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Synthesis of a Novel Volatile Platinum Complex for Use in CVD and a Study of the Mechanism of Its Thermal Decomposition in Solution

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Abstract: The synthesis, characterization, chemical vapor deposition, and mechanistic investigation of the thermal decomposition in aromatic solvents of *cis*-bis(η^2,η^1-pent-4-en-1-yl)platinum (**1**) are described. Complex **1** has a unique chelated structure, giving rise to enhanced volatility, and has proved useful for the chemical vapor deposition of thin platinum films under mild conditions. Films deposited on a glass slide in a hot walled glass tube at 175 °C have an elemental composition of 82% Pt and 18% C. Kinetic, deuterium labeling, and chemical trapping experiments indicate that the decomposition of **1** in aromatic solvents proceeds by reversible β-hydride elimination followed by reversible dissociation of 1,4-pentadiene to give a 3-coordinate platinum hydride intermediate (**9**). Reductive elimination of 1-pentene from **9** deposits metallic platinum. The rate of decomposition exhibits a significant β-deuterium isotope effect of $k_H/k_D = 3.8 \pm 0.3$. Added olefins are rapidly isomerized during the decomposition of **1**; trapping experiments with diphenylacetylene indicate that intermediate **9** is the highly active catalyst that is responsible for the alkene isomerization.

Introduction

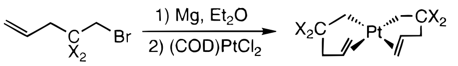
Chemical Vapor Deposition (CVD) is an important and widely used method of fabricating metal thin films from organometallic precursors. The technique involves the volatilization of an organometallic complex, which is then passed over a substrate and thermolyzed to deposit a metal film.[1] Ideally, the organic remnants of the thermolysis reaction remain in the gas phase and are easily removed. The temperatures of the thermolysis reactions are typically thousands of degrees lower than the temperatures required to generate films by other techniques. However, often the precursor decomposition reactions are not clean and heteroatoms from the ligands become incorporated into and reduce the quality of the resulting metal film. A fundamental understanding of the decomposition process should lead to the design of precursor complexes that undergo cleaner thermolysis reactions to produce higher quality metal films.

Due to the importance of thin platinum films for microelectronic[2−5] and catalytic[6] applications, there has been much interest in the design and study of organoplatinum complexes for use as precursors for CVD.[7−12] However, only a small number of organoplatinum complexes exhibit sufficient volatility necessary for the CVD technique, and even fewer undergo clean thermal decomposition to give platinum films. Puddephatt and co-workers recently reviewed several precursors for platinum CVD and reported that $(MeNC)_2PtMe_2$ produced films of the highest purity in the absence of added reagents: 88% Pt and 11% C.[8] Further studies showed that the addition of H_2 as a carrier gas drastically reduced the carbon contamination in platinum films for all organoplatinum precursors.[13]

We wish to report the synthesis of *cis*-bis(η^2,η^1-pent-4-en-1-yl)platinum (**1**), a novel, volatile organoplatinum complex that has proved useful for the deposition of unusually pure thin platinum films. We attribute the high volatility of **1** to the small, compact shape and low molecular weight imparted by the chelating pentenyl ligands. We have studied the thermolysis reactions of **1** in aromatic solvents extensively in both the presence and absence of added reagents. We have found evidence that a transient intermediate is a highly active olefin isomerization catalyst.

Results

Preparation and Characterization of 1. Treatment of $(COD)PtCl_2$ with pent-4-en-1-ylmagnesium bromide at 0 °C in Et_2O leads to the formation of **1** and free COD and precipitation of $MgCl_2$ (eq 1). Complex **1** was purified by sublimation and



(1)

1: X = H

1-β-d_4: X = D

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(1) Jensen, K. S.; Kern, W. In *Thin Film Processes*; Vossen, J. L., Kern, W., Eds.; Academic Press: Boston, 1991; Vol. II, pp 283−353.

(2) Bindra, P.; Roldan, J. *J. Electrochem. Soc.* **1985**, *132*, 2581−2589.

(3) Green, M. L.; Levy, R. A. *J. Met.* **1985**, *37*, 63−71.

(4) Shibli, S. M. A.; Noel, M. *J. Power Sources* **1993**, *45*, 139−152.

(5) Zimmerman, J. H. *J. Power Sources* **1991**, *36*, 253−267.

(6) Dossi, C.; Psaro, R.; Bartsch, A.; Fusi, A.; Sordelli, L.; Ugo, R.; Bellatreccia, M.; Zanoni, R.; Vlaic, G. *J. Catal.* **1994**, *145*, 377−383.

(7) Bradley, D. C. *Polyhedron* **1994**, *13*, 1111−1121.

(8) Dryden, N. H.; Kumar, R.; Ou, E.; Rashidi, M.; Roy, S.; Norton, P. R.; Puddephatt, R. J. *Chem. Mater.* **1991**, *3*, 677−685.

(9) Gozum, J. E.; Pollina, D. M.; Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688−2689.

(10) Puddephatt, R. J. *Polyhedron* **1994**, *13*, 1233−1234.

(11) Xue, Z.; Strouse, M. J.; Shuh, D. K.; Knobler, C. B.; Kaesz, H. D.; Hicks, R. F.; Williams, R. S. *J. Am. Chem. Soc.* **1989**, *111*, 8779−8784.

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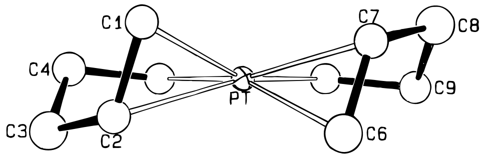
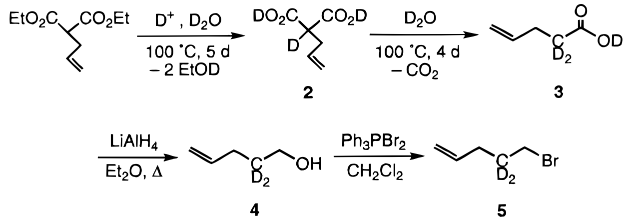


Figure 1. ORTEP drawing of **1**.

Scheme 1



isolated as yellow crystals in 85% yield. Recrystallization from an ethanol/pentane (1/1) solution at −15 °C resulted in crystals that were suitable for X-ray diffraction. Complex **1** is an air- and moisture-stable, low-melting (40−41 °C), volatile solid, which is moderately thermally sensitive in the solid state. It decomposes within 2 weeks at room temperature, but is stable indefinitely at −15 °C.

The ^{1}H NMR spectrum of **1** displays three distinct alkene resonances at δ 3.25 (d, 2 H, J_{HH} = 9 Hz, J_{PtH} = 28 Hz), 3.65 (d, 2 H, J_{HH} = 16 Hz, J_{PtH} = 40 Hz), and 4.45 (m, 2 H). The upfield shift of the resonances from those of the free alkene and the magnitude of the Pt−H coupling constants are consistent with π-coordination of the terminal C═C bond of the pentenyl ligand to platinum. The alkyl resonances appear as overlapping multiplets centered at δ 2.00 (m, 12 H) and could not be resolved. The five resonances present in the ^{13}C NMR spectrum all exhibit ^{195}Pt coupling and have been assigned based on the chemical shifts, the magnitude of the C−Pt coupling constants, and DEPT experiments: δ 28.70 (s, J_{CPt} = 40 Hz, β-CH$_2$), 32.31 (s, J_{CPt} = 811 Hz, α-CH$_2$), 33.76 (s, J_{CPt} = 24 Hz, γ-CH$_2$), 80.00 (s, J_{CPt} = 50 Hz, ═CH$_2$), 113.1 (s, J_{CPt} = 40 Hz, CH). The assignment for the β-carbon resonance is further supported by a deuterium labeling study (vide infra). The molecular ion appears in the electron ionization mass spectrum at *m/e* = 333 (^{195}Pt), which is consistent with a monomeric structure.

A single crystal X-ray diffraction study confirmed that **1** is monomeric, having two pentenyl ligands bound to platinum in a chelated fashion (Figure 1). The platinum is essentially square-planar coordinate; the two π-bound alkenes are oriented cis to one another and each is trans to a σ-bound carbon. The chelating pentenyl rings are related by a C_2 axis of symmetry.

The chelated structure of **1** results in several interesting structural features. As the pentenyl ring is puckered, aliphatic hydrogens may appear in a pseudo-axial or pseudo-equatorial position. The dihedral angle between the alkenes and the square plane is 69°; the π-bound alkenes are tipped 21° from the perpendicular (generally the most stable for platinum π-complexes)[14] conformation. Finally, the molecule is very compact, measuring less than 6.3 Å across its widest span (C3−C8).

Preparation and Characterization of 1-*β*-*d*$_4$. Isotopically labeled **1**-β-d_4 was prepared from the corresponding labeled alkyl bromide. The synthesis of 5-bromo-4,4-dideuterio-1-pentene (**5**) is shown in Scheme 1. A solution of diethyl (allyl)malonate in D$_2$O in the presence of a catalytic amount of acid was heated at reflux for 1 day. Monodeuterated diacid **2** was detected by ^{1}H NMR spectroscopy, but was not isolated. Continued heating for an additional 4 days led to the complete conversion of **2** to dideuterated acid **3**. Reduction with LiAlH$_4$ followed by treatment with PPh$_3$Br$_2$ gave bromide **5**. Integration of the resonances in the ^{1}H NMR spectrum of **5** indicated that deuterium incorporation was greater than 95%. A ^{2}H NMR spectrum of **5** confirmed that deuterium was present exclusively in the β-position.

