Adding a small amount of naphthalene to the solution of **3** in *n*-hexane only increases the intensity of naphthalene peaks. The intensity of the weak band does not increase, and it is attributable to a transition localized on $PtH_2(PMe_3)_2$.

Thermodynamic Studies. The isomerization of *trans*-**3** to *cis*-**3** was followed by ^{31}P NMR spectroscopy in acetone-d_6 between −40 and −80 °C. Although the cis isomer dominates in this solvent, its concentration steadily decreases as the temperature is lowered. If a solution of the dihydride was prepared at −80 °C and allowed to warm up in the NMR probe, the same equilibrium ratios were measured. A plot of ln K vs. $1/T$ is a straight line that yields $\Delta H = 0.3 \pm 0.1$ kcal/mol and $\Delta S = +3.7$ cal/(mol K) for the isomerization trans $\rightleftharpoons$ cis.

The isomerization was also monitored in toluene-d_8 to determine the effect of a change in solvent polarity. Only 15% of cis isomer is present in this solvent at −40 °C. The low concentration of this isomer produces more scatter in the Van't Hoff plot of the data than is observed for the study carried out in acetone-d_6. Approximate values obtained from a least-square fit of the data are $\Delta H = 0.5 \pm 0.2$ kcal/mol and $\Delta S = -1.4$ cal/(mol K). Although these values are not identical with those determined in acetone-d_6, nor are they as accurate, the heat of isomerization still lies between 0 and +1 kcal/mol.

The relative stabilities of cis and trans platinum dihydrides have been calculated in theoretical studies of oxidative addition of hydrogen to bis(phosphine)platinum(0).[20-24] In these studies, attempts were made to explain the known preference of platinum dihydrides for the trans geometry; however, there have been no quantitative experiments to test the results of these calculations. The most recent study, by Kitaura et al.,[23] employed the restricted Hartree–Fock (RHF) and SD–CI[24] methods in their study of the system $PtH_2(PH_3)_2$. In their best calculations, the energy differences between cis and trans isomers were within a few kilocalories per mole. An earlier study Noell and Hay[21] used GVB calculations to determine that, for $PtH_2(PH_3)_2$, the trans isomer was 4 kcal/mol more stable than the cis isomer. They also studied the experimentally attainable system $PtH_2(PMe_3)_2$ and calculated an energy difference of 23 kcal/mol in favor of the trans isomer. This predicts a greater thermodynamic driving force for producing trans dihydrides. A more recent GVB calculation of Low and Goddard[22] suggests that the geometries used in the previous[21] study may not be optimum.

The results of our study of $PtH_2(PMe_3)_2$ are more in accord with the calculated data for $PtH_2(PH_3)_2$. We find an enthalpy difference of less than 1.0 kcal/mol in both polar and nonpolar solvents, with the *trans*-dihydride only slightly more stable than the cis isomer. When crystals of *trans*-**3** are dissolved at −80 °C and the ^{31}P NMR spectrum is recorded (within $^1/_2$ h) at −80 °C, only an equilibrium mixture is observed. Because the isomerization trans $\rightleftharpoons$ cis occurs rapidly at −80 °C the barrier to isomerization must be small; however, isomerization is not so rapid that coalescence of the NMR resonances occurs. This places the barrier to isomerization in the 10–20 kcal/mol range. It is not clear whether the slight preference for *trans*-**3** isomer is steric. For example solutions of $PtH_2(PMe_3)_2$ contain about 10 times more cis isomer than for $PtH_2(PEt_3)_2$.[26] Space-filling CPK models suggest that even *cis*-$PtH_2(PMe_3)_2$ is sterically crowded. It is possible that the hypothetical PH_3 complex would favor the cis isomer to an even greater extent than in **3**. Applying the rule[39] that ligands with strong trans influences (such as H^-) prefer to be cis, one would have expected the cis isomer to be favored for PtH_2L_2 (L = phosphorus donor) complexes in the absence of steric effects.

Mechanism of Formation of 3 via 2. Spectroscopic (NMR) examination of the reaction mixture obtained by combining **1** with 2 equiv of sodium naphthalide at −80 °C under hydrogen reveals that *trans*-$PtHCl(PMe_3)_2$ (**2**) rather than **3** is produced. Complex **2** also forms by treating **1** with 1 equiv of sodium naphthalide under hydrogen at room temperature and can be isolated in high yield as colorless crystals from this reaction mixture. This compound was prepared previously[40a] by hydrazine reduction of the dichloride and found to be too unstable for purification. Recently Flood and Statler[40b] observed **2** as the product from pyrolysis of *trans*-PtCl(4-Me-pentyl)$(PMe_3)_2$. Although highly air sensitive in solution, crystals of **2** are stable in vacuo for several days at room temperature. If it is allowed to stand for ~1 h in carbon tetrachloride solution, **2** slowly reverts to **1**. The Pt–H stretch at 2177 cm^{-1} exhibited by the complex in benzene solution proves to be more convenient for characterization than the 2183-cm^{-1} stretch (in reactive carbon tetrachloride) as reported by Chatt and Shaw.[40a] This stretch is shifted to 2220 cm^{-1} in the solid-state (KBr pellet) IR spectrum in which the Pt–Cl stretch at 262 cm^{-1} and the Pt–P stretch at 348 cm^{-1} were also observed.

