

X-ray Crystallographic, Chemical, and Spectroscopic Studies of the Palladium Dichloride Complexes of Cyclonona-1,5-diene, Cycloocta-1,5-diene, Cycloocta-1,4-diene, and Cyclohepta-1,4-diene

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Abstract: The crystal structures of three of the title complexes are reported and discussed; the fourth complex, dichloro(cyclohepta-1,4-diene)palladium(II), was characterized spectroscopically. The coordinated diene ring conformations are compared to the minimum energy conformations recently calculated by molecular mechanics methods. It is concluded that cycloocta-1,5-diene and cyclohepta-1,4-diene change little on complexation, while cycloocta-1,4-diene and cyclonona-1,5-diene coordinate in conformations which are "excited" when referenced to the free diene conformational energy profile. In the case of cyclonona-1,5-diene, a significant activation energy barrier separates the free diene conformation (chair) and that appropriate for chelation (twist-boat chair). The expected kinetic limitation on chelation is experimentally indicated by the formation of cyclononadiene-bridged palladium dichloride oligomers as kinetic products, followed by slow formation of the chelated thermodynamic product. Free diene/coordinated diene-exchange reactions are observed and discussed, and the dichloro(cycloocta-1,4-diene)palladium(II) to dichloro(cycloocta-1,5-diene)palladium(II) rearrangement is described. Anomalously large high-field shifts are observed in the ^{13}C NMR for the coordinated homoallylic carbons of the two 1,4 dienes. Crystal data follow: $[\text{PdCl}_2\cdot\text{COD-1,5}]$, $P2_12_12_1$, $a = 6.886$ (5) Å, $b = 12.271$ (7) Å, $c = 11.000$ (9) Å; $[\text{PdCl}_2\cdot\text{CND-1,5}]$, $P2_1/n$, $a = 7.493$ (2) Å, $b = 12.344$ (6) Å, $c = 11.061$ (3) Å, $\beta = 90.88$ (2)°; $[\text{PdCl}_2\cdot\text{COD-1,4}]$, $P\bar{1}$, $a = 7.161$ (6) Å, $b = 7.917$ (9) Å, $c = 9.441$ (7) Å, $\alpha = 82.57$ (6)°, $\beta = 109.10$ (5)°, $\gamma = 114.80$ (5)°.

There has been considerable recent activity in the area of molecular mechanics calculations applied to calculation of reaction energy profiles for conformational interconversions of medium rings.¹ We have initiated a systematic study of the chemical consequences of medium-ring conformational analysis as it applies to the kinetics and thermodynamics of medium-ring diene chelation in square-planar metal complexes. Examination of the available data¹ indicates that the observed conformation of a coordinated diolefin can differ dramatically from the most stable free conformation. Differences in metal-diolefin complex formation rates and equilibrium constants should therefore have significant contributions from the conformational energy changes that the diolefin undergoes during the formation of the bidentate chelate ring.

Molecular mechanics calculations have been reported for the *cis,cis*-diolefins cycloocta-1,5-diene (COD-1,5),^{1a-d,f,g} cycloocta-1,4-diene (COD-1,4),^{1e-h} cyclonona-1,5-diene (CND-1,5)ⁱⁱ and cyclohepta-1,4-diene (CHD-1,4).¹⁸ Within this group of dienes, only for CHD-1,4 and COD-1,5 are the stable free conformations suitable for bidentate chelation. Appreciable free energy increases are expected on rearrangement of CND-1,5 and COD-1,4 to the chelating conformation.

In view of the preceding comments and in view of the paucity of accurate structural data for palladium-diolefin complexes,² we have undertaken detailed structural and spectroscopic analyses for the palladium(II) chloride complexes of the three aforementioned dienes. By means of X-ray crystallography we have determined molecular structures for $[\text{PdCl}_2\cdot\text{COD-1,5}]$, $[\text{PdCl}_2\cdot\text{CND-1,5}]$, and $[\text{PdCl}_2\cdot\text{COD-1,4}]$. Suitable crystals of $[\text{PdCl}_2\cdot\text{CHD-1,4}]$ could not be obtained. Proton and ^{13}C NMR, IR, and Raman studies have been carried out for $[\text{PdCl}_2\cdot\text{CHD-1,4}]$ as well as the other three complexes. We also report preliminary studies of the reaction of COD-1,5 with $[\text{PdCl}_2\cdot\text{CND-1,5}]$ and of the thermal rearrangement of $[\text{PdCl}_2\cdot\text{COD-1,4}]$ to $[\text{PdCl}_2\cdot\text{COD-1,5}]$.

Experimental Section

Materials. a. CND-1,5,³ COD-1,4,⁴ and CHD-1,4⁵ were prepared by literature methods. COD-1,5 was purchased from Aldrich Chemical Co.

Dichlorobis(benzonitrile)palladium(II) was prepared by the Kharasch procedure.⁶ The complexes $[\text{PdCl}_2\cdot\text{COD-1,5}]$,⁷ $[\text{PdCl}_2\cdot\text{COD-1,4}]$,⁴ and $[\text{PdCl}_2\cdot\text{CND-1,5}]$ ³ were prepared by literature methods. Microanalysis was performed by Galbraith Laboratory, Knoxville, Tenn. Palladium was determined by ignition.

b. Preparation of Dichloro(cyclohepta-1,4-diene)palladium(II). Cyclohepta-1,4-diene (0.90 g, 0.96 mmol) and dichlorobis(benzonitrile)palladium(II) (3.3 g, 0.86 mmol) were stirred with 40 mL of benzene for 30 min. The resultant yellow powder was filtered, washed with ether, and dried in vacuo. The yield was 2.10 g (90%); mp 167–172 °C (dec). Anal. Calcd for $\text{C}_7\text{H}_{10}\text{PdCl}_2$: C, 30.97; H, 3.77; Cl, 26.28; Pd, 39.22. Found: C, 30.80; H, 3.68; Cl, 26.14; Pd, 39.72. A solution of the complex in CDCl_3 liberates cyclohepta-1,4-diene quantitatively on reaction with $\text{CN}^-/\text{D}_2\text{O}$.

