

to 0.04. The discrepancy indices were $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.071$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.067$. In the last cycle of refinement, the maximum shift per error was 0.03. A final difference Fourier map showed the largest peak to be less than $0.24 \text{ e } \text{Å}^{-3}$. The final error of an observation of unit weight was 1.71.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for

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Registry No. 1, 31250-06-3; 3, 96165-39-8; dineopentylmagnesium, 19978-31-5; neopentyl chloride, 753-89-9.

Supplementary Material Available: Tables for 3 of all bond angles and bond lengths, anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

Thermal Rearrangement, Oxypalladation, and Molecular Structure of "Boat-Chair" Dichloro(3-methylcycloocta-1,4-diene)palladium(II)

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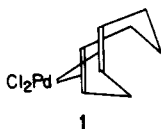
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In contrast to cycloocta-1,4-diene, which is found chelated to PdCl_2 in a high-energy boat-boat conformation, the methylated analogue dichloro(3-methylcycloocta-1,4-diene)palladium(II) (i.e., $[\text{PdCl}_2\text{-MeCOD-1,4}]$) has the hydrocarbon moiety chelated in the more stable boat-chair conformation, with the methyl group in the equatorial position. These structural results are discussed in terms of the free 1,4-diene conformational profile derived experimentally and theoretically by Anet and Yavari (*J. Am. Chem. Soc.* 1977, 99, 6986-6991). The molecular structure of $[\text{PdCl}_2\text{-MeCOD-1,4}]$ was determined by X-ray crystallography. Crystal data: space group $P2_1/n$ with $a = 8.113$ (1) Å, $b = 10.875$ (3) Å, $c = 11.758$ (2) Å, $\beta = 91.21$ (1)°, $V = 1037.1$ (6) Å³, $Z = 4$. The refinement was based on 2088 reflections with $I > 3\sigma(I)$ with final $R = 2.3\%$ and $R_w = 3.8\%$. Structural parameters are compared with a related series of $[\text{PdCl}_2\text{-diene}]$ complexes. The complex $[\text{PdCl}_2\text{-MeCOD-1,4}]$ rearranges thermally via allylic hydrogen migration to dichloro(*eq*-3-methylcycloocta-1,5-diene)palladium(II), followed by equilibration of the latter with dichloro(*ax*-3-methylcycloocta-1,5-diene)palladium(II) (the *eq/ax* equilibrium mixture is ca. 1.8:1 at 45 °C). Reaction of $[\text{PdCl}_2\text{-MeCOD-1,4}]$ with methoxide leads to methoxypalladation to form a 1,4,5- $\eta^3\text{-}\sigma,\pi$ -cyclooctenyl chelate.

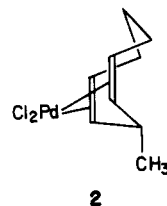
Introduction

In a previous report from this laboratory¹ we explored medium-ring diene conformational effects on the kinetics and thermodynamics of the metal chelation process. We have shown that a much better understanding of the rates and structural results of diene chelation can be accomplished through consideration of the conformational profiles of the free dienes. One very intriguing result of the previous study¹ was the finding that cycloocta-1,4-diene (COD-1,4) binds PdCl_2 in the unexpected boat-boat (BB) conformation 1. The BB conformation is an energy

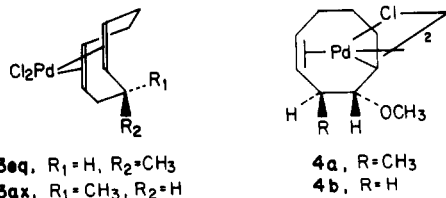


maximum for free COD-1,4, and our analysis led to the conclusion that 1 arises from initial monodentate chelation of twist boat (TB) COD-1,4, followed by kinetic trapping of BB at the second substitution (chelation) step.

We now report the synthesis and structural characterization of dichloro(3-methylcycloocta-1,4-diene)palladium(II), $[\text{PdCl}_2\text{-MeCOD-1,4}]$, 2. We find that the methyl group has perturbed the 1,4-diene conformational energy profile such that we now obtain exclusively the complexed



boat-chair (BC) conformation 2. We also report observations on the thermal rearrangement of 2 to 3eq and 3ax, and we establish 4a as the product of methoxide attack on 2 and 4b as the product of methoxide attack on 1.