Bromide **5** was treated with Mg, then (COD)PtCl$_2$ to give **1**-β-d_4 in 50% yield after sublimation (eq 1). Resonances at δ 1.85 (s, broad, 1 D) and 2.17 (s, 1 D, J_{PtD} = 18 Hz) are the only two features present in the ^{2}H NMR spectrum; the deuterium atoms remain exclusively in the β-position of the pentenyl ligand upon coordination to platinum. Based on the assumption that the through-bond coupling along Pt−C5−C4−H is maximized when the dihedral angle is 180° and smallest when the angle is 90°, the resonance at δ 2.17 (exhibiting J_{PtD} = 18 Hz) has been assigned to the deuterium atoms in the pseudo-equatorial position of the puckered chelate ring. The broadness of the second deuterium resonance probably results from a smaller, unresolved coupling to platinum. In the ^{13}C NMR spectrum of **1**-β-d_4, the resonance at δ 28.70 (quin, J_{CD} = 20 Hz) confirms that the deuterium atoms are present in the β-position. The mass spectrum of **1**-β-d_4 exhibits the molecular ion at *m/e* at 337 (^{195}Pt), 4 amu greater than that for **1**. Since no scrambling or D−H exchange was detected, we conclude that the deuterium incorporation in **1**-β-d_4 is similar to that for bromide **5** (greater than 95%).

Chemical Vapor Deposition. (a) Platinum Films. Chemical vapor deposition studies were performed in both a hot wall, low pressure (10^{-3} Torr) glass tube and a hot stage, high vacuum (10^{-7} Torr) stainless steel reaction vessel. Film formation in the hot tube experiments results from a combination of gas phase and surface decomposition pathways, whereas the hot stage emphasizes surface reactivity.[1] Because of the high volatility of **1**, it was not necessary to heat the precursor reservoir to obtain a reasonable rate of film growth.

There was no indication of substrate selectivity for experiments performed with the hot stage reactor; similar platinum films were obtained on copper and glass substrates held at 200 °C. The elemental composition of the films on a copper substrate, determined by Auger electron spectroscopy, were consistently 65% Pt, 25% C, and 10% Cu. The composition remained constant to a depth of 1250 Å, at which point the percentage of copper increased dramatically.

The thermolysis of **1** in a vertical hot tube reactor (Figure 2a) resulted in the formation of a highly reflective platinum mirror at temperatures as low as 175 °C on a glass substrate. The purity of the resulting films showed no temperature dependence, as AES showed similar atomic compositions for experiments at 220 and 275 °C. After sputtering away the upper 400 Å of the film to remove contamination from contact with lab atmosphere, film composition was consistently 82% Pt and 18% C. These values remained constant to a depth of 4000 Å, at which point the depth profile analysis was terminated. A scanning electron micrograph of a film formed on a glass slide at 275 °C shows an approximate average particle diameter of 60 nm and no indication of a predominant crystallographic orientation (Figure 3). The lower level of carbon contamination in these films (as compared to the hot stage experiments) indicates that gas phase decomposition pathways are significant for this process.

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(12) Xue, Z.; Thridanam, H.; Kaesz, H. D.; Hicks, R. F. *Chem. Mater.* **1992**, *4*, 162−166.

(13) Kumar, R.; Roy, S.; Rashidi, M.; Puddephatt, R. J. *Polyhedron* **1989**, *8*, 551−553.

(14) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801−3812.

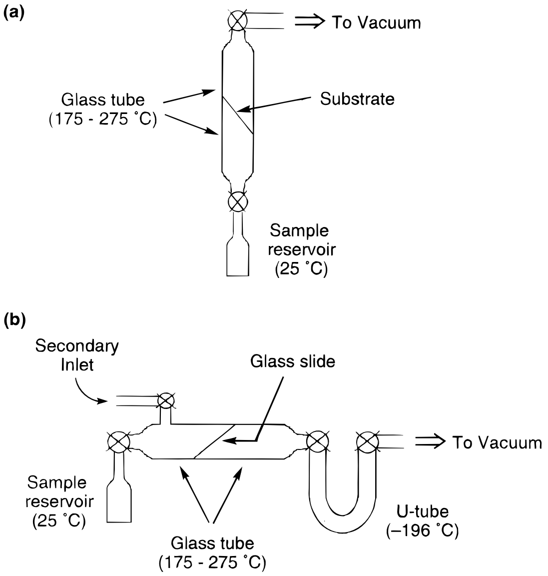


Figure 2. Schematic representations of (a) a vertical hot tube reactor and (b) a horizontal hot tube reactor equipped with a cold trap.

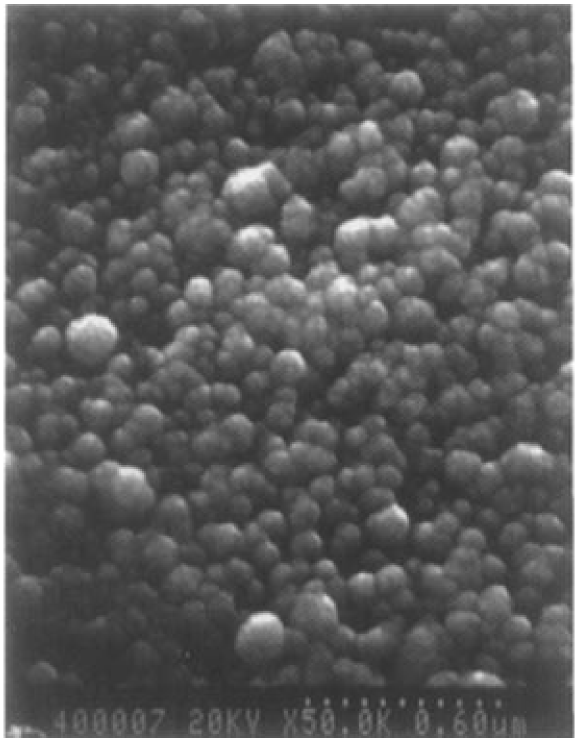
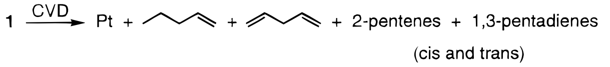


Figure 3. Scanning electron micrograph of the thin Pt film formed from the CVD of **1** on a glass slide at 275 °C.

(b) Organic Products. A horizontal hot tube reactor equipped with a U-tube cold trap (−196 °C) and a secondary inlet was employed to isolate the volatile products formed under CVD conditions (Figure 2b). The organic products from the thermolysis of **1** at 220 °C and 10 mTorr were analyzed by ^{1}H NMR spectroscopy and gas chromatography. The olefins 1-pentene, 2-pentene, 1,3-pentadiene, and 1,4-pentadiene were formed in approximately equal amounts (eq 2). This distribution

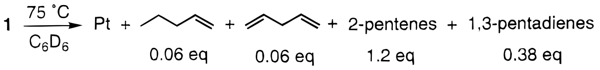


(2)

did not change with temperature or pressure. Similar results were observed for the thermolysis of **1** in a lead glass reactor (used to minimize wall effects).

The labeled olefin 1,1-dideuterio-1-pentene was introduced through the secondary inlet into the horizontal reactor both during and after the deposition of **1**. In both cases, none of the recovered labeled olefin (analyzed by ^{1}H and ^{2}H NMR spectroscopy) had isomerized.

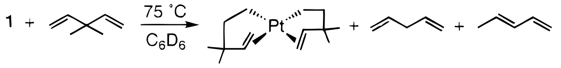
Thermolysis of 1 in Aromatic Solvents. The thermolysis of **1** in benzene-d_6 at 75 °C for 8 h results in the deposition of colloidal platinum and a mixture of olefins: 1-pentene (0.06 equiv), 2-pentene (1.2 equiv), 1,4-pentadiene (0.06 equiv), and 1,3-pentadiene (0.38 equiv) (total = 1.7 equiv) (eq 3). These ratios remained constant throughout the thermolysis and were independent of temperature. No higher alkenes, which could result from the coupling of radicals, were detected. Thermolysis of **1** in the presence of added mercury, which has been shown to trap colloidal platinum species,[15] did not affect the distribution of the organic products. Similar results were obtained when the thermolysis was conducted in the presence of O_2, H_2O, and $CHCl_3$, in different solvents (toluene-d_8 and cyclooctane), and in silylated and lead glass reaction vessels.



(3)

Added olefins (1-hexene, *trans*-3-hexene, and 1,1-dideuterio-1-pentene) were isomerized to a mixture of their isomers *during* the thermolysis of **1**, but were not isomerized when added to the reaction mixture after the decomposition of **1** was complete. Similarly, 1,4-pentadiene was isomerized to a mixture of *cis*- and *trans*-1,3-pentadiene when thermolyzed with **1**. Kinetic studies of the 1,4-pentadiene isomerization have shown that the isomerization rate of the diene exhibits first-order behavior and is similar to the rate of decomposition of **1**. Furthermore, added 1,4-pentadiene strongly inhibits the decomposition of **1** (vide infra).

