Chloropalladation of *exo*-9-Methylbicyclo[6.1.0]non-4-ene. Inversion of Configuration at Carbon Bound to Palladium and at Carbon Bound to Chlorine

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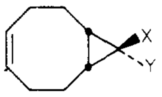
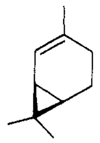
Reaction of the title bicyclic olefin with $PdCl_2(PhCN)_2$ in $CDCl_3$ gives bis(μ-chloro)bis[1,4,5-η-8-(α-chloroethyl)cyclooctenyl]dipalladium(II). Single-crystal X-ray diffraction was employed to determine the molecular structure of this chlorine-bridged dimer. Crystal data: $C_{10}H_{16}Cl_2Pd$, monoclinic, $a = 7.867$ (2) Å, $b = 12.651$ (2) Å, $c = 13.172$ (2) Å, $\beta = 119.4$ (1)°, space group $P2_1/C$, $Z = 4$. The final R factor is 6.3% for 1143 diffractometer collected intensities having $I \geq \sigma(I)$. The important stereochemical features are (i) the anti orientation of Pd and α-chloroethyl, which indicates inversion at cyclopropane carbon on electrophilic attack by palladium, and (ii) the sequence ordering on C_9, which indicates inversion at C_9 on nucleophilic attack by chlorine. The reaction of the dimer complex with aqueous cyanide ion proceeds quantitatively with retention at C_1 to form the trans (at cyclopropane) epimer of the title bicyclic. The probable mechanism of the ring closure is discussed.

Introduction

In previous reports from this laboratory, we have discussed chloropalladation reactions of bicyclo[6.1.0]non-4-ene,[1] bicyclo[5.1.0]oct-3-ene,[2] *N*-carbethoxy-8-azabicyclo[5.1.0]oct-3-ene,[3] and *exo*- and *endo*-9-methylbicyclo[6.1.0]non-4-ene (**1a** and **1b**), respectively.[4] More recently, Bäckvall and co-workers[5] have described the chloropalladation of the vinylcyclopropane (+)-car-2-ene (**2**), which was observed to form two palladium π-allylic products with a solvent-dependent product ratio. Thus, in (+)-2-carene the cyclopropane carbon that becomes allylic on chloropalladation undergoes predominant inversion of configuration in benzene. In reviewing electrophilic attack on cyclopropane rings, DePuy noted that much of the interest in such reactions derives from potential control of stereochemistry in the (up to three) new asymmetric centers developed on ring opening.[6] We now report that chloropalladation of cyclopropane in **1a** proceeds solely with inversion of configuration at both newly formed asymmetric carbon centers.



1a, X = CH_3, Y = H
b, X = H, Y = CH_3



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Experimental Section

Instrumentation. ^1H NMR spectra were obtained at 90 MHz by using a Varian EM390 instrument; ^{13}C NMR spectra were obtained at 22.39 MHz by using a Bruker WH-90 instrument. X-ray intensity data were collected at room temperature by using an Enraf-Nonius CAD-4 automated diffractometer.

Table I. Crystallographic Data and Data Collection Conditions for $C_{10}H_{16}Cl_2Pd$

formula	$C_{10}H_{16}Cl_2Pd$
space group	$P2_1/c$ (no. 14)
M_r, Daltons	313.55
a, Å	7.867 (2)
b, Å	12.651 (2)
c, Å	13.172 (2)
β, deg	119.4 (1)
V, Å^3	1142.3 (6)
Z	four based on monomer (each dimer sits on a crystallographic center of symmetry)
d_{calcd}, g/cm^3	1.832
d_{obsd}, g/cm^3	1.830[a]
cryst size, mm × mm × mm	0.305 × 0.102 × 0.102
radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)
scan type	ω-2θ
scan width (ΔW), deg	0.75 + 0.35 tan θ
max counting time, s	2 < 2θ ≤ 40°, 120 s
	40 < 2θ ≤ 50°, 240 s
collectn range	2 ≤ 2θ ≤ 50°
no. of unique data	2005
no. of unique data $I > 1.0\sigma(I)$	1143
no. of variables	116
R	0.063[b]
R_w	0.057[c]
esd	1.51[d]
largest parameter shift	0.31[d]
largest peak, e/Å^3	1.535[e]

[a] By flotation in mixed halo solvents. [b] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [c] $R_w = [\Sigma w (| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$ and $w = 4F^2/L^2\sigma(I)$, where L is the reciprocal Lorentz-polarization correction and $\sigma(I) = [P + (t/20)^2 B + (0.045I)^2]^{1/2}$. Here P is the number of counts during the scan, t is the scan counting time in seconds, and B is the sum of the background counts. [d] From final refinement, as a fraction of standard deviation. [e] From final difference Fourier.

