"In-Plane" Coordinated Double Bonds. Molecular Structures, Spectroscopy, and Stability of 5-Methylenecyclooctene and 5-Methylenecycloheptene Complexes of Platinum(II)

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A series of platinum(II) complexes having coordinated olefin constrained to lie in the square plane of coordination has been synthesized and characterized. The diolefin chelates used in this work are 5-methylenecycloheptene (MCH) and 5-methylenecyclooctene (MCOT). Since this class of compounds is of marginal stability, the diolefins, synthesis conditions, and metal substrates must be carefully chosen [e.g., all attempts to prepare Pd(II) analogues result in facile chloropalladation]. Analysis of X-ray and NMR data leads to the conclusion that the "in-plane" olefin is more weakly bound to platinum than is the "out-of-plane" olefin, and the principal source of instability is the close contact of terminal exocyclic carbon and gem-cis atom [2.82 (1) Å for C9 and Cl2 in (MCOT)PtCl$_2$ (**4a**), for example]. Several lines of evidence indicate that MCH forms more stable complexes than does MCOT [e.g., MCH displaces MCOT from (MCOT)PtCl$_2$ to yield (MCH)PtCl$_2$]. Reaction of (MCH)PtCl$_2$ with (C$_6$H$_5$)Sn(CH$_3$)$_3$ leads to either (MCH)PtClPh (**6**) or (MCH)PtPh$_2$ (**7**). The phenyl ligand in the former complex has large cis and trans influences (seen in X-ray and NMR results) of opposite sign. Virtually any diene displaces MCOT from (MCOT)PtCl$_2$. Even bridging bromide is a better ligand than the exocyclic olefin in MCOT. Thus (η^4-MCOT)PtBr$_2$ (**4b**) readily dimerizes to [(η^2-MCOT)PtBr(μ-Br)]$_2$. The kinetics and thermodynamics of this dimerization/dedimerization are reported. In the course of the present work, the molecular structures of the following five compounds were determined by X-ray diffraction: **4a**, **4b**, **6**, **7**, and dichloro-[(1,2,5,6-η^4)-2,5-dimethyl-1,5-hexadiene]platinum(II) (**9**). Crystal data for **4a**: C$_9$H$_{14}$Cl$_2$Pt, space group C2/c with a = 14.954 (2) Å, b = 7.233 (2) Å, c = 18.726 (5) Å, β = 94.01 (2)°, V = 2021 (1) Å^3, Z = 8. Crystal data for **4b**: C$_9$H$_{14}$Br$_2$Pt, space group C2/c with a = 15.317 (3) Å, b = 7.427 (2) Å, c = 18.920 (3) Å, β = 93.68 (1)°, V = 2148 (1) Å^3, Z = 8. Crystal data for **6**: C$_{14}$H$_{17}$ClPt, space group Pbca with a = 12.380 (2) Å, b = 12.757 (4) Å, c = 16.559 (3) Å, V = 2615 (2) Å^3, Z = 8. Crystal data for **7**: C$_{20}$H$_{22}$Pt, space group P2$_1$2$_1$2$_1$ with a = 6.250 (3) Å, b = 14.694 (4) Å, c = 17.796 (5) Å, V = 1634 (2) Å^3, Z = 4. Crystal data for **9**: C$_8$H$_{14}$Cl$_2$Pt, space group P2$_1$/n with a = 7.633 (3) Å, b = 12.147 (1) Å, c = 11.048 (1) Å, β = 97.84 (2)°, V = 1014.8 (6) Å^3, Z = 8.

Introduction

The chemical reactivity of metal-coordinated olefins is a topic of much current experimental[5] and theoretical[6] interest. Nucleophilic attack on coordinated olefins is crucial to many stoichiometric and catalytic processes, such as hydrogenation, polymerization, isomerization, oxidation, and hydrosilation.[7] In general, nucleophilic attack on a metal-coordinated olefin can occur from outside or inside the coordination sphere, e.g. 1. Attack from outside the

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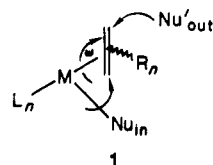
coordination sphere proceeds with overall trans stereochemistry (trans ligometalation), while attack from inside the coordination sphere results in cis stereochemistry (cis ligand migration). The overall rate of nucleophilic attack, the relative rates of potentially competitive external vs.

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internal nucleophilic attack pathways, and the regioselectivity of nucleophilic attack will depend on a number of factors such as (a) the nature of L$_n$M (cf. 1), (b) the identities of Nu and Nu', (c) the substitution pattern on the olefin (R$_n$), (d) asymmetry in the metal–olefin carbon bond lengths, (e) the barrier to rotation around ω, and (f) the fixed value of ω if rotation is restrained, as in a chelated diene for example.

In an extensive analysis of nucleophilic attack on coordinated olefins, Hoffmann and co-workers concluded that, for d^8 square-planar systems, olefins having $\omega \sim 0°$ would be deactivated with respect to those having $\omega \sim 90°$ for external nucleophilic attack,[6b,c] with the reverse order prevailing for internal nucleophilic attack.[6e] In order to test the ω-dependent reactivity predictions[6b,c,e] and clear up uncertainties about the general ability to synthesize stable "in-plane" $\omega \sim 0°$ olefin systems, we have synthesized complexes of 5-methylenecycloheptene (2, MCH) and 5-methylenecyclooctene (3, MCOT) with PtCl$_2$. In complexes of 2 and 3 with PtCl$_2$ the normal ground-state

2   3
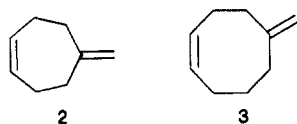
preference[6e,8-12] for $\omega \sim 90°$ is overcome by the geometric constraints of the ligands, and the $\omega \sim 0°$ and $\omega \sim 90°$ geometries are simultaneously available for competitive nucleophilic attack. We present here syntheses, structures, and spectral properties of complexes 4-7, all of which have the "crossed" $\omega \sim 0°$, 90° olefin geometries. In addition we compare 4 and 5 to model complexes 8 and 9, for which we also present spectral and structural data, and we discuss the bonding in the various complexes at hand. In subsequent papers we will discuss reactions with neutral and anionic nucleophiles that lead to nucleophilic addition to the platinum-coordinated olefin.

4a: X = Cl
b: X = Br
  5   7   8
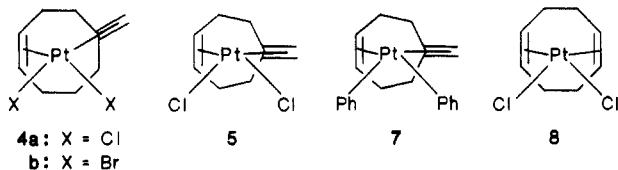
Experimental Section

General Data. The ^{1}H NMR spectra were recorded at 199.50 MHz by using a JEOL 200 instrument (reference δ 7.27, CHCl$_3$). The ^{13}C NMR spectra were recorded at 50.15 MHz with the same instrument (reference δ 77.0, CDCl$_3$ center peak). The ^{195}Pt NMR spectra were recorded at 64.3 MHz with a widebore Nicolet 300 instrument (reference δ 0.0, aqueous K$_2$PtCl$_6$, $\Delta\nu_{1/2}$ = 50 Hz). ^{1}H and ^{13}C NMR spectra are assigned by using appropriate decoupling and pulse sequence techniques, as necessary. Unless stated otherwise, all NMR spectra were determined in CDCl$_3$.

The IR spectra were recorded on a Perkin-Elmer 283 spectrometer with polystyrene calibration at 3027.1 and 1601.4 cm^{-1} (abbreviations: m, medium; s, strong; w, weak; br, broad). Neat 5-methylenecyclooctene was examined as a film between NaCl plates. Solid complexes were examined as Nujol mulls between NaCl plates or between polyethylene windows in the 500–200 cm^{-1}

region. Certain complexes were studied in CDCl$_3$ solution cells with KBr windows.

