Crystallographic and NMR Studies of Dichloro(η^4-1,2-divinylcyclohexane)palladium Complexes: Regio- and Stereochemistry of Nucleophilic Attack

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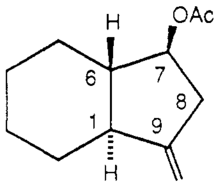
Dichloro(η^4-*trans*-1,2-divinylcyclohexane)palladium in solution adopts a square-planar geometry with the cyclohexane ring in a chair conformation and the olefinic groups nearly parallel and aligned perpendicular to the coordination plane. The cis isomer is fluxional in solution, equilibrating between two degenerate chair conformations with a barrier of 48.1 kJ/mol (T_c = 238 K). By favoring one conformation via introduction of a sterically demanding trimethylsilyl group, it is shown that nucleophilic attack, leading to oxidative cyclization, occurs exclusively at the olefinic group in the equatorial position. The crystal structures of the *trans*- and *cis*-1,2-divinylcyclohexane complexes, determined by X-ray diffraction, closely resemble their structures in solution. The trans complex shows monoclinic symmetry ($P2_1/n$) with a = 6.923 (1), b = 20.528 (5), c = 8.277 (2) Å, β = 105.25 (4)°, and Z = 4. The cis compound is triclinic ($P1$) with a = 6.329 (1), b = 7.738 (1), c = 12.473 (2) Å, α = 107.07 (1), β = 83.48 (1), and γ = 105.89 (1)°. The unit cell contains two crystallographically independent formula units. The structural models have been refined to the final linear R values of 0.040 (1720 observations) and 0.029 (3255 reflections) for the trans and the cis complexes, respectively.

Introduction

Palladium(II) complexes of nonconjugated dienes have been the subject of extensive structural studies, both experimentally[1] and theoretically.[2] Such complexes are unstable in the presence of nucleophiles and react to yield σ,π-palladium complexes, which may undergo further reactions to yield organic products.[1a] Although most of these reactions are stoichiometric with respect to palladium, such transformations have found important applications, for example, in the synthesis of natural products.[3]

We have recently shown that a variety of 1,5-dienes undergo oxidative cyclization in the presence of the Pd(II)-regenerating catalyst system $Pd(OAc)_2$–MnO_2–*p*-benzoquinone in acetic acid, to yield acetoxymethylenecyclopentanes.[4] Cyclizations of *trans*- and *cis*-1,2-divinylcyclohexane are highly stereoselective, yielding the cyclized products 1 and 2, respectively. The reactions are thought to proceed via palladium(II) diene complexes,



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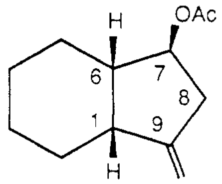

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which are subsequently attacked by acetate ion. To gain insight into the mechanism of these oxidative cyclizations and, in particular, to explain the high stereoselectivity observed, dichloropalladium diene complexes were prepared to serve as models for the catalytic intermediates.

Results

NMR Investigations. Palladium(II) chloride complexes[5] of *trans*- and *cis*-1,2-divinylcyclohexane[6] were prepared from the dienes and $PdCl_2(PhCN)_2$ in toluene, and their structures and dynamic behavior studied by NMR and X-ray crystallography.

The ^1H NMR spectrum of dichloro(η^4-*trans*-1,2-divinylcyclohexane)palladium (3) in $(CD_3)_2CO$ shows that the cyclohexane ring assumes a chair conformation, with diaxial coupling constants in the range 11.4–12.9 Hz and

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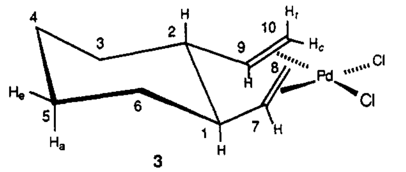
(5) The formation of 2 from *cis*-1,2-divinylcyclohexane was also effected by substituting $PdCl_2$ for $Pd(OAc)_2$.

(6) Palladium complexes of *cis*-divinylcyclohexane have been prepared previously, although they were not subjected to structural investigations: (a) Trebellas, J. C.; Olechowski, J. R.; Jonassen, H. B. *J. Organomet. Chem.* **1966**, *6*, 412. (b) Heimbach, P.; Molin, M. *J. Organomet. Chem.* **1973**, *49*, 477.



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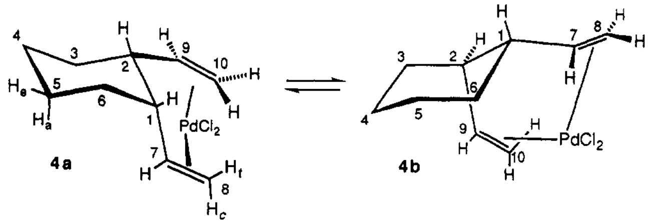
diequatorial and axial–equatorial couplings of about 3.5 Hz. The large coupling constant J_{H_1,H_6} (11.6 Hz) indicates that the substituents occupy equatorial positions. The two olefinic groups are nonequivalent, showing separate resonances in both the ^1H and ^{13}C NMR spectra. The orientation of these groups was deduced from the coupling constants J_{H_2,H_9} and J_{H_1,H_7}, determined to be 10.0 and 5.6 Hz, respectively. According to the modified Karplus equation,[7] the former coupling corresponds to a dihedral angle H_2–C_2–C_9–H_9 of approximately 155°, whereas the latter may correspond to either 30° or 125°, implying roughly parallel or perpendicular orientation of the two double bonds, respectively. To differentiate between these two orientations, NOE difference experiments were undertaken. From the results (Table I), the large dihedral angle H_2–C_2–C_9–H_9 was confirmed by the effect observed for H_{3a} (4.2%) and H_1 (2.6%) upon saturation of H_9. A larger effect was observed for H_7 (6.1%) upon irradiation of H_1 (and vice versa), suggesting the dihedral angle H_1–C_1–C_7–H_7 is 30° (and not 125°) and, thus, the olefinic bonds roughly parallel. Two identical conformations, interconverting by rotation of the C_1–C_7 and C_2–C_9 bonds, are possible for **3**. This rotation is slow on the NMR time scale, even at 70 °C, and occurs probably only after dissociation of the complex. The olefinic carbon–hydrogen coupling constants of approximately 163 Hz, typical for sp^2-hybridized carbon atoms,[7] suggest that the double bonds retain their planar olefinic character on coordination to palladium.

