Synthesis and Characterization of an Unusual Platinum(II) Alkene Complex with an η^2-Arene Interaction

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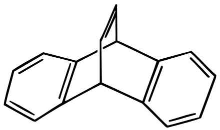
Received April 16, 1999

Dichloro(9,10-dihydro-9,10-ethenoanthracene)platinum(II) has been synthesized and characterized by NMR spectroscopy and X-ray crystallography. The crystal structure shows that the alkene fragment serves as an anchor to place one of the aromatic rings in close enough proximity for an η^2-arene−platinum interaction. Thus, the ethenoanthracene functions as a bidentate ligand.

Introduction

Platinum(II) alkene complexes are well-known organometallic species. The bonding of alkenes to a metal center can be described qualitatively as donation of the alkene π electrons into an empty orbital on the metal with simultaneous back-donation of metal electrons into the empty π^* orbital of the alkene.[1] In most square-planar d^8 metal alkene complexes the alkene is aligned in an upright perpendicular orientation with respect to the coordination plane.[2] Hoffmann and co-workers have performed calculations which indicate that this preference is not due to electronic factors but instead is due to the alkene avoiding steric interactions with the cis ligands.[3] Several examples have been reported in which Pt(II) is bonded to an alkene that is actually aligned in the in-plane orientation.[4] Many of these examples of in-plane alkenes that have been observed have the common feature of mutually perpendicular double bonds. In these cases one double bond is coordinated in the more common upright orientation while the other double bond is forced to coordinate with the in-plane orientation. In contrast, the lack of steric crowding in the (η^3-methylallyl)(triphenylphosphine)(styrene)platinum(II) cation appears responsible for the ability of the styrene to coordinate in a virtually in-plane orientation.[5] According to Miki and co-workers, the lack of steric congestion is achieved as a result of the small bite angle of the η^3-allyl ligand. However, it is important to note that the alkene−Pt bond distances are longer than those reported in other platinum(II) complexes with styrene, indicative of a weaker coordination of the styrene in this complex. Since steric factors play such an important role in the orientation of the ligand about the metal center, it follows that a ligand which encounters severe steric congestion when it coordinates in the normal upright orientation might adopt an in-plane orientation. To evaluate the feasibility of this premise, studies were initiated using 9,10-dihydro-9,10-ethenoanthracene (**1**).



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If this ligand coordinates in the typical upright orientation, one of the ligand's six-membered rings would be placed in the same space as a substituent located in the cis coordination site. Rotation of the alkene into the in-plane orientation would alleviate the steric problems. One of the six-membered rings would then be directed above the coordination plane, while the other would be directed away from the metal coordination sphere. The reaction of ethenoanthracene with platinum(II) salts and the characterization of the product obtained will be described herein. Additional related studies with allylbenzene and 1,4-dihydronaphthalene will also be discussed.

Results and Discussion

The synthesis of the platinum(II) ethenoanthracene complex was carried out by reacting Zeise's dimer with a stoichiometric amount of ethenoanthracene in a toluene−ether solvent mixture to yield a bright orange

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[1] (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939. (c) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

[2] Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985.

[3] Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

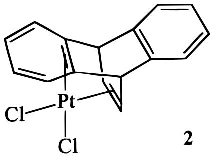
[4] (a) Wright, L. L.; Wing, R. M.; Rettig; M. F.; Wiger, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 5949. (b) Wright, L. L.; Wing, R. M.; Rettig, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 610. (c) Rakowsky, M. H.; Woolcock, J. C.; Wright, L. L.; Green, D. B.; Rettig, M. F.; Wing, R. M. *Organometallics* **1987**, *6*, 1211.

[5] Miki, K.; Kai, Y.; Kasai, N.; Kurosawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 2482.