UV–visible spectra were obtained on a Cary 219 or a Hewlett-Packard 8451A diode array instrument.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or by MicAnal, Tucson, AZ.

Reagent grade chemicals and solvents, including CDCl$_3$ and 2,5-dimethyl-1-5-hexadiene, were purchased from Aldrich or Mallinckrodt. Potassium tetrachloroplatinate, K$_2$PtCl$_4$, was a loan from Johnson Matthey Co. Sodium tetrachloroplatinate Hydrate was purchased from Strem Chemicals. 5-Methylenecycloheptene (2, MCH),[13] phenyltrimethylstannane,[14] dichloro[(1,2,5,8-η^4)-5-methylenecycloheptene]platinum(II) [5, (MCH)PtCl$_2$],[12] 4-cycloocten-1-one,[15] and bis(μ-chloro)dichlorobis(η^2-ethylene)diplatinum(II) (10),[16] dichloro[(1,2,5,6-η^4)-cycloocta-1,5-diene]-platinum(II) [8, (COD)PtCl$_2$],[17a] and dichloro[(1,2,5,6-η^4)-2,5-dimethyl-1,5-hexadiene]platinum(II) (9)[17b] were prepared by literature methods.

Preparation of Compounds. 5-Methylenecyclooctene (MCOT, 3). This compound was prepared by a Wittig reaction on 4-cycloocten-1-one (29.1 g). Distillation resulted in a 10-g (38–42 °C, 2.5 mmHg) fraction of pure 5-methylenecyclooctene.[17c]

^{1}H NMR: δ 5.75–5.55 (m, 2 H, —CH=), 4.76 (s, 1 H, =CHH), 4.74 (s, 1 H, =CHH), 2.3–1.9 (m, 8 H, —CH$_2$—), 1.6–1.4 (m, 2 H, —CH$_2$). ^{13}C NMR: δ 151.1 (C5); 130.1, 130.0 (C1, C2); 112.6 (C9); 39.4, 32.9, 29.0, 25.8, 25.2 (C3, C4, C6, C7, C8). IR (cm^{-1}): 3040 (w), 3010 (m), 2960 (s), 2930 (m), 1640 (m), 1440 (m), 885 (s), 720 (m).

Dichloro[(1,2,5,9-η^4)-5-methylenecyclooctene]platinum(II) [4a, (MCOT)PtCl$_2$]. Bis(μ-chloro)dichlorobis(η^2-ethylene)diplatinum(II) (10) (315 mg, 0.535 mmol) was dissolved in a mixture of 10 mL of benzene (dried over 4-Å molecular sieves) and 1 mL of reagent grade acetone. 5-Methylenecyclooctene (141 μL, 1.07 mmol) was added dropwise over a period of several minutes to the warmed (40 °C), stirred benzene solution of 10. Within a few minutes the orange color of the solution changed to yellow and a finely divided pale yellow precipitate formed. Stirring at 40 °C was continued for 45 min, and then hexane (40 mL) was added to complete the precipitation of the product. After being stirred for an additional 45 min at room temperature, the reaction mixture was chilled (–30 °C) for 2 h and filtered, and the solid product was placed in a vacuum desiccator for complete drying. The yield of pale yellow solid was 225 mg (54%). The product is mildly sensitive to water, but it can be handled in air at room temperature for short periods of time. The product should be stored in a tightly capped vial below 0 °C. Anal. Calcd for C$_9$H$_{14}$PtCl$_2$: C, 27.76; H, 3.43. Found: C, 27.85; H, 3.64.

^{1}H NMR of 4a (CDCl$_3$): δ 6.15 (m, 1 H, J_{Pt-H} = 78 Hz, —CH=), 5.68 (m, 1 H, J_{Pt-H} = 76 Hz, =CH—), 5.23 (s, 1 H, J_{Pt-H} = 59 Hz, =CHH), 4.78 (s, 1 H, J_{Pt-H} = 67 Hz, =CHH), 3.0–1.9 (m, 10 H, 5 CH$_2$). ^{13}C NMR of 4a: δ 100.5 (J_{Pt-C} = 147 Hz, C1 or C2), 93.6 (J_{Pt-C} = 148 Hz, C2 or C1), 89.2 (J_{Pt-C} = 85 Hz, C9), 136.4 (J_{Pt-C} = 69 Hz, C5), and C3, C4, C6, C7, C8 at δ 37.5, 36.5 (J_{Pt-C} = 24 Hz), 34.2, 26.9 (J_{Pt-C} = 25 Hz), 25.7 (J_{Pt-C} = 66 Hz). ^{195}Pt NMR of 4a: δ –3720 ($\Delta\nu_{1/2}$ = 200 Hz). IR of 4a (cm^{-1}, 0.1 M in CDCl$_3$): 3050–2925 (s, br), 1540 (m), 1420–1440 (m, br), 460 (m), 445 (m), 315 (s), 290 (s) (the latter four peaks are also observed in Nujol).

Growth of Single Crystals of 4a. Dissolution of 4a in 1:1 dichloromethane/toluene followed by slow evaporation at 7 °C (refrigerator) led to large yellow crystals.

Dibromo[(1,2,5,9-η^4)-5-methylenecyclooctene]platinum(II) [4b, (MCOT)PtBr$_2$]. MCOTPtCl$_2$ (220 mg) was dissolved in 30 mL of 1:1 benzene/dichloromethane. The solution of MCOTPtCl$_2$ was shaken with 3 mL of 0.46 M aqueous LiBr in a 50-mL separatory funnel. The lower (aqueous) fraction was removed, and

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the process was repeated with nine more 3-mL aliquots of LiBr solution. As the extractions proceeded, the color of the organic layer changed from yellow to orange. After an aqueous wash, the organic layer was dried over MgSO$_4$ and filtered, and the solvents were removed to leave orange MCOTPtBr$_2$ (0.165 g, 56%, presumed to be a mixture of monomer **4b** and dimer **11**). Anal. Calcd for C$_9$H$_{14}$PtBr$_2$: C, 22.61; H, 3.16. Found: C, 22.80; H, 3.15.

Growth of Single Crystals of 4b. A few milligrams of orange powder isolated as described above was dissolved in 1:1 dichloromethane/toluene. After 5 days of slow evaporation at 7 °C, the beaker contained yellow platelets (**4b**) and orange powder (presumed to be **11**). A yellow platelet was selected and mounted for X-ray data collection.

^{1}H NMR of **4b** (monomer, i.e. several yellow platelets separated by hand from the above described crystal growth mixture): δ 6.45 (m, 1 H, J_{Pt-H} = 68 Hz, —CH=), 5.70 (m, 1 H, J_{Pt-H} = 68 Hz, =CH—), 5.45 (s, 1 H, J_{Pt-H} = 56 Hz, =CHH), 4.62 (s, 1 H, J_{Pt-H} = 64 Hz, =CHH), 2.8–2.0 (m, 10 H, 5 CH$_2$).

^{1}H NMR of **11** (dimer, i.e. orange powder separated by hand from the above described crystal growth mixture—NMR had peaks due to both **4b** and **11**, but **4b** peaks are easily "subtracted"): δ 5.7–5.3 (m, 2 H, —CH=CH—), 4.86 (s, 1 H, =CHH), 4.81 (s, H, =CHH), 2.8–1.8 (m, 10 H, 5 CH$_2$). ^{13}C NMR (mixture of **4b** and **11** because lengthy signal averaging led to equilibration of monomer (dimer)): δ 149.5, 148.1 (C5), 115.2, 100.2 (=CH$_2$), 93.7, 91.3, 89.3, 88.8 (—CH=CH—), 38.5, 36.9, 36.7, 34.9, 32.9, 30.0, 29.5, 28.6, 27.2, 24.8 (10 CH$_2$).