Preparation of Compounds. The complex bis(μ-chloro)bis[1,4,5-η-8-(α-chloroethyl)cyclooctenyl]dipalladium(II) (**3**) was prepared by chloropalladation of **1a** as described earlier.[4] The related complex bis(μ-chloro)bis[1,4,5-η-cyclooctenyl]dipalladium(II) (**4**) was prepared as described in the literature.[7]

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $C_{10}H_{16}Cl_2Pd$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Pd(1)	0.4830 (1)	0.09620 (6)	0.39878 (6)	0.0333 (1)	0.00415 (4)	0.00996 (5)	−0.0017 (2)	0.0169 (1)	0.0018 (1)
Cl(1)	0.2791 (4)	0.0446 (2)	0.4783 (2)	0.0410 (7)	0.0065 (2)	0.0152 (2)	0.0030 (5)	0.0285 (5)	0.0059 (3)
Cl(2)	0.1503 (4)	0.4908 (2)	0.3606 (3)	0.0429 (9)	0.0072 (2)	0.0160 (3)	0.0061 (7)	0.0204 (7)	−0.0038 (4)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(1)	0.276 (1)	0.1942 (8)	0.2843 (7)	4.9 (2)	H(3A)	0.457 (10)	0.125 (7)	0.114 (6)	5.0
C(2)	0.275 (1)	0.1838 (9)	0.1695 (7)	5.0 (2)	H(3B)	0.536 (10)	0.261 (7)	0.170 (6)	5.0
C(3)	0.471 (1)	0.1815 (9)	0.1821 (8)	5.0 (2)	H(4)	0.670 (9)	0.092 (7)	0.292 (6)	5.2
C(4)	0.626 (1)	0.1422 (8)	0.2999 (8)	5.2 (2)	H(5)	0.822 (10)	0.176 (7)	0.463 (6)	4.5
C(5)	0.706 (1)	0.1971 (8)	0.4007 (7)	4.5 (2)	H(6A)	0.681 (8)	0.313 (7)	0.492 (5)	4.9
C(6)	0.675 (1)	0.3100 (9)	0.4251 (7)	4.9 (2)	H(6B)	0.781 (10)	0.352 (7)	0.412 (6)	4.9
C(7)	0.486 (1)	0.3633 (9)	0.3458 (8)	4.8 (2)	H(7A)	0.490 (10)	0.419 (7)	0.397 (6)	4.8
C(8)	0.306 (1)	0.3045 (7)	0.3388 (6)	3.7 (2)	H(7B)	0.474 (11)	0.368 (6)	0.283 (6)	4.8
C(9)	0.122 (1)	0.3758 (8)	0.2736 (7)	4.9 (2)	H(8)	0.309 (7)	0.298 (6)	0.419 (5)	3.7
C(10)	−0.063 (2)	0.3232 (11)	0.2497 (10)	7.2 (3)	H(9)	0.135 (10)	0.400 (7)	0.197 (6)	4.9
H(1)	0.161 (9)	0.172 (7)	0.285 (6)	4.9	H(10A)	−0.079 (10)	0.293 (8)	0.199 (6)	7.2
H(2A)	0.201 (10)	0.239 (7)	0.107 (6)	5.0	H(10B)	−0.033 (11)	0.301 (8)	0.334 (7)	7.2
H(2B)	0.218 (10)	0.111 (6)	0.136 (6)	5.0	H(10C)	−0.152 (12)	0.369 (8)	0.220 (7)	7.2

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)^*h^2 + B(2,2)^*k^2 + B(3,3)^*l^2 + B(1,2)^*hk + B(1,3)^*hl + B(2,3)^*kl)]$. Estimated standard deviations in the least significant digits are shown in parentheses.