10.1021/om990272e CCC: $18.00

crystalline solid. A comparison of the ^{1}H NMR spectrum of the complex with that of the free ethenoanthracene indicates clearly that the ethenoanthracene coordinates to the metal via the ethene fragment. The multiplet corresponding to the alkene protons was shifted from 7.40 to 5.50 ppm and displayed coupling to ^{195}Pt. The protons on the bridgehead carbons shift slightly from 5.50 to 5.65 ppm upon coordination of the ligand to the metal. The hydrogens on the aromatic rings of the free ligand display characteristic quartets at 6.78 and 7.32 ppm. In the complex these quartets split into two sets of quartets, giving a total of four resonances attributed to the aromatic hydrogens located at 7.65, 7.50, 7.35, and 7.15 ppm. This is consistent with a breaking of the symmetry of the organic fragment such that the two aromatic rings are no longer equivalent. The ^{13}C NMR spectrum provides more information about the manner in which the symmetry has been altered.

The ^{13}C NMR spectrum of free ethenoanthracene shows five resonances. Upon coordination to platinum eight resonances are present and dramatic changes in chemical shifts are observed. The resonances assigned to the bridging ethene carbons shift from 139 to 75 ppm, a shift of 64 ppm, and display coupling to ^{195}Pt ($J_{\mathrm{Pt,C}} =$ 151 Hz). Prior to coordination the quaternary carbons are equivalent and appear at 146 ppm. Upon coordination they split into two resonances, one at 146 ppm and one at 100 ppm. This dramatic shift of one of the quaternary carbons was unexpected. The remaining carbons of the aromatic rings which originally gave rise to two resonances appear as four resonances in the complex. Upon inspection of these NMR data it became apparent that the structure of the material isolated was not the expected in-plane-coordinated ethenoanthracene. Instead, the ethenoanthracene seemed to be coordinating as a bidentate ligand (**2**).



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To clarify the structure of this new material, a single-crystal X-ray diffraction study was performed. X-ray-quality crystals were obtained by slow evaporation of a chloroform solution of the complex. The molecular structure determined clearly shows that the complex is not a dimer in which the ligand is monodentate. Instead, the ethenoanthracene coordinates in a bidentate fashion through the C1−C2 bond as expected and through the C11−C16 bond in one of the arene rings, as shown in Figure 1. The bidentate nature of the coordination requires the orientation of the coordinated double bond to be upright and not the anticipated in-plane orientation.

The complex crystallizes in the space group *Cc* with two independent molecules related by a pseudo-inversion center with one solvent molecule ($CHCl_3$) per asymmetric unit which breaks the symmetry. Crystallographic data are tabulated in Table 1, and selected bond distances are provided in Table 2. The two molecules differ slightly in structure, but they have the same key features. By focusing on one of these molecules, it is possible to gain some insight into the relative strengths of the metal−ligand interactions. The bond length for the platinum to the midpoint of the C1−C2 double bond is 1.98(4) Å. In comparison, the bond distance from the midpoint of the C11−C16 bond of the aromatic ring to the platinum atom is 2.22(4) Å. This difference in bond lengths reflects a difference in the relative strengths of interaction with the metal such that the C1−C2 double bond is coordinating more strongly to the metal. This qualitative analysis of the bonding interactions can be extended further. Viewing the complex from above the coordination plane, as shown in Figure 2, reveals further information about the arene−platinum interaction. The coordinated aromatic ring appears to have bent back from the metal center. The aromatic rings in this ligand are normally coplanar with the bridgehead carbons, as observed in