Chloro[(1,2,5,8-η^4)-5-methylenecycloheptene)]phenylplatinum(II) (6). Dichloro[(1,2,5,8-η^4)-5-methylenecycloheptene]platinum(II) (61.7 mg, 0.165 mmol) was dissolved in 6.6 mL of CH$_2$Cl$_2$, and trimethylphenyltin (30.8 μL, 0.165 mmol) was added with stirring. After 2 h, the reaction was quenched by the addition of 20 mL of hexanes. After removal of volatile solvents (rotary evaporator), the remaining solid was washed with hexanes to remove residual tin compound and chromatographed (CH$_2$Cl$_2$) on a small Florisil column. A golden yellow fraction was collected, and the solvent was removed (42 mg, 61%). Anal. Calcd for C$_{14}$H$_{17}$PtCl: C, 40.42; H, 4.12. Found: C, 40.31; H, 4.24.

^{1}H NMR of **6**: δ 7.4–6.9 (m, 5 H, phenyl), 5.05 (s, 2 H, J_{Pt-H} = 27 Hz, =CH$_2$), 4.53 (m, 2 H, J_{Pt-H} = 78 Hz, —CH=CH—), 2.9–2.2 (m, 8 H, 4 CH$_2$). ^{13}C NMR of **6**: δ 164.9 (phenyl B1) 133.8 (phenyl CB2, CB6), 128.4 (phenyl CB3, CB5), 124.5 (phenyl CB4), 104.9 (C8), δ 86.3 (J_{Pt-C} = 225 Hz, C1 and C2), 34.9 and 31.9 (C3–C7, C4–C6).

Crystal Growth. A few milligrams of **6** was dissolved in 1:1 CH$_2$Cl$_2$/heptane. Slow evaporation at 4 °C resulted in pale yellow needles. One crystal was selected and was cut with a razor blade to give more uniform dimensions for X-ray exposure.

Diphenyl[(1,2,5,8-η^4)-5-methylenecycloheptene]platinum-(II) (7). Dichloro[(1,2,5,8-η^4)-5-methylenecycloheptene]platinum(II) (30.8 mg, 0.082 mmol) was dissolved in 5.0 mL of CH$_2$Cl$_2$, and trimethylphenyltin (30.8 μL, 0.165 mmol) was added to the solution. The reaction mixture was stirred 30 min and the solvent was removed (rotary evaporation). The solid product was washed with hexanes to remove tin compounds, dissolved in CH$_2$Cl$_2$, and chromatographed (CH$_2$Cl$_2$/Florisil). A pale yellow fraction was collected, which yielded 25 mg of off-white **7** (0.55 mmol, 67%) upon removal of CH$_2$Cl$_2$.

Because of the thermal instability of **7**, we were unable to obtain satisfactory elemental analysis.

^{1}H NMR of **7**: δ 7.4–6.7 (m, 10 H, phenyl), 5.15 (m, 2 H, J_{Pt-H} = 47 Hz, —CH=CH—), 4.87 (s, 2 H, J_{Pt-H} = 48 Hz, =CH$_2$), 2.9–2.2 (m, 8 H, 4 CH$_2$).

Crystal Growth. **7** (2.6 mg) was dissolved in 1:1 CH$_2$Cl$_2$/toluene. Slow evaporation for 6 days in the dark at 4 °C resulted in almond-colored needles. During X-ray data collection the crystal turned dark red.

Dichloro(5-methylenecycloheptene)platinum(II) (5). ^{1}H NMR of **5**: δ 5.75 (m, 2 H, J_{Pt-H} = 68 Hz, —CH=CH), δ 4.80 (s, 2 H, J_{Pt-H} = 59 Hz, =CH$_2$), δ 3.2–2.3 (m, 8 H, CH$_2$). ^{13}C NMR of **5**: δ 140.4 (J_{Pt-C} = 52 Hz, C5), 100.2 (J_{Pt-C} = 169 Hz, C1, C2), 89.4 (J_{Pt-C} = 70 Hz, C8), 38.4, 32.1 [(C3, C8) and/or (C4/C7)].

Dichloro[(1,2,5,6-η^4)-cycloocta-1,5-diene]platinum(II) [8, (COD)PtCl$_2$]. ^{1}H NMR of **8**: δ 5.6 (m, 4 H, J_{Pt-H} = 67 Hz, —CH=CH—); 3.0–2.0 (m, 8 H, CH$_2$). ^{13}C NMR of **8**: δ 100.8 (J_{Pt-C} = 152 Hz, C1, C2, C5, C6), 3.10 (C3, C4, C7, C8).

Dichloro[(1,2,5,6-η^4)-2,5-dimethyl-1,5-hexadiene]platinum(II) [9, (HEX)PtCl$_2$]. ^{1}H NMR of **9**: δ 5.06 (s, 2 H, J_{Pt-H} = 69 Hz, =CHH), 4.20 (s, 2 H, J_{Pt-H} = 68 Hz, = CHH), 2.6–2.2 (m, 4 H, —CH$_2$CH$_2$—), 2.05 (s, 6 H, J_{Pt-H} = 29 Hz, CH$_3$). ^{13}C NMR of **9** (CD$_2$Cl$_2$): δ 129.6 (J_{Pt-C} = 115 Hz, C2 and C5), 75.7 (J_{Pt-C} = 148 Hz, C1 and C6), 39.1 (C3 and C4), 26.6 (J_{Pt-C} = 22 Hz, methyl C).

Bis(μ-chloro)dichlorobis(η^2-ethylene)diplatinum(II) (10). ^{195}Pt NMR of **10**: δ –2680 (Δ$\nu_{1/2}$ = 100 Hz, major peak), –2656 (Δ$\nu_{1/2}$ = 500 Hz, minor peak); trans and cis isomers, respectively?

Reference NMR Spectra. We include here reference NMR spectra (CDCl$_3$) for free ligands 5-methylenecycloheptene (MCH), 2,5-dimethyl-1,5-hexadiene (HEX), and cycloocta-1,5-diene (COD).

(a) ^{1}H NMR of MCH: δ 5.80 (m, 2 H, —CH=CH—), 4.65 (s, 2 H, =CH$_2$), δ 2.31–2.1 (m, 8 H, CH$_2$). ^{13}C NMR of MCH: δ 163.6 (C5), 135.7 (C1, C2), 109.8 (C8), 36.1, 28.6 (C3, C4, C6, C7).

(b) ^{1}H NMR of HEX: δ 4.74–4.67 (br, 4 H, =CH$_2$), 2.16 (s, 4 H, —CH$_2$CH$_2$—), 1.73 (s, 6 H, CH$_3$). ^{13}C NMR of HEX: δ 145.5 (C2, C5), 110.1 (C1, C6), 36.0 (C3, C4), 22.3 (methyl).

(c) ^{1}H NMR of COD: δ 5.5 (m, 4 H, —CH=CH—), 2.25 (m, 8 H, CH$_2$). ^{13}C NMR of COD: δ 128.3 (C1, C2, C5, C6), 27.9 (C3, C4, C7, C8).

Coordinated Olefin Displacement Series. A series of equilibrations [(diolefin)PtCl$_2$ + diolefin' ⇌ (diolefin')PtCl$_2$ + diolefin] was set up, in order to establish the relative binding abilities of the various diolefins. Typically, to 400 μL of 0.2 M (diolefin)PtCl$_2$ in CDCl$_3$ was added enough diolefin' such that diolefin' was in slight excess. The displacement reaction was followed by ^{1}H NMR until equilibrium was reached (a few hours to a few days).