Dichloro(η^4-*cis*-1,2-divinylcyclohexane)palladium (**4**) is fluxional at room temperature, as shown by the pairwise identity of the ^1H NMR signals. However, at −90 °C, the ^1H NMR spectrum shows the presence of a single conformer with two nonequivalent olefinic groups. From variable-temperature ^1H NMR studies, the barrier to conformational change was calculated to be 48.1 kJ/mol[8] (T_c 238 K for coalescence of H_7 and H_9), which is close to the barrier to ring flipping for the free diene (calculated to be 43.9 kJ/mol, T_c 228 K). Therefore, the effect of coordination to palladium on the conformational change is only 4.2 kJ/mol, suggesting a geometrically nondemanding coordination between the olefinic groups and palladium. However, the conformational change of **4** must occur while the ligand is at least partially coordinated to palladium, since dissociation is slower than ring flipping, as judged from the separate ^1H NMR signals of the complex and the free ligand even at room temperature. This situation is different from that of **3**, which must dissociate prior to conformational change.

The orientation of the vinyl groups in **4** could be deduced from low-temperature ^1H NMR spectroscopy. The coupling constants J_{H_1,H_7} and J_{H_2,H_9} were found to be 0 and 10.5 Hz, respectively. According to the modified Karplus equation,[7] these coupling constants correspond to dihedral angles H_1–C_1–C_7–H_7 and H_2–C_2–C_9–H_9 of approximately 90° and 160°, respectively (structure **4b**), which implies,



4a ⇌ 4b

as in **3**, nearly parallel olefinic groups.

Crystallographic Description of the Structures. Crystal data and fractional atomic coordinates are shown in Tables II and III, respectively. Selected bond distances and bond angles are listed in Table IV. Tables V and VI show the calculated ring puckering parameters and selected torsional angles, respectively. Perspective views of the different isomers and conformers of the dichloro(1,2-divinylcyclohexane)palladium complexes are shown in Figures 1 and 2. The crystal structures are illustrated in Figures 3 and 4.

The crystal of the *cis*-1,2-divinylcyclohexane complex of $PdCl_2$ contains two crystallographically independent conformers, in agreement with the NMR results, labeled A and B in Figure 1. The fluxionality of this molecule can probably be the reason for the wide distribution of the bond lengths and bond angles around the average values in these structures. Nevertheless, the calculated mean values (with the rmsd's indicated in square brackets, when averaged over more than three values), 1.53 [6] Å for C–C single bonds in the cyclohexane rings, 1.50 [4] Å for the C–C and 1.39 [5] Å for the C=C bonds within the vinylic groups, are normal values for such bonds and agreeable with the corresponding mean values, 1.53 [1], 1.51, and 1.36 Å, calculated for the *trans*-1,2-divinylcyclohexane moiety. The contact distances between the Pd atom and the vinylic carbon atoms range from 2.18 to 2.30 Å in the cis isomer and between 2.20 and 2.25 Å in the trans isomer, with the mean values of 2.22 [4] and 2.23 [2] Å, respectively. The rotation of the double bond about the palladium–olefin midpoint vector is 4 and 8° for the C_7–C_8 and C_9–10_{10} bonds of the cis-isomer A, respectively, 12 and 2° for the corresponding bonds of isomer B, and 0 and 9° for these bonds in the trans isomer.[9] The six-membered ring adopts an almost ideal chair conformation in all these forms of 1,2-divinylcyclohexane. It is also confirmed by the ring-puckering parameters, calculated according to Cremer and Pople[10] (cf. Table V). The ideal values for chair conformation are θ = 0° or 180°, q_2 = 0 Å, and $q_3 = \pm Q$ Å.[10] When the cis isomer changes conformation from A to B, the vinylic substituents at C_1/C_2 also change their positions from near equatorial/axial in A to near axial/equatorial in B. In the trans isomer, however, both vinylic groups have equatorial positions (cf. Table VI). It should be noted that the orientation of the vinylic groups in both complexes is similar to that observed in solution.

The crystal structures, in both the "cis" and the "trans" crystals, seem to be held together by weak intermolecular interactions of the van der Waals' type.

Nucleophilic Attack. The structural studies of **3** and **4** presented above demonstrate that the two olefinic groups in both **3** and **4** coordinate differently to palladium. To investigate whether this difference in coordination leads to a difference in reactivity, it was necessary to choose a diene whose cyclization product(s) revealed the olefinic

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(11) (a) Klyne, W.; Prelog, W. *Experientia* **1960**, *16*, 521. (b) Stanford, Jr., R. H.; Waser, J. *Acta Crystallogr.* **1972**, *A28*, 213.

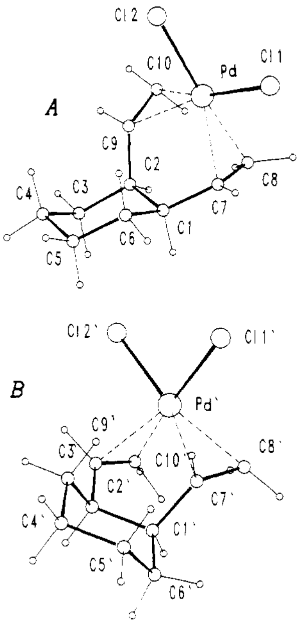


Figure 1. Perspective views of the two conformers of dichloro(*cis*-1,2-divinylcyclohexane)palladium complex: (top) form A; (bottom) form B. Atoms are labeled as in the text.

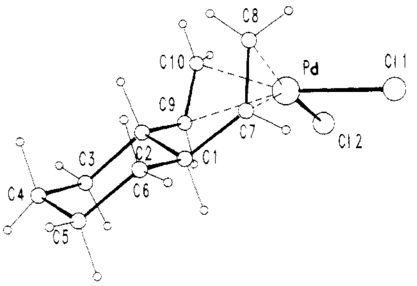


Figure 2. Perspective view of the *trans*-1,2-divinylcyclohexane complex of palladium dichloride, with atoms labeled for reference in the text.

Table I. NOE Data on Dichloro(*trans*-1,2-divinylcyclohexane)palladium

proton irradiated	proton affected (%)	proton irradiated	proton affected (%)
H_{10t}	H_{10c} (4.2)	H_7	H_{10c} (2.5) H_{8c} (8.4) H_1 (6.1)
H_{8t}	H_{8c} (3.8)		
H_9	H_{10c} (6.2) H_{8c} (3.0) H_1 (2.6) H_{3a} (4.2)	H_1	H_7 (6.1) H_9 (2.6) H_{3a} (4.0) H_{5a} (4.6)

