Platinum(0) Complexes of Cyclic Alkynes and Allenes from Base-Induced Dehydrohalogenation of Bromocycloalkenes

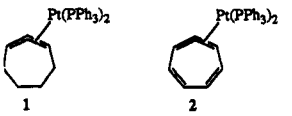
Zheng Lu, Khalil A. Abboud, and W. M. Jones*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received October 14, 1992

Summary: Treatment of 1-bromocycloheptene or a mixture of 1-, 2-, and 3-bromocycloheptatrienes with t-BuOK in the presence of $(Ph_3P)_3Pt$ has been confirmed to lead to predominant formation of $(Ph_3P)_2Pt$ π-complexes of the corresponding cyclic allenes. In contrast, reaction of these same halides and 1-bromocyclohexene with LDA in THF in the presence of $(Ph_3P)_3Pt$ leads exclusively to $(Ph_3P)_2Pt$ complexes of the corresponding cyclic akynes. These reactions provide the first metal complexes of cycloheptadienynes and a convenient alternate method for the preparation of Pt(0) complexes of cyclohexyne and cycloheptyne. The mechanism of formation of the complex of 1,2-cycloheptadiene is briefly discussed and an X-ray crystal structure of one of the cyclheptadienyne complexes is reported.

Reaction of 1-bromocycloheptene[1] and a mixture of bromocycloheptatrienes[2] with t-BuOK in the presence of $(Ph_3P)_3Pt$ have been reported to give reasonable yields of Pt(0) complexes of the corresponding cyclic allenes (**1** and **2**, respectively). In this paper we confirm the previous



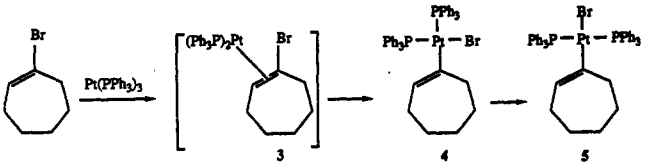
1 **2**

reports, comment on the mechanism of formation of the 1,2-cycloheptadiene adduct, and report our finding that the regiochemistry of the t-BuOK elimination can be reversed by a change in base; reaction of 1-bromocycloheptene, the mixture of bromocycloheptatrienes, and also 1-bromocyclohexene with LDA in the presence of $(Ph_3P)_3Pt$ gives Pt(0) complexes of strained cyclic alkynes[3] in modest to good yields. These reactions give none of the allene complexes. An X-ray crystal structure of one of the cycloheptadienyne complexes is also reported.

Results and Discussion

Consistent with the report of Visser and Ramakers,[1] we have found that reaction of 1-bromocycloheptene with t-BuOK (in THF; Visser and Ramakers may have used DMSO) in the presence of $(Ph_3P)_3Pt$ gives the 1,2-cycloheptadiene complex **1**. This adduct was implied[1] to have arisen from simple trapping of the free allene. However two observations make us doubt that this is the mechanism in THF. First, when a solution of essentially colorless 1-bromocycloheptene is added to an orange, saturated THF solution of $(Ph_3)_3Pt$ at room temperature, the orange color is instantly discharged, giving a pale yellow solution. Second, although experimental problems [primarily the low solubility of $(Ph_3P)_3Pt$] precluded reliable kinetic studies, qualitatively, the reaction of t-BuOK with 1-bromocycloheptene in the presence of $(Ph_3P)_3Pt$ at room tempeature is significantly faster than in its absence. These two observations taken together suggest that **1** may arise from reaction of base with an intermediate platinum complex rather than trapping of a free cyclic allene.

To search for viable intermediates, 1-bromocycloheptene was allowed to react at room temperature with $(Ph_3P)_3Pt$ in the absence of base. As mentioned above, the color of the solution changed instantly, and examination of the ^{31}P NMR after 15 min showed significant formation of a new, unstable product. Based on ^1H and ^{31}P NMR spectra, this is believed to be the cis insertion product **4**.[5] Due to its instability, we were unable to obtain a satisfactory ^{13}C NMR spectrum of **4**. On standing, **4** isomerized[6,7] to its known trans isomer **5**.[8] From the ^{31}P NMR, reaction of neither the presumed cis insertion adduct nor its trans isomer with t-BuOK produced any trace of **1**. Therefore they cannot be intermediates in the formation of the allene complex **1**.