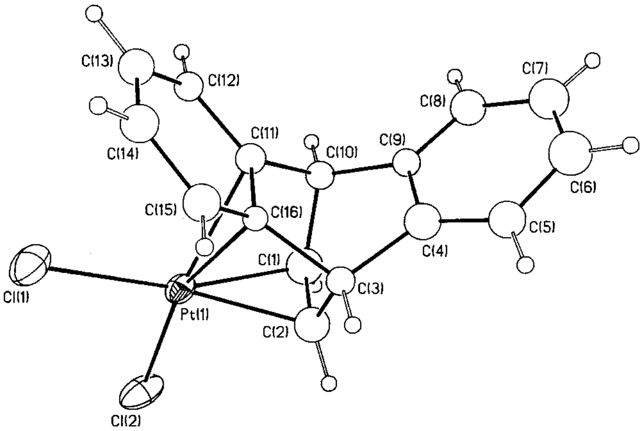


Figure 1. ORTEP drawing of dichloro(9,10-dihydro-9,10-ethenoanthracene)platinum(II) showing 35% probability thermal ellipsoids and atom labeling.

Table 1. Crystal Data for $C_{16}H_{12}Cl_2Pt{\cdot}0.5CHCl_3$

formula	$C_{16}H_{12}Cl_2Pt{\cdot}0.5CHCl_3$
fw	529.96
cryst syst	monoclinic
space group	*Cc* (No. 9)
a, Å	7.969(2)
b, Å	17.898(5)
c, Å	22.897(9)
β, deg	98.57(3)
V, Å^3	3229(2)
Z	8
D_{calcd}, g cm^{-3}	2.18
μ, mm^{-1}	9.35
transmissn coeff	0.75/0.96
no. of obsd data	2179
$R(F_o)^a$	0.0590
$R_w(F_o)^b$	0.0800

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table 2. Bond Lengths (Å)

Pt(1)−Cl(1)	2.326(10)	Pt(1)−Cl(2)	2.270(9)
Pt(1)−C(1)	2.13(4)	Pt(1)−C(2)	2.10(3)
Pt(1)−C(11)	2.33(2)	Pt(1)−C(16)	2.34(3)
C(1)−C(2)	1.43(5)	C(1)−C(10)	1.50(4)
C(2)−C(3)	1.42(4)	C(3)−C(16)	1.57(4)
C(3)−C(4)	1.50(4)	C(4)−C(9)	1.44(4)
C(4)−C(5)	1.33(4)	C(5)−C(6)	1.39(5)
C(6)−C(7)	1.41(5)	C(7)−C(8)	1.39(5)
C(8)−C(9)	1.39(4)	C(9)−C(10)	1.49(3)
C(10)−C(11)	1.56(4)	C(11)−C(12)	1.42(4)
C(11)−C(16)	1.50(4)	C(12)−C(13)	1.40(5)
C(13)−C(14)	1.42(4)	C(14)−C(15)	1.37(4)
C(15)−C(16)	1.35(5)		

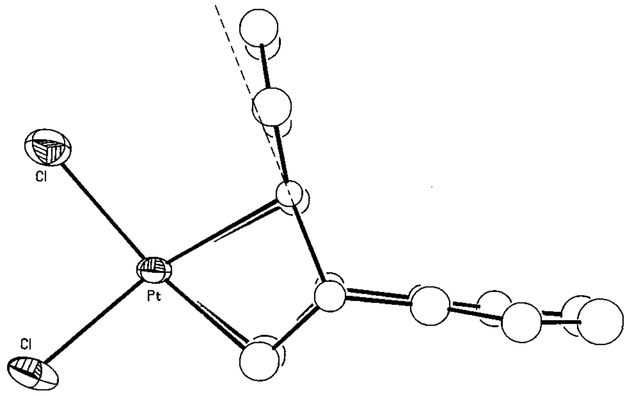


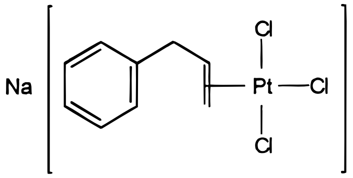
Figure 2. Top view of dichloro(9,10-dihydro-9,10-ethenoanthracene)platinum(II).

the uncoordinated portion of the complex. The coordination of the aromatic ring bends the ring back 11° away from the normal orientation. This is clear evidence of π back-bonding between the metal and the coordinated aromatic ring carbons. This loss of planarity upon coordination has been well-documented for metal alkene complexes.[6]