Table II. Crystal Data and Some Experimental Details (Esd's, Where Given, Are in Parentheses)

	cis	trans
compd	dichloro(1,2-divinylcyclohexane)palladium	
formula	$C_{10}H_{16}Cl_2Pd$	
M_w	313.54	
approx cryst size, mm	0.45·0.45·0.15	0.38·0.15·0.07
cryst color	yellow	yellow
space group	$P\bar{1}$	$P2_1/n$
a, Å	6.329 (1)	6.923 (1)
b, Å	7.738 (1)	20.528 (5)
c, Å	12.473 (2)	8.277 (2)
α, deg	107.07 (1)	90.0
β, deg	83.48 (1)	105.25 (4)
γ, deg	105.89 (1)	90.0
cell vol, Å^3	561.3 (2)	1134.9 (5)
Z	2	4
D_c, g cm^{-3}	1.855	1.835
$F(000)$	312	624
$\mu_{Mo\,K\alpha}$, cm^{-1}	20.67	20.45
$N_{unique,tot}$	3494	1953
N_{used}	3255 [$F > 6\sigma(F)$]	1720 [$F > 2\sigma(F)$]
no. of variables	242	134
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.029	0.040
$R_w = [\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.042	0.046

group that was attacked. For this purpose, *cis,cis*-1,2-divinyl-4-(trimethylsilyl)cyclohexane (**5**) was chosen. The palladium(II) chloride complex of **5** (**6**) was prepared by the addition of $PdCl_2(PhCN)_2$ to a mixture of 8-(trimethylsilyl)-(*E*,*Z*)-1,5-cyclodecadiene, 1-(trimethylsilyl)-

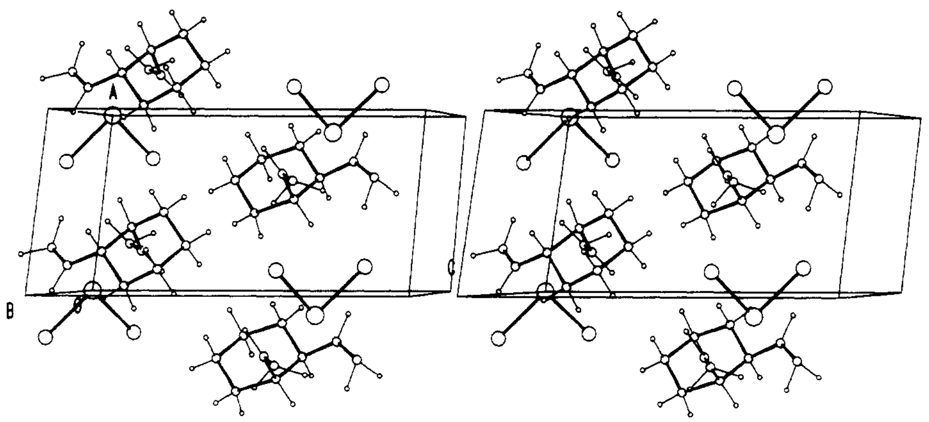


Figure 3. Stereoscopic packing illustration of the crystal structure of (*cis*-1,2-divinylcyclohexane)palladium dichloride complex.

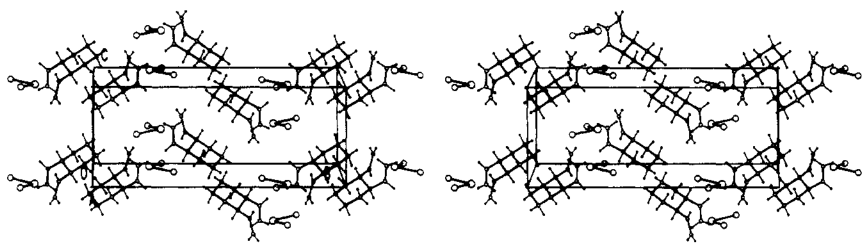
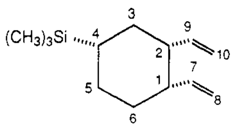


Figure 4. Stereoscopic illustration of the crystal structure of dichloro(*trans*-1,2-divinylcyclohexane)palladium complex.



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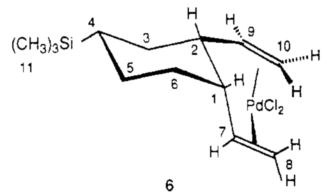

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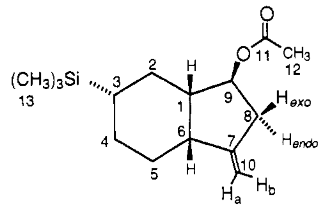
(E,E)-1,4,9-decatriene, and 1-(trimethylsilyl)-(Z,E)-1,4,9-decatriene (obtained from butadiene and trimethylvinylsilane).[12] This resulted in coordination of palladium(II) to the 1,5-diene only, followed by stereospecific Cope rearrangement of the cyclic silane to yield the pure cis,cis-isomer **6**. This was shown by NMR (by the appearance of H_4, for example, as a triplet of triplets with diaxial coupling constants of 12.9 Hz and axial–equatorial coupling constants of 4.0 Hz) to exist in a single chair conformation, with the bulky trimethylsilyl group in an equatorial position. The coupling constants J_{H_1,H_7} and J_{H_2,H_9} were found to be 10.5 and 0 Hz, respectively, suggesting a conformation similar to that of the unsubstituted cis isomer.

Treatment of **6** with bis(diphenylphosphino)ethane afforded the free diene **5**, which was shown by ^{1}H NMR to exist as a single isomer. Oxidative cyclization of **5**, with the catalyst system employed previously,[4c] would thus lead to **7** or **8**, depending on whether nucleophilic attack occurs



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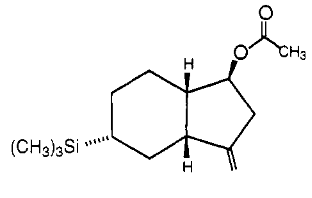

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on the equatorial or the axial double bond, respectively. The results clearly show that only **7** was obtained, demonstrating that nucleophilic attack occurred exclusively on the equatorial double bond.

The structure of **7** was deduced by NMR studies, using double-resonance experiments for the determination of coupling constants. The chair conformation of the six-membered ring was retained, as evidenced by a complete assignment of the coupling constants. The resonances at δ 2.03 and 2.90 (C_6D_6) were assigned to the bridgehead protons, H_6 being identified as the proton resonating at lower field. This is supported by couplings of H_6 to H_{10a} and H_{10b} (1.5 Hz), H_{5a} (2.0 Hz) and H_{5e} (2.0 Hz), and is consistent with the relative shift order of bridgehead protons observed in analogous [4,2,0]cyclononanes.[4c] The bridgehead proton at δ 2.03 is coupled to a quartet at δ 0.55 with J = 13.0 Hz, assigned to H_{2a}. This proton is coupled to H_3, which appears as a triplet of triplets at δ 0.35 and is the proton attached to the carbon bearing the silyl group. Further support for this structure comes from J_{H_1,H_9}, which was found to be 0 Hz, indicating a dihedral angle H_1–C_1–C_9–H_9 of about 90°, compatible only with structure **7**.