Equilibration of Dibromo[(1,2,5,9-η^4)-5-methylenecyclooctene]platinum(II) (4b) and Bis(μ-bromo)dibromobis-[(1,2-η)-5-methylenecyclooctene]diplatinum(II) (11). Examination of both ^{1}H and ^{13}C NMR of putative monomeric η^4-**4b** led to observation of concentration-dependent "free" exocyclic olefin. This process was treated as a dimerization with bridging bromide replacing exocyclic olefin, described as follows (eq 1 and 2).

$$2 \text{ monomer } \mathbf{4b} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ dimer } \mathbf{11} \qquad (1)$$
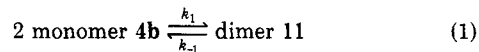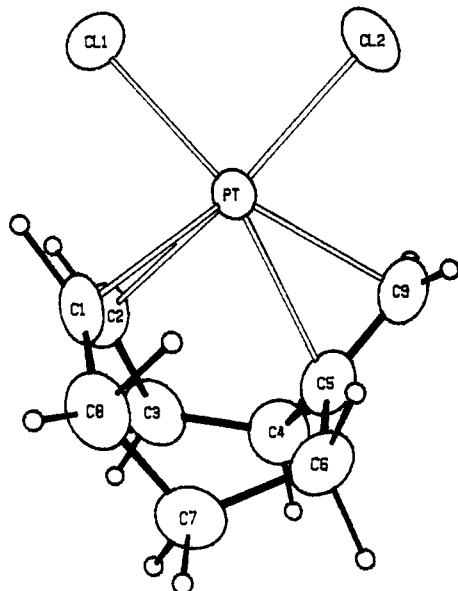
$$K = k_1/k_{-1} = [\mathbf{11}]/[\mathbf{4b}]^2 \qquad (2)$$

Integration of the ^{1}H NMR of the **4b**/**11** mixture as a function of concentration gave K = 54 ± 4 (26 ± 2°, CDCl$_3$). This equilibrium constant was found to be independent of temperature between 0 and 48 °C.

The ^{195}Pt NMR of 69.6 mg of **4b** in 3.0 mL of CDCl$_3$ (0.049 M, equilibrated for 4 h) revealed two Pt environments, once again indicating monomer/dimer equilibration. The major resonances are observed at δ –4130 (Δ$\nu_{1/2}$ = 230 Hz, η^4-monomer **4b**) and –3090 (Δ$\nu_{1/2}$ = 460 Hz, η^2-dimer **11**, trans). A minor peak at δ –3105 (Δ$\nu_{1/2}$ = 670 Hz) may be due to **11**, cis. The peaks at δ –3090 and –3105 are at their expected positions on the basis of the ^{195}Pt NMR of **10** (given above) and on comparison of the ^{195}Pt NMR spectra of **4a** and **4b** [Δ(halogen)-induced Δδ(^{195}Pt)]. The equilibrium constant for dimerization (eq 1) was estimated to be 90 ± 30 from the relative intensities of the peaks at δ –4130, –3090, and –3105.

The equilibrium constant for dimerization (eq 1) was also estimated by ultraviolet absorption (360 nm, 24 °C). Ten solutions with total platinum concentration ranging from 0.00125 to 0.040 M gave absorbance values at 360 nm that resulted in the best values for ε$_{monomer}$ = 1180 ± 13 cm^{-1} M^{-1}, ε$_{dimer}$ = 1250 ± 23 cm^{-1} M^{-1}, and K = 70 ± 10 upon least-squares fitting of the ε(360 nm) data with ε$_{monomer}$, ε$_{dimer}$, and K as parameters.

The rate constants k_1 and k_{-1} (eq 1) were determined in CDCl$_3$ by a relaxation technique[18] with observation at 360 nm. Equilibrated solutions, 0.0010–0.01 M in platinum (expressed as monomer), were perturbed by dilutions, which would increase monomer concentration no more than 10%. The characteristic relaxation time (τ) is obtained as the diluted solution approaches

(18) (a) Bernasconi, C. F. *Relaxation Kinetics*; Academic: New York, 1976. (b) Espenson, J. H. *Chemical Kinetics and Reaction Mechanism*; McGraw-Hill: New York, 1981. (c) Swinehart, J. H.; Castellan, G. W. *Inorg. Chem.* **1964**, *3*, 278.

Figure 2. Dichloro[(1,2,5,6-η^4)-2,5-dimethyl-1,5-hexadiene]-platinum(II) (**9**) viewed directly above the coordination plane. Angles (see also Table II) (deg): C4–C5–C8, 116.2 (5); C3–C2–C7, 113.5 (5).

Figure 1. Dichloro[(1,2,5,9-η^4)-5-methylenecyclooctene]platinum(II) (**4a**) viewed directly above the coordination plane. Selected nonbonded distances (see also Table II) (Å): Cl2–C9, 2.82 (1); Cl1–C1, 3.02 (1); Cl1–C2, 3.16 (1). Angles (see also Table II) (deg): C4–C5–C6, 118.4 (9); C1–C2–C3, 128.6 (8); C2–C1–C8, 129.2 (8). Best plane (deg): Pt–C1–C2/Pt–C5–C9, 100.3.

equilibrium. A plot of τ^{-2} vs. [Pt]$_{total}$ gave k_1 = 9.2 × 10^{-3} M^{-1} s^{-1}, k_{-1} = 1.2 × 10^{-4} M^{-1} s^{-1}, and K = k_1/k_{-1} = 77.

Crystallography. X-ray structure analyses were carried out in the same manner for each of the structures. Space groups were determined and cell constants verified by examination of oscillation and Weissenberg photographs. In addition, for (MCOT)PtCl$_2$, precession and cone-axis photographs were also taken. For (MCOT)PtBr$_2$, no photographs were taken. Because of the similarity of the bromide crystal in size, shape, and color to the (MCOT)PtCl$_2$ crystal, data collection was started without preliminary film work and the structure was solved by using the Pt coordinate from the (MCOT)PtCl$_2$ atoms file.

The identity of the crystal selected for X-ray analysis was verified in each case by ^{1}H NMR on several of the remaining crystals.
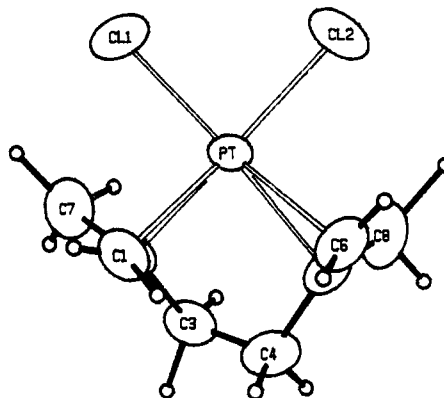
Cell constants were determined by least-squares refinements on the basis of ca. 25 carefully centered reflections having 2θ as large as possible.

Intensity data were collected at room temperature on an Enraf-nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, with a crystal-to-counter distance of 21 cm and pulse-height discrimination set to accept ca. 95% of the intensity of a well-centered reflection. Scattering factors (neutral atoms) were taken from ref 19a and were corrected for both the real and imaginary parts of the anomalous dispersion where appropriate. The Enraf-Nonius SDP+ program package was used throughout.
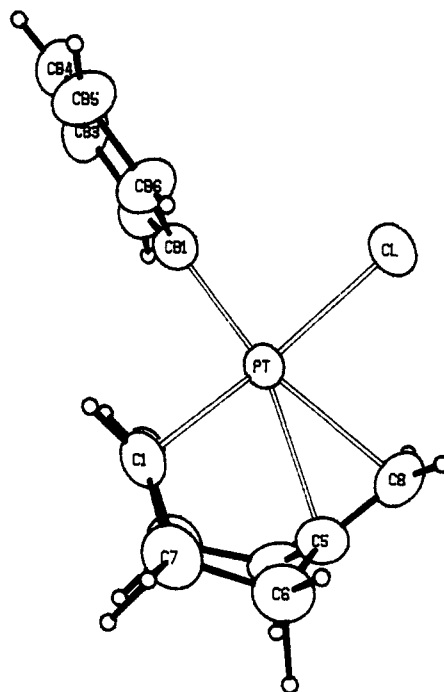
For compounds **4a**, **4b**, and **6**, all hydrogen atoms were located, all non-hydrogen atoms were refined anisotropically, and hydrogen atom thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom. For compound **9**, one methyl hydrogen (H8B) could not be refined and its position was fixed. During data collection for compound **7**, crystal degradation was encountered. Thus for **7**, with the largest number of atoms of any of the compounds studied, only the platinum atom was refined anisotropically and the hydrogen atoms were not located. Also for **7** the sign of *hkl* was chosen to minimize the *R* factor (anomalous scattering).