The ^{13}C NMR data can now be reevaluated in light of this monomeric structure. The shift of one of the quaternary aromatic carbons now is completely understandable. Upon coordination to the platinum it shifts toward TMS by 46 ppm. The ethene carbons (C1−C2) shift by 64 ppm toward TMS. These shifts are as expected for an η^2 bonding interaction with substantial π back-bonding. The magnitudes of the shifts provide additional direct evidence of the relative bonding interactions for the two portions of the ligand with the platinum. The smaller change in chemical shift of the quaternary carbons of the aromatic ring demonstrates that the bond between C11 and C16 has not been altered as much by bonding to the metal as has the C1−C2 bond, again indicative of a weaker Pt−arene bonding interaction.

This η^2-arene coordination is unusual. Most examples of arene coordination to transition metals involve η^6 coordination, as in (arene)Cr(CO)$_3$ complexes, or η^2 coordination with at least one of the coordinating carbons being unsubstituted.[7] What we have observed seems to be equivalent to the η^2 coordination of a tetrasubstituted alkene. Complexes with tetrasubstituted alkenes have been of interest but have rarely been isolated in stable form. The preference of this particular ligand to coordinate in a bidentate η^4 manner is most likely due to increased stability of the upright perpendicular orientation of the C1−C2 bond. Rather than coordinate in the less favorable in-plane orientation, one of the aromatic rings coordinates to the metal, and this cleaves the chloride bridges. Thus, in this situation the alkene fragment serves as an anchor to place the aromatic ring in close enough proximity to allow for a binding interaction.

Upon analysis of the structure of this complex, it was of interest to see if other arenes could be bound to Pt(II) in a similar fashion. Allylbenzene was considered a promising candidate for further work, since it has the same relative distance between the arene ring and the alkene fragment. A direct reaction between allylbenzene and Na$_2$[PtCl$_4$] was carried out, yielding Na[PtCl$_3$(η^2-CH$_2$=CHCH$_2$C$_6$H$_5$)] (**3**). This is a simple Zeise's salt type product with the alkene portion coordinated to the Pt and the arene uncoordinated.



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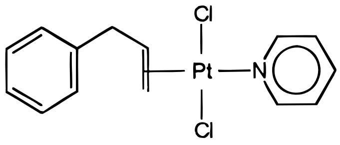
Upon treatment of **3** with 1 equiv of pyridine, *trans*-(pyridine)(η^2-allylbenzene)dichloroplatinum(II) (**4**) is isolated. The elemental analysis is consistent with this formulation, as is the ^{1}H NMR spectrum. Again the alkene portion shows three unique resonances in the spectrum, and each is coupled to the ^{195}Pt. Both allylic protons are clearly visible in the spectrum, as are the aromatic protons. Attempts to remove the pyridine from **4** and open up a coordination site for the arene to bond to yielded a white solid. The same white solid was isolated from the direct reaction of allylbenzene with Zeise's dimer. The ^{1}H NMR spectrum of this material shows that the alkene portion of the molecule is coordinated, as evidenced by the ^{195}Pt coupling. In **3** and **4** the aromatic resonances are all at chemical shifts greater than 7.2 ppm, but in this new material the aromatic resonances are shifted to 6.8 ppm. The two allylic protons are still visible in the spectrum, indicating that this material is not an η^3-allyl complex. When the ^{13}C NMR spectrum was acquired, only seven resonances were observed. The three carbons of the allyl fragment are easily identifiable at 93, 64, and 39 ppm, with the resonances at 93 and 64 ppm showing ^{195}Pt coupling, but there are only four aromatic carbons in the spectrum. The quaternary carbon at 148 ppm shows weak Pt coupling, and one of the other aromatic carbon resonances also shows weak Pt coupling, but with only four aromatic resonances the arene cannot be coordinating in a simple static η^2 manner.