Discussion

It has been assumed[1a,2] and confirmed in a few cases[13] that 1,5-diene complexes of palladium and platinum have the two double bonds aligned almost parallel to one another and perpendicular to the coordination plane. The only exceptions are those dienes that are geometrically constrained, forcing one double bond to be parallel to the coordination plane.[1b,14] The expected mode of coordination has been found in the palladium(II) diene complexes prepared in this study, with torque angles close to those previously reported.[13d] However, the conformation of the noncoordinating part of the molecule seems to be even more important than the conformation of the olefinic groups, resulting in a geometry that deviates from the one expected to give the maximum orbital overlap with the metal. In **4**, for example, the cyclohexane ring assumes a chair conformation, which flips without the olefinic groups decoordinating completely. This suggests that a strict adherence to a precise perpendicular geometry of the olefinic groups to the coordination plane in metal diene complexes is not necessary, only that the olefinic groups are free to assume the desired conformation.

Nucleophilic attack trans to palladium at either of the two double bonds of the cis-isomer **4** would lead to the

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] of the Non-Hydrogen Atoms of the *cis*- and *trans*-1,2-Divinylcyclohexane Complexes of Palladium Dichloride (Esd's in Parentheses)

atom	x/a	y/b	z/c	U_{eq}, Å^2
		Cis Isomer		
Pd	0.00000	0.00000	0.00000	0.0275 (1)
Cl(1)	−0.2652 (3)	−0.0401 (3)	−0.1224 (2)	0.0414 (3)
Cl(2)	−0.2421 (3)	−0.1929 (3)	0.0965 (2)	0.0432 (3)
C(1)	0.2275 (5)	0.3999 (4)	0.0806 (4)	0.0398 (3)
C(2)	0.3621 (4)	0.3134 (4)	0.1404 (4)	0.0395 (3)
C(3)	0.4451 (5)	0.4475 (4)	0.2466 (3)	0.0422 (3)
C(4)	0.2653 (5)	0.5116 (5)	0.3256 (4)	0.0529 (3)
C(5)	0.1338 (5)	0.5971 (4)	0.2706 (4)	0.0502 (3)
C(6)	0.0410 (4)	0.4786 (4)	0.1653 (3)	0.0349 (3)
C(7)	0.1495 (4)	0.2717 (4)	−0.0310 (3)	0.0317 (3)
C(8)	0.2456 (4)	0.1482 (4)	−0.1010 (3)	0.0309 (3)
C(9)	0.2280 (4)	0.1296 (4)	0.1446 (3)	0.0292 (3)
C(10)	0.2675 (4)	−0.0371 (4)	0.0821 (3)	0.0248 (3)
Pd′	−0.11519 (4)	0.59424 (4)	0.70691 (2)	0.0281 (1)
Cl(1′)	0.1318 (3)	0.7909 (3)	0.6160 (2)	0.0412 (3)
Cl(2′)	0.1499 (3)	0.6341 (3)	0.8314 (2)	0.0399 (3)
C(1′)	−0.4814 (4)	0.2784 (4)	0.5745 (3)	0.0295 (3)
C(2′)	−0.3575 (3)	0.1839 (4)	0.6274 (3)	0.0267 (3)
C(3′)	−0.1745 (4)	0.1359 (4)	0.5563 (4)	0.0387 (3)
C(4′)	−0.2498 (5)	−0.0069 (5)	0.4342 (4)	0.0594 (3)
C(5′)	−0.3694 (5)	0.0897 (4)	0.3778 (3)	0.0504 (3)
C(6′)	−0.5605 (4)	0.1541 (4)	0.4517 (4)	0.0389 (3)
C(7′)	−0.3386 (4)	0.4716 (4)	0.5625 (4)	0.0387 (3)
C(8′)	−0.3819 (5)	0.6456 (5)	0.6179 (4)	0.0573 (3)
C(9′)	−0.2646 (5)	0.3133 (4)	0.7355 (4)	0.0387 (3)
C(10′)	−0.3590 (5)	0.4567 (5)	0.8132 (4)	0.0487 (3)
		Trans Isomer		
Pd	0.16680 (5)	0.22861 (2)	0.00834 (4)	0.0309 (1)
Cl(1)	0.3147 (2)	0.3270 (1)	−0.0142 (2)	0.0474 (5)
Cl(2)	−0.1382 (2)	0.2798 (1)	−0.0280 (2)	0.0459 (5)
C(1)	0.2966 (8)	0.1220 (3)	−0.1896 (7)	0.038 (2)
C(2)	0.1645 (8)	0.0854 (3)	−0.1010 (6)	0.039 (1)
C(3)	0.0524 (9)	0.0310 (3)	−0.2154 (7)	0.046 (2)
C(4)	0.2003 (11)	−0.0149 (3)	−0.2670 (8)	0.061 (3)
C(5)	0.3389 (11)	0.0214 (3)	−0.3477 (8)	0.065 (3)
C(6)	0.4494 (9)	0.0768 (3)	−0.2377 (7)	0.050 (2)
C(7)	0.4027 (7)	0.1785 (3)	−0.0855 (6)	0.037 (2)
C(8)	0.4643 (7)	0.1825 (3)	0.0851 (6)	0.041 (2)
C(9)	0.0196 (8)	0.1310 (3)	−0.0523 (7)	0.037 (2)
C(10)	0.0297 (9)	0.1454 (3)	0.1100 (7)	0.044 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\alpha^*_i\alpha^*_j a_i a_j$.

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Table IV. Selected Intramolecular Bond Distances (Å) and Angles (deg) Involving the Non-Hydrogen Atoms of the *cis*-1,2-Divinylcyclohexane (A and B) and of the *trans*-1,2-Divinylcyclohexane Complexes of Palladium Dichloride (Esd's Are Given in Parentheses)