3 **4** **5**

Intrigued by the rapid color change upon initial mixing and the knowledge that Bennett[9] had found evidence for π-complexes of dihaloalkenes as intermediates in the preparation of cycloalkyne complexes of $(Ph_3P)_2Pt$, the reaction of 1-bromocycloheptene with $(Ph_3P)_3Pt$ in THF was examined at −30 °C. Indeed, at this temperature the ^{31}P NMR showed formation of a low-concentration transient (Figure 1). Although isolation was not possible, its ^{31}P chemical shifts and platinum–phosphorus coupling constants (δ = 25.4 and 28.4 ppm; J = 3206 and3502 Hz) compare well with those reported for **6** (δ = 23.9 and 27.6 ppm; J = 3013 and 3893 Hz).[10] It therefore seems likely that **1** arises from dehydrohalogenation of an initially

(1) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc. Chem. Commun.* **1972**, 178.

(2) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228.

(3) $(Ph_3P)_2Pt$ complexes of cycloheptyne, cyclohexyne, and cyclopentyne have been prepared by Bennett[4] by Na/Hg reduction of the corresponding dibromocycloalkenes in the presence of $(Ph_3P)_3Pt$. All of these reactions are believed to proceed by reduction of initially formed π-complexes.

(4) For an excellent review, see: Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

(5) For examples of insertion of platinum into carbon–halogen bonds, see: (a) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc.* **1971**, 2667. (b) Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103.

(6) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705.

(7) This isomerization is strongly solvent dependent, occurring very rapidly in CH_2Cl_2, quite slowly in benzene, and at an intermediate rate in THF.

(8) Winchester, W. R. Ph.D. Dissertation, University of Florida, 1985.

(9) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(10) Stang, P. J.; Kowalski, M. H.; Schiavellim, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, 3347. Yoshida, T. *J. Am. Chem. Soc.* **1971**, *93*, 3797.

0276-7333/93/2312-1471$04.00/0

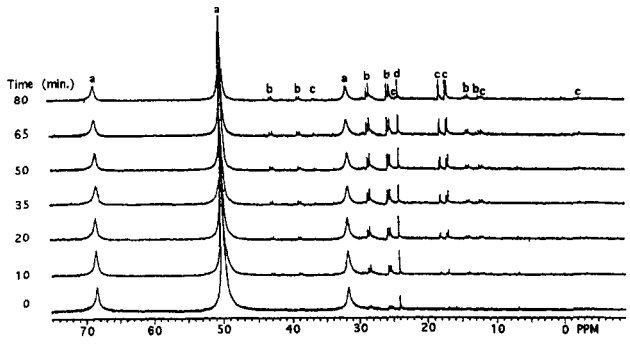
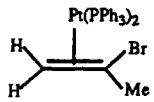


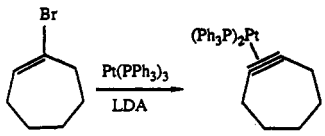
Figure 1. Time-arrayed ^{31}P NMR spectrum of the reaction mixture of 1-bromocycloheptene and $Pt(PPh_3)_3$ in THF at −30 °C. Peaks marked a are $Pt(Ph_3)_3$, b are suggested to be the π-complex **3**, c are the cis insertion product **4**, and d is Ph_3PO.



6

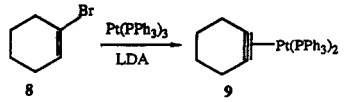
formed π-complex **3** rather than trapping of the strained hydrocarbon intermediate. However, at this stage, this suggestion must be taken as tentative.