Thermolysis of **1** in toluene-d_8 in the presence of 3,3-dimethyl-1,4-pentadiene completely inhibited the formation of colloidal platinum (eq 4). While free 1,3- and 1,4-pentadiene were evolved, no 1- or 2-pentene was detected by ^{1}H NMR spectroscopy. Unfortunately, the resulting organoplatinum complexes (formed in a ratio of 5:1:1) could not be completely purified. However, the similarity of the ^{1}H NMR spectrum of the major product to that of **1** is consistent with the structural formulation for **6**. Resonances at δ 3.17 (dd, 2 H, $J_{HH} = 9$ Hz, $J_{PtH} = 25$ Hz), 3.62 (dd, 2 H, $J_{HH} = 15$ Hz, $J_{PtH} = 40$ Hz), and 4.14 (m, 2 H) are characteristic of a chelated pentenyl ligand. Two singlets at δ 1.06 (s, 6 H) and 1.23 (s, 6 H) correspond to the axial and equatorial methyl groups of **6**. The tetramethyl substituted analog has a greater thermal stability than **1**, as temperatures greater than 105 °C are required for the decomposition of **6**.



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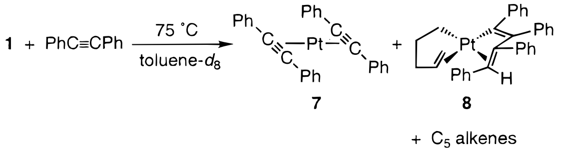
(4)

Thermolysis of 1 with Diphenylacetylene. Thermolysis of **1** in the presence of diphenylacetylene at 75 °C in toluene-d_8 completely inhibited the deposition of colloidal Pt(0), leading to the formation of organoplatinum complexes **7** and **8** (eq 5).



(5)

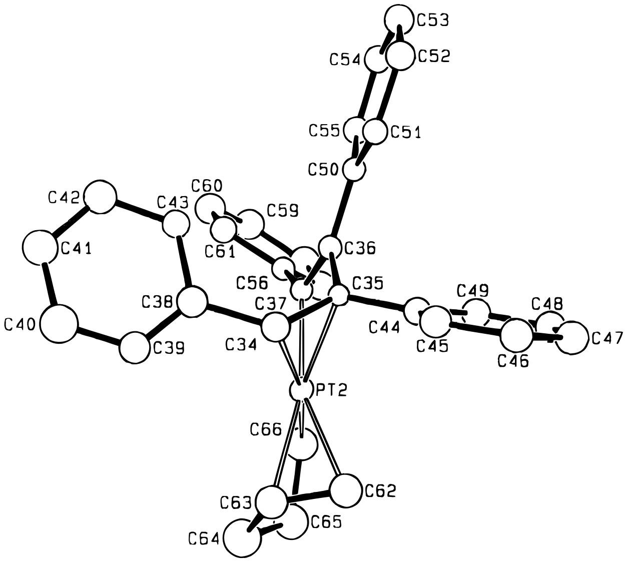


Figure 4. ORTEP drawing of one of the two independent molecules in the asymmetric unit of **8**.

In addition, the ratio of 1-pentene and 1,4-pentadiene to their thermodynamically favored isomers, 2-pentene and 1,3-pentadiene, is drastically increased. The distribution of the pentenes and pentadienes, as well as the yields of **7** and **8**, is markedly dependent on the concentration of diphenylacetylene. At low concentrations of diphenylacetylene (5 equiv), bis(diphenylacetylene)platinum (**7**), which has been characterized previously,[16] is the major organoplatinum product. As the concentration of diphenylacetylene is increased, the yields of 1-pentene, 2-pentene, 1,3-pentadiene, and **7** all approach zero, while the yields of novel organoplatinum product (**8**) and 1,4-pentadiene both approach 1 equiv.

Complex **8** was isolated from the reaction mixture in 51% yield by chromatography on silica followed by recrystallization from a toluene/hexane solution. The low temperature (255 K) ^{1}H NMR spectrum of **8** exhibits alkyl resonances at δ 1.50 (m, 3 H) and 2.00 (m, 3 H), and olefinic resonances at δ 3.24 (d, 1 H, $J_{HH} = 9$ Hz, $J_{PtH} = 41$ Hz), 3.92 (d, 1 H, $J_{HH} = 15$ Hz, $J_{PtH} = 49$ Hz), and 5.38 (m, 1 H) that are characteristic of a chelated pentenyl ligand.[17] In addition, there is a vinyl resonance at δ 5.95 (s, 1 H, $J_{PtH} = 18$ Hz) and several aryl resonances having a cumulative integration of 20 protons. There are 25 distinct carbon resonances in the ^{13}C NMR spectrum. The molecular ion appears at *m/e* = 691 in the mass spectrum.

A single crystal X-ray diffraction study indicates that **8** has retained one chelating pentenyl ligand and has added a chelating 1,2,3,4-tetraphenylbuta-1,3-dien-1-yl ligand (Figure 4). There is one toluene solvate molecule, which has different intermolecular contacts to the two independent molecules of **8** in the asymmetric unit. The molecules have very similar structural parameters and are related by a pseudo-2-fold screw axis. Each Pt is essentially square-planar coordinate in which the two σ-bound carbons are oriented cis to one another and each is trans to a coordinated π-bond. The stereochemistry about the terminal double bond of the tetraphenylbutadienyl ligand is trans.[18−22]

Kinetics. The thermolysis of **1** was monitored by following the disappearance of **1** (0.069 M in toluene-d_8) by ^{1}H NMR spectroscopy in a sealed tube at 87 °C. In the absence of added reagents, the decomposition of **1** to colloidal platinum, pentenes, and pentadienes obeyed clean first-order kinetics ($k_{obs} = 4.15 \times 10^{-4}$ s^{-1}). There was no induction period, nor any evidence of an autocatalytic reaction. The decomposition of **1** is slightly accelerated by added diphenylacetylene ($k_{obs} = 1.1 \times 10^{-3}$ s^{-1}; [PhC≡CPh] = 0.34 M), and strongly inhibited by added 1,4-pentadiene ($k_{obs} = 1.9 \times 10^{-5}$ s^{-1}; [1,4-pentadiene] = 0.97 M). No intermediates were detected in any of the preceding reactions.

The effect of diphenylacetylene concentration on the rate of decomposition of **1** has been thoroughly investigated. As 1,4-pentadiene is produced during the course of the reaction, free 1,4-pentadiene was added in order to maintain pseudo-first-order conditions. The decomposition of **1** (0.028 M in toluene-d_8; [1,4-pentadiene] = 0.32 M; monitored by ^{1}H NMR spectroscopy at 77 °C) is accelerated by diphenylacetylene, but the rate appears to saturate at higher concentrations of the alkyne (Figure 5a). Because of concentration limitations (due to solubility and detection), the saturation point could not be reached under these conditions.

Fortunately, the maximum diphenylacetylene-independent or "saturation" rate was achieved in the experiments conducted without added 1,4-pentadiene. In the absence of added 1,4-pentadiene, the rate of decomposition of **1** at 77 °C showed no dependence on the concentration of diphenylacetylene (Figure 5b). These data were combined with those from the experiments in the presence of 1,4-pentadiene to construct an inverse plot of 1/k_{obs} vs [1,4-pentadiene]/[PhC≡CPh] (Figure 5c).[23] The rate at saturation for the decomposition of **1** ($k_{sat} = 3.08 \pm 0.25 \times 10^{-4}$ s^{-1}) was calculated from the intercept of the inverse plot. The activation parameters ($\Delta H^{\ddagger} = 32.3 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = 18 \pm 1$ eu, 77 °C) for the decomposition of **1** under saturation conditions were determined from a temperature dependence study (62.5−93 °C).

Thermolysis of 1-*β*-*d*$_4$. The decomposition of **1**-β-d_4 (0.028 M in toluene-d_8) under saturation conditions ([PhC≡CPh] = 0.60 M; [1,4-pentadiene]$_0$ = 0 M) at 77 °C was monitored by ^{1}H NMR spectroscopy. The measured rate constant was 0.80 ± 0.02 × 10^{-4} s^{-1}, showing that the reaction exhibits a substantial β-deuterium isotope effect of $k_H/k_D = 3.8$. The only organic product, 2-deuterio-1,4-pentadiene, was identified by ^{1}H NMR spectroscopy and GC/MS. The organoplatinum products, identified by ^{1}H NMR spectroscopy, were a mixture of **7** and **8**. From the ^{1}H and ^{2}H NMR spectra it is apparent that deuterium atoms are present only in the pentenyl ligand of **8**; no deuterium atoms were detected in the terminal vinyl position of the butadienyl ligand. A mass spectrum of the mixture of organoplatinum products indicates that both **8**-d_2 and **8**-d_3 are present.

Reaction with H$_2$. Upon treatment with H$_2$, solid **1** decomposes rapidly at room temperature to yield colloidal

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[15] Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinsky, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819−1830.

[16] Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 759−760.

[17] At room temperature the NMR spectra are broad. At low temperature a small amount (<5%) of a minor isomer was detected. The fluxional process was not investigated.

[18] Isomerization to give the *E* isomer is common for alkyne insertion reactions (see refs 19−22).