Experimental Section

General Data. NMR spectra were determined by using a Varian EM 390 instrument (90-MHz ¹H) or a JEOL 200 FX instrument (200-MHz ¹H). $[\text{PdCl}_2\text{-COD-1,4}]^2$ and bis(benzo-

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(1) Rettig, M. F.; Wing, R. M.; Wiger, G. R. *J. Am. Chem. Soc.* 1981, 103, 2980-2986.

nitrile)dichloropalladium(II)³ were prepared by literature methods. Microanalysis was performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Compounds. 3-Methylcycloocta-1,4-diene (MeCOD-1,4). The procedure of Yashuda et al.⁴ was modified as follows: a 5-L round-bottomed flask was fitted with a mechanical stirrer, reflux condenser, and gas inlet and outlet valves. The flask was purged with helium, and a steady helium flow was maintained throughout the procedure. To the flask were added 388 mL of tetrahydrofuran, 142 g of triethylamine, 36.5 g of chopped potassium (we did not find it necessary to use a potassium dispersion), and 202 g of cycloocta-1,3-diene. The mixture was stirred vigorously and gently heated with a heating mantle to 50 °C. Stirring and heating was maintained until the potassium was completely consumed (ca. 4 h). At this point the reaction mixture was a deep red color. The heating mantle was then replaced with an ice bath, and a solution of 80 mL of methyl iodide in 300 mL of tetrahydrofuran was added dropwise. After the addition was complete, the ice bath was removed and the mixture was stirred at room temperature for 2 h at which time it was light beige in color. Addition of 250 mL of water was followed by extraction of the mixture with pentane (3 × 500 mL). The combined pentane extracts were washed with 2 M HCl (3 × 300 mL) and water (2 × 400 mL). The extracts were dried over MgSO₄, and the solvents were removed on a rotary evaporator. Distillation yielded 65 g of a 3:1 mixture of 3-methylcycloocta-1,4-diene and -cycloocta-1,3-diene. This mixture was used without further purification in the preparation of the palladium complexes. The palladium complex obtained ([PdCl₂·MeCOD-1,4]) was identical with that obtained using 3-methylcycloocta-1,4-diene which had been purified by gas chromatography.

Dichloro(3-methylcycloocta-1,4-diene)palladium(II), [PdCl₂·MeCOD-1,4], 2. To a solution of 4.30 g (11.2 mmol) of dichlorobis(benzonitrile)palladium(II) in 15 mL of CH₂Cl₂ was added 2.0 mL of the mixture of MeCOD-1,4 and MeCOD-1,3 described above. Precipitation began within 30 s, and stirring was continued for an additional 15 min. Addition of 10 mL of diethyl ether was followed by filtration. The precipitate was washed with ether (3 × 10 mL) and was air-dried. The yield was 2.33 g (7.79 mmol) of bright yellow powder (70%, decomp pt 158–165 °C).

¹H NMR (200 MHz, CDCl₃): δ 6.3–5.9, H₁, H₅, m; δ 5.2–5.0, H₂, H₄, dd, *J*_s ≈ 6.8, 7.0 Hz; δ 4.2–4.0, H₃, sextet, coupling to CH₃, H₂, H₄, all ~7 Hz; δ 2.9–2.5, 2 H; δ 2.4–2.0, 4 H; δ 1.59, CH₃, d, *J* = 7.0 Hz. ¹³C NMR (50 MHz, CDCl₃): δ 117.3, C₁ and C₅; δ 84.1, C₂ and C₄; δ 31.4, C₆ and C₈; δ 29.8, C₃; δ 24.6, C₇; δ 18.6, CH₃.

Bis(μ-chloro)bis[1,4,5-η³-(2-methoxy-3-methyl)cyclooctenyl]dipalladium(II), 4a. [PdCl₂·MeCOD-1,4] (330 mg, 1.10 mmol) was added to a mixture of NaHCO₃ (100 mg, 1.19 mmol) in 15 mL of anhydrous methanol. The mixture was stirred rapidly for 20 min during which time the color of the solid changed to white. The white solid (salts plus product) was isolated by filtration and was washed with CH₂Cl₂ (2 × 15 mL). The CH₂Cl₂ fractions were combined with the methanol filtrate, followed by concentration to 3 mL, at which time considerable solid was present. After addition of 20 mL of pentane, the white solid was filtered and air-dried to yield 310 mg (0.525 mmol) of off-white solid **4a** (95%, decomp pt 160–165 °C). Anal. Calcd for C₂₀H₃₄O₂Cl₂Pd₂: C, 40.71; H, 5.80. Found: C, 40.72; H, 5.77.

¹H NMR (200 MHz, CDCl₃): δ 5.75–5.6, H₅, *J*_{5,4} = 9.0 Hz, *J*_{5,6} = 6.0, 7.0 Hz; δ 5.26–5.15, H₄, dd, *J*_{4,5} = 9.0 Hz, *J*_{4,3} = 5.6 Hz; δ 3.92–3.78, H₁, "q", *J*_{1,2} = 6.0 Hz, *J*_{1,7} = 5.5, 5.5 Hz; δ 3.50–3.38, H₂, dd, *J*_{2,1} = 6.0 Hz, *J*_{2,3} = 9.0 Hz; δ 3.27, -OCH₃, s; δ 2.6–2.35, H₃ and H₆ or H₆', m; δ 2.24–1.95, H₆' or H₆, H₇ and H₇', m; δ 1.6–1.35, H₈ or H₈', m, *J*_{8,8'} = 15.7 Hz, also *J* to H₁ = 5.8 Hz plus additional *J*s to H_{7,7'} totalling ≤ 8.5 Hz; δ 1.25, CH₃, d, *J*_{CH₃,3} = 6.0 Hz; δ 1.05–0.98, H₈' or H₈, m, *J*_{8,8'} = 15.7 Hz, *J* to H₁ = 3.5 Hz, additional *J*s to H_{7,7'} = 5.5, 5.5 Hz. In order to assign the δ 3.92–3.27 absorption to H₁ in **4a**, the acetylacetonate (acac) derivative was prepared by using Ti(acac)₃.⁵ In the acac derivative,