Absorption corrections were done as follows:

Compound 4a: analytical based on careful measurement of crystal faces.

(19) (a) Cromer, D. T.; Waber, J. T. *International Tables For X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158. (c) Atom coordinates for **8** taken from Syed, A.; Stevens, E. D.; Cruz, S. G. *Inorg. Chem.* **1984**, *23*, 3673–3674.

Figure 3. Chloro[(1,2,5,8-η^4)-5-methylenecycloheptene]-phenylplatinum(II) (**6**) viewed directly above the coordination plane. Selected nonbonded distances (see also Table II) (Å): Cl–C8, 3.04 (1); CB1–C1, 2.91 (2); CB1–C2, 2.89 (2). Angles (see also Table II) (deg): C4–C5–C6, 118 (1); C1–C2–C3, 121 (1); C2–C1–C7, 123 (1). Best plane (deg): Cl–Pt–CB1/CB1–CB2–CB3–CB4–CB5–CB6, 84.0; Pt–C1–C2/Pt–C5–C8, 89.7.

Compound 9: empirical based on a psi scan near χ = 90°. The minimum transmission (T_{min}) was 63%, and the average (T_{av}) was 85% on the basis of an arbitrary maximum of 100%.

Compounds 4b, 6, and 7. Empirical PSI scan corrections were supplemented by an empirical fit of a Fourier expansion to the ΔF's of the isotropically refined structures, using the program DIFABS.[19b]

For **4b**. A psi scan gave T_{min} = 17% and T_{av} = 69%. DIFABS gave minimum absorption = 0.79 and maximum absorption = 1.18, with the average correction = 0.99.

For **6**. A psi scan gave T_{min} = 92% and T_{av} = 96%. DIFABS gave minimum absorption = 0.88 and maximum absorption = 1.18, with the average correction = 1.0.

For **7**. A psi scan gave T_{min} = 82% and T_{av} = 94%. DIFABS gave minimum absorption = 0.77 and maximum absorption = 1.14, with the average correction = 1.00.

Analytical corrections were done on **6** and **7** but proved less satisfactory. All structures were refined in full-matrix least squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the w is defined as $4F_o^2/[\sigma(F_o^2)]^2$.

Table I. Summary of Crystal Data

	4a	4b	6	7	9
formula	$C_9H_{14}Cl_2Pt$	$C_9H_{14}Br_2Pt$	$C_{14}H_{17}ClPt$	$C_{20}H_{22}Pt$	$C_8H_{14}Cl_2Pt$
space group	$C2/c$	$C2/c$	$Pbca$	$P2_12_12_1$	$P2_1/n$
M, daltons	388.21	477.12	415.83	457.49	376.2
a, Å	14.954 (2)	15.317 (3)	12.380 (2)	6.250 (3)	7.633 (3)
b, Å	7.233 (2)	7.427 (2)	12.757 (4)	14.694 (4)	12.147 (1)
c, Å	18.726 (5)	18.920 (3)	16.559 (3)	17.796 (5)	11.048 (1)
β, deg	94.01 (2)	93.68 (1)			97.84 (2)
V, Å^3	2021 (1)	2148 (1)	2615 (2)	1634 (2)	1014.8 (6)
Z	8	8	8	4	8
d_{calcd}, g/cm^3	2.55	2.96	2.11	1.86	2.44
cryst. size (mm × mm × mm)	0.36 × 0.22 × 0.20	0.3 × 0.2 × 0.2	0.22 × 0.08 × 0.09	0.33 × 0.13 × 0.08	
radiatn (graphite monochromated)	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
scan width (ΔW), deg	1.00 + 0.350 tan θ	1.00 + 0.350 tan θ	1.00 + 0.350 tan θ	1.00 + 0.350 tan θ	1.00 + 0.350 tan θ
max counting time, s (2θ limits, deg)	120 (4 ≤ 40), 240 (>40)	180 (≤40), 240 (>40)	120 (≤30), 180 (>30)	120	180 (≤40), 240 (>40)
collectn range, deg	4 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 45	2 ≤ 2θ ≤ 40	2 ≤ 2θ ≤ 50
no. of unique data	1773	1882	1708	911	2314
no. of unique data [$I > 3\sigma(I)$]	1530	1614	1098	809	2169
no. of variables	151	151	196	90	139
R,[a] %	3.7	3.3	2.4	3.3	2.3
R_w,[b] %	5.0	4.5	2.9	4.5	3.3
esd	2.1	1.8	0.9	1.5	1.4
largest parameter shift[c]	0.71	0.04	0.77	0.02	0.26
largest peak, e/Å^3[d]	0.8 (1)	0.6 (1)	0.5 (1)	0.5 (1)	0.9 (2)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 4F_o^2/[\sigma(F_o^2)]^2$, and $\sigma(I) = [P + 4B + (0.045I)^2]^{1/2}$. Here P is the number of counts during the scan and B is the sum of the background counts. [c] From final refinement. [d] From final difference Fourier.

Table II. "Core" Bond Distances, Angles, and NMR Parameters for (Diene)PtX₂, X = Cl, Br, or Phenyl

parameter	(MCOT)-PtCl₂ (4a)	(MCOT)-PtBr₂[e] (4b)	(COD)-PtCl₂[b] (8)	(HEX)-PtCl₂ (9)	(MCH)-PtCl₂[d] (5)	(MCH)PtPhCl (6)	(MCH)-PtPh₂ (7)
r_{Pt-C1}, Å	2.190 (9)	2.205 (9)	2.172 (6)	2.153 (5)	2.23 (1)	2.13 (1)	2.22 (2)
r_{Pt-C2}, Å	2.165 (8)	2.189 (9)	2.154 (5)	2.264 (5)	2.24 (1)	2.16 (1)	2.26 (2)
r_{Pt-C5}, Å	2.344 (8)	2.34 (2)	2.176 (6)	2.268 (4)	2.28 (1)	2.44 (1)	2.36 (2)
$r_{Pt-C6,8,or9}$, Å	2.209 (8)	2.21 (1)	2.178 (6)	2.168 (5)	2.31 (1)	2.36 (1)	2.29 (2)
r_{C1-C2}, Å	1.40 (1)	1.40 (1)	1.375 (8)	1.387 (7)	1.38 (2)	1.36 (2)	1.34 (3)
$r_{C5-C6,C8orC9}$, Å	1.34 (1)	1.34 (2)	1.387 (8)	1.370 (7)	1.37 (2)	1.33 (2)	1.24 (2)
r_{Pt-X1}, Å	2.314 (2)	2.454 (1)	2.315 (1)	2.300 (1)	2.306 (3)	1.99 (1)(phenyl)	2.04 (2)
r_{Pt-X2}, Å	2.313 (3)	2.455 (1)	2.309 (1)	2.315 (1)	2.298 (3)	2.334 (3) Cl	2.04 (2)
angle X1–Pt–X2, deg	84.59 (9)	84.60 (3)	89.78 (5)	87.19 (6)	86.6 (2)	85.5 (3)	84.4 (7)
ω, C1–C2, deg	82.3	83.3	83.3	86.7	90.0	88.2	88.4
ω, C5–C6, C8, or C9, deg	4.8	4.8	84.2	73.7	0.0	1.9	7.2
$^1J_{Pt-C1}$, Hz	147[a]	c	152	148	169	225	c
$\Delta\delta(C1)$[f]	−29.5[a]	c	−27.5	−34.4	−35.5	−49.4	c
$^2J_{Pt-H}(C1)$, Hz	78[a]	68	67	69[a]	68	78	47
$^1J_{Pt-C2}$, Hz	148[a]	c	152	115	169	225	c
$\Delta\delta(C2)$	−36.4[a]	c	−27.5	−15.9	−35.5	−49.4	c
$^2J_{Pt-H(C2)}$, Hz	76[a]	68	67		68	78	47
$^1J_{Pt-C5}$, Hz	69	c	152	115	52	not observed	c
$\Delta\delta(C5)$	−14.7	c	−27.5	−15.9	−23.2		c
$^2J_{Pt-H(C5)}$, Hz			67				
$^1J_{Pt-C6,8,or9}$, Hz	85	c	152	148	70	0	c
$\Delta\delta(C6, 8, or 9)$	−23.4	c	−27.5	−34.4	−20.4	−4.9	c
$^2J_{Pt-H(C6,8,or9)}$, Hz	59, 67	56.64	67	68[a]	59	27	48