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Casas et al.[7c] have observed similar NMR behavior in a platinum(II) complex of 2-benzylpyridine. In their complex, the nitrogen of the pyridine serves as the anchor for an arene so that it is capable of binding as an η^2-arene. Their crystal structure shows that the arene is bound as a weak η^2-arene in the solid state, but in solution they have observed a fluxional behavior such that both ortho carbon atoms of the arene display

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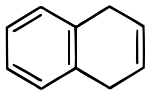
[6] Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

[7] (a) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31. (b) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135. (c) Casas, J. M.; Fornies, J.; Martin, A.; Menjon, B. *Organometallics* **1993**, *12*, 4376. (d) Li, C.-S.; Jou, D.-C.; Cheng, C.-H. *Organometallics* **1993**, *12*, 3945. (e) Liu, C.-H.; Li, C.-S.; Cheng, C.-H. *Organometallics* **1994**, *13*, 18.

weak coupling to the platinum. Cheng et al.[7d,e] have also found a similar situation with a palladium complex. In their work they have found that an η^2-aryl group is able to rotate in a manner such that it slips between two limiting η^2-arene orientations. While our system uses a different functional group to anchor the arene in the vicinity of the platinum, it likely uses the same types of motions. The added degree of rotational freedom between the alkene and arene fragments present in allylbenzene gives rise to the different coordination geometry that it adopts, as compared to that of the ethenoanthracene complex.

In an effort to remove this flexiblility and isolate an analogue of **2**, 1,4-dihydronaphthalene (**5**) was reacted with Pt(II). When Zeise's dimer was reacted with 1,4-dihydronaphthalene, a product with an empirical formula of $PtCl_2(C_{10}H_{10})\cdot 0.5$(toluene) was isolated. Unfortunately this material was insoluble in $CDCl_3$, CD_2Cl_2, and d_6-acetone and falls apart in DMSO. We were thus unable to characterize this material by NMR spectroscopy, nor were we able to obtain crystals. If the ligand is bound in a bidentate manner, compound **6** could be formed. On the other hand, if this is a dimeric structure, we may have isolated a simple Zeise's dimer analogue with the 1,4-dihydronaphthalene coordinated as an η^2-alkene (compound **7**). Without NMR or X-ray evidence it is not possible to distinguish between the two structures. Thus, while 1,4-dihydronaphthalene does form a complex with platinum(II), 9,10-dihydro-9,10-ethenoanthracene is the only ligand that we have been able to show definitively to form a simple η^2-arene complex.



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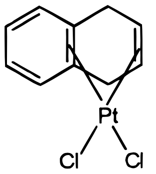

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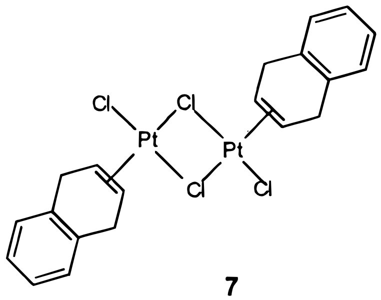

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In conclusion, the ethenoanthracene is unusual in that it does coordinate in an η^4 fashion, using the alkene fragment to anchor the arene in place. This allows for the ethenoanthracene to function as a bidentate ligand with the equivalent of an η^2 tetrasubstituted alkene. We believe the specific locked conformation of the ethenoanthracene may be necessary for this unusual type of η^2-arene coordination.

Experimental Section

General Considerations. Zeise's salt[9] and Zeise's dimer[8] were prepared using standard literature methods. 9,10-Dihydro-9,10-ethenoanthracene was provided by Steve Ittel, Central Research and Development, E. I. DuPont de Nemours and Co. All other alkenes were used as received (Aldrich). Elemental analyses were performed by Midwest Micro Laboratory. NMR spectra were measured at 300 MHz (^{1}H) and 75 MHz (^{13}C), and coupling constants are reported in hertz.