	cis isomer, A	cis isomer, B	trans isomer
	Distances		
Pd-Cl(1)	2.294 (2)	2.314 (2)	2.294 (2)
Pd-Cl(2)	2.326 (2)	2.312 (2)	2.306 (2)
Pd-C(7)	2.184 (3)	2.233 (4)	2.236 (6)
Pd-C(8)	2.178 (3)	2.300 (4)	2.203 (5)
Pd-C(9)	2.254 (4)	2.236 (4)	2.244 (5)
Pd-C(10)	2.198 (4)	2.176 (4)	2.223 (6)
C(1)-(C7)	1.497 (5)	1.560 (4)	1.514 (7)
C(2)-(C9)	1.455 (4)	1.494 (5)	1.503 (8)
C(7)-(C8)	1.324 (4)	1.406 (5)	1.366 (7)
C(9)-(C10)	1.370 (4)	1.459 (5)	1.359 (8)
	Angles		
C(9)-Pd-C(10)	35.8 (1)	38.6 (2)	35.4 (2)
C(8)-Pd-C(10)	88.9 (1)	92.0 (2)	91.2 (2)
C(8)-Pd-C(9)	88.6 (1)	108.2 (2)	90.9 (2)
C(7)-Pd-C(10)	101.1 (1)	91.2 (2)	101.6 (2)
C(7)-Pd-C(9)	80.4 (1)	81.3 (2)	80.9 (2)
C(7)-Pd-C(8)	35.4 (1)	36.1 (2)	35.8 (2)
Cl(2)-Pd-C(10)	87.3 (1)	88.8 (2)	86.1 (2)
Cl(2)-Pd-C(9)	92.3 (1)	87.4 (1)	91.8 (2)
Cl(2)-Pd-C(8)	172.2 (1)	162.1 (1)	171.0 (2)
Cl(2)-Pd-C(7)	152.4 (1)	161.7 (1)	153.1 (2)
Cl(1)-Pd-C(10)	163.3 (1)	169.4 (1)	162.0 (2)
Cl(1)-Pd-C(9)	160.8 (1)	151.9 (1)	162.6 (2)
Cl(1)-Pd-C(8)	90.2 (1)	85.6 (1)	89.9 (2)
Cl(1)-Pd-C(7)	87.6 (1)	93.0 (1)	89.7 (2)
Cl(1)-Pd-Cl(2)	91.5 (1)	90.3 (1)	90.1 (1)
Pd-C(7)-C(1)	105.2 (3)	107.2 (2)	105.1 (4)
C(1)-C(7)-C(8)	127.5 (3)	125.4 (3)	127.4 (5)
Pd-C(7)-C(8)	72.1 (2)	74.6 (2)	70.8 (3)
Pd-C(8)-C(7)	72.5 (2)	69.3 (2)	73.4 (3)
Pd-C(9)-C(2)	111.2 (3)	107.6 (2)	108.7 (4)
C(2)-C(9)-C(10)	125.2 (3)	126.6 (3)	122.4 (5)
Pd-C(9)-C(10)	69.9 (2)	68.5 (2)	71.5 (3)
Pd-C(10)-C(9)	74.3 (2)	73.0 (2)	73.1 (3)

Table V. Ring-Puckering Parameters[a] for the Cyclohexane Rings in the Dichloropalladium Complexes of *cis*- and *trans*-1,2-Divinylcyclohexane (Esd's in Parentheses)

compd	q_2, Å	ϕ_2/ϕ, deg	q_3, Å	Q, Å	θ, deg
cis isomer, A	0.031 (3)	100 (7)	0.544 (4)	0.544 (4)	3.3 (3)
cis isomer, B	0.050 (3)	−38 (4)	−0.571 (3)	0.573 (3)	174.9 (3)
trans isomer	0.033 (6)	37 (10)	0.576 (6)	0.576 (6)	3.3 (6)

[a] Calculated according to Cremer and Pople.[10]

Table VI. Selected Torsional Angles,[a] Calculated for the *cis*- and *trans*-1,2-Divinylcyclohexane Complexes of Palladium Dichloride (Esd's[b] in Parentheses)

compd	atoms involved	angle, deg
cis isomer, A	C(7)-C(1)-C(6)-C(5)	178.8 (3)
	C(9)-C(2)-C(3)-C(4)	−67.5 (4)
	H(1)-C(1)-C(7)-H(7)	−83[c]
	H(2)-C(2)-C(9)-H(9)	156[c]
cis isomer, B	C(7′)-C(1′)-C(2′)-C(3′)	−65.2 (4)
	C(9′)-C(2′)-C(3′)-C(4′)	179.7 (3)
	H(1′)-C(1′)-C(7′)-H(7′)	−176[c]
	H(2′)-C(2′)-C(9′)-H(9′)	93[c]
trans isomer	C(7)-C(1)-C(6)-C(5)	−178.1 (5)
	C(9)-C(2)-C(3)-C(4)	179.2 (5)
	H(1)-C(1)-C(7)-H(7)	−45[c]
	H(2)-C(2)-C(9)-H(9)	−165[c]

[a] Right-hand rule according to Klyne and Prelog.[11a] [b] Esd's are calculated according to Stanford and Waser.[11b] [c] None of the hydrogen positions are refined (cf. the text). The uncertainties in the torsional angles, including H positions, are assumed to be between 6 and 8°.

observed compound **2** from palladium-catalyzed oxidative cyclization of *cis*-1,2,divinylcyclohexane. However, the results of the cyclization of the silicon derivative show that only the olefinic group in the equatorial position is attacked, at least in that process which goes on to form product. This implies that one of the conformational enantiomers of **4** (one chair conformation) leads to a product with 1*R*,6*S*,7*S* configuration and the other to a product with opposite absolute configuration. However, for the trans-compound **3**, nucleophilic addition to the two olefinic groups would result in products with different stereochemistry, whereas only the stereoisomer with 1*S**,6*S**,7*S** configuration (**1**) was observed in the cyclization of *trans*-1,2-divinylcyclohexane.[4c] If a palladium(II) diene complex, analogous to **3**, is, in fact, a true intermediate in the oxidative cyclization of *trans*-1,2-divinylcyclohexane, then only one double bond must be attacked. As noted previously, this phenomenon has been demonstrated unequivocally in the cyclization of the trimethylsilyl derivative **5**, which gave **7** as the major product with no evidence of the other regioisomer. The formation of only one stereoisomer from *trans*-1,2-divinylcyclohexane can thus be rationalized assuming the exclusive nucleophilic addition to C_9 in **3** or to C_7 after rotation of the C_1–C_7 and C_2–C_9 bonds. Since the two conformations are identical, they lead to identical products, the absolute configuration of the product being determined by the absolute configuration of the starting diene.

Summary. Dichloro(*trans*- and *cis*-1,2-divinylcyclohexane)palladium exist in solution and in the solid state in conformations with nearly parallel olefinic bonds. Both complexes equilibrate between two degenerate conformations, the former via dissociation, the latter while complexed to palladium. This study shows that, for palladium diene complexes, not only are the olefinic bonds coordinated differently to the metal but the small electronic differences cause nucleophilic attack to only one of the bonds.

Experimental Section

NMR spectra were run on a Bruker WP 200 MHz or a Bruker AM 400 spectrometer equipped with a B-VT 1000 variable-temperature unit. ^1H, $^{13}C[H]$ (composite-pulse, broad-band ^1H decoupled ^{13}C), and ^{13}C NMR spectra were assigned with the aid of distortionless enhancement by polarization transfer (DEPT), heteronuclear correlation (^1H–^{13}C) and double-quantum phase-sensitive COSY experiments (^1H–^1H). Microanalyses were performed by Analytical Laboratories, Engelskirchen, Germany.

Bis(benzonitrile)dichloropalladium was prepared from benzonitrile and palladium dichloride according to Kharasch et al.[15] *cis*- and *trans*-1,2-divinylcyclohexane were purchased from Fluka. 1,2-Bis(diphenylphosphino)ethane, obtained from Aldrich, was recrystallized from heptane before use. Triphenyl phosphite was purchased from Merck, butadiene from Fluka, and trimethylvinylsilane from Aldrich. $Ni(COD)_2$ was prepared according to literature methods.[16] For the NOE difference experiment, a solution of dichloro(*trans*-1,2-divinylcyclohexane)palladium in $(CD_3)_2CO$ was deoxygenated by using the freeze–thaw method.[17]

Toluene was dried and distilled from sodium benzophenone ketyl, hexane was fractionally distilled, and dichloromethane was distilled over P_2O_5.