Spectral Measurements. ^1H NMR spectra were obtained by using a Varian EM-390 90 MHz instrument, in conjunction with a Nicolet Signal averager when low solubility was a problem. ^{13}C NMR spectra were obtained by using a Bruker WH 90 instrument operating at 22.639 MHz. IR spectra were obtained with a Perkin-Elmer 283 instrument. Ligands were examined as films between NaCl plates; solid complexes were examined in NaCl or KBr pellets or as Nujol mulls between polyethylene windows for the low-frequency vibrations. Raman spectra were obtained by using a Spex Ramalog instrument. Neat liquids were placed in a capillary tube support and were excited with the green 4130-Å line.

Crystal Growth. $[\text{PdCl}_2\cdot\text{CND-1,5}]$. These crystals were obtained directly from the reaction mixture of bicyclo[6.1.0]non-4-ene and dichlorobis(benzonitrile)palladium(II) in benzene.³ The initially formed insoluble $\text{Pd}_3\text{Cl}_6(\text{CND-1,5})_2$ was left standing overnight to yield large

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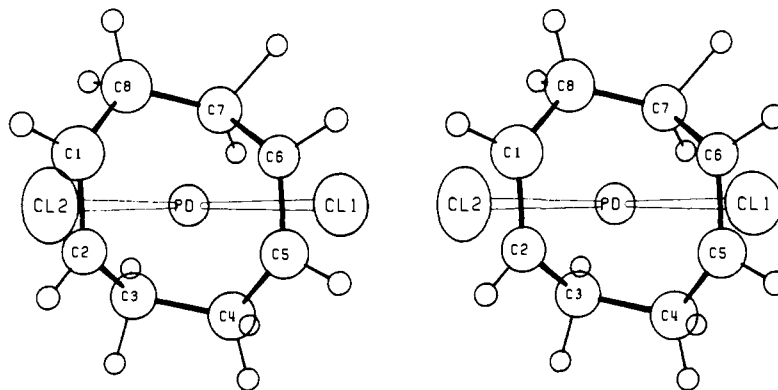


Figure 1. Stereopair drawing of the molecular structure of $[\text{PdCl}_2\cdot\text{COD-1,5}]$.

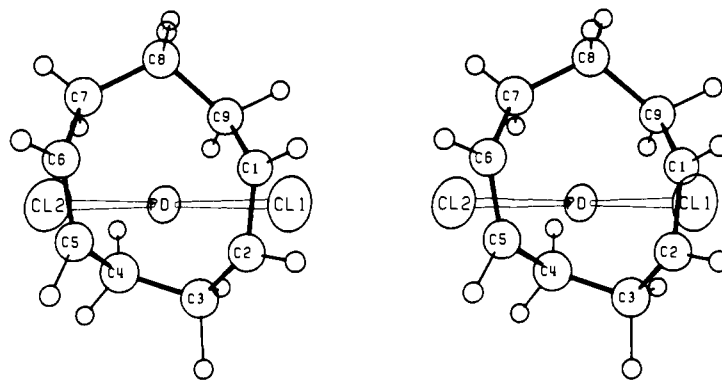


Figure 2. Stereopair drawing of the molecular structure of $[\text{PdCl}_2\cdot\text{CND-1,5}]$.

orange needles of composition $[\text{PdCl}_2\cdot\text{CND-1,5}]$.

$[\text{PdCl}_2\cdot\text{COD-1,5}]$. A 10-mL beaker containing 50 mg of dichlorobis(benzonitrile)palladium(II) dissolved in 5 mL of CH_2Cl_2 was placed inside a 100-mL beaker. A layer of COD-1,5 (ca. 2 mm deep) was placed in the large beaker surrounding the small beaker. The large beaker was closed off, and after 24 h, most of the CH_2Cl_2 had left the small beaker, leaving mixed crystals of $[\text{PdCl}_2\cdot\text{COD-1,5}]$ and $[\text{PdCl}_2\cdot 2\text{PhCN}]$. The former was present primarily as yellow needles, while the latter had a darker, clustered appearance. A yellow needle was selected for X-ray analysis.

$[\text{PdCl}_2\cdot\text{COD-1,4}]$. A 10-mL beaker filled with a saturated solution of $[\text{PdCl}_2\cdot\text{COD-1,4}]$ was placed in a 50-mL beaker. Hexane was carefully added to the large beaker until it layered over the CH_2Cl_2 solution in the small beaker. The large beaker was sealed off, and after 24 h, yellow crystals were present in the small beaker. These were suitable for X-ray analysis.

Crystallography. X-ray structure analysis was carried out in the same basic manner for each of three structures. After a crystal was selected for X-ray analysis, an ^1H NMR spectrum was taken by using several of the remaining crystals to verify the formulation of the material. The identity of the olefinic component of the complex was checked by cyanide displacement and ^1H NMR identification. Space groups were determined by examination of precession and cone axis photographs, and cell constants were determined by least-squares refinement on the basis of 12 carefully centered reflections having 2θ in excess of 35° . The α_1 line from our molybdenum tube was assumed to have $\lambda = 0.70923 \text{ \AA}$. Densities were measured by flotation in chlorocarbon mixtures.

Intensity data were collected by using graphite-monochromated $\text{Mo K}\alpha$ radiation, with a crystal-to-counter distance of 40 cm and pulse-height discrimination set to accept ca. 90% of reflection 400 in the $[\text{PdCl}_2\cdot\text{CND-1,5}]$ crystal.