Dichloro(9,10-dihydro-9,10-ethenoanthracene)platinum(II)·0.5(toluene) (2). To 0.315 g (0.536 mmol) of $[(C_2H_4)PtCl_2]_2$ (Zeise's dimer) dissolved in 25 mL of diethyl ether and 5 mL of toluene was added 0.219 g (1.073 mmol) of 9,10-dihydro-9,10-ethenoanthracene. The solution was stirred vigorously under N_2 for 6 h. Upon concentration of the resulting solution, a bright orange solid was produced. Filtration yielded 0.46 g of the desired product with 0.5 equiv of toluene cocrystallized for an 85% yield. ^{1}H NMR ($CDCl_3$): δ 7.65 (m, 2 H), 7.50 (m, 2 H), 7.35 (m, 2 H), 7.15 (s, toluene C_6H_5-), 7.20 (m, 2 H), 5.60 (m, H3 and H10), 5.50 (m, $J_{Pt,H} = 95$, H1 and H2), 2.38 (s, toluene $-CH_3$). ^{13}C NMR ($CDCl_3$): δ 146 (C4, C9), 135, 131, 127, 124, 100 (C11, C16), 75 ($J_{Pt,C} = 151$, C1, C2), 52 (C3, C10). IR (Nujol): 3069, 1595, 1584, 1530, 1488, 1355, 1301, 1294, 1192, 1178, 1158, 1111, 1084, 1023, 984, 975, 948,928, 781, 767, 756, 740, 720, 701, 622 cm^{-1}. Anal. Calcd for $C_{19.5}H_{16}Cl_2Pt$: C, 45.36; H, 3.10; Cl, 13.74; Pt, 37.79. Found: C, 45.97; H, 3.11; Cl, 13.92; Pt, 38.0.

Sodium (η^2-allylbenzene)trichloroplatinate(II) (3). To a solution of 0.474 g (1.08 mmol) of $Na_2[PtCl_4]\cdot 4H_2O$ dissolved in 30 mL of *n*-propanol was added 0.60 mL (4.5 mmol) of allylbenzene. The solution was covered, allowed to stand overnight, and then filtered to remove the insoluble NaCl byproduct. The filtrate was concentrated almost to dryness. Upon addition of hexanes a yellow solid precipitated. Filtration yielded 0.37 g of the desired product for a 77% yield. ^{1}H NMR (d_6-acetone): δ 7.45 (d, 2H), 7.30 (t, 2H), 7.20 (t, 1H), 5.05 (m, $J_{Pt,H} = 66$, 1H), 4.30 (d, $J_{Pt,H} = 66$, 1H), 4.14 (d, $J_{Pt,H} = 81$, 1H), 3.53 (dd, 1H), 3.10 (dd, 1H). IR (Nujol): 1630, 1010, 740, 695, 595 cm^{-1}. Anal. Calcd for $NaPtCl_3C_9H_{10}$: C, 24.40; H, 2.28. Found: C, 24.13; H, 2.31.

***trans*-Dichloro(η^2-allylbenzene)(pyridine)platinum(II) (4).** To a solution of 0.278 g (0.628 mmol) of $Na[PtCl_3(\eta^2\text{-}C_9H_{10})]$ in 15 mL of H_2O was added 51 μL (0.634 mmol) of pyridine. A light yellow solid precipitated. The product was collected by filtration to give 0.25 g of product for an 86% yield. Occasionally the initial product of the reaction was a viscous oil. In these cases the H_2O was decanted off and hexanes were added to the oil. Stirring for about 30 min usually produced the desired yellow solid in comparable yields. ^{1}H NMR ($CDCl_3$): δ 8.80 (d, $J_{Pt,H} = 30$, 2H), 7.88 (t, 2H), 7.13−7.48 (m, 6H), 5.85 (m, $J_{Pt,H} = 60$, 1H), 4.85 (d, $J_{Pt,H} = 60$, 1H), 4.74 (d, $J_{Pt,H} = 60$, 1H), 3.70 (dd, 1H), 3.36 (dd, 1H). IR (Nujol): 1607, 1244, 1217, 1155, 1106, 1066, 1017, 996, 765, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NCl_2Pt$: C, 36.28; H, 3.27; N, 3.03. Found: C, 36.37; H, 3.26; N, 3.02.