Dichloro(*trans*-1,2-divinylcyclohexane)palladium (3). *trans*-1,2-Divinylcyclohexane (218 mg, 1.6 mmol) was added, with stirring, to a solution of bis(benzonitrile)dichloropalladium (621

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(16) Bogdanovic, B.; Kröner, M.; Wilke, G. *Liebigs Ann. Chem.* **1966**, *699*, 1.
(17) Air was removed under vacuum while the sample was frozen with liquid N_2. The system was closed and warmed to room temperature. This process was repeated several times to ensure an oxygen-free sample.

mg, 1.6 mmol) in toluene (20 mL). The yellow precipitate, which formed after 5 min, was filtered, washed with toluene and hexane, and dried under vacuum for 1 h (yield 320 mg, 64%). The solid was characterized as dichloro(*trans*-1,2-divinylcyclohexane)palladium by ^{1}H and ^{13}C NMR techniques and by X-ray diffraction. Crystals were obtained by allowing an acetone solution to sit at 5 °C for three days. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, 297 K) δ 6.75 (m, $J_{7,8t}$ = 15.6 Hz, $J_{7,8c}$ = 8.85 Hz, $J_{1,7}$ = 5.6 Hz, 1 H, H_7), 5.91 (m, $J_{9,10t}$ = 15.3 Hz, $J_{9,10c}$ = 8.05 Hz, $J_{2,9}$ = 10 Hz, 1 H, H_9), 5.75 (dd, $J_{9,10c}$ = 8.05 Hz, $J_{10t,10c}$ = 2.4 Hz, 1 H, H_{10c}), 5.34 (dd, $J_{9,10t}$ = 15.3 Hz, $J_{10c,10t}$ = 2.4 Hz, 1 H, H_{10t}), 5.02 (d, $J_{7,8t}$ = 15.6 Hz, 1 H, H_{8t}), 4.72 (d, $J_{7,8c}$ = 8.85 Hz, 1 H, H_{8c}), 3.02 (ddt, $J_{1,7}$ = 5.6 Hz, $J_{1,6e}$ = 3.2 Hz, $J_{1,2}$ = $J_{1,6a}$ = 11.6 Hz, 1 H, H_1), 1.88 (m, 2 H), 1.75 (m, 3 H), 1.53 (ddt, $J_{6e,6a}$ = 11.4 Hz, $J_{6a,5e}$ = 3.5 Hz, $J_{1,6a}$ = $J_{6a,5a}$ = 12.9 Hz, 1 H, H_{6a}), 1.37 (qt, $J_{5a,6a}$ = $J_{5a,4a}$ = $J_{5a,5e}$ = 12.9 Hz, $J_{5a,6e}$ = $J_{5a,4e}$ = 3.5 Hz, 1 H, H_{5a}), 1.23 (qt, $J_{4a,5a}$ = $J_{4a,3a}$ = $J_{4a,4e}$ = 12.9 Hz, $J_{4a,5e}$ = $J_{4a,3e}$ = 3.5 Hz, 1 H, H_{4a}), 1.05 (ddt, $J_{3a,3e}$ = 11.7 Hz, $J_{3a,4a}$ = 3.5 Hz, $J_{2,3a}$ = $J_{3a,4a}$ = 12.8 Hz, 1 H, H_{3a}). ^{13}C[H] NMR ($(CD_3)_2CO$, 400 MHz, 297 K)[18] δ 131.42 (C_7), 127.26 (C_9), 97.64 (C_{10}), 84.85 (C_8), 51.03 (C_1), 44.65 (C_2), 33.91 (C_6), 30.96 (C_3), 25.43 (C_5), 25.17 (C_4). ^{13}C–^{1}H couplings of the olefinic region were observed by using a gated decoupling experiment: $J(C_{10}–H_{10t,c})$ = 163 Hz, $J(C_8–H_{8t,c})$ = 159 Hz, $J(C_9–H_9)$ = 161 Hz, $J(C_7–H_7)$ = 163 Hz. Anal. Calcd for $C_{10}H_{16}PdCl_2$: C, 38.30; H, 5.14. Found: C, 37.92; H, 4.79.

Dichloro(*cis*-1,2-divinylcyclohexane)palladium (4). *cis*-1,2-Divinylcyclohexane (250 mg, 1.9 mmol) was added to a solution of bis(benzonitrile)dichloropalladium (730 mg, 1.9 mmol) in toluene (20 mL), according to the preparation of diene complexes by Jensen.[19] After this stirred for 5 min, a bright yellow solid precipitated. The solid was filtered, washed with toluene and hexane, and dried under vacuum for 1 h (yield 520 mg, 87%). Single crystals were obtained by allowing a CH_2Cl_2 solution to sit at 5 °C for 2 weeks. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz, 297 K) δ 6.50 (m, 2 H, $H_7(H_9)$),[20] 5.45 (d, J = 7.5 Hz, 2 H, $H_{8c}(H_{10c})$), 4.80 (d, J = 15 Hz, 2 H, H_{8t} (H_{10t})), 2.65 (m, 2 H, $H_1(H_2)$), 1.80 (m, 8 H). ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, 183 K) δ 6.45 (dd, $J_{7,8t}$ = 15.5 Hz, $J_{7,8c}$ = 9.0 Hz, 1 H, H_7), 6.30 (m, $J_{9,10t}$ = 15.5 Hz, $J_{9,10c}$ = 8.0 Hz, $J_{2,9}$ = 10.5 Hz, 1 H, H_9), 5.63 (dd, $J_{9,10c}$ = 8.0 Hz, $J_{10t,10c}$ = 2.0 Hz, 1 H, H_{10c}), 5.57 (dd, $J_{9,10t}$ = 15.5 Hz, $J_{10c,10t}$ = 2.0 Hz, 1 H, H_{10t}), 5.34 (d, $J_{7,8t}$ = 15.5 Hz, 1 H, H_{8t}), 4.75 (d, $J_{7,8c}$ = 9.0 Hz, 1 H, H_{8c}), 3.02–0.8 (m, 10 H).