[a] Reverse assignment to related atom possible. [b] Distance data from ref 19c. [c] ^{13}C results unavailable because of long-term solution problems: monomer/dimer (4b) or thermal decomposition (7). [d] Distance data for orientation 1, model 2: see ref 12. [e] Additional distances for 4b (numbering scheme same as that given for Figure 1) (Å): Br2–C9, 2.90 (2); Br1–C1, 3.15 (1); Br1–C2, 3.28 (1). Additional angles for 4b (deg): C4–C5–C6, 118 (2); C1—C2–C3, 125 (1); C2–C1–C8, 129 (1). Best planes for 4b (deg): Pt–C1–C2/Pt–C5–C9, 99.0. [f] $\Delta\delta(C)$ is coordination chemical shift (negative shift is toward Me₄Si reference).

Details of the crystallographic results are given in Table I. Selected distances and angles are given in Table II and the figure captions.

Results and Discussion

### A. Preparation of Compounds.

The near absence[20,21] of literature reports of d^8 square-planar "in-plane" coordinated olefins could indicate that such compounds cannot in general be prepared or are subjected to rapid decomposition. Indeed our earliest efforts in this area involved

(20) (a) (MCH)PtCl₂ (5): Anderson, C. B.; Michalowski, J. T. *J. Chem. Soc., Chem. Commun.* 1972, 459–460. (b) (MCH)PtCl₂ (5): ref 12.

(21) (a) (η^3-Methallyl)(triphenylphosphine) ("in-plane" styrene)platinum(II) cation: Miki, K.; Kai, Y.; Kasai, N.; Kurosawa, H. *J. Am. Chem. Soc.* 1983, *105*, 2482–2483. (b) Similar to ref 21a except (Z)-but-2-ene "in-plane": Miki, K.; Yamatoya, K.; Kasai, N.; Kurosawa, H.; Emoto, M.; Urabe, A. *J. Chem. Soc., Chem. Commun.* 1984, 1520–2.
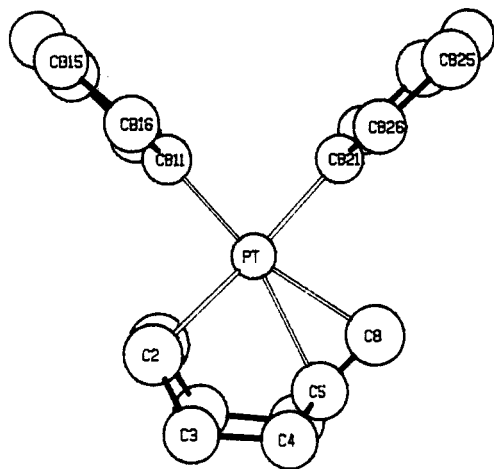
Figure 4. Diphenyl[(1,2,5,8-η^4)-5-methylenecycloheptene]platinum(II) (7) viewed directly above the coordination plane. Selected nonbonded distances (see also Table II) (Å): CB21–C8, 2.81 (2), CB11–C1, 3.02 (2); CB11–C2, 3.08 (2). Angles (see also Table II) (deg): C4–C5–C6, 121 (2); C1–C2–C3, 122 (2); C2–C1–C7, 119 (3). Best plane (deg): CB11–Pt–CB21/CB11–CB12–CB13–CB14–CB15–CB16, 91.3; CB11–Pt–CB21/CB21–CB22–CB23–CB24–CB25–CB26, 94.5.

reaction of bis(benzonitrile)dichloropalladium(II) with 2, 3, and derivatives of 7-methylenebicyclo[2.2.1]hept-2-ene (12). In the cases 2 and 3, the palladium reagent rapidly


12
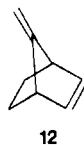
chloropalladates at room temperature to give uncharacterized product mixtures.[22] With 12 and derivatives extremely fast chloropalladation of the "presumed" in-plane double bond proceeds as in eq 3.[23]

(3)
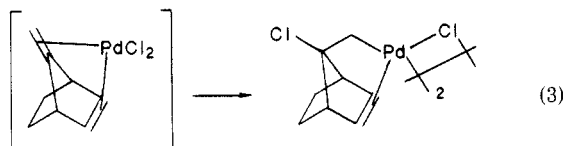
In contrast to the palladium(II) results, it was found by Anderson and Michalowski[20a] that 5-methylenecycloheptene reacts readily with PtCl$_4^{2-}$ in methanol[24] to give the 1:1 adduct MCH·PtCl$_2$, the first apparent in-plane coordinated olefin. This structure was indeed later confirmed by us by X-ray crystallography.[12] The stability of (MCH)PtCl$_2$ (5) is no doubt in part related to the overall rarity of chloroplatination as a kinetically viable reaction pathway. Since we had concluded[12] that for MCH the boat conformation is 4–5 kcal/mol less stable than the chair configuration, it was natural to assume that other potential in-plane diene ligands, which would not have to conformationally destabilize to chelate,[25] would give rise to in-

(22) (a) Unpublished results from this laboratory. (b) The reaction of MCOT with PdCl$_2$(PhCN)$_2$ has also been reported to yield a *characterized* chloropalladation product (Cl at C5, Pd at C9, Cl-bridged dimer). We however have been unable to reproduce the results: see ref 17c.

(23) Wiger, G.; Albelo, G.; Rettig, M. F. *J. Chem. Soc., Dalton Trans.* 1974, 2242–2247.

(24) PtCl$_4^{2-}$/alcohol/diene, "standard" conditions for (diene)PtCl$_2$ synthesis, see: Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 6, pp 632–680.

(25) For effects of conformation on chelation, see: Rettig, M. F.; Wing, R. M.; Wiger, G. R. *J. Am. Chem. Soc.* 1981, *103*, 2980–2986.

plane complexes even more stable than (MCH)PtCl$_2$. Our expectation is that 5-methylenecyclooctene (MCOT, 3) has a ground-state "tub" configuration similar to that of cyclooocta-1,5-diene.[26] Inspection of molecular models indicated that it would be feasible for the tub to chelate with the exocyclic olefin nearly in-plane. With the preceding considerations in mind, we were surprised to find that the "standard" conditions[12,20a,24] for synthesis of (diene)PtCl$_2$ failed for diene = MCOT. Thus it appears that Cl⁻ is too poor as a leaving group or that ROH is too competitive as an entering group to accommodate chelate ring closure to form (MCOT)PtCl$_2$.

The synthesis of (MCOT)PtCl$_2$ was finally accomplished as shown in eq 4, where the penultimate leaving group is

$$^1/_2[(C_2H_4)PtCl(\mu\text{-Cl})]_2 + MCOT \xrightarrow[\text{or CDCl}_3]{CH_2Cl_2}$$
$$(MCOT)PtCl_2 + C_2H_4 \quad (4)$$
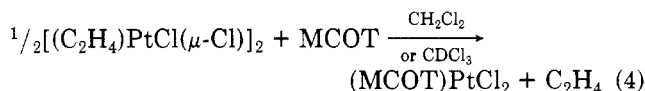
bridging chloride, the ultimate leaving group is ethylene, and there is no interference from the solvent. Thus (MCOT)PtCl$_2$ can be synthesized, but contrary to expectations it is less stable overall than (MCH)PtCl$_2$. We will comment further on relative stabilities in a later section of the paper.