Careful examination of the ^{31}P and the ^{195}Pt NMR spectra of the crude product from the reaction of 1-bromocycloheptene with t-BuOK in THF showed the presence of a minor product in addition to the allene complex. This new product was found to be the known[9] cycloheptyne adduct **7** by comparing all the ^{1}H, ^{31}P, and ^{195}Pt NMR spectrum of the crude products with those of authentic **7**. The allene and alkyne complexes were formed in a ratio of about 4:1. Somewhat to our surprise, when LDA was substituted for t-BuOK in the same solvent, the sole product (82% yield) was **7**.[11]



7

Whereas 1-bromocycloheptene reacts with t-BuOK in the presence of $(Ph_3P)_3Pt$ to give the cyclic allene adduct, attempts to repeat this for the six-membered homologue in THF or, probably, DMSO[1] failed. The reason for this failure is unclear. However, as with the seven-membered ring, reaction of **8** with LDA gives the platinum–cyclohexyne adduct **9** in 83% yield.



8 **9**

In earlier work,[13] we reported that the mixture of bromocycloheptatrienes **10–12** react with t-BuOK in THF in the presence of $(Ph_3P)_3Pt$ to give the cycloheptatetraene complex **2**. Unfortunately, little was learned from a closer examination of this reaction because the mixture of bromocyclohepatrienes reacts quite rapidly with either base to give heptafulvalene[14] or $(Ph_3P)_3Pt$ to give the cis insertion product which rearranges at room temperature to the known trans isomers,[8] even at temperatures as low as −50 °C. Neither the cis nor trans insertion isomers gave the cycloheptatetraene complex **2** when treated with t-BuOK in THF which excludes either of these as possible intermediates. Attempts to detect a π-complex at any temperature failed. The question of how **2** arises must therefore remain open, although it should be mentioned that **2** has been found to be in thermal equilibrium with **13** (in toluene[15]), suggesting that the lifetime of cycloheptatetraene may be long enough to be trapped.

As with 1-bromocycloheptene and 1-bromocyclohexene, substitution of LDA for t-BuOK changed the course of the reaction and led to exclusive formation of the cycloheptadienyne complexes **14** and **15** in a ratio of about 8:1; no trace of the allene complex **2** or the unknown cumulene complex **16** could be detected by ^{31}P NMR (Scheme I).

Although a single crystal of one of the cycloheptadienyne complexes (**14**) was obtained for an X-ray study, on a macroscale the two complexes could not be separated. Structure assignments in solution are therefore based on NMR spectra of the mixture. Chemical shift assignments for H3 and H7 in **14** and **15** are based on their Pt–H 2D NMR spectra. Assignments for the remaining hydrogens and all carbons are based on COSY and C–H 2D NMR spectra. Details are given in the Experimental Section. The crystal structure of **14** is shown in Figure 2, and selected bond distances and angles are listed in Table I. The seven-membered ring is bent along the C3–C7 line. The plane containing atoms C7, C1, C2, and C3 (average esd is 0.006 Å) forms an angle of 153(1)° with the plane containing atoms C3–7 (average esd is 0.05 Å). The former forms an angle of 174(1)° with the plane of C1, C2, and Pt. The ring bond distances exhibit relatively high esd's, an indication of large ring atomic vibrations or displacements in the molecule. As a result, C7 bond distances could not be used to assign C7 as the lone sp^3 C atom of the ring. This assignment, however, is made based on the bond angle C1–C7–C6, 115.0(2)°, which is the smallest in the ring.

Experimental Section

NMR spectra were recorded on a Varian VXR-300 or General Electric QE-300 with TMS as the reference for ^{1}H and ^{13}C NMR, 80% H_3PO_4 as the refrence for ^{31}P NMR, and a saturated solution of K_2PtCl_6 in D_2O as the reference for ^{195}Pt NMR. IR spectra were obtained from KBr pellets using a Perkin Elmer 1600 FTIR and mass spectra on a Finnigan Mat 95Q. X-ray data were collected on a Siemens P3m/v diffractometer equipped with a graphite monochromator. Elemental analyses were performed with a Carlo Erba 1106 Elemental Analyzer. THF was purified by distillation under nitrogen atmosphere from sodium/benzophenone. Hexane was dried with 4A molecular sieves and degassed by bubbling nitrogen gas through it for 5 h. Potassium *tert*-butoxide, lithium diisopropylamide (LDA), and most other reagents including NMR solvents were obtained from Aldrich and used without further purification. The mixture of 1-bromo-2-bromo- and 3-bromocyclohepta-1,3,5-triene (**10–12**),[16] tris(triphenylphosphine)platinum(0),[17] 1-bromocycloheptene,[1] 1-bro-

(11) Reversal in regiochemistry of elimination of HX to give strained cyclic allenes and alkynes has been previously reported[12] but none leading to the formation of metal complexes.