there is no absorption at δ 3.92–3.78; instead there is an overlapped two hydrogen multiplet centered at δ 3.4 (H₁ and H₂). This upfield shift of H₁ is diagnostic of H₁(acac) compared to H₁(chlorine-bridged dimer).⁵

The coupling constants in the previous paragraph were confirmed by homonuclear decoupling.

Bis(μ-chloro)bis(1,4,5-η³-6-methylcycloocta-4,7-dienyl)dipalladium(II), 5. A solution of 208 mg of [PdCl₂·MeCOD-1,4] (0.69 mmol) in 25 mL of CH₂Cl₂ was cooled to 0 °C, followed by addition of 97 μL of Et₃N (0.70 mmol). The cooled solution lightened in color during the first few minutes, and stirring at 0 °C was continued for 1 h. The resulting CH₂Cl₂ solution was chromatographed (Florasil/CH₂Cl₂), and the first yellow band was collected. Evaporation of most of the CH₂Cl₂, followed by addition of hexanes, led to a white solid which was isolated by filtration. The yield was 118 mg (0.225 mmol, 65%). ¹H NMR (90 MHz, CDCl₃): δ 6.41, "q", three *J*s ≈ 8 Hz each, vinyl H; δ 5.71, ddd, *J*s ≈ 11.4, 2.5, 1.5 Hz, vinyl H; δ 5.46, d, *J* ≈ 8 Hz, vinyl H; δ 5.1–4.7, m, vinyl H; δ 3.75, "t", two *J*s ≈ 6 Hz; PdCH; δ 2.6–0.7, remaining eight hydrogens, including methyl doublet (*J* = 7.2 Hz) at δ 1.38. The ¹H NMR spectrum of **5** is directly derivative of that of the non-methyl analogue,⁶ when the differences expected for 6-equatorial methyl substitution are considered.

Reaction of Bis(μ-chloro)bis(1,4,5-η³-6-methylcycloocta-4,7-dienyl)dipalladium(II), 5, with C₆H₆/HCl. The *σ*-allyl dimer **5** (107 mg, 0.20 mmol) was dissolved in 20 mL of CH₂Cl₂ and was cooled to 0 °C. To the cooled CH₂Cl₂ solution was added 1.1 mL of a solution of 0.4 M HCl in benzene. The solution was stirred at 0 °C for 1 h, followed by evaporation of most of the solvent and addition of hexane to force precipitation of 75 mg of solid (70%). The product was found by ¹H NMR to be a 1:1 mixture of starting [PdCl₂·MeCOD-1,4], **2**, and dichloro(*eq*-3-methyl-1,5-cyclooctadiene)palladium(II), **3eq**. After 20 days at room temperature, a solution of this 1:1 **2**/**3eq** mixture was converted to 1.8:1 **3eq**/**3ax** (no **2** observed after 20 days).

Reaction of 3-Methylcycloocta-1,5-diene (3-MeCOD-1,5) with Dichlorobis(benzonitrile)palladium(II). Deuteriochloroform solutions of 3-MeCOD-1,5 were obtained by shaking the corresponding palladium chloride complexes (from complete thermal rearrangement of [PdCl₂·MeCOD-1,4]) with aqueous cyanide. The CDCl₃ layer was washed with water, followed by addition of PdCl₂(PhCN)₂. The reactions were conducted under a variety of conditions, always resulting in a ca. 1:1.5 mixture of products, as shown ¹H NMR. These are the same two products observed in the thermal rearrangement of [PdCl₂·MeCOD-1,4]. The 1:1.5 mixture (**3eq**/**3ax**) equilibrates to ca. 1.8:1 (**3eq**/**3ax**) over several days at room temperature or overnight at 45 °C.

[PdCl₂·MeCOD-1,4]: Crystal Growth and Determination of Structure by X-ray Crystallography. The crystal was grown by layering hexane over a dichloromethane solution which was saturated with [PdCl₂·MeCOD-1,4]. After a day, yellow crystals were present. X-ray data collected (Enraf-Nonius CAD-4 automated diffractometer), structure solution by the heavy-atom method, and refinement were routine (program package: Enraf-Nonius CAD-4 SDP Plus, Version 1.1). The X-ray results are summarized in Tables I and II and in Figures 1 and 2.