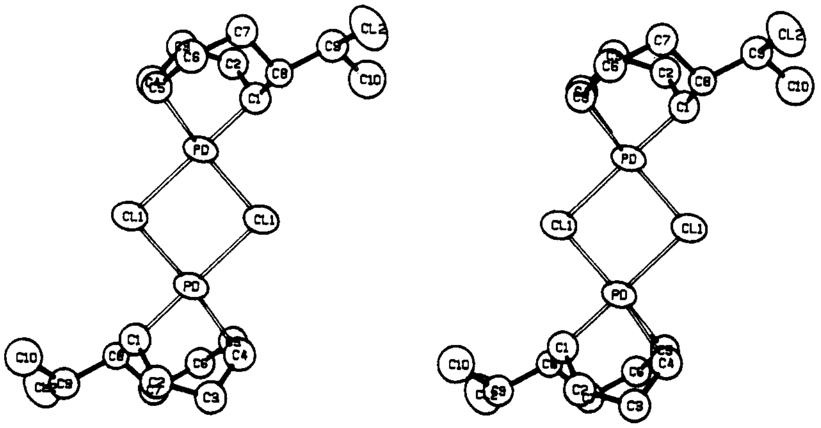


Figure 1. Stereopair drawing of 3. The view is normal to the square plane, over the bridge centroid (hydrogens omitted for clarity).

Spectral properties of 4 were identical with those published.[7]

Reaction of Complexes 3 and 4 with CN^-/D_2O. In a typical experiment, 0.4 mL of a $CDCl_3$ solution 0.05 M in 4 is shaken for 20 s with 0.5 mL of D_2O which is 1 M in KCN. After layer separation, the organometallic product $\{[(CN)_x\mathit{Pd}(\sigma\text{-cyclooctenyl})]^{(-x+1)}\}$ is found (by NMR) to be in the D_2O layer: ^1H NMR (D_2O, referenced to $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$) δ 5.85–5.3 (2 H, m, olefin), 2.5–1.1 (11 H, remaining hydrogens); ^{13}C NMR (D_2O, broad-band ^1H decoupled, internal reference dioxane, peaks reported here referenced to Me_4Si) δ 132.5, 131.5, 40.4, 37.9, 30.5, 29.9, 28.9, 25.7.

The reaction of complex 3 with CN^-/D_2O was reported earlier.[4] In this case the organic product (see Results and Discussion) remains in the $CDCl_3$ layer.

Crystal Growth. Complex 3. Gas diffusion of pentane into a nearly saturated solution of 3 in $CHCl_3$ led, after 24 h, to rather thick pale yellow needles. One of these needles was selected for the X-ray investigation.

X-ray Data and Structure Determination. A summary of crystal data is presented in Table I. Room-temperature X-ray photographic data from precession and cone axis photographs showed the crystal to be monoclinic with systematic extinctions ($h0l$, $l = 2n$; $0k0$, $k = 2n$) consistent with the space group $P2_1/c$ (No. 14). Data reduction and structure solution/refinement were accomplished by using the Enraf-Nonius structure solution programs (version 18.2). The cell constants were based on least-squares refinement of 25 carefully centered high-angle reflections. The atom positional and thermal parameters are listed in Table II. A full list of bond distances and bond angles is presented in Tables III and IV, respectively. Tables of observed and calculated structure factors as well as additional molecular geometry results are available as supplementary material.