(12) For example, see: (a) Montgomery, L. K.; Applegate, L. E. *J. Am. Chem. Soc.* **1967**, *89*, 5305. (b) Ball, W. J.; Landor, S. R. *Proc. Chem. Soc.* **1961**, 143. (c) Ball, W. J.; Landor, S. R. *J. Chem. Soc.* **1962**, 2298.

(13) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, 2228.

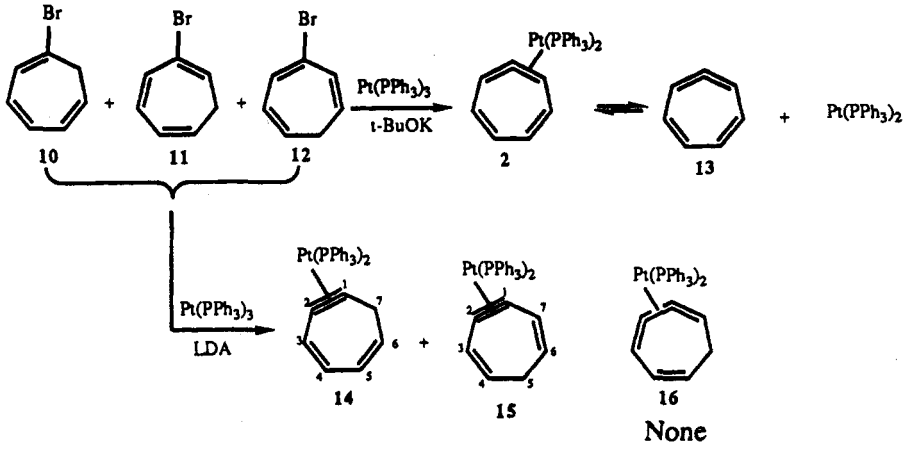
(14) Ennis, C. L.; Jones, W. M. *J. Am. Chem. Soc.* **1967**, *89*, 3069.

(15) Lu, W. M.; Jones, W. M. Submitted to *Organometallics*.

(16) Fohlish, B. J.; Haug, E. *Chem. Ber.* **1971**, *711*, 82.

(17) Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* **1968**, *11*, 105.

Scheme I



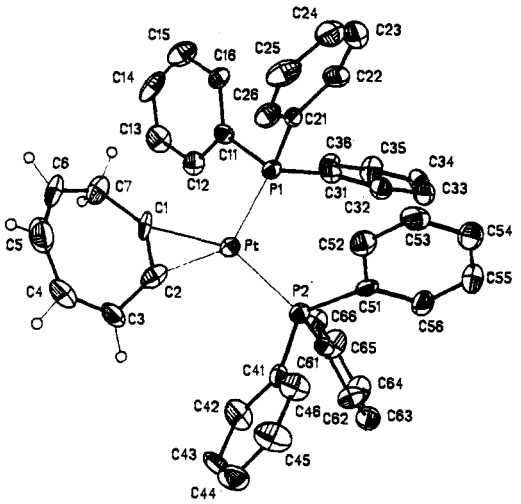


Figure 2. Molecular structure and crystallographic numbering scheme for complex 14.