Results and Discussion

Molecular Structure of [PdCl₂·MeCOD-1,4]. The molecular structure of [PdCl₂·MeCOD-1,4] (Figures 1 and 2) is very similar to that of [PdCl₂·COD-1,4], reported by us earlier.¹ The principal difference is of course the BC conformation of coordinated MeCOD-1,4 observed here in contrast to the BB conformation found for coordinated

(5) (Acetylacetonato) [1,4,5-η³-(2-methoxy-3-methyl)cyclooctenyl]palladium(II) was prepared as an NMR sample only using Ti(acac) and **4a** in CDCl₃, followed by filtration of TiCl₄ by means of a cotton plug. The ¹H NMR of the product was exactly as expected on the basis of our earlier results with very similar (acetylacetonato)cyclooctenylpalladium(II) systems (Albelo, G.; Wiger, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510–4519).

(6) (a) Agami, C.; Levisalles, J.; Rose-Munch, F. *J. Organomet. Chem.* **1972**, *35*, C59. (b) *J. Chem. Soc., Chem. Commun.* **1974**, 505–506. (c) Dahan, F. *Acta Crystallogr. B: Struct. Crystallog. Cryst. Commun.* **1976**, *B32*, 1941–1943.

(2) Tayim, H. A.; Kharboush, M. *Inorg. Chem.* **1971**, *10*, 1827–1828.

(3) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(4) Yashuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

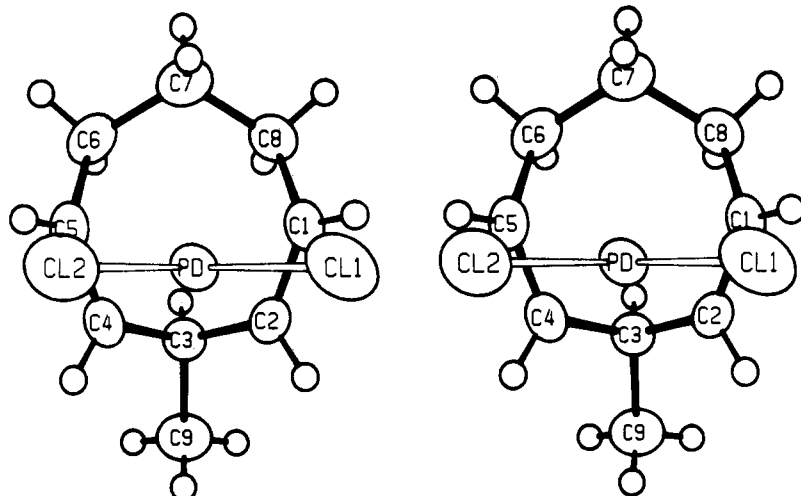


Figure 1. Stereopair drawing of the molecular structure of $[\text{PdCl}_2 \cdot \text{MeCOD-1,4}]$.

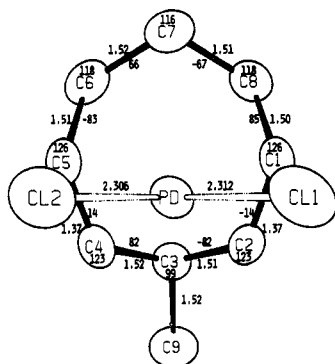


Figure 2. Bond lengths and angles and torsion angles of the coordinated diene 3-methyl-COD-1,4. Esds are as follows: $r(\text{Pd}-\text{Cl})$, ± 0.001 Å; $r(\text{C}-\text{C})$, ± 0.003 Å, CCC angle, $\pm 0.2^\circ$; torsion angles, $\pm 0.3^\circ$.

COD-1,4. On comparison of carbon torsion angles observed here for $[\text{PdCl}_2 \cdot \text{MeCOD-1,4}]$ to those calculated for BC COD-1,4 by Anet and Yavari,⁷ we observe a significant "flattening" of the portion of the coordinated ring around C7. Thus the 66–67° dihedral angles around C7 are compared to $\pm 87^\circ$ calculated for free COD-1,4.⁷ This flattening is the response of the coordinated ring to the nonbonded $\text{Pd} \cdots \text{H}7$ (axial) interactions distance of 2.90 (2) Å. The C1–C2–C3–C4–C5 ring geometry observed here is very similar to that observed earlier by us for $[\text{PdCl}_2 \cdot \text{COD-1,4}]$.¹

Inspection of Table II reveals that the PdCl_2 -diolefin structural parameters are essentially the same for $[\text{PdCl}_2 \cdot \text{MeCOD-1,4}]$ and $[\text{PdCl}_2 \cdot \text{COD-1,4}]$. Comparison of the latter two structures to that of $[\text{PdCl}_2 \cdot \text{COD-1,5}]$ reveals the principal differences as follows: (a) the 1,4 dienes have smaller olefin bite angles and correspondingly large CIPdCl angles; and (b) the rotation of the double bonds about the Pd–midpoint axes (torque) is 3–4 times greater in the COD-1,4s compared to the COD-1,5.