The ^1H NMR (benzene-d_6) spectrum of **2** exhibits a hydride resonance at −16.2 ppm (^1J(Pt–H) = 1308 Hz, ^2J(P–H) = 17 Hz) as well as a virtual triplet at 1.2 ppm (^1J(Pt–H) = 33 Hz, ^2J(P–H) = 7 Hz) corresponding to the phosphine methyl protons. The $^{31}P\{^1H\}$ NMR (acetone-d_6) spectrum of **2** exhibits a singlet at −13.7 ppm (^1J(Pt–P) 2609 Hz). All the spectroscopic data are consistent with a trans structure for **2**.

To conclusively establish the identity of **2**, its crystal structure was determined. Selected distances and angles are given in Tables IV and V. Complex **2** exhibits a nearly square-planar geometry (Figure 3) although the P(1)–Pt–P(2) angle of 176.0 (2) slightly bends away from the chloride ligand. The chloride is situated mutually cis to each of the phosphorus atoms with P(1)–Pt–Cl and P(2)–Pt–Cl angles of 92.0 (2) and 91.4 (2)°, respectively. The hydride could not be located but is assumed to be trans to Cl.

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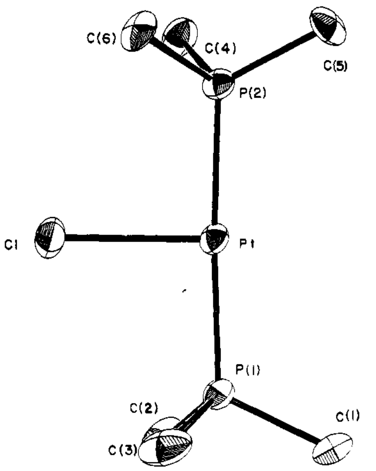


Figure 3. ORTEP diagram of *trans*-$\mathrm{PtHCl(PMe_3)_2}$; ellipsoids at 50% probability.

The pronounced trans influence[39] of the hydride is reflected in the Pt–Cl distance of 2.423 (6) Å that is appreciably longer than the sum of the atomic radii of 2.30 Å or the Pt–Cl distance of 2.294 (9) Å reported[41] for *trans*-$\mathrm{PtCl_2(PEt_3)_2}$. An analogous result has been obtained for *trans*-$\mathrm{PtHCl(PPh_2Et)_2}$ for which a Pt–Cl distance of 2.422 (9) Å was determined.[42] Again, the electronic nature of the $\mathrm{PMe_3}$ derivative, as reflected by Pt–P bond distances (2.280 (6) and 2.281 (6) Å), is similar to that of the bulkier $\mathrm{PPh_2Et}$ analogue (2.267 (8) and 2.269 (8) Å).

Although there are numerous examples for the preparation of metal hydride complexes under reducing conditions, little is known about mechanistic details. The best understood cases[43] are those where H_2 oxidatively adds to a low-valent metal complex. Treatment of **2** with 1 equiv of sodium naphthalide under hydrogen results in the exclusive formation of **3**. When this is taken together with the low-temperature NMR experiments discussed above, one sees that incorporation of hydride follows the process

$$\mathbf{1} + \mathrm{Na(np)} \xrightarrow{H_2} \mathbf{2} + \mathrm{Na(np)} \xrightarrow{H_2} \mathbf{3} \qquad (3)$$

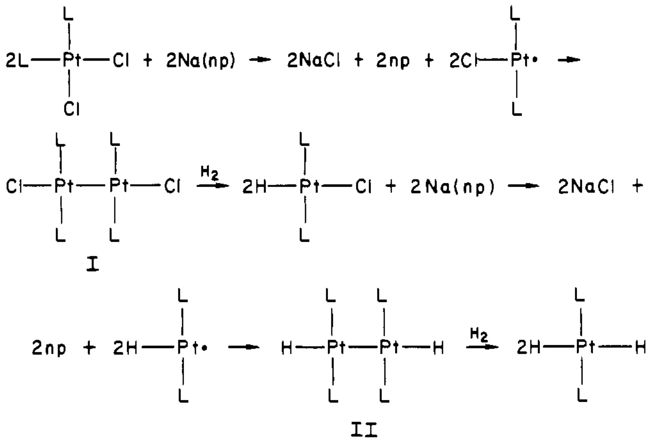
This implies a kinetic preference for the reaction of sodium naphthalide with **1** over the reaction with **2**. Indeed, the reaction (under H_2) between 1 equiv of Na(np), 1 equiv of **1** and 1 equiv of **2** at 0 °C yields an additional equivalent of **2** and no **3** by ^{31}P NMR spectroscopy. In the control experiment (eq 4) hydride–chloride exchange was not observed.