Table I. Bond Lengths (Å) and Angles (deg) for the Non-H Atoms of Complex 14

Pt–P(1)	2.275(4)	Pt–P(2)	2.270(3)
Pt–C(1)	2.058(11)	Pt–C(2)	2.00(2)
C(1)–C(2)	1.31(2)	C(1)–C(7)	1.41(2)
C(2)–C(3)	1.42(3)	C(3)–C(4)	1.31(3)
C(4)–C(5)	1.37(3)	C(5)–C(6)	1.37(4)
C(6)–C(7)	1.38(3)		
P(1)–Pt–P(2)	107.16(12)	P(1)–Pt–C(1)	105.1(5)
P(2)–Pt–C(1)	147.7(5)	P(1)–Pt–C(2)	142.3(4)
P(2)–Pt–C(2)	110.2(4)	C(1)–Pt–C(2)	37.5(6)
Pt–C(1)–C(2)	68.6(9)	Pt–C(1)–C(7)	155.1(14)
C(2)–C(1)–C(7)	136.0(2)	Pt–C(2)–C(1)	73.9(9)
Pt–C(2)–C(3)	157.0(10)	C(1)–C(2)–C(3)	128.3(14)
C(2)–C(3)–C(4)	121.0(2)	C(3)–C(4)–C(5)	129.0(2)
C(4)–C(5)–C(6)	131.0(2)	C(5)–C(6)–C(7)	128.0(2)
C(1)–C(7)–C(6)	115.0(2)		

mocyclohexene,[18] *trans*-(bromo)(1-η-cycloheptenyl)bis(triphenylphosphine)platinum[8] and *trans*-(bromo)(1-η^1-cyclohepta-1,3,5-trienyl)bis(triphenylphoshine)platinum[8] were prepared according to literature procedures.

Preparation of (1,2-η^2-Cycloheptadiene)bis(triphenylphosphine)platinum (1). Visser[1] reported the preparation of 1 but gave no experimental details. We used the following procedure. Tris(triphenylphosphine)platinum (0.5 g, 0.51 mmol) and 0.11 g (1.0 mmol) of t-BuOK were dissolved in 10 mL of THF. To this solution was added 0.1 g (0.57 mmol) of 1-bromocycloheptene in 2 mL of THF dropwise at room temperature. After the solution was stirred for 2 h, the mixture was filtered through silica gel. The products, 1 and 7 (4:1), were precipitated by adding excess hexane. The products were further purified by recrystallization from THF/hexane. Yield: 0.29 g (70%). The ^{1}H NMR chemical shifts are the same as those reported by Visser. Additional NMR data for 1: ^{31}P NMR (121 MHz, toluene-d_8) δ 30.6 (d, $^1J_{Pt-P}$ = 3135 Hz, $^2J_{P-P}$ = 35 Hz), 34.5 (d, $^1J_{Pt-P}$ = 317 Hz, $^2J_{P-P}$ = 35 Hz); ^{195}Pt NMR (64 MHz, toluene-d_8) δ −4939 (dd, $^1J_{Pt-P1}$ = 3137 Hz, $^1J_{Pt-Pt2}$ = 3170 Hz).

Preparation of *cis*-(Bromo)(1-η^1-cycloheptenyl)bis(triphenylphosphine)platinum (4). Tris(triphenylphosphine)-platinum (0.25 g, 0.25 mmol) was dissolved in 5 mL of THF. To this solution was quickly added 0.1 g (0.57 mmol) of 1-bromocycloheptene in 2 mL of THF. After this mixture was stirred 10 min at room temperature, excess hexane was added until a precipitate was formed. The product 4 was collected by carefully decanting the supernatant solution, washing the precipitate with hexane, and drying on a vacuum line: yield 0.14 g (63%); mp 215 °C dec; IR 3055 w, 2908 m, 2847, w, 1480 m, 1435 s, 1400 w, 1185 w, 1095 s, 1028 w, 999 w, 742 s, 693 vs, 544 m, 522 vs; ^{1}H NMR (300 MHz, CD_2Cl_2, −20 °C), δ 7.1–1.8 (aromatics, 30 H), 5.62 (br, 1 H), 2.58 (br, 1 H), 1–2 (br, 9 H); ^{31}P NMR (121 MHz, C_6D_6) δ 17.7 (td, $^1J_{Pt-P}$ = 4742 Hz, $^2J_{P-P}$ = 13 Hz), 18.6 (td, $^1J_{Pt-P}$ = 1458 Hz, $^2J_{P-P}$ = 13 Hz); ^{195}Pt NMR (64 MHz, C_6D_6) δ −4567.6 (dd, $^1J_{Pt-Pt}$ = 1458 Hz, $^1J_{Pt-p2}$ = 4751 Hz). Due to its instability, a sample pure enough for elemental analysis could not be obtained.