Attempted Synthesis of Dichloro(η^4-allylbenzene)platinum(II). 1. Using the method of Busse et al.,[8] a solution of 31 mg (0.067 mmol) of *trans*-dichloro(η^2-allylbenzene)(pyridine)platinum(II) in 10 mL of diethyl ether was added to 1.5 g (55 mequiv) of Dowex 50W-8X ion-exchange resin in a 50 mL Erlenmeyer flask. After it was stirred vigorously for 1 h, the solution was filtered. The resin was washed twice with 5 mL portions of ether. The combined filtrate and washes were treated with 1.5 g of fresh resin and stirred for 1 h. The mixture was again filtered, and the resin was washed as above. The combined filtrate and washes were treated a third time with 1.5 g of fresh resin. The final combined filtrate and washes were dried over Na_2SO_4 and then evaporated to

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(8) Busse, P. J.; Greene, B.; Orchin, M. *Inorg. Synth.* **1980**, *10*, 181.

dryness, yielding a tacky dark orange solid. Extraction of this material with ether and subsequent evaporation of the ether yielded a white solid in very low yield.

2. Allylbenzene (0.207 mL, 1.56 mmol) was slowly added to a solution of Zeise's dimer (0.459 g, 0.780 mmol) in 40 mL of diethyl ether. The resulting solution was stirred under a very slow stream of N_2 gas until the solution volume was reduced to 10 mL. The reaction vessel was then sealed and allowed to stand for 16 h. Upon further concentration and cooling, a light tan solid was produced. The product was collected by filtration and washed three times with small portions of ether. A white solid (0.125 g) was isolated. Additional small amounts of this product could be obtained upon evaporation of the filtrate. ^1H NMR ($CDCl_3$): δ 6.91 (d, 3H), 6.81 (m, 2H), 5.12 (m, $J_{Pt,H} =$ 88, 1H), 4.27 (t, $J_{Pt,H} = 88$, 1H), 3.96 (d, 1H), 3.82 (d, 1H), 2.65 (d, $J_{Pt,H} = 125$, 1H). ^{13}C NMR (CD_2Cl_2): δ 148 ($J_{Pt,C} = 75$), 131, 126, 124 ($J_{Pt,C} = 46$), 93 ($J_{Pt,C} = 264$), 64 ($J_{Pt,C} = 225$), 39. IR (Nujol): 3039, 1579, 1238, 1165, 1112, 1049, 1031, 1009, 943, 901, 822, 740, 665 cm^{-1}. Anal. Calcd for $C_9H_{10}Cl_2Pt$: C, 28.12; H, 2.62; Cl, 18.46; Pt, 50.80. Found: C, 31.86; H,2.61; Cl, 9.71.

Dichloro(1,4-dihydronaphthalene)platinum(II)·0.5-(toluene). To 0.315 g (0.536 mmol) of $[(C_2H_4)PtCl_2]_2$ (Zeise's dimer) dissolved in 25 mL of diethyl ether and 5 mL of toluene was added 2.068 g (15.9 mmol) of 1,4-dihydronaphthalene. The solution was stirred vigorously under N_2 for 6 h. Upon concentration of the resulting solution, a bright orange solid was produced. Filtration yielded 0.110 g of a product with an empirical formula consistent with the desired product with 0.5 equiv of toluene cocrystallized for a 23% yield. IR (Nujol): 1649, 1194, 1018, 959, 890, 836, 724, 665 cm^{-1}. Anal. Calcd for $C_{13.5}H_{14}Cl_2Pt$: C, 36.66; H, 3.19; Cl, 16.03; Pt, 44.13. Found: C, 36.76; H, 3.13; Cl, 15.85.