BC vs. BB Conformations in the PdCl_2 Chelates. We have observed only the BC product from reaction of 3-MeCOD-1,4 with $\text{PdCl}_2(\text{PhCN})_2$, in direct contrast to the earlier observation of only the BB form in the absence of the methyl group (in neither case does ^1H or ^{13}C NMR indicate the presence of more than one coordinated conformer, nor does examination of the Dreiding models suggest any possibility of $\text{BB} \leftrightarrow \text{BC}$ interconversion when the chelate is intact. The fact that both conformers can be observed ligated to PdCl_2 implies that the structural preference for BB (COD-1,4) is kinetic, as we argued

Table I. Summary of Crystal Data for $[\text{PdCl}_2 \cdot \text{MeCOD-1,4}]$,
2

formula	$\text{PdCl}_2\text{C}_9\text{H}_{14}$
mol wt	299.52
space group	$P2_1/n$
cell const	
a, Å	8.113 (1)
b, Å	10.875 (3)
c, Å	11.758 (2)
β , deg	91.21 (1)
cell vol, Å ³	1037.2 (7)
formula units/cell	4
D(calcd), g/cm ³	1.92
cryst shape, size	prism; $010-0\bar{1}0 = 0.508$ mm, $101-\bar{1}0\bar{1} = 0.204$ mm, $\bar{1}02$, $10\bar{2} = 0.152$ mm, and 001 $= 0.76$ mm from center of crystal
abs corr, anal. (based on above cryst dimens)	transmiss coeff: Max, 76%; min, 66%
radiatn	graphite monochromated Mo $K\alpha$ ($\lambda = 0.7107$ Å)
data collectn method	ω -2 θ scans
scan width $\Delta\omega$, deg	$0.75 + 0.35 \tan \theta$
max counting time, s	$2\theta < 40^\circ$, 120 s; $2\theta > 40^\circ$, 240 s
collect range, deg	$2 \leq 2\theta \leq 55$
no. of unique data	2383
no. of unique data $I \geq 3\sigma(I)$	2088
no. of variables	166
R, %	2.3
R_w , %	3.8
esd unit weight	1.43
largest parameter shift/error	0.13
largest peak in final diff map, e/Å ³	0.8 ± 0.1

earlier.¹ In the case of unligated free COD-1,4 both experiment and theory⁷ point to the TB as the predominant conformer near room temperature. An initially complexed η^2 TB must pass BB (and be trapped as the BB chelate) on the way to BC chelate (the BC is not observed for COD-1,4). In the present case, we are forced to conclude either (a) that the initial η^2 complexation of the first double bond on TB MeCOD-1,4 is kinetically inhibited, thus allowing direct reaction with a small concentration of BC or (b) that BC is the predominant (only?) conformer present for MeCOD-1,4 and therefore formation of the BC complex proceeds directly. On the basis of Anet and Yavari's work and citations therein,⁷ overall preference for BC in free Me-COD-1,4 is quite plausible. Our qualitative examination of Dreiding models does not indicate any obvious interactions which favor BC over TB in MeCOD-1,4 compared to COD-1,4 nor does metal access to η^2 -olefin in TB MeCOD-1,4 appear to be diminished any less than

(7) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* 1977, 99, 6986–6991.

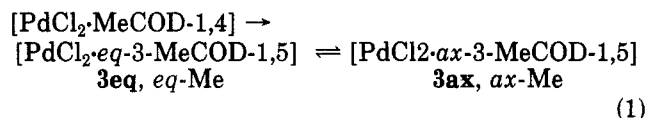
Table II. Selected Distances (Å) and Angles (deg) and Calculated Structure Parameters for [PdCl₂•diene]

	[PdCl ₂ •MeCOD-1,4]	[PdCl ₂ •COD-1,4] ^a	[PdCl ₂ •COD-1,5] ^f
Pd—Cl	2.244 (2)	2.258 (9)	2.199 (5)
Pd—C2	2.202 (2)	2.200 (9)	2.208 (5)
Pd—C4	2.199 (2)	2.209 (9)	
Pd—C5	2.249 (2)	2.211 (9)	2.204 (8)
Pd—C6			2.213 (8)
C=C ^b	1.372 (3)	1.37 (1)	1.384 (7)
	1.369 (4)	1.37 (1)	1.385 (7)
Pd-olefin midpoints ^b	2.115	2.122	2.092
	2.116	2.100	2.097
olefin midpoint—Pd-olefin midpoint "bite" angle	81.5	81.6	86.3
Cl—Pd—Cl angle	91.38 (3)	91.9 (1)	90.31 (5)
shortest olefin carbon nonbonded Cl dist ^c	3.14, 3.47, 3.45, 3.11	3.15, 3.50, 3.42, 3.12	3.16, 3.28, 3.29, 3.20
α, ^{b,d} deg	16, 18	16, 20	26, 40
β, ^{c,d} deg	78, 89, 85, 78	82, 87, 90, 71	79, 75, 71, 69
twist, ^{b,e} deg	2, 1	2, 6	2, 3
torque, ^{b,e} deg	22, 23	21, 18	6, 5
tilt, ^{b,e} deg	2, 2	3, 0	0, 0
PdCl ₂ plane to olefin midpoint, ^b Å	0.079, 0.107 ^f	0.16, 0.04 ^f	0.037, -0.002