Preparation of *cis*-(Bromo)(1-η^1-cyclohepta-1,3,5-trienyl)-bis(triphenylphoshine)platinum. The procedure used for preparation of 4 was followed using a mixture of 10, 11, and 12 instead of 1-bromocycloheptene. Only 10 reacted: yield 64%; mp 162 °C dec; IR 3055 w, 2907 m, 2847 1, 1480 m, 1435 s, 1185 w, 1095 s, 1028 w, 999 w, 742 s, 693 vs, 544 m, 522 vs; ^{1}H NMR (300 MHz, CD_2Cl_2, −30 °C) δ 7.5–7.8 (aromatics, 12 H), 7.3–7.4 (aromatics, 18 H), 5.7–6.1 (m, 4 H), 5.12 (br, 1 H), 3.16 (br, 1 H), 0.95 (br, 1 H); ^{31}P NMR (121 MHz, CD_2Cl_2, −30 °C) δ 16.3 (td, $^1J_{Pt-P}$ = 1569 Hz, $^2J_{P-P}$ = 14.6 Hz), 15.8 (td, $^1J_{Pt-P}$ = 4580 Hz, $^2J_{P-P}$ = 14.6 Hz); ^{195}Pt NMR 64 MHz, CD_2Cl_2, −30 °C) δ −4538.7 (dd, $^1J_{Pt-P1}$ = 1570 Hz, $^1J_{Pt-P1}$ = 1570 Hz, $^1J_{Pt-P2}$ = 4598 Hz). Due to instability of this product, a sample pure enough for elemental analysis was not obtained.

Preparation of (1,2-η^2-Cycloheptyne)bis(triphenylphosphine)platinum (7). Bennett[10] has prepared both 7 and 9 by reducing 1,2-dibromocycloheptene and 1,2-dibromocyclohexene with sodium amalgam in the presence of tris(triphenylphosphine)-platinum. We used the following procedure to prepare these complexes. For 7, 0.5 g (0.51 mmol) of tris(triphenylphosphine)-platinum and 0.1 g (1 mmol) of LDA were dissolved in 10 mL of THF. To this solution was added 0.1 g (0.57 mmol) of 1-bromocycloheptene in 2 mL of THF dropwise at room temperature. After 2 h, the solution was filtered through silica gel. Addition of excess hexane induced precipitation of 7. The product was further purified by recrystallization from THF/hexane. Yield: 0.34 g (82%). The ^{1}H NMR chemical shifts are the same as those reported by Bennett.[10] Additional NMR data:

(18) Wittig, G.; Fritze, P. *Ann. Chem.* **1968**, *711*, 82.

^{195}Pt NMR (64 MHz, toluene-d^8) δ −4698 (t, $^1J_{Pt-P}$ = 3435 Hz). The cyclohexyne complex **9** was prepared in the same way. Yield: 83%. Additional NMR data: ^{195}Pt NMR (64 MHz, toluene-d_8) δ −4658 (t, $^1J_{Pt-P}$ = 3388 Hz).