[19] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002−3011.

[20] Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505−5512.

[21] Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 189−198.

[22] Clark, H. C.; Fiess, P. L.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 177−188.

[23] Since 1,4-pentadiene is produced during the course of the reaction, the value for [1,4-pentadiene] was set to 0.014 M, the average of the amount produced. However, use of values ranging from 0.0001 to 0.028 M for this concentration gives similar plots.

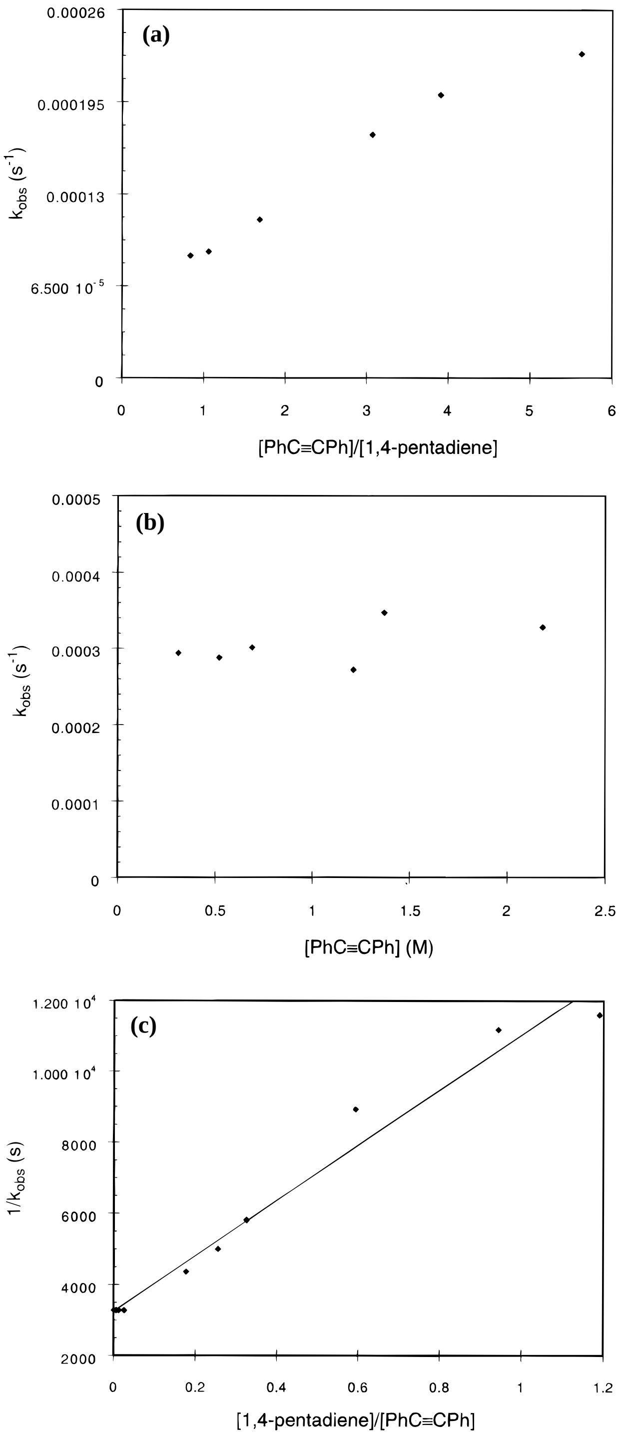
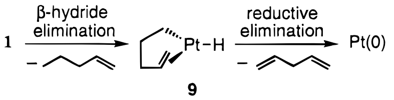
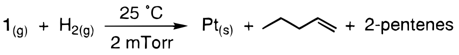


Figure 5. Kinetic data for the decomposition of **1** in the presence of PhC≡CPh (77 °C, toluene-d_8): (a) the plot of the observed rate constant for the decomposition of **1** with respect to the concentration of diphenylacetylene in the presence of added 1,4-pentadiene; (b) the plot of the observed rate constant for the decomposition of **1** with respect to the concentration of diphenylacetylene in the absence of added 1,4-pentadiene; (c) the inverse plot.

platinum. Because of our reactor design (Figure 2a), this facile reaction prevented detailed CVD studies as platinum deposited before reaching the substrate (a suitable gas inlet/substrate arrangement will permit film analysis). In a closed system in both solution and the solid state, the final organic product was pentane, presumably resulting from hydrogenation of the olefins catalyzed by Pt(0). Hydrogenation was avoided by treating the vapor of **1** with hydrogen gas under dynamic vacuum (0.2 Torr) using the apparatus shown in Figure 2b. Again, platinum deposited rapidly at room temperature and the organic products were collected at 77 K. Spectroscopic analysis showed that 1-pentene and 2-pentene were formed in approximately equal amounts (eq 6).

Scheme 2





(6)

Discussion

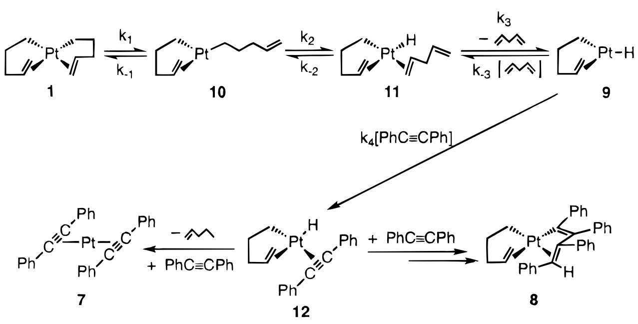
Chemical Vapor Deposition. The pent-4-en-1-yl ligand has shown great promise as a ligand for the preparation of organometallic CVD precursors. The chelating ligand has a low molecular weight and leads to a compact structure enhancing the volatility of the resulting organometallic complex. Most important for CVD applications, we have demonstrated that the chelated bis-pentenyl complex of platinum undergoes a facile, low energy, relatively clean decomposition reaction that deposits thin platinum films. Thermolysis of **1** in a hot tube CVD reactor (Figure 2a) produced films of unusually high purity for an organoplatinum precursor, comparable to Puddephatt's (MeNC)$_2$-PtMe$_2$ complex (vide supra).[8] In addition, **1** decomposes under unusually mild conditions. Unfortunately, the facile reaction of **1** with dihydrogen at 25 °C precluded detailed CVD studies using dihydrogen as a carrier gas with the present CVD apparatus.

Mechanism. Initially, we expected the thermal decomposition of **1** to involve β-hydride elimination and dissociation of 1,4-pentadiene to give a three-coordinate platinum hydride intermediate (**9**), followed by reductive elimination of 1-pentene to deposit a platinum film (Scheme 2). However, analysis of the volatile products from CVD experiments showed a mixture of the expected kinetic products (1-pentene and 1,4-pentadiene) and an approximately equivalent amount of their thermodynamically favored isomers 2-pentene and 1,3-pentadiene (predominately trans isomers). While control experiments are difficult to rigorously conduct in a heterogeneous system, we made a serious effort to determine whether alkene isomerization is catalyzed by the platinum film. The fact that an isotopically labeled alkene (1,1-dideuterio-1-pentene) did not isomerize when introduced into the CVD reactor both during and after the decomposition of **1** suggests that the film is not a catalyst for alkene isomerization.

In order to study the thermolysis of **1** as quantitatively as possible, we investigated the decomposition of **1** in aromatic solvents, a relatively nonpolar medium. The thermolysis of **1** in benzene-d_6 gives the same organic products as those observed under CVD conditions. However, the ratio of the expected kinetic products, 1-pentene and 1,4-pentadiene, to 2-pentene and 1,3-pentadiene is very low. The decomposition obeys clean, first-order kinetics. There is no evidence for autocatalysis by either colloidal platinum or other products. As no decadienes are produced and no free radical abstraction of hydrogen or chlorine atoms was observed when the reaction was conducted in the presence of CHCl$_3$, a mechanism involving homolytic cleavage of the Pt−C σ-bond to give pentenyl radicals is unlikely.

Added 1,4-pentadiene severely retards the rate of decomposition of **1**, which could reflect either of two equilibria for the decomposition process: association of 1,4-pentadiene with **1**, or reversible dissociation of 1,4-pentadiene from **1**. Since we

Scheme 3



do not detect the formation of a 1,4-pentadiene adduct (or the disappearance of **1**), we exclude the associative mechanism. Thus, reversible dissociation of 1,4-pentadiene from **1** must precede (or be) the rate determining step in the mechanism of decomposition of **1**.[24−30] That 3,3-dimethyl-1,4-pentadiene is incorporated into the platinum complex (to form **6**) during the thermolysis of **1** is further evidence for the reversibility of 1,4-pentadiene dissociation.

Although added 1,4-pentadiene inhibits the decomposition of **1**, it is slowly isomerized to *cis*- and *trans*-1,3-pentadiene. Similarly, added alkenes (1-hexene and 1,1-dideuterio-1-pentene) rapidly isomerize to a mixture of their isomers *during*, but not before or after, the thermal decomposition of **1** in aromatic solvents. Since alkene isomerization occurs only during the decomposition of **1** and obeys first-order kinetics, we conclude that a transient intermediate platinum complex that is a highly active olefin isomerization catalyst is formed during the thermolysis.