Details of the crystallographic results are in Table I. Soon after we completed the $[\text{PdCl}_2\cdot\text{COD-1,5}]$ structure, we became aware of an earlier accurate structure of the same complex.^{8a} The earlier structure is

(8) (a) Benckroun, L.; Herpin, P.; Julia, M.; Saussine, L. *J. Organomet. Chem.*, 1977, 128, 275. (b) A reviewer indicated to us that a third X-ray investigation of $[\text{PdCl}_2\cdot\text{COD-1,5}]$ had been carried out: Howells, M. A. M. "The Structure and Synthesis of Metal Cyclic Diolefin Compounds", Ph.D. Thesis, University of Iowa, 1973 (*Chem. Abstr.* 1973, 81, 120776). Here a crystal of $[\text{PdCl}_2\cdot\text{COD-1,5}]$ which was polymorphic (space group $Pbca$) to ours was studied. The details of the molecular structure are essentially the same as reported herein.

slightly superior to ours, and we therefore have used those atom coordinates in the Results and Discussion sections of this paper (the root-mean-square error between the two structures is 0.03 \AA ; substantially more intensities were collected by Herpin et al.,^{8a} and we therefore use their data even though either structure would lead us to the same conclusions).^{8b}

Exchange Reactions with CND-1,5 and COD-1,5 Competing for PdCl_2 .

(a) $[\text{PdCl}_2\cdot\text{CND-1,5}]$ and Excess COD-1,5. A CDCl_3 solution was prepared with initial concentrations 0.034 M $[\text{PdCl}_2\cdot\text{CND-1,5}]$ and 0.34 M COD-1,5. The reaction was monitored by ^1H NMR. After 2.5 h at room temperature, $[\text{PdCl}_2\cdot\text{COD-1,5}]$ was barely detectable. After the initial 2.5 h, the solution was heated to and maintained at 50°C . At 50°C , conversion to $[\text{PdCl}_2\cdot\text{COD-1,5}]$ plus free CND-1,5 was ca. 30% complete in 2 h, 90% complete in 19 h, and 100% complete in 43 h. The solution remained homogeneous throughout the study.

(b) $[\text{PdCl}_2\cdot\text{COD-1,5}]$ and Excess CND-1,5. A CDCl_3 solution was prepared with initial concentrations 0.030 M $[\text{PdCl}_2\cdot\text{COD-1,5}]$ and 0.3 M CND-1,5. The solution was placed in a 50°C bath, and the reaction was monitored periodically by ^1H NMR. Equilibrium was reached at ca. 17 h, when integration of the δ 6.6 and δ 6.3 multiplets ($[\text{PdCl}_2\cdot\text{CND-1,5}]$ and $[\text{PdCl}_2\cdot\text{COD-1,5}]$, respectively) indicated a 1/6 ratio of $[\text{PdCl}_2\cdot\text{CND-1,5}]$ to $[\text{PdCl}_2\cdot\text{COD-1,5}]$. No further change in this ratio was observed after 26 more hours at 50°C . At that time (43 h total), the solution was evaporated to dryness under high vacuum, and the resultant mixture of solid complexes was shaken with aqueous CN^-/ether . The ether layer was analyzed gas chromatographically, and a 15/85 CND-1,5 to COD-1,5 mole ratio was observed, confirming the ^1H NMR conclusions.

Rearrangement of $[\text{PdCl}_2\cdot\text{COD-1,4}]$ to $[\text{PdCl}_2\cdot\text{COD-1,5}]$. A solution of $[\text{PdCl}_2\cdot\text{COD-1,4}]$ in CDCl_3 (ca. 0.03 M) was placed in a 50°C bath. After 17 h, there was $\sim 40\%$ conversion to $[\text{PdCl}_2\cdot\text{COD-1,5}]$ (^1H NMR integration in the coordinated olefinic hydrogen region). After 42 h, the conversion to $[\text{PdCl}_2\cdot\text{COD-1,5}]$ was found to be $>90\%$. No other products were observed; the solution remained homogeneous with no decomposition to metallic palladium.

Results

A. Structures. In the three complexes for which we have structural data the central palladium(II) is essentially in a square-planar environment defined by the two chlorines and by the midpoints of the carbon-carbon bonds (Figures 1-3). In Figure 4, we give details of coordinated diene bond lengths, bond

Table I. Summary of Crystal Data for PdCl₂·Diene

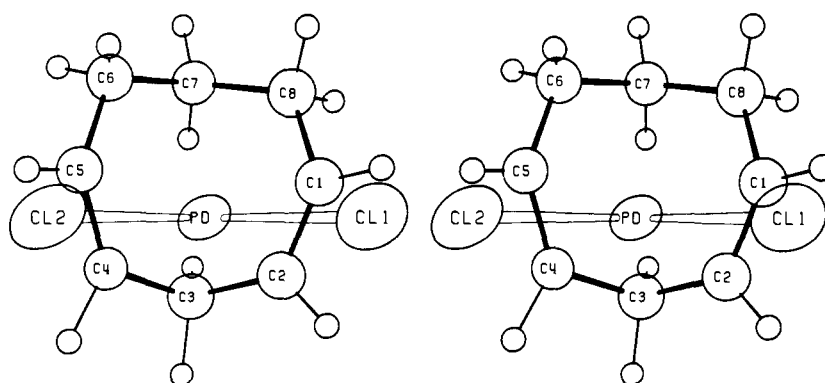
	[PdCl ₂ ·COD-1,5]	[PdCl ₂ ·CND-1,5]	[PdCl ₂ ·COD-1,4]
mol wt	285	299	285
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
cell constants			
<i>a</i> , Å	6.886 (5)	7.493 (2)	7.161 (6)
<i>b</i> , Å	12.271 (7)	12.344 (6)	7.917 (9)
<i>c</i> , Å	11.000 (9)	11.061 (3)	9.441 (7)
α , deg	90	90	82.57 (6)
β , deg	90	90.88 (2)	109.10 (5)
γ , deg	90	90	114.80 (5)
cell vol, Å ³	929	1023	455
formula units/cell	4	4	2
calcd/obsd density, g cm ⁻³	2.04/1.99	1.94/1.91	2.08/2.11
crystal shape/size	octahedron	0.4 × 0.2 × 0.2 mm	0.4 × 0.2 × 0.2 mm long direction is 2 $\bar{1}\bar{1}$
data collectn method	θ -2 θ scan	θ -2 θ scan	θ -2 θ scan
scan speed (2 θ)	2°/min	2°/min	2°/min
scan range (2 θ)	1.5 + 0.692 tan θ	1.5 + 0.692 tan θ	1.5 + 0.692 tan θ
bkgd counting time, s	20	20	20
std reflctns	3/50	3/50	3/50
std dev of stds, %	2.9 for 200, 2.6 for 040, 2.2 for 003	5.9 for 400, 5.4 for 040, 6.0 for 004	3.0 for 400, 3.2 for 080, 3.5 for 006
2 θ range	3-45°	3-50°	3-30°, 40-45°
unique reflctns	745	1353	1329
no. of reflctns obsd (<i>I</i> > 2 σ)	721	1151	1203
<i>R</i> , %	3.6	3.5	3.8
<i>wR</i> , %	4.5	3.8	4.3
σ	1.64	1.06	1.10