Preparation of (1,2-η^2-Cyclohepta-3,5-dien-1-yne)bis(triphenylphoshine)platinum (14) and (1,2-η^2-Cyclohepta-3,6-dien-1-yne)bis(triphenylphoshine)platinum (15). Tris(triphenylphosphine)platinum (0.5 g, 0.5 mmol) and LDA (0.15 g, 1.4 mmol) were dissolved in 12 mL of THF. To this solution was added a mixture of 0.15 g (0.88 mmol) of **10**, **11**, and **12** in 2 mL of THF dropwise at −10 °C. The solution was then warmed to room temperature and filtered through silica gel. Hexane (40 mL) was added to the filtrate. Any resulting precipitate was removed by filtration through silica gel. The product (0.17 g of a mixture of **14** and **15**) of yellow crystals was obtained by slow evaporation of the solvent: yield 43%; mp 165–175 °C dec; IR 3051 w, 3006 w, 2810 w, 1963 w, 1712 m, 1478 s, 1433 s, 1307 w, 1182 m, 1094 s, 1026 m, 998 m, 860 w, 744 s, 696 s, 678 m, 543 s, 522 s, 510 s, 500 s, 426 m; MS *m/e* 809 (M^+); **14** and **15** could not be separated, but their NMR resonances could be clearly assigned except in the phenyl region (which is 7.0–8.0 ppm in the ^{1}H NMR and 128, 129, 134, and 138 ppm in the ^{13}C NMR). For **14**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.32 (d, H7, $^1J_{Pt-H}$ = 30.2 Hz, $^3J_{H-H}$ = 4.7 Hz), 5.22 (m, H6), 5.75 (m, H5), 5.77 (m, H4), 5.88 (d, H3, $^3J_{Pt-H}$ = 40.3 Hz, $^3J_{H-H}$ = 8.8 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 28.9 (C7), 125.1 (C6), 127.8 (C5), 126.8 (C4), 121.2 (C3); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 28.0 (for both of the P nuclei, but their coupling constants to the Pt are different: $^1J_{Pt-P1}$ = 3370.2 Hz, $^1J_{Pt-P2}$ = 3404.4 Hz); ^{195}Pt NMR (64 MHz, CD_2Cl_2) δ −4667. For **15**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.38 (d, H3 and H7, $^1J_{Pt-H}$ = 33.0 Hz, $^3J_{H-H}$ = 8.8 Hz), 5.10 (m, H4 and H6), 2.42 (t, H5, $^3J_{H-H}$ = 7.0 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 123.2 (C3 and C7), 114.2 (C4 and C6), 30.0 (C5); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 27.2 ($^1J_{Pt-P}$ = 3392.4 Hz); ^{195}Pt NMR (64 MHz, CD_2Cl_2) δ −4689. Anal. Calcd for $C_{43}H_{36}P_2Pt$: C, 63.78; H, 4.48. Found: C, 63.76; H, 4.55.

X-ray Structure of 14: $C_{43}H_{36}P_2Pt$, M_r = 809.7, monoclinic, $P2_1/c$, a = 13.544(2) Å, b = 17.235(3) Å, c = 16.163(2) Å, β = 107.93(1)°, V = 3590(1) Å^3, Z = 4, D_{calc} = 1.498 g cm^{-3}, Mo Kα (λ = 0.710 69 Å), T = 298 K, R = 0.0449, and R_w = 0.0456 for 2811 reflections [$I \geq 3\sigma(I)$].

All data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 69 Å). A total of 40 reflections with 20.0° ≤ 2θ ≤ 22.0° were used to refine the cell parameters. A total of 587 reflections were collected using the ω-scan method. Four reflections 9040, 113, 031) were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was <1.02%). Absorption corrections were applied based on measured crystal faces using SHELXTL plus;[19] absorption coefficient, μ = 40.3 cm^{-1}; minimum and maximum transmission were 0.561 and 0.674, respectively.

The structure was solved by the heavy-atom method in SHELXTL plus[19] from which the location of the Pt atoms were obtained. The rest of the non-hydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in SHELXTL plus[19] using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. A total of 415 parameters were refined, and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, $I_{intensity} = (I_{peak} - I_{background})$(scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography* (1974).[20] Scattering factors for non-hydrogen atoms were taken to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography* (1974).[20] Scattering factors for non-hydrogen atoms were taken from Cromer and Mann (1968)[21] with anomalous-dispersion corrections from Cromer and Liberman (1970),[22] while those of hydrogen atoms were from Stewart, Davidson, and Simpson (1965).[23]

Acknowledgment. The authors gratefully acknowledge support of this work by the National Science Foundation and the University of Florida Division of Sponsored Research.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, bond lengths and angles, crystallographic data, and anisotropic thermal parameters for **14** (11 pages). Ordering information is given on any current masthead page.

OM920633P

(19) Shedrick, G. M. (1990). SHELXTL plus. Nicolet XRD Corporation, Madison, WI.
(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, AL (Present distributor, D. Reidel: Dordrecht), 1974; Vol. IV, p 55.
(21) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(22) Cromer, D. T.; Lieberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.