The catalytically active intermediate can be trapped chemically with diphenylacetylene. As the alkyne concentration is increased, the yields of the expected kinetic products 1-pentene and 1,4-pentadiene increase at the expense of the isomerized products 2-pentene and 1,3-pentadiene, indicating that diphenylacetylene inhibits olefin isomerization. At very high concentrations of the alkyne, only 1,4-pentadiene is produced; alkene isomerization and the formation of 1-pentene have been eliminated.

A kinetic study showed that added diphenylacetylene results in only a slight rate acceleration for the decomposition and clean first-order behavior in **1**. The reaction is inhibited by added 1,4-pentadiene, and at high ratios of alkyne to diene the reaction reaches saturation (the rate is no longer dependent on the concentration of diphenylacetylene). These data indicate that the alkyne captures a platinum intermediate and does not create a new decomposition pathway by direct reaction with **1**.

The results summarized above for the decomposition of **1** can be rationalized by the mechanism shown in Scheme 3. Initial, reversible pentenyl de-chelation to give **10**, followed by β-hydride elimination to yield **11** and reversible 1,4-pentene dissociation, leads to three-coordinate platinum hydride intermediate **9**. In the gas phase or in solution in the absence of traps, reductive elimination of 1-pentene from **9** deposits metallic platinum. In aromatic solvents diphenylacetylene rapidly traps **9** to give alkyne adduct **12**. Intermediate **12** may then reductively eliminate 1-pentene, and be trapped by a second equivalent of diphenylacetylene to give **7**, or consecutively insert two molecules of diphenylacetylene to yield **8**. Our evidence indicates that **9** is a highly active isomerization catalyst and catalyzes the isomerization of kinetic products 1-pentene and 1,4-pentadiene to 2-pentene and 1,3-pentadiene, respectively. The lower than theoretical yield of organic products (ca. 85%) in the absence of diphenylacetylene presumably results from a secondary decomposition pathway.

Using the steady-state assumption, the rate law associated with the mechanism illustrated in Scheme 3 can be derived; it is given in eq 7. At high ratios of [PhC≡CPh]/[1,4-pentadiene],

$$\text{Rate} = \frac{k_1k_2k_3k_4[\text{PhC}{\equiv}\text{CPh}][\mathbf{1}]}{k_{-1}k_{-2}k_{-3}[\text{1,4-pentadiene}] + (k_2k_3 + k_{-1}k_3 + k_{-1}k_{-2})k_4[\text{PhC}{\equiv}\text{CPh}]} = k_{\text{obs}}[\mathbf{1}] \qquad (7)$$

the [1,4-pentadiene] term becomes negligible and the expression for k_{obs} becomes a constant value (eq 8). Thus, the rate law

$$k_{\text{obs}} = \frac{k_1k_2k_3}{k_2k_3 + k_{-1}k_3 + k_{-1}k_{-2}} \qquad (8)$$

for the above mechanism predicts the experimentally observed rate saturation at high ratios of [PhC≡CPh]/[1,4-pentadiene]. Furthermore, the large, positive entropy of activation (18 ± 1 eu) suggests that substantial rotational and/or translational freedom is acquired in or before the rate determining transition state. This is consistent with the presence of de-chelation in the pre-equilibrium steps and with the proposed rate-limiting dissociation of 1,4-pentadiene.

While alkene de-chelation cannot be detected kinetically, there is much theoretical and experimental evidence that direct β-hydride elimination from a four-coordinate square-planar d^8 complex with a constrained configuration, such as **1**, must be a high energy process. In a theoretical investigation, Thorn and Hoffmann concluded that β-hydride elimination proceeds much more readily from a three-coordinate d^8 intermediate.[31] Whitesides and co-workers have extensively studied the decomposition reactions of L_2PtR_2 (L = phosphine; R = alkyl) complexes and have found that the lowest energy β-hydride eliminations occur in systems where a phosphine dissociates to give a three-coordinate $LPtR_2$ intermediate.[32−34] When phosphine dissociation is inhibited by using a chelating phosphine, β-hydride elimination does not take place until much higher temperatures are reached.[34] Furthermore, Thorn and Hoffmann have calculated that the lowest energy transition state for β-hydride elimination involves a PtCCH dihedral angle of 0°.[31] Whitesides and co-workers have shown that β-hydride elimination is severely retarded in constrained platinum metallacycles that cannot achieve this angle.[35,36] Finally, Flood and co-workers have estimated the Pt−alkene bond strength to be less than 28

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(24) There are several examples of square-planar d^8 organometallic complexes, having strong σ-donating, trans-activating alkyl ligands, which undergo substitution by dissociation of a neutral ligand to give a three-coordinate 14-electron intermediate (see refs 25−30).

(25) Alibrandi, G.; Bruno, G.; Lanza, S.; Minniti, D.; Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1987**, *26*, 185−190.

(26) Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481−1490.

(27) Frey, U.; Helm, L.; Merbach, A. E.; Romeo, R. *J. Am. Chem. Soc.* **1989**, *111*, 8161−8165.

(28) Lanza, S.; Minniti, D.; Romeo, R.; Moore, P.; Sachinidis, J.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 542−543.

(29) Minniti, D.; Alibrandi, G.; Tobe, M. L.; Romeo, R. *Inorg. Chem.* **1987**, *26*, 3956−3958.

(30) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631−2634.

(31) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079−2090.

(32) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550−1557.

(33) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 1676−1678.

(34) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258−5270.

(35) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521−6528.

(36) Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1473−1480.

kcal/mol for a complex with a chelating pentenyl ring similar to that in complex **1**.[37] Under the reaction conditions employed for the thermolysis of **1** (77 °C), there would be sufficient energy to break such a bond.

We propose that β-hydride elimination occurs in a pre-equilibrium step, prior to the rate determining dissociation of 1,4-pentadiene. The observed β-deuterium isotope effect ($k_H/k_D = 3.8$) is of a magnitude normally interpreted as evidence for direct involvement of C−H bond-breaking in the rate determining step. However, Whitesides and co-workers have reported similar values (2.3 and 3.0) for equilibrium kinetic isotope effects for platinum dialkyl complexes.[26,32] Furthermore, Jones and Feher have observed an equilibrium kinetic isotope effect of $k_H/k_D = 2.7$ in a rhodium system.[38]

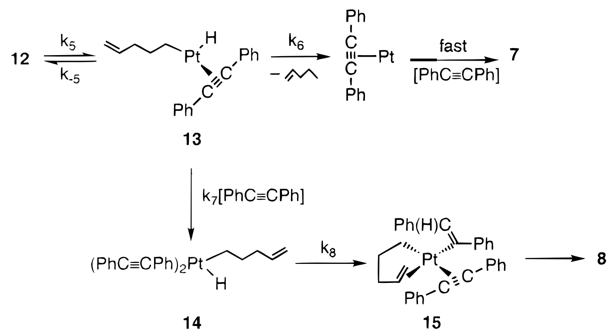
In the presence of diphenylacetylene we cannot rigorously exclude an associative mechanism in which there is a direct equilibrium between **11** and **12** (in such a mechanism the rate would saturate at k_2, the β-hydride elimination step). However, diphenylacetylene does not react directly with **1** and our kinetic results obtained in the absence of diphenylacetylene have shown that substitution of 1,4-pentadiene in **11** proceeds by a dissociative mechanism. Thus, we believe that a mechanism involving the associative attack of diphenylacetylene on **11** and the reverse reaction of attack by 1,4-pentadiene on **12** is unlikely.

Organoplatinum Products. The conversion of intermediate alkyne adduct **12** to products **7** and **8** occurs after the rate determining step, making direct investigation of this part of the process difficult. However, we can draw some conclusions about the reaction pathways from the fact that the ratio of **8**/**7** increases with increasing diphenylacetylene concentration. Presumably, **7** results from reductive elimination of 1-pentene from **12** followed by rapid reaction with diphenylacetylene. Product **8** appears to result from the insertion of diphenylacetylene into the platinum−hydride bond of **12** followed by the insertion of a second molecule of alkyne into the resulting platinum−vinyl bond to give the chelated product.

A mechanism involving the direct attack of diphenylacetylene on **12** to accelerate alkyne insertion (and prevent reductive elimination) would account for the observed dependence of the relative yields of **7** and **8** on alkyne concentration. However, theoretical calculations indicate that the low energy pathway for alkyne insertions in platinum(II) systems proceeds from four-coordinate square-planar complexes.[31] There is much experimental evidence to substantiate this prediction.[19,20,22,39] In addition, as mentioned above, we have not obtained any evidence for the associative attack of diphenylacetylene on **1** or any 4-coordinate intermediate in this system. Thus, we disfavor an associative mechanism for the conversion of **12** to **8**.