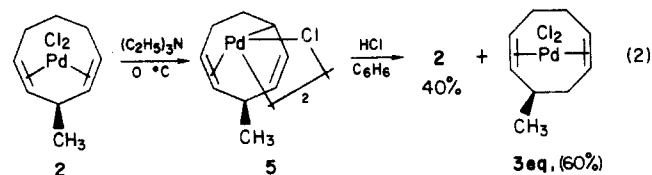
^a From ref 1. ^b C1=C2 and C4=C5, or C5=C6, respectively. ^c Olefin carbon in increasing numerical order. ^d Definition of α, and β: Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* 1976, 14, 33-61. ^e Defined in ref 1. ^f PdCl₂ plane lies between midpoints and C1, C5. ^g Benchekroun, L.; Herpin, P.; Julia, M.; Saussine, L. *J. Organomet. Chem.* 1977, 128, 275.

about half (methyl interference to coordination) compared to COD-1,4. This latter observation suggests strongly that we would observe BB MeCOD-1,4 (trapped) if a significant concentration of TB MeCOD-1,4 were present. Thus we are led to conclude that BC is the strongly dominant ground-state conformer in free MeCOD-1,4.

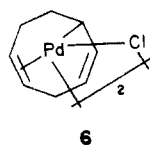
Rearrangement of [PdCl₂•MeCOD-1,4] to [PdCl₂•MeCOD-1,5]. We reported earlier¹ that [PdCl₂•COD-1,4] rearranges thermally to [PdCl₂•COD-1,5]. Since BB COD-1,4 has been calculated to be ca. 4 kcal/mol destabilized compared to TB or BC COD-1,4⁷ and since COD-1,5 is coordinated in a geometry similar to its ground-state TB form, we argued that there is a conformational contribution of several kilocalories per mole contributing to driving the [PdCl₂•COD-1,4] to [PdCl₂•COD-1,5] rearrangement. We now find that [PdCl₂•MeCOD-1,4] rearranges analogously (eq 1).



In order to assign **3eq** and **3ax** as equatorial and axial methyls, respectively, we carried out the sequence shown in eq 2. Reaction of [PdCl₂•COD-1,5] with Et₃N is known⁶



to lead to the non-methylated σ-allyl dimer **6** (characterized by X-ray crystallography, also prepared by us from [PdCl₂•COD-1,4] and [PdCl₂•COD-1,5]) analogous to **5**. We have prepared both dimers **6** and **5** and we conclude that



the structures are identical (except for the methyl) on the basis of extremely similar NMR spectra (**5** is a single

stereoisomer—only one methyl doublet). On reaction of **5** with acid, the 1,4-diene is regenerated as **2** (indicating that methyl is equatorial in **5**) and the 1,5 product is exclusively the δ 1.46 methyl product. Since the methyl stereochemistry is retained in **2** → **5** → **2**, we expect also retention in **2** → **5** → **3eq**. This identifies **3eq** as the epimer with the δ 1.46 methyl. Our assignment of **3eq** and **3ax** is in agreement with the results of Heimbach and Molin, who obtained the epimeric **3eq/3ax** mixture in a totally independent manner.⁸

It is noteworthy here that on reaction with HCl/C₆H₆ **2** gives comparable amounts of 1,4- and 1,5-dienes. We have found that under the same conditions dimer **6** gives [PdCl₂•COD-1,5] exclusively. These results suggest a steric role for methyl in inhibiting protonation at C₄ in **5** to form **3eq**, thus making protonation at C₆ competitive in formation of **2**.

As indicated in eq 1, the kinetic product of the 1,4 → 1,5 rearrangement is the product with the equatorial methyl group found at δ 1.46 (CDCl₃). Thus, after [PdCl₂•MeCOD-1,4] (0.9 M) was dissolved in CDCl₃ and the mixture thermostated at 45 °C, it was found that **3eq** was detected (14%) after 1 h (no **3ax**) and after 5 h the product mixture was 65% [PdCl₂•MeCOD-1,4], 26% **3eq**, and 9% **3ax** (axial δ (CH₃) 1.30 in **3ax**). After 32 h, the mixture was 9% [PdCl₂•MeCOD-1,4], 58% **3eq**, and 33% **3ax**. After three more days in the bath, the mixture was 65% **3eq** and 35% **3ax**.