Table II. Selected Distances (Å) and Angles (Deg)

	[PdCl ₂ ·COD-1,5]	[PdCl ₂ ·CND-1,5]	[PdCl ₂ ·COD-1,4]
Pd-olefin midpoint distance	2.092	2.099	2.122
olefin midpoint-Pd olefin midpoint "bite" angle	2.097	2.130	2.100
Cl-Pd-Cl angle	86.3	92.3	81.6
shortest olefin carbon nonbonded Cl distances	90.3	90.1	91.9
	3.16, 3.20	3.13, 3.12	3.15, 3.12
	3.28, 3.29	3.17, 3.30	3.50, ^a 3.42 ^b

^a Pd-C₂. ^b Pd-C₄.Table III. PdCl₂·Diene: Calculated Structural Parameters

	[PdCl ₂ ·COD-1,5]	[PdCl ₂ ·CND-1,5]	[PdCl ₂ ·COD-1,4]
α , deg	26, 40 ^a	37, 9 ^a	16, 20 ^a
β , deg	79, 75, 71, 69 ^b	78, 68, 86, 78 ^b	82, 87, 90, 71 ^b
twist, deg	2, 3 ^c	4, 14 ^c	2, 6 ^c
torque, deg	6, 5 ^c	4, 12 ^c	21, 18 ^d
tilt, deg	0, 0 ^c	2, 2 ^c	3, 0 ^d
PdCl ₂ plane to olefin midpoint, Å	0.075, 0.066	0.201, 0.142	0.33, 0.08

^a Bond 1, bond 2. See ref 9. ^b Olefin carbon in increasing order of numbering. See Figures 1-3. ^c C₁=C₂ and C₅=C₆, respectively. ^d C₁=C₂ and C₄=C₅, respectively.Figure 3. Stereopair drawing of the molecular structure of [PdCl₂·COD-1,4].

angles, and dihedral angles. The bond lengths and angles about palladium are collected in Table II.

The Palladium-Olefin Interaction. Ittel and Ibers⁹ have sug-

gested structural parameters (α , β) for characterization of the metal-olefin interaction. These parameters are interpreted as measures of hybridization changes at olefinic carbons. We have calculated these parameters and they are found in Table III. In addition Table III contains additional structural parameters,

(9) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.*, 1976, 14, 33.

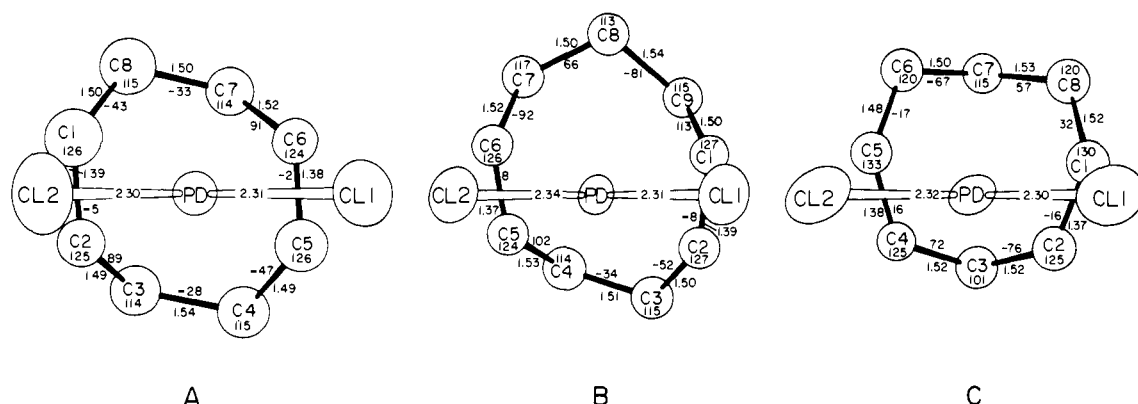


Figure 4. Bond lengths, angles, and torsion angles for coordinated dienes: A, [PdCl₂·COD-1,5]; B, [PdCl₂·CND-1,5]; C, [PdCl₂·COD-1,4]. Esd's are as follows: $r(\text{Pd}-\text{Cl})$, ± 0.002 Å; $r(\text{C}-\text{C})$, ± 0.01 Å; CCC angle, $\pm 0.6^\circ$; torsion angles, $\pm 0.8^\circ$.

Table IV. Infrared/Raman Spectroscopic Results for Diene and PdCl₂·Diene^a

diene	free diene $\nu(\text{C}=\text{C})$ (as films between NaCl plates)	PdCl ₂ · diene $\nu(\text{C}=\text{C})$ (NaCl pellets)	$\Delta\nu^b$	PdCl ₂ · diene $\nu(\text{Pd}-\text{Cl})$ (Nujol/ polyethylene)
CND-1,5	1650	1525	-125	323, 289
COD-1,5	1650 ^c	1515	-135	331, 290
COD-1,4	1640 ^c	1518	-122	330, 293
CHD-1,4	1647	1508	-139	320, 297

^a All results in cm⁻¹. Infrared results excepting footnote c.
^b Shifts in $\nu(\text{C}=\text{C})$ on coordination. ^c Raman results.