Two phenyl containing complexes, namely, (MCH)-PtPhCl (6) and (MCH)PtPh$_2$ (7), may be prepared from (MCH)PtCl$_2$ and PhSnMe$_3$ or Ph$_2$Hg by an aryl transfer reaction.[27] Complexes 6 and 7 are stable with respect to further phenyl migration (for example to C8). In contrast to the behaviors of 6 and 7, attempts to arylate (MCOT)PtCl$_2$ (4a) or (MCOT)PtBr$_2$ (4b) with (aryl)SnR$_3$ lead to fast aryl transfer to Pt, followed by rapid aryl migration to C9. These aryl transfer/migration reactions will be discussed in a subsequent paper in this series.

B. Structural and NMR Considerations. 1. Crystal Structures. To date we have completed structural work on five examples of "in-plane" coordinated olefins, namely, 4a, 4b, 5,[12] 6, and 7. We also determined the structure of gem-disubstituted 9 as a model for the gem disubstitution that characterizes our exocyclic systems, and we present literature[19b] results for (COD)PtCl$_2$ to model the vicinal-disubstitution characteristic of the endocyclic olefins in our systems. There are a number of common structural features among the in-plane systems: (1) X1–Pt–X2 angles are significantly smaller than 90°; (2) r_{Pt-X1} and r_{Pt-X2} are not significantly different (when X1 = X2); (3) the close approach of in-plane terminal carbon to the cis ligand on platinum (see figure captions; for 4a, for example, Cl2–C9 is 2.82 (1) Å, which is 0.6–0.7 Å less than the sum of van der Waals radii); (4) longer Pt–exocyclic olefin bonds compared to Pt–endocyclic olefin bonds; (5) a systematic determination of shorter exocyclic C=C bonds compared to endocyclic C=C bonds (not significant for any *individual* case at the 99.5% confidence level, however); (6) generally longer Pt–C5 bonds compared to Pt–C6, C8, or C9 (the esd's for 5 for Pt–C5 and Pt–C8 are ±0.01 Å, so the distances are not significantly different). For comparison purposes, we note the following from the models 8 and 9: (1) for 8, the Cl–Pt–Cl angle is very close to 90° [at 89.78 (5)°]; (2) the Cl–Pt–Cl angle in 9 is closed to 87.19 (6)°, presumably due to interaction of Cl and CH$_3$; (3) Pt–C2 and Pt–C5 in 9 are ca. 0.1 Å longer than Pt–C1 and Pt–C6 in the same molecule, which is consistent with the usual pattern of increased olefin–carbon–metal bond length with electron-donating substituents.[28]

(26) See ref 25 for related ideas and leading references.

(27) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* 1978, 357–368.

Upon comparison of the in-plane systems to the models, we make several observations. First, it is apparent that the in-plane complexes as a whole are in general destabilized, as can be seen from the bond length patterns, in the nonbonded cis ligand repulsion, and in the closure of X1–Pt–X2 to as little as 84.4 (7)° (in **7**). Second, the asymmetry in the Pt–exocyclic olefin interaction, which could accelerate nucleophilic addition at C5,[29] is maximized in **4a** and **4b** and is probably a combination of the gem-disubstitution pattern and chelate ring constraints (the analogous interactions in the MCH derivatives are less asymmetric for example). Third, if we use the X1–Pt–X2 angles as an overall measure of "strain" around platinum, we can see in the structures reasons for the enhanced stability of (MCH)PtCl$_2$ (ClPtCl angle = 86.6 (2)°) over (MCOT)PtCl$_2$ (ClPtCl angle = 84.6 (1)°), even though the latter is not "conformationally destabilized" as is the former.[12]

Comparison of the three MCH systems **5**, **6**, and **7** leads to interesting observations. Monophenylation of **5** to form **6** is accompanied by a significant trans influence (average bond length increase for Pt–C5 and Pt–C8 of ca. 0.10 Å. In addition to the trans influence in **6**, we see an almost equally large cis influence of *opposite sign*[30] (Pt–C1 and Pt–C2 shorten by an average of ca. 0.10 Å). One might expect that, in cis diphenyl compounds, the cis and trans influences would oppose one another and cancel. Indeed, in **7**, the olefinic carbons return to positions close to those in **5**.

We noted earlier that olefins **2** and **3** are unstable with respect to spontaneous chloropalladation. The palladium structures **4a** and **5** may be good models for the activated complexes in chloropalladation of **2** and **3**, with olefinic carbons, Pd, and Cl in a near in-plane arrangement ideal for cis addition.

Finally, we observe that the distances involving olefinic carbon are identical within our error limits for the chloro and bromo structures **4a** and **4b**. The fact that the exocyclic olefin in **4b** is displaced by bridging bromide in solution (analogous chemistry for **4a** not observed) is therefore related to enhanced nucleophilicity of bromide compared to chloride, and not to inherent weakening of the Pt–C5,C9 bond in **4b** compared to that in **4a**.

2. NMR. ^{1}H and ^{13}C NMR results along with selected bond lengths and angles are presented in Table II for the seven diolefin complexes under study. We have noted above that the in-plane olefinic carbons are systematically more distant from platinum than are the endocyclic olefinic carbons. Comparison of NMR parameters gives a consistent view of the relative strengths of the interaction. Thus for **4a** and **5**, for example, J_{Pt-C} (out-of-plane) is 2–3 times greater than J_{Pt-C} (in-plane). (The hydrogens attached to these carbons also show diminished coupling to platinum in the in-plane orientation, but the differences are much less than for J_{Pt-C}.) With the J_{Pt-C} and r_{Pt-C} data in Table II we have found a general monotonic increase in J_{Pt-C} as r_{Pt-C} decreases. For example, extremes in J_{Pt-C} are observed for **6**, where extremes in r_{Pt-C} are also observed. Indeed on the basis of bond lengths compound **6** appears to have both the strongest and the weakest Pt-olefin interactions in Table II. The three potential NMR criteria of stability, namely, J_{Pt-C}, J_{Pt-H}, and $\Delta\delta$, inde-

pendently mirror the character of the bonds in **6**. Thus for the endocyclic —CH=CH— bond in **6** the J_{Pt-C} of 225 Hz, $\Delta\delta(^{13}C)$ of –49.4 ppm, and J_{Pt-H} of 78 Hz are the largest values in the table, while the corresponding values for >C=CH$_2$ in **6** are the smallest. For complex **7**, with the second phenyl trans to the endocyclic olefin, we are able only to observe ^{1}H NMR, and the J_{Pt-H} values are consistent with the X-ray results: reduction of endocyclic J_{Pt-H} compared to that of **6** and increase of exocyclic J_{Pt-H} compared to that of **6**. We note here that the relative cis and trans influences of phenyl, which were observed in the bond lengths, is mirrored in the NMR parameters. We also note that similar NMR parameters[31a] for (R)(Cl)-(COD)Pt, R = phenyl, benzyl, or methyl, suggest that the opposed cis and trans effects are not aryl π-system dependent.

It is useful to compare the (MCOT)PtCl$_2$ (**4**) and (MCH)PtCl$_2$ (**5**) NMR parameters to the models (COD)-PtCl$_2$ (**8**) and (HEX)PtCl$_2$ (**9**). The endocyclic parameters of **4a**, **5**, and **8** are quite similar, which suggests that the endocyclic interaction of MCH and MCOT with platinum(II) is well-modeled by COD. The exocyclic NMR parameters for **4** and **5** are quite similar, and these are in turn similar to **9** with the exception of J_{Pt-C}, which are roughly doubled in **9** compared to those of **4a** or **5**.