Direct reaction of 3-methyl-COD-1,5 with PdCl₂(PhCN)₂ gives a kinetic product mixture in solution that is 1:1.5 **3eq/3ax**.⁹ Chromatography (Florasil, CH₂Cl₂) leads to a

(8) Heimbach, P.; Molin, M. *J. Organomet. Chem.* 1973, 49, 483-494. These workers obtained **3eq/3ax** mixtures on reaction of PdCl₂(PhCN)₂ with *trans*- or *cis*-3-methyl-*cis*-1,2-divinylcyclobutanes. Axial/equatorial methyls were assigned by Heimbach and Molin by comparison with a number of other methylated complexed COD-1,5s which they obtained ultimately from divinylcyclobutanes. Thus for Δδ(**3eq-3ax**), Heimbach and Molin find that the vinyl proton 2 adjacent to equatorial methyl in **3eq** is shielded 0.37 ppm with respect to the remaining three vinyl protons. Our **3eq** in CDCl₃ shows virtually the same shielding effect for H₂ (0.42 ppm in CDCl₃).

(9) The experimental result suggests a slight preference for the free TB 3-methyl-COD-1,5 with equatorial methyl. Preferred initial attack by Pd(II) on the open (outside) face of the first double bond, followed by TB → TB' conversion and chelation, should lead to overall kinetic preference for axial methyl, as we observe.

benzonitrile free solid product with the same 1:1.5 **3eq/3ax** formulation. A solution of this purified **3eq/3ax** mixture (45°, 3 days) led to establishment of the 65:35 **3eq/3ax** equilibrium mixture noted above. Thus this equilibrium position has been approached from both sides. Molecular mechanics¹⁰ calculations for coordinated and uncoordinated (twist boat) 3-methylcycloocta-1,5-diene predict an axial/equatorial methyl free energy difference of 0.0 ± 0.5 kcal/mol. This free energy difference is observed experimentally, based on the 65:35 **3eq/3ax** equilibrium mixture ($\Delta G^\circ \approx -0.4$ kcal/mol for $3ax \rightleftharpoons 3eq$).

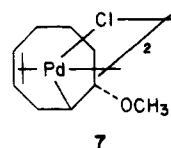
The double-bond migration reaction (eq 1) proceeds to an equilibrium position having residual $[PdCl_2 \cdot MeCOD-1,4]$ at $\leq 0.5\%$ of the mixture (analysis by 200-MHz ¹H NMR), which suggests $\Delta G^\circ \leq -2.5$ kcal/mol for the reaction. Molecular mechanics calculations¹⁰ for $[PdCl_2 \cdot COD-1,4]$ (boat-chair) and for $[PdCl_2 \cdot COD-1,5]$ (twist boat) suggest $\Delta G^\circ \approx -4.5$ kcal/mol for the rearrangement.¹¹ The majority of the enthalpy (~ 2.4 kcal/mol) results from the Pd-H7(axial) induced ring flattening which we mentioned earlier.

The overall isomerization process (eq 1) can be viewed as hydrogen migrations of two kinds, but sharing common features. In the $2 \rightarrow 3eq$ rearrangement one allylic H₅ must go to C₄ and the **3eq** \rightarrow **3ax** could proceed via axial allylic H₃ dissociation, followed by return to the opposite face to become equatorial H₃ in **3ax**. We have noted that the rates of the $2 \rightarrow 3eq \rightarrow 3ax$ steps are comparable and that the allylic deprotonation reactions of $[PdCl_2 \cdot COD-1,5]$ with Et₂N and **2** with Et₃N are also comparably fast (minutes at 0 °C). We note further that σ -allyls **5** and **6** react with acid to form (at least in part) coordinated 1,5-dienes. The facts at hand suggest that the 1,4 \rightarrow 1,5 rearrangement and the C₃ epimerization are mediated by the acidity of singly allylic protons in the 1,4- and 1,5-dienes. At this time, we cannot comment definitively on what moiety may be the important base here; however, we have shown that the reactions do proceed as before in acid-washed (Dowex 7, H⁺) CDCl₃.

Oxypalladation of $[PdCl_2 \cdot COD-1,4]$ and $[PdCl_2 \cdot MeCOD-1,4]$. In response to the theoretical analysis of Eisenstein and Hoffman¹² concerning nucleophilic attack on coordinated olefins, we recently published¹³ an

experimental study of the relationship of asymmetry in olefin binding to the kinetically preferred site of nucleophilic attack on coordinated olefin. Since there are differences in C₁, C₂, C₄, and C₅ bond lengths to palladium in the coordinated COD-1,4 and MeCOD-1,4 (see above) it was of interest to determine whether oxypalladation (with CH₃O⁻) would proceed under kinetic or thermodynamic control.