X-ray Crystal Structure of Dichloro(9,10-dihydro-9,-10-ethenoanthracene)platinum(II). An orange crystal of $C_{16}H_{12}Cl_2Pt\cdot 0.5CHCl_3$ was mounted on a thin glass fiber for data collection. Single-crystal intensity measurements were made at 21 ± 1 °C using $\omega-2\theta$ scans ($2\theta_{max} = 45°$) on a Nicolet R3mV diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Of the 5489 reflections measured ($-h,\pm k,\pm l$), 2321 were unique ($R_{int} = 0.066$) and 2179 were observed ($I > 3\sigma(I)$). The data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method, expanded by standard difference Fourier searches, and refined by using full-matirix least-squares techniques. All heavy atoms other than those of the olefinic ligand were refined anisotropically; the latter were refined isotropically. Hydrogen atoms were included at idealized positions ($d_{C-H} =$ 0.96 Å) with a refined isotropic group thermal parameter (U_H = 0.07(2) Å^2).

The compound crystallized in the monoclinic space group *Cc* with eight molecules per unit cell. In addition, the unit cell contains four chloroform solvent molecules. Two independent molecules of the platinum complex within the asymmetric unit are related by a pseudo-inversion center, and there are no significant differences in the bonding parameters or conformations of the two molecules. It is the presence of only one solvent molecule in the asymmetric unit which breaks the symmetry and prevents crystallization in the centrosymmetric space group *C*2/*c*. A centrosymmetric packing would require that the chloroform molecule have crystallographically imposed symmetry, that the chloroform molecule be disordered about a symmetry element, or that an additional chloroform molecule be present. Translation of the origin, such that the approximate inversion center in the space group *Cc* coincides with any of the real inversion centers of the space group *C*2/*c* (e.g. 0.25, 0.25, 0 or 0, 0, 0) does not move the chloroform molecule to any symmetry site. There is also no evidence of any disorder involving the chloroform molecule. A systematic search for vacant cavities within the unit cell, using a modified (W. R. Schiedt and local) version of the program CAVITY,[10] revealed no significant holes within which a missing chloroform molecule could lie. The largest cavity found was approximately 4.6 Å across at its maximum dimension. By comparison, the cavity occupied by the chloroform molecule in this structure has a maximum dimension of about 7.8 Å. Additional evidence for the choice of space group lies in the chemically reasonable structure observed for both molecules of the complex. The severe distortion from idealized geometries of chemically equivalent groups often observed for centrosymmetric structures refined in acentric space groups[11] is not seen. Final verification of the choice comes from a comparison of final residuals for models refined in the two enantiomeric settings for space group *Cc*. One model gives residuals of $R =$ 0.0590, $R_w = 0.0800$, and $S = 1.49$; the model generated by reversing the signs of all atomic coordinates gives $R = 0.0618$, $R_w = 0.0856$, and $S = 1.59$. The reported values of the atomic coordinates and all derived parameters correspond to the model giving significantly lower residuals.

Structure solution, refinement, and calculation of derived results were performed using the SHELXTL[12] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[13] and the real and imaginary anomalous dispersion corrections were those of Cromer.[14]

Acknowledgment. Funding for this work was provided in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and The Duke Endowment. Sincere gratitude is also extended to Dr. Steve Ittel for his generous and insightful input on this project.

Supporting Information Available: Tables containing complete crystallographic data, atomic coordinates for all non-hydrogen atoms and equivalent isotropic thermal parameters, all bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters, ORTEP diagrams for both molecules one and two, and a description of the data collection and refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990272E

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