$$\mathbf{1} + \mathbf{3} \nrightarrow \mathbf{2} \qquad (4)$$

The mechanism whereby one hydrogen from H_2 is transferred to Pt to form **2** and then **3** was puzzling. Initially we expected that **3** formed via reduction of **1** to a $\mathrm{Pt(PMe_3)_2}$ species followed by oxidative addition of H_2 ($\mathrm{PtL_2}$ complexes are known[7-9] with bulky phosphine ligands). The preceding observations exclude this possibility. An alternative mechanism for the formation of **2** and **3** is depicted in Scheme I.

The role of $\mathrm{np^-}$ as an electron-transfer agent is supported by the observation (by ^{1}H NMR spectroscopy) of np and only traces (<5%) of dihydronaphthalene following the conversions **1** → **2** and **2** → **3**. Dihydronaphthalene and Tetralin are the products observed[44] when $\mathrm{np^-}$ functions as a base rather than as an electron-transfer agent. The basic nature of $\mathrm{np^-}$ was an important consideration because Kaska and co-workers[45] have used dehydrochlorination reactions of rhodium hydridochlorides with $\mathrm{NaN(SiMe_3)_2}$ as a route to reactive dihydrides. We have shown that $\mathrm{NaN(SiMe_3)_2}$ and H_2 can effect the **2** → **3** conversion but not **1** → **2**; however, this apparently is unrelated to the mechanism of naphthalide reductions described here.

Scheme I



Confirmation of H_2 as the primary source of hydride hydrogen was established by combining **1**, D_2, and Na(np). By IR analysis [ν(Pt–D) = 1600 cm^{-1} and ν_{bend} (Pt–D) = 575 cm^{-1}] and ^{2}H NMR spectroscopy (–16.1 ppm, ^1J(Pt–D) = 200 Hz, ^2J(D–P) = 2.4 Hz) **2**-d_1 formed in greater than 90% isotopic purity. In the control experiment **2** and D_2 did not produce **2**-d_1 over a 1-day period. A similar labeling experiment could not be performed for the **2** → **3** conversion since $\mathrm{PtH_2L_2}$ acts as an efficient catalyst[26] for H_2/D_2 scrambling. The observation, by IR spectroscopy, that small amounts of **3** (and large amounts of Pt metal) form when **1** is treated with 2Na(np) in the absence of H_2 can be attributed to abstraction of hydrogen from THF. Another case is known[17] where $\mathrm{PtL_2}$ abstracts hydrogen from THF solvent to form dihydrides.

There is precedent for a complex like I of Scheme I. The reaction between $\mathrm{PtCl_2(dppm)}$ [dppm = bis(diphenylphosphine)methane] and $\mathrm{NaBH_4}$ yields[46] $\mathrm{ClPt(\mu\text{-}dppm)_2PtCl}$ upon refluxing. Hydrogen addition to dimers[47] I and II may occur either across the Pt–Pt bond or by oxidative addition to one metal followed by hydrogen migration.

The bulkier *trans*-$\mathrm{PtHCl(PEt_3)_2}$ complex[40a,48] could also be prepared from *cis*-$\mathrm{PtCl_2(PEt_3)_2}$, Na(np), and H_2; however, this method did not prove successful with *cis*-$\mathrm{PtCl_2(PPh_3)_2}$, which decomposed when treated with Na(np) and H_2. Since *trans*-$\mathrm{PtHCl(PPh_3)_2}$ can be synthesized by other methods[40a,49] the failure with the Na(np) method can be attributed to the bulk of the $\mathrm{PPh_3}$ ligands that may hinder the essential dimer formation process of Scheme I.

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Registry No. **1**, 15630-86-1; *trans*-**2**, 91760-38-2; *trans*-**3**, 80581-71-1; *cis*-**3**, 80540-35-8; *cis*-$\mathrm{PtCl_2(SEt_2)_2}$, 15442-57-6.

Supplementary Material Available: Tables of anisotropic temperature factors for *trans*-$\mathrm{PtH_2(PMe_3)_2}$ and *trans*-$\mathrm{PtHCl(PMe_3)_2}$ (2 pages). Ordering information is given on any current masthead page.

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