The reaction of $[PdCl_2 \cdot COD-1,4]$ with methoxide has been reported¹⁴ to yield complex **7**, which would result



from CH₃O⁻ attack (presumably externally or trans) on C₅. Unfortunately, no mention of spectroscopic or structural experimental results in support of structure **7** claimed was made. However we do note that the "most distant carbon" criterion¹² would target C₅ as the (kinetically activated) site of nucleophilic attack. On the basis of our study of Dreiding models, the resultant 1,3,4- η^3 -cyclooctenyl structure (e.g., **7**) would be highly strained relative to the isomeric 1,4,5- η^3 structure. Thus actual observation of the 1,3,4- η^3 structure as a kinetic product would provide further good support for the Eisenstein and Hoffman¹² model of coordinated olefin reactivity.

We have prepared the methoxy adducts of both $[PdCl_2 \cdot MeCOD-1,4]$, i.e., **4a**, and $[PdCl_2 \cdot COD-1,4]$, i.e., **4b**. We have shown by extensive analysis of the ¹H NMR spectra (Experimental Section)—first of **4a** and then of **4b**—that the isolated methoxypalladation products are in fact 1,4,5- η^3 chelates as shown in structures **4**. Thus these products share the same 1,4,5- η^3 chelate structure with all other known σ, π -cyclooctenyls (excluding π -allyls).^{6b,c,15} The 1,3,4- η^3 structure type therefore remains unobserved, although such a chelate could be on the 1,4,5- $\eta^3 \rightarrow$ 1,3- η^3 rearrangement pathway (σ, π - π -allyl rearrangement).¹⁶

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Registry No. 1, 31741-66-9; 2, 96129-19-0; 3 eq, 41626-41-9; 3 ax, 41626-40-8; **4a**, 96129-20-3; **4b**, 96150-62-8; 5, 96150-63-9; MeCOD-1,4, 49826-93-9; COD-1,3, 1700-10-3; 3-MeCOD-1,5, 56564-88-6; $[PdCl_2 \cdot COD-1,5]$, 12107-56-1; (acetylacetonato)-[1,4,5- η^3 -(2-methoxy-3-methyl)cyclooctenyl]palladium(II), 96129-21-4; dichlorobis(benzonitrile)palladium(II), 14220-64-5.

Supplementary Material Available: Tables of structure factors, positional and thermal parameters, and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

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(10) Molecular Mechanics—The Warshal, Lifson, Gelin and Karplus "CFF3" program (see: Niketic, S. R.; Rasmussen, K. "The Consistent Force Field", Springer Verlag: New York, 1977) which uses steepest descent followed by Newton-Raphson energy minimization was modified to use the Buckingham form for the nonbonded repulsions. A recent modification of Allinger's MM2 force field (Jaime, C. S.; Osawa, E. *Tetrahedron* **1983**, *39*, 2769) was used. Calculations for complexed olefin included the following in order to accommodate the effects of metal-olefin bonding: r_{C-C} increased to 1.375 Å, k_{C-C} reduced to 7.1 mdyn/Å, and r_{C-O} reduced to 14.4 mdyn/rad. Palladium was included in the calculated as follows: Pd-C_{sp²}, $k = 2.08$ mdyn/Å, $r_0 = 2.12$ Å, Pd-Cl, $k = 1.39$ mdyn/Å, $r_0 = 2.30$ Å; Cl-Pd-Cl, $k = 0.139$ mdyn/rad, $\alpha_1 = 90.0^\circ$, and C_{sp²}-Pd-Cl, $k = 0.278$ mdyn/rad, $\alpha_0 = 91.25^\circ$. Since the spectroscopic and kinetic data are only available for Pt(II), we calibrated with use of Pt(II) data and transferred the parameters to Pd(II). Structure comparisons of analogous Pd(II) and Pt(II) systems indicate that no rescaling of constants is justified. The palladium values emerged from two Pt(II) calibrations: first the vibrational spectrum of PtCl₄²⁻ (Sabatini, A.; Sacconi, L.; Schetting, V. *Inorg. Chem.* **1964**, *3*, 1775-6) was fit (± 5 cm⁻¹) and second the olefin rotation barrier for (ethylene)PtCl₃⁻ was "fit" to the 9-14 kcal/mol range commonly observed (Miya, S.; Saito, K. *Inorg. Chem.* **1981**, *20*, 187-8. Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1969**, 53) for Pt(II)-olefin rotation. Our calculated ΔH^\ddagger for (ethylene)PtCl₃⁻ (above parameters) is 11.5 kcal/mol.

(11) The molecular mechanics approach applied to $[PdCl_2 \cdot COD-1,4]$ (boat-boat) suggest $\Delta G^\circ \approx -8$ kcal/mol for rearrangement to $[PdCl_2 \cdot COD-1,5]$ (twist boat).

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