Table V. ¹H NMR Spectral Results for PdCl₂·Diene and for Free Diene in CDCl₃ at 298 K^a

diene	free	PdCl ₂ ·diene	hydrogen coordi- nation shift ^b
CND-1,5			
olefinic	5.9-5.6 (m), 5.6-5.2 (m)	6.75-6.5 (br)	ca. 1
aliphatic	2.1-1.2	3.0-1.6 (m)	
COD-1,5			
olefinic	5.5 (br)	6.30 (br)	0.8
aliphatic	2.25	3.1-2.1 (m)	
COD-1,4			
olefinic (H ₂ , H ₄)	5.8-5.5 (q, $J \approx 5$ Hz)	5.4 (q, $J \approx 7$ Hz)	-0.25
(H ₁ , H ₅)	5.5-5.1 (m)	6.3-5.9 (br)	0.8
aliphatic (H ₃)	2.8 (t, $J \approx 4.5$ Hz)	3.9-3.1 (m)	ca. 0.7
(H ₆ , H ₈)	2.4-2.1 (m)	2.9-1.8 (br)	
CHD-1,4			
olefinic	5.65 (m)	5.8 (m), 5.6 (m)	0.15, -0.05
aliphatic (H ₃)	2.9-2.7 (m)	3.7-3.2 (m)	0.6-0.7
(H ₇ , H ₈)	2.3-2.1 (m)	3.0-2.0 (m)	

^a Chemical shifts in ppm (δ) referenced to tetramethylsilane: m = multiplet; br = broad; q = quintet (not first order). ^b Positive coordination shifts to low field; negative to high field.

namely, olefin "twist", "torque", and "tilt". "Twist" distortion is best described as rotation of the C=C bond about the carbon-carbon axis. The magnitude of this angle is a measure of the deviation of the best plane of the olefin from perpendicularity to the palladium to olefin-midpoint vector. We define "torque" to be the extent of rotation of the double bond about the palladium to olefin-midpoint vector, away from the "normal" perpendicular orientation and toward the "in-plane" orientation. "Tilt" describes distortions from perpendicularity of the carbon-carbon bond and the palladium to olefin-midpoint vector.

Table VI. ¹³C NMR Spectral Results for PdCl₂·Diene and for Free Diene in CDCl₃ at 298 K^a

diene	free	PdCl ₂ ·diene ^b	carbon coordi- nation shift
CND-1,5			
olefinic	130.9, 129.8	116.4, 115.4	ca. -14.5
other	28.6, 26.6, 24.3	31.5, 30.4, 27.0	
COD-1,5			
olefinic	128.3	116.6	-11.7
other	27.9	31.0	
COD-1,4			
olefinic (C ₁ , C ₅)	128.4	118.9	-9.5
(C ₂ , C ₄)	130.4	76.6	-53.8
other (C ₃)	29.4	24.4	-5.0
(C ₇)	23.0	24.4	1.4
(C ₆ , C ₈)	24.8	31.5	6.7
CHD-1,4			
olefinic (C ₁ , C ₅)	128.4	118.2	-10.2
(C ₂ , C ₄)	131.2	84.4	-46.8
other (C ₃)	28.6	25.9	-2.7
(C ₆ , C ₇)	27.0	28.5	1.5

^a Chemical shifts in ppm referenced to tetramethylsilane. ^b In CD₂Cl₂ resonances for PdCl₂·1,4-COD: 120.3, 78.0, 33.1, 25.9, 25.8 ppm (C₃ and C₇ are resolved in CD₂Cl₂ but not in CDCl₃).

B. Spectroscopic Measurements. Vibrational Spectra. Results for free ligands and palladium complexes are presented in Table IV.

¹H and ¹³C NMR Spectra. The NMR results are collected in Tables V and VI.

CND-1,5 and [PdCl₂·CND-1,5]. The olefinic carbon and hydrogen resonances have not been individually assigned in this work. On the basis of carbon resonance peak heights, we assign the δ 28.6 signal to the unique CH₂ carbon in the free diene. This assignment would carry over to the 30.4 ppm resonance in the complex. The carbon spectrum of [PdCl₂·CND-1,5] is temperature independent down to -63 °C in CDCl₃.

COD-1,5 and [PdCl₂·COD-1,5]. These assignments are straightforward.

COD-1,4 and [PdCl₂·COD-1,4]. The proton spectrum of COD-1,4 was assigned with the initial reasonable assumption that the nonfirst-order "triplet" at δ 2.8 is due to the doubly allylic 3-hydrogens. The remaining assignments are readily obtained through double resonance experiments. The 3-hydrogens were strongly coupled to the δ 5.8-5.5 multiplet and are not noticeably coupled to the δ 5.5-5.1 multiplet. Similarly, the allylic hydrogens (δ 2.4-2.1) are strongly coupled to H₁ and H₅ at δ 5.5-5.1 and not noticeably coupled to H₂ and H₄. Furthermore, irradiation of the δ 2.4-2.1 resonance collapses the δ 1.5-1.1 resonance to a singlet, as expected. The olefinic carbon resonances in the free diene were assigned earlier by Anet and Co-workers, using selective

^1H decoupling.¹⁶ These assignments would also follow from peak height and electronegativity arguments (the 29.4- and 23.0-ppm peaks are about half the height of all the other carbon peaks). The ^1H NMR spectrum of $[\text{PdCl}_2\text{-COD-1,4}]$ was assigned by ^1H decouplings in a manner analogous to the free diene. Irradiation of the δ 5.4 multiplet in $[\text{PdCl}_2\text{-COD-1,4}]$ collapses the doubly allylic (H_3) proton resonance at δ 3.9–3.1 to an AB quartet ($J_{\text{AB}} \approx 15$ Hz). Given the ^1H assignments, the olefinic carbons in the complex were assigned by selective proton decoupling. Thus, in CD_2Cl_2 , selective irradiation of the δ 5.4 ^1H multiplet while acquiring the ^{13}C spectrum led to the observation of only the carbon resonance at 78.0 ppm and selective irradiation of the δ 6.3–5.9 ^1H multiplet led to the observation of only the 120.3-ppm carbon signal. On the basis of the peak heights observed in CD_2Cl_2 , the highest field carbon resonances (which overlap in CDCl_3) would be assigned to C_3 and C_7 .