Dichloro(*cis*,*cis*-1,2-divinyl-4-(trimethylsilyl)cyclohexane)palladium (6). 9-(Trimethylsilyl)-(*Z*,*E*)-1,5-cyclodecadiene was prepared as a mixture with 1-(trimethylsilyl)-(*E*,*E*)-1,4,9-decatriene and 1-(trimethylsilyl)-(*Z*,*E*)-1,4,9-decatriene, from trimethylvinylsilane and butadiene (1:2), according to Heimbach et al.[12] $Ni(COD)_2$, together with 1 mol equiv of triphenyl phosphite, was employed as the catalyst system. After heating for 6 h at 60 °C, the contents were fractionally distilled (using a Büchi bulb-to-bulb distillation apparatus) up to 150 °C, giving a clean mixture of the cyclic decadiene and the two decatrienes. Reaction of 448 mg (2.1 mmol) of the mixture (approximately 50% is the cyclized product as determined from ^{1}H NMR) with bis(benzonitrile)dichloropalladium (460 mg, 1.2 mmol) in toluene (30 mL) gave dichloro(*cis*,*cis*-1,2-divinyl-4-(trimethylsilyl)cyclohexane)palladium (188 mg, 0.5 mmol) as determined by ^{1}H NMR. The product, precipitated out of toluene as a yellow solid, was washed with toluene and hexane and then dried under vacuum for 1 h. ^{1}H NMR ($CDCl_3$, 200 MHz, 297 K) δ 6.55 (dd, $J_{9,10t}$ = 15.5 Hz, $J_{9,10c}$ = 8.5 Hz, 1 H, H_9), 6.32 (ddd, $J_{7,8t}$ = 15.5 Hz, $J_{7,8c}$ = 8.5 Hz, $J_{1,7}$ = 10.5 Hz, 1 H, H_7), 5.90 (dd, $J_{7,8c}$ = 8.5 Hz, $J_{8c,8t}$ = 2.0 Hz, 1 H, H_{8c}), 5.00 (ddd, $J_{7,8t}$ = 15.5 Hz, $J_{8c,8t}$ = 2.0 Hz, $J_{9,10c}$ = 8.5 Hz, 2 H, H_{8t}, H_{10c}), 4.68 (d, $J_{9,10t}$ = 15.5 Hz, 1 H, H_{10t}), 2.75 (m, 1 H, H_1), 2.55 (m, 1 H, H_2), 2.39 (q, $J_{3a,2}$ = $J_{3a,3e}$ = $J_{3a,4}$ = 12.9 Hz, 1 H, H_{3a}), 2.15 (m, 1 H, H_{5e}), 1.70 (m, 4 H, H_{3e}, H_{5a}, H_{6a}, H_{6e}), 0.78 (tt, $J_{4,3a}$ = $J_{4,5a}$ = 12.9 Hz, $J_{4,3e}$ = $J_{4,5e}$ = 4.0 Hz, 1 H, H_4), 0.05 (s, 9 H, H_{11}). Anal. Calcd for $C_{13}H_{24}SiPdCl_2$: C, 40.48; H, 6.27. Found: C, 40.26; H, 6.10.

***cis*,*cis*-1,2-Divinyl-4-(trimethylsilyl)cyclohexane (5).** In a typical experiment, 1,2-bis(diphenylphosphino)ethane (31 mg, 0.08 mmol) was added to a mixture of dichloro(*cis*,*cis*-1,2-divinyl-4-(trimethylsilyl)cyclohexane)palladium (31 mg, 0.08 mmol) in CH_2Cl_2 (30 mL). Immediately, the cloudy solution turned a bright clear orange. The CH_2Cl_2 was removed under vacuum, and the residue extracted with hexane (40 mL). Careful evaporation of the hexane (the product is volatile) gave *cis*,*cis*-1,2-divinyl-4-(trimethylsilyl)cyclohexane (15 mg, 94% yield) as a clear oil. The spectroscopic properties (^{1}H NMR) were identical with those reported for *cis*,*cis*-1,2-divinyl-4-(trimethylsilyl)cyclohexane, prepared by heating 8-(trimethylsilyl)-(*E*,*Z*)-1,5-cyclodecadiene.[12]

Cyclization of *cis*,*cis*-1,2-Divinyl-4-(trimethylsilyl)cyclohexane (7). *cis*,*cis*-1,2-Divinyl-4-(trimethylsilyl)cyclohexane (92 mg, 0.44 mmol) was added to a well-stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), MnO_2 (43.5 mg, 0.5 mmol), and *p*-benzoquinone (10.8 mg, 0.1 mmol) in 2.5 mL of acetic acid. After this stirred at room temperature for 7.5 h, H_2O (1 mL) was added, and the mixture extracted with petroleum ether (5 × 5 mL). The organic phase was washed with 2 M NaOH (3 × 5 mL) and then with H_2O (3 × 5 mL) and dried over Mg_2SO_4. Separation using a convex gradient elution on silica gel[21] (gradient system hexane/CH_2Cl_2/methanol) afforded the desired compound (34 mg, 29% yield) along with minor amounts of Me_3Si-containing impurities (shown by ^{1}H NMR). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K)[22] δ 4.97, 4.84 (2 H, H_{10a}, H_{10b}), 4.76 (1 H, H_9), 2.79 (2 H, H_{8endo}, H_6), 2.41 (1 H, H_{8exo}), 2.04–1.97 (5 H, H_1, H_{5e}, 3 × H_{12}), 1.61–1.51 (2 H, H_{2e}, H_{5a}), 1.38 (1 H, H_{4e}), 1.08 (1 H, H_{4a}), 0.55 (1 H, H_{2a}), 0.43 (1 H, H_3), –0.11 (9 H, H_{13}). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 4.96, 4.91 (m, $J_{10a,10b}$ = 1 Hz, $J_{10a,6}$ = $J_{10b,6}$ = 1.5 Hz, $J_{10a,8exo}$ = $J_{10a,8endo}$ = $J_{10b,8exo}$ = $J_{10b,8endo}$ = 2.0 Hz, 2 H, H_{10a}, H_{10b}), 4.85 (d, $J_{9,8exo}$ = 6.0 Hz, 1 H, H_9), 2.90 (m, $J_{5a,6}$ = $J_{5e,6}$ = 2.0 Hz, 1 H, H_6), 2.65 (m, 1 H, H_{8exo}), 2.45 (m, 1 H, H_{8endo}), 2.03 (m, $J_{2a,1}$ = 13.0 Hz, 1 H, H_1), 1.98 (m, $J_{5e,5a}$ = 13.5 Hz, $J_{5e,4e}$ = 6.5 Hz, $J_{5e,4a}$ = 3.5 Hz, 1 H, H_{5e}), 1.65 (s, 3 H, 3 × H_{12}), 1.60 (m, 1 H, H_{2e}), 1.45 (m, $J_{5a,5e}$ = $J_{5a,4a}$ = 13.5 Hz, $J_{5a,4e}$ = 4.5 Hz, 1 H, H_{5a}), 1.28 (m, $J_{4e,4a}$ = 13.0 Hz, $J_{4e,3}$ = 2.5 Hz, $J_{4e,5e}$ = 6.5 Hz, $J_{4e,5a}$ = 4.5 Hz, 1 H, H_{4e}), 1.12 (qd, $J_{4a,4e}$ = $J_{4a,3}$ = $J_{4a,5a}$ = 13.0 Hz, $J_{4a,5e}$ = 3.5 Hz, 1 H, H_{4a}), 0.55 (q, $J_{2a,2e}$ = $J_{2a,3}$ = $J_{2a,1}$ = 13.0 Hz, 1 H, H_{2a}), 0.35 (tt, $J_{3,2a}$ = $J_{3,4a}$ = 13.0 Hz, $J_{3,2e}$ = $J_{3,4e}$ = 2.5 Hz, 1 H, H_3), –0.10 (s, 9 H, H_{13}). ^{13}C(^{1}H) NMR ($CDCl_3$, 100.6 MHz, 297 K)[23] δ 170.84 (1 C, C_{11}), 149.86 (1 C, C_9), 105.89 (1 C, C_{10}), 78.21 (1 C, C_7), 46.16, 40.45 (2 C, C_1, C_6), 37.58, 26.43, 25.45, (3 C, C_4, C_5, C_8), 24.32 (1 C, C_3), 21.38 (2 C, C_{12}, C_2), –3.65 (3 C, C_{13}).