A second, more plausible mechanism that accounts for the observed dependence of the product yields on alkyne concentration is shown in Scheme 4. Rapid, reversible de-chelation of the pentenyl ligand generates transient intermediate **13**. Reaction with free diphenylacetylene forms **14**, and accounts for the observed alkyne concentration dependence. Irreversible alkyne insertion produces **15** and prevents reductive elimination. A second insertion of diphenylacetylene into the platinum vinyl bond of **15** gives **8**. Because reductive elimination of 1-pentene could potentially occur from **12** and **14** as well as **13**, we conclude that the alkyne trapping and insertion steps must be faster than reductive elimination of the alkene.[40]

Scheme 4



Isomerization of Kinetic Alkene Products. Many transition metal hydride complexes have been shown to catalyze alkene isomerization through consecutive steps of alkene insertion and β-hydride elimination.[41] Our kinetic studies have indicated that alkene insertion/β-hydride elimination is a reversible step in the decomposition of **1**. The fact that added olefins are isomerized exclusively *during* the thermolysis of **1** necessitates the presence of a transient intermediate that is a highly active alkene isomerization catalyst. It is reasonable to conclude that intermediate **9** is responsible for the isomerization of the expected kinetic products of the thermolysis of **1**, 1-pentene, and 1,4-pentadiene. The fact that the trapping of **9** with diphenylacetylene leads to a drastic reduction in isomerization supports this conclusion. Furthermore, **9** has an open coordination site, which would facilitate the complexation and isomerization of added alkenes. Presumably, diphenylacetylene inhibits alkene isomerization through preferential occupation of the open coordination site.

Relationship between the Thermal Decomposition of 1 Under Nonpolar Solution and CVD Conditions. Detailed kinetic studies of the decomposition of **1** are more straightforward to carry out in solution than in the CVD reactor itself. In the absence of direct mechanistic studies under CVD conditions, we cannot be certain that the mechanism that we have elucidated in solution is necessarily the same as that which operates under CVD conditions. However, the pentene and pentadiene products observed in the hot tube experiments are the same as those seen in solution. The differences observed in the product ratios between the CVD and solution phase reactions can be attributed to the increased contact time in solution. Thus, it is likely that an intermediate platinum hydride is formed during the hot tube thermolysis reaction and that its behavior parallels that seen in nonpolar solutions. While we cannot determine if the platinum hydride complex is present in the gas phase or on the platinum surface, our CVD experiments indicate that gas phase decomposition pathways are significant for the hot tube reactions (vide supra). The carbon contamination of the Pt films presumably results from the secondary decomposition pathway proposed for the decomposition of **1** in aromatic solvents in the absence of diphenylacetylene.

Summary

We have described the synthesis of a novel, volatile organoplatinum(II) complex (**1**), which has proved useful for the

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[37] Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634−2643.

[38] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650−1663.

[39] Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *87*, C45−C47.

[40] A mechanism involving rapid, reversible alkyne insertion would also account for the observed effect of diphenylacetylene concentration. However, to our knowledge, there have been no reports of facile β-hydride elimination from a vinyl complex.

[41] Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1992.

chemical vapor deposition of thin platinum films of relatively high purity (82% Pt). We attribute the unusual volatility of **1** to the compact structure imparted by the two chelating pent-4-en-1-yl ligands. A comprehensive investigation of the mechanism of decomposition of **1** in aromatic solvents revealed the presence of a transient three-coordinate platinum hydride (**9**) that catalyzes the isomerization of the kinetic products 1-pentene and 1,4-pentadiene to 2-pentene and 1,3-pentadiene. The intermediate isomerization catalyst was chemically trapped with diphenylacetylene.

Experimental Section

General. For a description of the instrumentation and general procedures used, please see earlier papers from these laboratories.[42,43]

Unless otherwise specified all reagents were purchased from commercial suppliers and used without subsequent purification. Diethyl ether, toluene, hexamethyldisiloxane, and benzene were distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents were vacuum transferred from sodium benzophenone ketyl. Diphenylacetylene was purified by sublimation. The reagents (COD)$PtCl_2$,[35] 2,2-dimethyl-3-butenal,[44] and $R_2C{=}PPh_3$ (R = H, D) were prepared according to literature procedures. Powderless gloves were worn during all sample or CVD chamber manipulations. All CVD substrates (glass slide, silicon wafer, or copper foil) were washed with 2-propanol and distilled H_2O and dried under a stream of argon prior to use. Argon (99.9%) and hydrogen (99.999%) were used as received.

Chemical Vapor Deposition. Three types of CVD chambers were used in this study: a hot stage reactor, a vertical hot wall reactor, and a horizontal hot wall reactor equipped with a U-tube cold trap. The hot stage reactor consisted of an evacuated (10^{-7} Torr) stainless steel chamber equipped with a heatable sample stage (a copper block resistively heated by a current passing through a tungsten wire) and a sample/carrier gas/reactive gas inlet placed ~5 cm from the hot stage. In this device, only the sample stage was heated. The remainder of the chamber was kept at ambient temperature.

The vertical hot wall reactor consisted of a dynamically pumped (10^{-3} Torr) 60 cm long Pyrex tube, at one end of which was placed the CVD precursor. This section of the tube was kept at room temperature during the CVD run. Approximately 20 cm from this area was a 20 cm long hot zone in which the CVD substrate was placed. The hot zone of the reaction chamber was wrapped with a layer of heating tape and then a layer of aluminum foil. The temperature was interactively controlled and monitored via a thermocouple placed between the heating tape and the glass tube. The system was heated at 300 °C for 1 h prior to use (the precursor reservoir was cooled to −196 °C during this period). The system was designed so that a controlled flow of either a carrier gas (Ar) or a reactive gas (H_2) could pass over the precursor and toward the hot zone.

The precursor reservoir and hot zone of the horizontal hot tube reactor were similar to those for the vertical reactor. In addition, the horizontal reactor was equipped with a secondary inlet between the precursor reservoir and the hot zone. Volatile products were collected in a U-tube (cooled to −196 °C) connected to the end of the hot tube. The experiments were conducted under both static and dynamic vacuum (10 mTorr). At the conclusion of each type of CVD experiment (typically 1 h), the reaction chamber or hot stage was slowly cooled (while under dynamic vacuum) to room temperature.

The compositions of the platinum films from the hot stage and vertical hot tube experiments were determined by Auger electron spectroscopy, the film adherence was tested with Scotch tape (passed in all cases), and the film morphology was analyzed by scanning electron microscopy at the University of Illinois Materials Research Lab. Volatile products from the horizontal hot wall reactor experiments were vacuum transferred into a solvent (benzene or benzene-d_6) and analyzed by NMR spectroscopy and gas chromatography.

(η^1,η^2-C_5H_9)$_2$Pt (1). A 100-mL Schlenk flask was charged with Mg (0.122 g, 5.02 mmol), 1 crystal of I_2, and Et_2O (20 mL). The mixture was stirred under N_2 for 1 h, and 5-bromo-1-pentene (0.60 mL, 5.1 mmol) was added by syringe. The mixture was stirred for 6 h, then cooled to 0 °C. The solution was transferred away from the undissolved Mg by cannula to a 100-mL Schlenk flask containing (COD)$PtCl_2$ (0.53 g, 1.4 mmol) in Et_2O (20 mL) under nitrogen at 0 °C. The mixture was stirred at 0 °C for 30 min. The excess Grignard reagent was quenched with distilled H_2O (0.5 mL) and the mixture was allowed to warm to room temperature. The solution was dried with magnesium sulfate and filtered through Celite, which was washed with Et_2O (60 mL). The combined filtrates were concentrated by rotary evaporation to a viscous yellow oil. The oil was purified by sublimation (25 °C, 10 mTorr) to yield yellow crystals (0.390 g, 83%). MS (EI) *m/e* Calcd: 332 (88%, ^{194}Pt), 333 (100%, ^{195}Pt). Found: 332 (90%), 333 (65%), indicating a mixture of M^+ and $(M - H)^+$. The base peak appeared at *m/e* = 259 (100%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 2.00 (m, 12 H), 3.25 (d, 2 H, $J_{HH} = 9$ Hz, $J_{PtH} = 28$ Hz), 3.65 (d, 2 H, $J_{HH} = 16$ Hz, $J_{PtH} = 40$ Hz), 4.45 (m, 2 H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ 28.70 (s, $J_{PtC} = 40$ Hz), 32.31 (s, $J_{PtC} = 811$ Hz), 33.76 (s, $J_{PtC} = 24$ Hz), 80.00 (s, $J_{PtC} = 50$ Hz), 113.1 (s, $J_{PtC} = 40$ Hz). DEPT90: δ 113.1 (CH). Mp 40−41 °C. Anal. Calcd for $C_{10}H_{18}Pt$: C, 36.03; H, 5.44. Found: C, 36.23; H, 5.48.

(η^1,η^2-$C_5H_7D_2$)$_2$Pt (1-β-d_4). Complex **1**-β-d_4 was prepared by the same method used for its protiated analog, replacing 5-bromo-1-pentene with 5-bromo-4,4-dideuterio-1-pentene. MS (EI) *m/e* Calcd: 336 (88%, ^{194}Pt), 333 (100%, ^{195}Pt). Found: 336 (100%), 337 (96%), indicating a mixture of M^+ and $(M - H)^+$. This mixture precluded analysis of deuterium incorporation by examination of the mass spectrum. ^{1}H NMR (400 MHz, C_6D_6, 298 K): same as **1** except for δ 2.00 (m, 8 H). ^{2}H NMR (60 MHz, C_6H_6, 298 K): δ 1.86 (s, 1 D, broad), 2.17 (s, 1 D, $J_{PtD} = 18$ Hz). ^{13}C NMR (75.5 MHz, C_6D_6, 298 K): δ 28.2 (quin, $J_{DC} = 20$ Hz, J_{PtC} could not be resolved), 32.1 (s, $J_{PtC} = 811$ Hz), 33.6 (s, $J_{PtC} = 26$ Hz), 80.0 (s, $J_{PtC} = 45$ Hz), 113.1 (s, $J_{PtC} = 45$ Hz). DEPT45: δ 32.1, 33.6, 80.0, 113.1.