CHD-1,4 and $[\text{PdCl}_2\text{-CHD-1,4}]$. The ^1H NMR spectrum of free CHD-1,4 is straightforwardly assigned on the basis of chemical shifts and integrals. We were unable to definitively assign the olefinic hydrogens in $[\text{PdCl}_2\text{-CHD-1,4}]$ because the material is so insoluble that we could not reliably decouple and observe the ^1H spectrum. The coordinated olefinic hydrogens are, however, very close in chemical shift. The carbon resonances in CHD-1,4 are assigned by analogy to Anet's assignments for COD-1,4. The 28.6-ppm resonance is about half the intensity of the remaining four and is assigned to C_3 , leaving the 27.0-ppm resonance to be assigned to $\text{C}_{6,7}$. The carbon resonances in $[\text{PdCl}_2\text{-CHD-1,4}]$ are assigned by analogy to assignments for $[\text{PdCl}_2\text{-COD-1,4}]$, as selective proton decoupling was not feasible. On the basis of peak heights, we assign the 25.3-ppm resonance to C_3 and the 28.5-ppm resonance to $\text{C}_{6,7}$.

Discussion

The Palladium–Olefin Interactions. One of our long-term objectives is to develop an understanding of how changes in the geometric arrangement of the coordinated olefin affect metal–olefin bond strength. A primary factor in bond strength is bond distance. Comparison of Pd to olefin midpoint distances (Table II) shows a range of distances too small to require comment (2.10 ± 0.03 Å). On the basis of the bond distance criterion, we conclude that the palladium–olefin bond strengths are very similar in these three complexes.

Successively greater distortions (Table III) from the “ideal” torque angle of 0° (cf. Ziese's anion¹⁰) are found in the order $[\text{PdCl}_2\text{-COD-1,5}]$ (torque = 6° and 5°), $[\text{PdCl}_2\text{-CND-1,5}]$ (torque = 4° and 12°), and $[\text{PdCl}_2\text{-COD-1,4}]$ (torque = 21° and 18°). A simple parameter which reflects this distortion is the angle of intersection of the olefinic C–C vectors. That angle is 9° , 17° , and 35° for the three complexes, respectively. “Torque” distortion is related to the well-known olefin rotation in square-planar d^8 complexes. The question of preferred orientation has been raised in recent publications.¹¹ There is agreement that, from an electronic standpoint, there is little preference for one torque angle over another. The dominant factor leading to the “normal” 0° torque angle appears to be steric interaction of olefinic carbon with cis ligands on the square plane. Such interactions have recently been analyzed in the molecular structure of dichloro(5-methylenecycloheptene)platinum(II), where both out-of-plane and in-plane coordinated double bonds are observed.¹² The olefinic carbon to cis chlorine distances in the present complexes are given in Table II. Here again there is little difference in “nonbonded” interactions from one complex to another. The highest torque angles (in $[\text{PdCl}_2\text{-COD-1,4}]$) are not sufficient to introduce a nonbonded distance significantly shorter than that found in the nearly “ideal” geometry of $[\text{PdCl}_2\text{-COD-1,5}]$.

The only remaining significant distortions observed are the 14° twist angle for C=C in $[\text{PdCl}_2\text{-CND-1,5}]$ and the relatively small diene bite angle in $[\text{PdCl}_2\text{-COD-1,4}]$. Both twist and bite angle distortions could be energetically costly, through significant loss of orbital overlap.

Cyclic Diolefin Conformations. Coordinated cycloocta-1,5-diene in $[\text{PdCl}_2\text{-COD-1,5}]$ is found in the C_2 twist-boat (TB) (or tub) form observed in the gas phase¹³ and in most of its metal complexes.¹⁴ The coordinated COD-1,5 ring conformation is very similar to that calculated by molecular mechanics methods^{1a} for the free COD-1,5 TB ground-state conformation. One concludes that free COD-1,5 does not undergo a significant conformational energy increase in order to adjust to the “coordinated” conformation. This conclusion, taken together with the near zero “torque” angles for COD-1,5, would lead to the expectation that the Pd–diene bond dissociation enthalpy is most positive for $[\text{PdCl}_2\text{-COD-1,5}]$, in comparison with the other complexes discussed below.

Cyclonona-1,5-diene has two relatively low energy conformations,¹¹ only one of which, the twist-boat chair (TBC), is capable of acting as a bidentate chelate. The TBC conformation is observed in $[\text{PdCl}_2\text{-CND-1,5}]$ and it is identical¹⁵ (excepting olefinic bond length increase) with the I-TBC conformation found by the Anet and Yavari,¹¹ using molecular mechanics methods. We believe that the conformational energy profile calculated for free CND-1,5 is a good indicator of the conformational energy “stored” in the coordinated CND-1,5. According to Anet and Yavari,¹¹ the I-TBC conformer is ca. 2.3 kcal/mol less stable than the ground C_2 conformation; we expect therefore that, from the conformational standpoint alone, the diene bond dissociation enthalpy in $[\text{PdCl}_2\text{-CND-1,5}]$ is 2–3 kcal/mol less positive than that for $[\text{PdCl}_2\text{-COD-1,5}]$. When one considers the narrow range of heats of formation for palladium–diene complexes,¹⁶ one concludes that a conformational change on coordination can be a major factor in differentiating one diolefin from another, as far as affinity for the metal is concerned. We will comment further on this point in a later section.

Anet and Yavari¹⁶ have also calculated the conformational energy profile for cycloocta-1,4-diene. Here there are two low-lying conformations but with a trivial (0.1 kcal/mol) energy separation. These conformations are the boat-chair (BC) of nearly C_s symmetry and the twist-boat (TB) of C_2 symmetry. Low-temperature ^1H and ^{13}C NMR studies¹⁶ of COD-1,4 are fully consistent with the conclusions drawn from the molecular mechanics calculations. There are no reports of electron diffraction studies of COD-1,4.