There are modest chemical shift differences between the dichloro and dibromo forms of (MCOT)PtX$_2$. The ^{195}Pt resonance, however, shifts by 410 ppm upon replacement of Cl with Br. We have used this fact to ensure that the metathesis reaction used to make the dibromo derivative is complete. Indeed ^{195}Pt NMR is a sensitive analytical tool for differentiating among and detecting a variety of platinum organometallics and coordination compounds.[31b] Specifically (MCOT)PtBr$_2$ (**4b**) readily dimerizes in solution so that the monomer **4b** and two different dimers are coexistent (Experimental Section). No such process is evident for (MCOT)PtCl$_2$. The ^{195}Pt–^{1}H coupling constants reinforce the X-ray observation that no change in Pt–olefin bonding has been induced as a result of replacing Cl by Br in the (MCOT)PtX$_2$ complex.

Overall the NMR parameters for the compounds under study give a picture that is in complete agreement with the X-ray structures of these complexes. Thus the X-ray structures reflect the solution structures, and the NMR data are a satisfactory monitor of the structural changes that occur during the reactions of these molecules.

C. Bonding. Although a great number of calculations have been done on Pt–olefin bonding, only a subset[6e-h,9,11,32,33] of these address the question of relative stabilities and/or reactivities of in-plane and out-of-plane olefin geometries. Typical experimental activation energies[10,34,35] for olefin rotation in square d^8 complexes have been measured by dynamic NMR to be 14–16 kcal/mol, and the calculations generally agree with this value. Furthermore there is unanimity that the origin of the barrier is steric, which is precisely our interpretation of

(28) See ref 24, pp 641 et seq.

(29) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320. (b) Wright, L. L.; Wing, R. M.; Rettig, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 610–612.

(30) "Opposite-sign" cis and trans influences of aryl ligands have been observed in platinum–phosphorus coupling constants: Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2117–2124.

(31) (a) Similar NMR parameters for chloro[(1,2,5,6-η^4)-cycloocta-1,5-diene](R)platinum(II): Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1975**, *97*, 721–727. (b) The use of ^{195}Pt NMR to distinguish between similar chloro and bromo complexes is well-established in coordination chemistry; see, e.g.: Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic: New York, 1978; Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247. Pregosin, P. S. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 285 and references cited therein.

(32) Hay, P. J. *J. Am. Chem. Soc.* **1984**, *103*, 1390–1393.

(33) Trzcinska, B. M.; Fackler, J. P.; Anderson, A. B. *Organometallics* **1984**, *3*, 319–323.

(34) Miya, S.; Saito, K. *Inorg. Chem.* **1981**, *20*, 287–288.

(35) Cramer, R.; Kline, J. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2519–2524.

the experimental X-ray results. Only Hay's calculations optimized both in-plane and out-of-plane geometries with the result that a 0.4-Å elongation of metal to olefin distance was predicted[32] for the in-plane double bond. We find the elongation experimentally to be near 0.1 Å and caution that failure to take the elongation into account theoretically would bias calculated metal–olefin overlap populations.

Ziegler and Rauk[11] have done the most detailed dissection of metal–olefin bonding contributions. The main difference between in- and out-of-plane orientations is the way in which π bonding factors. The in-plane interaction requires back-donation from a b_2-symmetry metal-based orbital, which is the same orbital from which a perpendicularly oriented trans phenyl group would accept electron density. That this competition in fact favors phenyl is clear from the rather short Pt–CB1 distance of 1.99 (1) Å to the phenyl ligand in 6. Thus the intrinsic weakening of the in-plane bond due to steric repulsion is amplified upon trans phenylation by σ polarization of the a_1-symmetry metal-based orbitals away from the in-plane olefin and by substantially reduced back-donation from b_2. The out-of-plane double-bond binding, on the other hand, is little affected by σ polarization effects and in fact experiences additional stabilization from the enhanced π back-bonding experienced as a result of the phenyl-group-induced diminution of charge density on platinum. Thus, the *trans* influence is ascribed primarily to σ polarization from and weak back-donation to the in-plane olefin, while the oppositely affected cis influence is ascribed to enhanced $d\pi$–$p\pi$ back-donation to the out-of-plane olefin.

In so far as it is possible to make a quantitative comparison, the bonding model and the experimental results are in agreement. However it is clear that additional work will be required in both areas, if we are to have a useful working and predictive knowledge of how metal coordination affects the chemistry of carbon–carbon double bonds.

D. Olefin Displacement Reactions—Thermodynamics. A quantitative measure of the weak coordination of in-plane double bonds comes from two types of olefin displacement studies and one synthetic observation.

First a relative displacement order for various diolefin ligands has been established (see Experimental Section). The observed order is as follows (a diolefin displaces all diolefins listed after it): dicyclopentadiene ~ COD-1,5 > dipentene ~ 4-vinylcyclohexene ≫ 5-methylenecycloheptene > 5-methylenecyclooctene.[36] This has been rather exhaustively studied, and we have yet to find a bidentate ligand, diolefin or otherwise, that will not displace 5-methylenecyclooctene from **4a**.

Second, we have found that coordinated Br⁻ is a sufficiently strong nucleophile to displace the exocyclic double bond from (MCOT)PtBr₂ forming a bromine-bridged dimer, 11. This process is readily monitored in solution
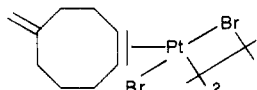
11

(DCCl₃ or D₂CCl₂) by using NMR spectroscopy (¹H or

¹⁹⁵Pt) or by using absorption spectroscopy at 360 nm. The average of four independently determined (Experimental Section) values of K determined from ¹H and ¹⁹⁵Pt NMR and UV-concentration studies is 70 ± 15 (from temperature dependence of K: $\Delta H = -1$ kcal/mol; $\Delta S = +5$ cal deg⁻¹ mol⁻¹). This equilibration places the exocyclic double bond of MCOT on a par with bridging Br as a ligand, and the positive ΔS for dimerization strongly suggests that the exocyclic double bond displacement greatly increases rotational/vibrational entropy in η^2- vs. η^4-MCOT.

Third, we note that the usual conditions for synthesis of (diolefin)PtCl₂ complexes (alcohol solvent, diolefin, and PtCl₄⁻)[12,20a,24] failed to yield any product when the diolefin was MCOT. This failure led us to postulate that the exocyclic olefin of MCOT will not displace terminal chloride or compete with alcohol solvents as an entering group. We then observed that (MCOT)PtCl₂ does form if the penultimate leaving group is *bridging* chloride and the solvent is nonnucleophilic (Experimental Section) (bridging bromide is competitive vide supra). These synthetic considerations confirm that MCOT is at the bottom of the (diolefin)PtCl₂ stability series.

E. Dynamics. It was noted that the **4b** ⇌ 11 equilibrium was established at a surprisingly slow rate in the (MCOT)PtBr₂ system. Thus the forward and reverse rate constants were measured by using a rapid dilution technique under the linearizing conditions suggested by Swinehart.[18c] The small dedimerization rate constant (eq 1, $k_{-1} = 1.2 \times 10^{-4}$ s⁻¹) shows that the exocyclic double bond is a very poor entering group.

Summary and Conclusions

In-plane coordinated double bonds are unstable, primarily due to steric interactions with cis ligands. The weakest of the ligands capable of forming an in-plane olefin–metal interaction is 5-methylenecyclooctene.

Kinetic studies indicate that a prime factor limiting the stability of the in-plane double bond is its poor ability to function as an entering group. Presumably this is due to the requirement that both the endo- and exocyclic double bonds of crossed olefin systems must be eclipsed with metal substituents in the 5-coordinate activated complex. Thus this may be unique to cross olefin ligands, and other putative models for the in-plane coordination may lead to more stable complexes.

We note finally the close correspondence of our NMR and X-ray results in assessment of relative stabilities of the platinum–diene complexes.

(36) The ordering of the first four dienes agrees with that found for Pd(II): Partenheimer, W. *Inorg. Chem.* **1972**, *11*, 743.