Thermolysis of 1 with PhC≡CPh: (η^2-PhC≡CPh)$_2$Pt (7). A glass bomb was charged with **1** (0.034 g, 0.102 mmol), PhC≡CPh (0.085 g, 0.48 mmol), and benzene (6 mL) under nitrogen. The solution was heated at 75 °C for 15 h and then evaporated to dryness. The brown residue was dissolved in Et_2O (3 mL) and stored at −35 °C for 15 h. The resulting white crystals were washed with Et_2O (2 × 1 mL) and dried *in vacuo* giving 0.028 g (0.051 mmol, 50%) of **7**. The identity of **7** was confirmed by comparison of ^{13}C NMR and IR spectral data with literature values.[16]

Thermolysis of 1 with PhC≡CPh: (η^1,η^2-C_5H_9)(η^1,η^2-C_4Ph_4H)Pt·0.5 toluene (8). A 30-mL glass bomb was charged with **1** (0.064 g, 0.19 mmol), PhC≡CPh (2.25 g, 12.6 mmol), and toluene (5 mL) under nitrogen. The solution was heated at 75 °C for 5 h and then was evaporated to dryness. The yellow residue was chromatographed on a column of silica (2 cm × 10 cm) under nitrogen using a solution of 90/10 hexanes/toluene as eluent. The excess diphenylacetylene eluted first, followed by a bright yellow band which was evaporated to dryness (0.080 g). The yellow solid was crystallized from a 75/25 hexanes/toluene solution (5 mL) stored at −35 °C for 4 days to yield 0.065 g (0.097 mmol, 51%) of yellow block-like crystals of **8**. MS (EI) *m/e* Calcd for ^{195}Pt: 621. Found: 621 (M^+, 78%). The base peak appeared at *m/e* = 552 ($M^+ - C_5H_9$, 100%). ^{1}H NMR (300 MHz, CH_2Cl_2, 255 K): major isomer (there is a small amount (5%) of what appears to be a minor isomer) δ 1.50 (m, 3H), 2.00 (m, 3H), 3.24 (d, 1 H, $J_{HH} = 9$ Hz, $J_{PtH} = 41$ Hz), 3.92 (d, 1 H, $J_{HH} = 15$ Hz, $J_{PtH} = 49$ Hz), 5.38 (m, 1 H), 5.91 (s, 1 H, $J_{PtH} = 19$ Hz), 6.94 (m, 2 H), 7.05 (m, 6 H), 7.30 (m, 8 H), 7.66 (m, 2H), 7.80 (m, 2H). ^{13}C NMR (101 MHz, CH_2Cl_2, 255 K, J_{PtC} could not be resolved in this experiment): δ 22.7, 26.7, 32.4, 76.4, 98.3, 103.0, 108.2, 124.7, 124.9, 126.6, 126.9, 127.1, 128.0, 128.1, 128.2, 128.5, 128.8, 129.1, 138.3, 138.6, 138.9, 140.7, 143.1, 156.4. IR (KBr): 555 (w), 694 (s), 729 (w), 750 (w), 763 (m), 1381 (w), 1441 (m), 1483 (w), 1492 (w), 1597 (w), 2850 (w), 2922 (w), 3018 (w), 3057 (w). Anal. Calcd for $C_{36.5}H_{34}Pt$ (**8**·0.5toluene): C, 65.65; H, 5.13. Found: C, 65.40; H, 5.18.

$H_2C{=}CHCH_2CD_2CO_2H$ (3). A 200-mL two-neck round-bottomed flask equipped with a reflux condenser was charged with D_2O (75 mL) under nitrogen. Acetyl chloride (0.40 mL, 5.6 mmol) was added

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(42) Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1995**, *117*, 1814−1827.

(43) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 3822−3835.

(44) Crawford, R. J.; Lutener, S.; Tokunaga, H. *Can. J. Chem.* **1977**, *55*, 3951−3954.

dropwise by syringe and the mixture was stirred for 5 min to generate a catalytic amount of acid. Diethyl (allyl)malonate (7.5 mL, 38 mmol) was added by syringe and the mixture was heated at reflux. The progress of the reaction was monitored by ^{1}H NMR spectroscopic analysis of aliquots from the reaction mixture. The reaction was complete after 5 days. The solution was cooled to room temperature and was extracted with Et_2O. The organic solution was dried over magnesium sulfate, filtered through Celite, and concentrated by rotary evaporation to give 3.35 g (87%) of **3** as a viscous off-white liquid. The ^{1}H NMR spectrum of **3** was compared to that of the parent 4-pentenoic acid. Spectroscopic data for **3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 2.35 (d, 2 H, $J_{HH} = 6$ Hz), 5.00 (dd, 1 H, $J_{HH} = 1$ Hz, $J_{HH} = 10$ Hz), 5.06 (dd, 1 H, $J_{HH} = 1$ Hz, $J_{HH} = 17$ Hz), 5.80 (m, 1 H). Spectroscopic data for $H_2C{=}CHCH_2CH_2CO_2H$: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 2.35 (m, 2 H), 2.44 (m, 2 H), 5.00 (dd, 1 H, $J_{HH} = 1$ Hz, $J_{HH} = 10$ Hz), 5.06 (dd, 1 H, $J_{HH} = 1$ Hz, $J_{HH} = 17$ Hz), 5.80 (m, 1 H).

$H_2C{=}CHCH_2CD_2CH_2OH$ (4). A 100-mL three-neck round-bottomed flask equipped with a reflux condenser was charged with $LiAlH_4$ (1.50 g, 39.5 mmol) and Et_2O (50 mL) under nitrogen. Complex **3** (2.0 g, 19 mmol) was added dropwise by syringe and the mixture was heated at reflux for 12 h. The flask was cooled to room temperature and 8 mL of 3% NaOH (aq) was added and the mixture was stirred for 30 min. The solution was filtered through Celite and concentrated by rotary evaporation to yield 1.54 g (17.5 mmol, 92%) of **4** as a clear liquid. The ^{1}H NMR spectrum of **4** was compared to that of the parent 4-penten-1-ol. Spectroscopic data for **4**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.67 (br s, 1 H), 2.10 (d, 2 H, $J_{HH} = 7$ Hz), 3.62 (s, 2 H), 4.97 (m, 2H), 5.80 (m, 1 H). Spectroscopic data for $H_2C{=}CHCH_2CH_2CH_2OH$: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.63 (m, 3 H, the resonances for the acidic proton and β-protons overlap), 2.10 (vq, 2 H, $J_{HH} = 8$ Hz), 3.62 (t, 2 H, $J_{HH} = 7$ Hz), 5.97 (m, 2 H), 5.80 (m, 1 H).

$H_2C{=}CHCH_2CD_2CH_2Br$ (5). A 300-mL three-neck round-bottomed flask equipped with a pressure-equalizing addition funnel was charged with *N*-bromosuccinimide (11.5 g, 64.6 mmol) and CH_2Cl_2 (100 mL) under nitrogen. The orange slurry was cooled to 0 °C and a solution of PPh_3 (16.0 g, 61.1 mmol) in CH_2Cl_2 was added by addition funnel over 20 min. Pyridine (2.2 g, 28 mmol) was added by syringe. To the maroon mixture, a solution of **4** (1.54 g, 17.5 mmol) in CH_2Cl_2 (50 mL) was added by addition funnel over 30 min. The mixture was stirred for 40 h at room temperature, then diluted with pentane (75 mL), filtered through Celite, and concentrated to a volume of 10 mL. The clear solution was vacuum transferred to a 25-mL round-bottomed flask. Pentane was removed by distillation (40 °C). Vacuum transfer of the remaining volatile materials afforded 0.400 g (2.64 mmol, 15%) of **5** as a clear liquid. The ^{1}H NMR spectroscopic and GC/MS data of **5** were compared to that of the parent 5-bromo-1-pentene. Spectroscopic data for **5**: GC/MS *m/e* (relative intensity) 111 ($CH_2CD_2{}^{81}Br^+$, 8%), 109 ($CH_2CD_2{}^{79}Br^+$, 9%), 71 ($CH_2{=}CHCH_2CD_2CH_2^+$, 100%), 70 (23%), 69 (30%), 68 (13%). The molecular ion was not detected. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.18 (d, 2 H, $J_{HH} = 7$ Hz), 3.37 (s, 2 H), 5.02 (m, 2 H), 5.78 (m, 1 H), no resonance was observed at δ 1.93, indicating greater than 95% deuterium incorporation. ^{2}H NMR (61 MHz, C_6H_6, 298 K): δ 1.42 (s). The GC data showed that contaminants were present in the sample of **5**. Spectroscopic data for **1**-d_4 indicated that the contaminants did not effect the incorporation of the pentenyl-d_2 ligand into the metal complex. Spectroscopic data for $H_2C{=}CHCH_2CH_2CH_2Br$: GC/MS *m/e* (relative intensity) 150 (M^+, ^{81}Br, 2%), 148 (M^+, ^{79}Br, 2%), 109 ($CH_2CH_2{}^{81}Br^+$, 7%), 107 ($CH_2CH_2{}^{81}Br^+$, 8%), 69 ($CH_2{=}CHCH_2CH_2CH_2^+$, 100%), 68 (24%), 67 (34%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.93 (m, 2 H), 2.18 (vq, 2 H, $J_{HH} = 7$ Hz), 3.37 (t, 2 H, $J_{HH} = 7$ Hz), 5.02 (m, 2 H), 5.78 (m, 1 H).