The TB conformation of COD-1,4 is not suitable as a chelate while the BC conformation would appear to be a highly effective

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chelating orientation. It is therefore surprising that the observed conformation for ligated COD-1,4 in [PdCl₂-COD-1,4] is not that corresponding to BC but rather most closely resembles the boat-boat (BB) conformation. The BB conformation (essentially the BC form with carbon 7 "flipped") is not an energy minimum in free COD-1,4; rather it is a transition state between TBC conformations of opposite chirality. The ligated "BB" conformation is similar¹⁷ to the BB conformation determined by Anet and Yavari. The observed symmetry is nearly C_s, but there is significant twisting of the olefinic double bonds and flattening of the two boat ends of the diene. The conformation is best described as a flattened boat-boat. The free C_s BB conformation was calculated to be 3.8 kcal/mol above the calculated TB and BC ground conformations. We believe that it is reasonable to use the 3.8-kcal/mol figure as a lower limit to the conformational energy "stored" in [PdCl₂-COD-1,4].

In order to understand the absence of the BC conformation, we have used the coordinates of Anet and Yavari,¹⁶ combined with the nearly identical nature of carbons 1-5 in the BC and BB forms, to calculate a structure for [PdCl₂-COD-1,4(BC)]. Molecular models indicate that the only significant hindrance in this compound would be interaction between the metal and the axial hydrogen on C₇. In our calculated structure this contact is at 2.2 ± 0.1 Å. This value is only slightly shorter the range of known Pd...H contacts,¹⁸ some of which are believed to be attractive at or near this distance. Since even the slightest adjustments in the coordinated geometry could increase this distance considerably, we conclude that the absence of the BC conformer in the complex cannot be attributed to thermodynamic instability. Rather a consideration of the total conformational energy diagram for COD-1,4 combined with the assumption that the complex formation occurs via a series of monosubstitutions with attachment of the metal at the least sterically hindered olefinic position has led us to the conclusion that the BC conformer is kinetically inaccessible as a chelate. Thus each reasonable stepwise substitution process leads to chelated BB along all paths to chelated BC. Chelated BB is a stable kinetic trap from which chelated BC does not form at a noticeable rate (a Pd-olefin dissociation would be required).

Favini and co-workers¹⁸ have used the molecular mechanics approach to calculate the most stable conformer of cyclohepta-1,4-diene. They have concluded that the symmetric (C_s) boat is the preferred conformer; however, mention was not made of the other possibility, namely, the twist-boat. In either case, CHD-1,4 would coordinate in a stable conformation, as either the C_s boat or the twist-boat are suitable as chelates.

Spectroscopic Observations. Vibrational Spectra. The results in Table IV show the expected decrease in the "Double-bond stretch" on coordination. The Δν's of 120-140 cm⁻¹ are within the expected range and are not particularly informative.

¹H and ¹³C Nuclear Magnetic Resonance Studies. One of the most dependable spectroscopic changes generally observed for olefins coordinated to PdCl₂ is the shift of the olefinic hydrogen resonance ca. 1 ppm to low field on coordination.³⁵ Such shifts are observed for [PdCl₂-COD-1,5] and [PdCl₂-CND-1,5] (Table V). However, both 1,4 diene complexes are anomalous, with two olefinic hydrogens shifted to high field and two to low field. If the olefinic resonance in [PdCl₂-COD-1,5] is considered "normal", then the analogous resonances in the 1,4-diene complexes are almost 1 ppm to higher field than expected. The ¹³C NMR results for the 1,4-diene complexes are also unexpected. A small upfield olefinic carbon shift is normally observed¹⁹ on coordination to PdCl₂ (cf. [PdCl₂-COD-1,5], Table VI). The expected behavior

is observed for the 1,5-diene complexes; however, the 1,4-diene complexes have normal and abnormal olefinic carbon resonances. The "inside" coordinated olefinic carbons (C₂ and C₄) are shifted to high field by 4-5 times the expected shift (Table VI), while carbons 1 and 4 exhibit a normal coordination shift. The unusual high-field C₂, C₄, H₂, and H₄ shifts may indicate a homoconjugative interaction in the 1,4-diene complexes. On careful comparison of Anet and Yavari's¹⁶ BB atom coordinates to the X-ray coordinates for [PdCl₂-1,4-COD], we find that the C₂-C₄ distance is shortened by 0.2 (to 2.35 Å) in the complex and that the C₂C₃C₄ bond angle is closed by 7° (to 101°) in the complex.²⁰ The structural results are consistent with the homoconjugation hypothesis.

Chemical Observations. Displacement of CND-1,5 from [PdCl₂-CND-1,5] with COD-1,5. We have mentioned above that the spectral and structural parameters for [PdCl₂-CND-1,5] and [PdCl₂-COD-1,5] are very similar. We contend that CND-1,5 would undergo a favorable (by ca. 2-3 kcal/mol) TBC → C₂ conformational change on liberation from the PdCl₂ moiety. If the metal-olefin bond dissociation energies for the two 1,5-diene complexes (without conformation change) are as similar as the structural and spectroscopic results would suggest, then the TBC → C₂ conformational relaxation could become the major factor driving displacement of CND-1,5 by COD-1,5. We have found that COD-1,5 will slowly and completely displace CND-1,5 from [PdCl₂-CND-1,5] (Experimental Section). In an effort to approximate the equilibrium constant for the reaction as written in eq 1, [PdCl₂-COD-1,5] was equilibrated with a 10-fold excess of [PdCl₂-CND-1,5] + COD-1,5 ⇌ [PdCl₂-COD-1,5] + CND-1,5 (1)

CND-1,5. The equilibrium concentrations led to a calculated *K* for eq 1 of ca. 3 × 10². With the assumption of a small entropy term, the Δ*H* for eq 1 is estimated to be -3 kcal/mol. The experimental enthalpy change can be entirely accounted for by the required C₂ → TBC conversion for CND-1,5. This result shows that a relatively small conformational enthalpy change has a dramatic effect when dienes compete for cis coordination positions.