Collection and Processing of X-ray Data. Crystals of the *cis*- and *trans*-divinylcyclohexane complexes of palladium dichloride, suitable for single-crystal X-ray diffraction studies, were grown from dichloromethane (over 2 weeks) and acetone (over 3 days) solutions, respectively, at 5 °C. The intensity data were collected at room temperature on a Siemens STOE/AED2 diffractometer equipped with a graphite monochromator and Mo Kα radiation (λ = 0.71069 Å, θ_{max} = 30°) using the ω–2θ scan technique. Data reductions included corrections for background, Lorentz, and polarization effects as well as for absorption effects. The absorption corrections were based on ψ scans of nine reflections from each crystal with χ angles near 90° and different θ values. The transmission factors varied between 0.25 and 0.60 (cis compound) and 0.29 and 0.42 (trans complex). The unit-cell parameters were refined by least-squares calculations using angular settings of well-centered strong reflections: 70 for the triclinic cis compound with 29° < 2θ < 49° and 51 for the monoclinic trans complex within the range 17° < 2θ < 36°. Crystal data are shown in Table II.

Structure Solutions and Refinements. The structures were solved by the Patterson method (SHELXS)[24] and refined by full-matrix least-squares treatment based upon |*F*| (SHELX).[25] The

(18) Assignments confirmed by a ^{1}H–^{13}C heteronuclear correlation experiment.

(19) Jensen, K. A. *Acta Chem. Scand.* **1953**, *7*, 866.

(20) Assume analogous assignment of peaks as in **3** and **6**.

(21) Baeckström, P.; Stridh, K.; Li, L.; Norin, T. *Acta Chem. Scand.* **1987**, *B41*, 442.

(22) Coupling constants were obtained from both $CDCl_3$ and C_6D_6 NMR spectra, and the assignments were confirmed by a double-quantum phase-sensitive COSY experiment.

(23) Assignments confirmed by a distortionless enhancement of polarization transfer (DEPT) experiment.

(24) Sheldrick, G. M. SHELXS 84: *Program for Crystal Structure Solution*; University of Göttingen, FR-Germany, 1984 (personal communication).

(25) Sheldrick, G. M. SHELX 76: *Program for Crystal Structure Determination*; University of Cambridge, England, 1976.

hydrogen atoms in both structures, except those of the cyclohexane rings in the cis compound, which were given assumed positions calculated after each cycle of the refinement, were located from difference electron density calculations, and their positions were kept riding on the respective mother atoms.

In the last stage of the refinements, the positions of the non-hydrogen atoms together with their anisotropic thermal parameters and isotropic temperature factors for the hydrogen positions were refined. In the case of the cis compound, for which an empirical extinction correction factor was also included, two group and four individual isotropic temperature factors were refined for the H atoms. In the case of the trans complex, each hydrogen has its own temperature factor refined.

Final R values together with some details of the refinement calculations are shown in Table II. The atomic scattering factors for the C and Cl atoms were taken from Cromer and Mann,[26] those for the Pd^{2+} ion from Cromer and Waber,[27] and those for the H atoms from Stewart et al.[28] The correction terms for the anomalous dispersion of the non-hydrogen atoms were taken from Cromer and Liberman.[29] Weights of the structure factors were calculated as $w = \text{const}/[\sigma^2(F) + g(F^2)]$ with g estimated to be 0.000 79 and 0.001 26 for the cis and trans complexes, respectively.

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Supplementary Material Available: Fractional atomic coordinates of the H atoms (Table VII), bond distances and bond angles (Table VIII), bond distances and bond angles involving the hydrogen atoms (Table IX), and anisotropic thermal parameters of the non-hydrogen atoms (Table X) (5 pages); lists of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Synthesis of [μ-1,9,10,11-η:4,5,6,12-η-Tricyclo[7.1.1.1^{4,6}]dodeca-1(11),4,6-(12),9-tetraene]bis(tricarbonyliron): The Smallest Cyclophane with Metal-Stabilized Antiaromatic Decks[1]

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The synthesis and structure of [μ-1,9,10,11-η:4,5,6,12-η-tricyclo[7.1.1.1^{4,6}]dodeca-1(11),4,6(12),9-tetraene]bis(tricarbonyliron) (1), a small cyclophane containing iron-stabilized antiaromatic decks of cyclobutadiene, is reported. Complex 1 crystallizes in the monoclinic space group $P2_1/a$, a = 12.455 (6) Å, b = 9.769 (4) Å, c = 7.156 (2) Å, β = 92.88 (3)°, and d(calcd, Z = 2) = 1.665 g cm^{-3}. The structure was resolved by direct methods using MULTAN80 and refined by least squares to R_f = 4.2% (R_w = 5.2%). The physical properties of 1 were examined and compared to [2.2]paracyclophane. The cyclobutadiene ligands are parallel to and lie directly over each other with no ring distortion, and there is a 20.6° out-of-plane bending of the aliphatic bridges away from the metal. The intradeck distance of 2.7 Å is the smallest observed for the cyclophanes. The carbonyl moieties are in the staggered conformation.

Introduction

The theory of interaction of molecular orbitals has spurred the study of many synthetic methods and reactions, inter alia, Diels–Alder reactions and photochemical cycloaddition reactions.[2] Cyclophanes, the most famous being [2.2]paracyclophane, have occupied the thoughts of theorists and experimentalists for many years.[3] Cyclophanes containing benzene are among those most investigated and show considerable cofacial π–π repulsions which result in the distortion of the benzene ring from planarity and increased reactivity.[3,4] These distortions have been confirmed by X-ray determinations and charge-transfer complex formation, and these observations are explained by increased electron density on the outer faces of these cyclophane systems with rehybridization of

(1) (a) Preliminary results were presented at the 3rd Chemical Congress of North America and 195th National Meeting of the American Chemical Society, Toronto, Canada, June 5–10, 1988, ORGN 365, and the 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14, 1989, ORGN 186. (b) C.M.A. was an Alexander von Humboldt Research Fellow, 1984–1985.
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