Thermolysis of 1 with PhC≡CPh: Sample Kinetic Trial. Under a nitrogen atmosphere at 21 °C a 1-mL volumetric flask was charged with **1** (0.0093 g, 0.028 mmol), diphenylacetylene (0.056 g, 0.31 mmol), and hexamethyldisiloxane (0.8 μL, internal standard). The mixture was diluted to a volume of 1.0 mL with toluene-d_8. The light yellow solution was transferred to a 5-mm NMR tube, which was then flame-sealed under nitrogen. The sample was placed in a NMR probe (Bruker AMX 300 MHz) preheated to 77 °C (temperature calibrated with an external 100% ethylene glycol standard). The reaction was monitored at 300 s intervals to greater than 3.5 half-lives by ^{1}H NMR spectroscopy.

3,3-Dimethyl-1,4-pentadiene.[45] A 50-mL Schlenk tube was charged with Ph_3PCH_2 (1.05 g, 3.80 mmol) and toluene (10 mL) under nitrogen. The yellow solution was cooled to 0 °C and 2,2-dimethyl-3-butenal (0.375 g, 3.81 mmol) in toluene (5 mL) was added by syringe. The resulting clear solution was filtered through acidic alumina, which was washed with toluene (2 × 2 mL). Distillation of the combined filtrates at 72 °C afforded 0.14 g (1.4 mmol, 37%) of 3,3-dimethyl-1,4-pentadiene as a clear liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.09 (s, 6 H), 4.95 (m, 4 H), 5.80 (m, 2 H). Bp 72 °C (experimental), 70 °C (reported).[45]

Thermolysis of 1 with 3,3-Dimethyl-1,4-pentadiene: Spectroscopic Evidence for (η^1,η^2-$CH_2CH_2C(Me)_2CH{=}CH_2)_2Pt$ (6). A 30-mL glass bomb was charged with **1** (0.048 g, 0.14 mmol), 3,3-dimethyl-1,4-pentadiene (80 μL, 0.6 mmol), and benzene (5 mL) under nitrogen. The solution was heated for 15 h at 75 °C, filtered through silica, and evaporated to dryness affording a yellow solid (0.040 g). Despite repeated chromatography and crystallization, the major product could only be partially separated from two minor products (ca. 15%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.06 (s, 6 H), 1.23 (s, 6 H), δ 3.17 (dd, 2 H, $J_{HH} = 9$ Hz, $J_{PtH} = 25$ Hz), 3.62 (dd, 2 H, $J_{HH} = 15$ Hz, $J_{PtH} = 40$ Hz), 4.14 (m, 2 H).

Thermolysis of 1-β-d_4 with PhC≡CPh. Under a nitrogen atmosphere at 21 °C a 1-mL volumetric flask was charged with **1**-β-d_4 (0.0094 g, 0.028 mmol), diphenylacetylene (0.153 g, 0.858 mmol), and hexamethyldisiloxane (0.8 μL, internal standard). The mixture was diluted to a volume of 1.0 mL with toluene-d_8. The light yellow solution was transferred to a 5-mm NMR tube, which was then flame-sealed under nitrogen. The sample was placed in a NMR probe (Bruker AMX 300 MHz) preheated to 77 °C (temperature calibrated with an external 100% ethylene glycol standard). The reaction was monitored at 300-s intervals to greater than 3.5 half-lives by ^{1}H NMR spectroscopy. After the reaction had reached completion (7 h) the volatile materials were vacuum transferred to another 5-mm NMR tube and analyzed by ^{1}H NMR spectroscopy and GC/MS. The spectroscopic data were consistent with those expected for 2-deuterio-1,4-pentadiene. The yield based on ^{1}H NMR integration was 92%. ^{1}H NMR (300 MHz, toluene-d_8, 298 K): δ 2.60 (d, 2 H, $J_{HH} = 6$ Hz), 4.92 (m, 4 H), 5.70 (m, 1H). GC/MS: *m/e* = 69 (M^+). The non-volatile materials were analyzed by ^{1}H NMR spectroscopy and mass spectrometry. The spectroscopic data were consistent with a mixture of **7** and **8**-d_x, where $x = 2$ or 3. The yield of **8**-d_x, based on ^{1}H NMR spectroscopy, was 60%. The yield of **7** could not be determined due to overlap of resonances in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz, C_6D_6, 298 K): notable features consistent with **8**-d_x, δ 1.50 (m), 3.24 (d, $J_{HH} = 9$ Hz, platinum coupling was not resolved), 3.92 (d, $J_{HH} = 15$ Hz, platinum coupling was not resolved), 5.38 (br), 5.91 (s, platinum coupling was not resolved), 7.66 (m), 7.80 (m); resonance consistent with **7**, δ 7.98 (d, 7 Hz); other resonances were obscured by the large concentration of free diphenylacetylene in the sample. MS (EI): *m/e* = 623 (60%) and 624 (60%), indicating a mixture of **8**-d_3 and **8**-d_2.

X-ray Crystallographic Analysis of (η^1,η^2-$C_5H_9)_2Pt$ (1). Clear yellow blocks of **1** were obtained by slow crystallization from a pentane/ethanol (1/1) solution at −15 °C. A fragment cut from one of these crystals was mounted on a glass fiber using Paratone N hydrocarbon oil. The crystal was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to −100 °C by a nitrogen flow low-temperature apparatus, which had been previously calibrated by a thermocouple placed at the sample position. Crystal quality was evaluated by measurement of intensities and inspection of peak scans. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry.

The 1737 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization affects. No corrections for crystal movement or decomposition were necessary. An empirical correction was made to the data based on the combined differences of F_{obs} and F_{clc} following refinement of all atoms with isotropic thermal parameters

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(45) Lukes, R.; Hofman, J. *Chem. Ber.* **1960**, *93*, 2556−2561.

($T_{max} = 1.66$, $T_{min} = 0.75$, no θ dependence).[46] The choice of the centric group $P\bar{1}$ was confirmed by the successful solution and refinement of the structure.

The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. The final residuals for 50 variables refined against the 1563 accepted data for which $F^2 > 3\sigma(F^2)$ were $R = 4.5\%$, $wR = 5.8\%$, and GOF = 2.81. The R value for all 1737 data was 5.0%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)_2$, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to 0.03 in the last cycles of refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[47]

Inspection of the residuals ordered in ranges of $\sin(\theta/\lambda)$, $|F_o|$, and parity and the value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 4.07 $e^-/Å^3$, and the lowest excursion −2.24 $e^-/Å^3$.

X-ray Crystallographic Analysis of (η^1,η^2-C_5H_9)(η^1,η^2-C_4Ph_4H)Pt·0.5 toluene (8). Clear yellow blocks of **8** were obtained by slow crystallization from a hexane/toluene (3/1) solution at −35 °C as described above. A fragment cut from one of these crystals was mounted in the X-ray beam and cooled to −110 °C as described for **1**. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry.

The 7345 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was performed, as the intensity standards varied randomly by approximately ±10%, far larger than any secular variation. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.82$ for the average curve, but also showed effects which suggested (together with the intensity standard variations) that the crystal was moving in the beam. An empirical correction was made to the data based on the combined differences of F_{obs} and F_{clc} following refinement of all atoms with isotropic thermal parameters and removal of 282 data in eight groups (see below) ($T_{max} = 1.31$, $T_{min} = 0.82$, no θ dependence).[46] The choice of the centric group $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. Removal of the bad data (as above) left 7063 unique data in the final data set.

The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.3 times the B_{eqv} of the atoms to which they were attached. They were included in structure factor calculations, but not refined. After inclusion of the hydrogen atoms it became obvious that some regions of data were systematically low in intensity. A total of 282 reflections were removed from the data set in 8 regions of consecutive collection numbers. After these were removed, the DIFABS absorption correction was performed. Attempts to refine the carbon atoms with anisotropic thermal parameters yielded chemically unreasonable results, probably due to high correlation between the two independent molecules in the unit cell. Thus, only the platinum atoms were refined with anisotropic thermal parameters.

The final residuals for 311 variables refined against the 5213 accepted data for which $F^2 > 3\sigma(F^2)$ were $R = 4.88\%$, $wR = 5.68\%$, and GOF = 1.86. The R value for all 7063 data was 7.10%. Data analysis was conducted as described for **1**. The largest peak in the final difference Fourier map had an electron density of 1.96 $e^-/Å^3$, and the lowest excursion was −0.27 $e^-/Å^3$. There was no indication of secondary extinction in the high-intensity low-angle data.

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Supporting Information Available: Tables of crystal and data collection parameters for **1** and **8**, positional parameters for **1**, tables of bond distances and angles, and representative kinetic data (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[46] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

[47] Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.