Kinetics of Formation of [PdCl₂-CND-1,5]. The conformational energy profile calculated by Anet and Yavari¹¹ for CND-1,5 suggests that the only populated conformations at room temperature are a pair of chiral C₂ "chairs". The chairs were found experimentally¹¹ to interconvert with Δ*G*[‡] of 10.3 ± 3 kcal/mol, in good agreement with the calculated "strain-energy" barrier of 11.4 kcal/mol. Between the C₂ "chairs" lie two energy minima corresponding to (potentially chelating) chiral TBC's, which lie 2.3 kcal/mol above the chairs (calculated). We now consider how the chair to TBC barrier of ca. 11 kcal/mol manifests itself. Formation of the chelate ring in [PdCl₂-CND-1,5] is presumed to involve successive nucleophilic substitutions on the square plane, with attack along the out-of-plane *z* axis followed by formation of a five-coordinate intermediate and finally square planar product.²¹ The first product formed would have a monodentate CND-1,5; a second substitution step would give chelated bidentate CND-1,5. In the absence of special effects, one would expect the activation energy for the second substitution reaction (chelation step) to approximate the activation energy for the first step, since both processes involve attack by carbon-carbon double bond and since the trans effect does not come into play for the cis-substitution process. However, the most reasonable pathway for the second substitution process would require the ligated CND-1,5 to assume the BC or TBC conformation, and in addition the already coordinated double bond would lie in the square coord-

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dination plane. Thus, the second double bond is in position to attack above the coordinated plane. Energetic differences between the perpendicular and in-plane coordinated olefin could contribute to the activation energy,^{11,12} and this, coupled with a very unfavorable energetic pathway for the chair to TBC activation energy,²² could dramatically inhibit the second substitution step to form the chelate ring. In our earlier published work³ involving [PdCl₂CND-1,5] we did in fact have positive indication that the chelation step was inhibited kinetically (without a good explanation for the inhibition). Thus, reaction of [PdCl₂·2PhCN] with CND-1,5 results in immediate precipitation of material with stoichiometry Pd₃Cl₆(CND-1,5)₂. We characterized the material as a "linear polymer" with bridging halogens and bridging dienes. This precipitate, over period of 24 h in contact with mother liquor, rearranges quantitatively to chelated [PdCl₂CND-1,5]. We now contend that monodentate CND-1,5 (probably as a chair) attacks a second palladium substrate in a kinetically controlled oligomerization process. The inhibited process (chelation) ultimately leads to the thermodynamic monomer product.

Rearrangement of [PdCl₂·1,4-COD] to [PdCl₂·1,5-COD]. Conversion of coordinated 1,4-COD to coordinated 1,5-COD should be favored by as much as 4 kcal/mol from the conformational energy standpoint alone, enough of a stabilization to overcome the fact that free COD-1,4 is more stable than free COD-1,5 by ca. 2 kcal/mol.^{1f,23} There are suggestions in the literature that metal ion promotion of the COD-1,4 to COD-1,5 rearrangement is possible.^{4,24} However, in every case reported there was the possibility of metals selectively binding and concentrating COD-1,5 which could have been present as an impurity in the COD-1,4 or COD-1,3 that was available (although very high purities were claimed). In the present case, at the beginning of reaction, no [PdCl₂COD-1,5] was detectable by ¹H NMR. As described in the Experimental Section, the initial [PdCl₂COD-1,4] resonances gradually disappeared and were replaced by [PdCl₂COD-1,5] resonances.²⁵ Given the present results, one would

expect that a mixture of COD-1,4 and COD-1,5 would be stoichiometrically converted completely to [PdCl₂COD-1,5], possibly again with a primary driving force being conformational relaxation in the coordination sphere. We suggest the general possibility of converting a mixture of olefins to a single coordinated olefin, given the conformational driving force and the low-energy pathway (in the present case probably involving Pd-H formation).

Conclusion

In this paper we have initiated a comprehensive study of metal-diolefin interactions. We have shown that relatively small conformational energy effects can have a major influence on the kinetics and thermodynamics of complex formation. We are now expanding the scope of this work to other diene systems and to calorimetric measurements of the enthalpies of diene complexation reactions.

Acknowledgment. We thank Professor F. Anet for supplying us with atom coordinates calculated as described in ref 1e,i. This work was partially supported by the National Science Foundation (Grant CHE-7822691 and an NSF Summer Faculty Fellowship to G.R.W.), by the University of California Intramural Research Fund, by a Cottrell Research Grant (G.R.W.), and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The department's Bruker WH-90 NMR instrument and Spex Ramalog were purchased in part by NSF equipment funds and by University Biomedical Sciences Support Funds.

Supplementary Material Available: A listing of structure factors (Table S1) and fractional coordinates, temperature factors, bond lengths, bond angles, and torsion angles (Table S2) for [PdCl₂CND-1,5] and A listing structure factors (Table S3) and fractional coordinates, temperature factors, bond lengths, bond angles, and torsion angles (Table S4) for [PdCl₂COD-1,4] (41 pages). Ordering information is given on any current masthead page.

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(25) The rapidity of formation of [PdCl₂COD-1,5] reported in ref 4 and 24 is surprising in view of our observation of the slowness of the homogeneous rearrangement. The earlier rapid formation of [PdCl₂COD-1,5] would be expected if COD-1,5 were initially present or possibly if the rearrangement followed a different path.

[2.2.2]Paracyclophane, a Novel Type of Metal Cation Complexing Agent (π -Prismand)

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Abstract: A novel type of cryptation involving only the π -binding sites of the cavity [2.2.2]paracyclophane is evidenced through solubility and ¹H NMR studies. The stability constant, in methanol, of the 1:1 complex of [2.2.2]paracyclophane with silver triflate is approximately 100-fold higher than those of the usual π -charge-transfer complexes of arenes with silver cation. The well-defined, sharp-melting, crystalline, 1:1 complex has been isolated and characterized.

Although many crown ethers contain aromatic rings,¹ there exist only a few claims of the aromatic subunit serving as a π donor in these systems in complexation with metal or ammonium salts.^{2,3} Sousa and co-workers⁴ have described the perturbation induced

by metal ion guests on the emission properties and ¹³C chemical shifts of the naphthalene unit of crown ether hosts.

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