Table III. Bond Distances (Å) for $C_{10}H_{16}Cl_2Pd$

C(1)-C(2)	1.521 (12)	C(1)-H(1)	0.91 (8)
C(2)-C(3)	1.474 (13)	C(2)-H(2A)	0.97 (7)
C(3)-C(4)	1.508 (13)	C(2)-H(2B)	1.00 (7)
C(4)-C(5)	1.349 (12)	C(3)-H(3A)	1.08 (7)
C(5)-C(6)	1.514 (12)	C(3)-H(3B)	1.14 (8)
C(6)-C(7)	1.498 (13)	C(4)-H(4)	0.79 (8)
C(7)-C(8)	1.532 (12)	C(5)-H(5)	0.92 (8)
C(8)-C(1)	1.523 (11)	C(6)-H(6A)	0.87 (8)
C(8)-C(9)	1.542 (11)	C(6)-H(6B)	0.96 (8)
C(9)-C(10)	1.497 (16)	C(7)-H(7A)	0.99 (8)
C(9)-Cl(2)	1.807 (9)	C(7)-H(7B)	0.83 (8)
Pd(1)-Cl(1)	2.396 (3)	C(8)-H(8)	1.06 (6)
Pd(1)-C(1)	2.015 (9)	C(9)-H(9)	1.13 (7)
Pd(1)-C(4)	2.178 (10)	C(10)-H(10A)	0.82 (10)
Pd(1)-C(5)	2.144 (9)	C(10)-H(10B)	1.04 (10)
		C(10)-H(10C)	0.84 (10)

Results and Discussion

Complex 3 is found to be a centrosymmetric dimer, resulting from chloropalladation of *exo*-9-methylbicyclo[6.1.0]non-4-ene with overall external cleavage of the cyclopropane rings. An ORTEP drawing of the structure is shown in the Figure 1. The centrosymmetric nature of the dimer is exact, since the molecule is positioned on a crystallographic center of symmetry.

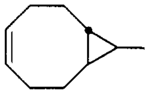
The palladium–carbon bonding is the expected 1,4,5-η^3 "σ,π" type interaction. The crucial stereochemical features are (i) the anti orientation of Pd(1)–C(1) and C(8)–C(9), which indicates inversion at C(1) on electrophilic attack

Table IV. Bond Angles (Deg) for $C_{10}H_{16}Cl_2Pd$

Pd(1)-C(1)-C(8)	110.3 (6)	C(3)-C(4)-H(4)	109.5 (62)	C(1)-C(8)-H(8)	107.6 (37)
Pd(1)-C(1)-C(2)	106.7 (7)	C(5)-C(4)-H(4)	122.4 (64)	C(7)-C(8)-C(9)	110.2 (7)
Pd(1)-C(1)-H(1)	102.5 (50)	Pd(1)-C(5)-C(6)	110.7 (6)	C(7)-C(8)-H(8)	113.0 (37)
C(8)-C(1)-C(2)	117.8 (8)	Pd(1)-C(5)-C(4)	73.2 (6)	C(9)-C(8)-H(8)	100.3 (37)
C(8)-C(1)-H(1)	108.0 (50)	Pd(1)-C(5)-H(5)	105.4 (47)	Cl(2)-C(9)-C(8)	108.6 (6)
C(2)-C(1)-H(1)	110.6 (48)	C(6)-C(5)-C(4)	129.3 (9)	Cl(2)-C(9)-C(10)	106.4 (7)
C(1)-C(2)-C(3)	113.9 (8)	C(6)-C(5)-H(5)	108.2 (50)	Cl(2)-C(9)-H(9)	105.9 (37)
C(1)-C(2)-H(2A)	117.6 (46)	C(4)-C(5)-H(5)	119.6 (49)	C(8)-C(9)-C(10)	114.8 (8)
C(1)-C(2)-H(2B)	108.1 (45)	C(7)-C(6)-C(5)	119.5 (9)	C(8)-C(9)-H(9)	103.1 (37)
C(3)-C(2)-H(2A)	106.0 (47)	C(7)-C(6)-H(6A)	101.6 (53)	C(10)-C(9)-H(9)	117.5 (39)
C(3)-C(2)-H(2B)	101.7 (45)	C(7)-C(6)-H(6B)	106.7 (45)	C(9)-C(10)-H(10A)	99.2 (74)
H(2A)-C(2)-H(2B)	108.3 (57)	C(5)-C(6)-H(6A)	110.4 (53)	C(9)-C(10)-H(10B)	104.8 (52)
C(2)-C(3)-C(4)	112.7 (8)	C(5)-C(6)-H(6B)	101.5 (46)	C(9)-C(10)-H(10C)	99.5 (70)
C(2)-C(3)-H(3A)	103.5 (40)	H(6A)-C(6)-H(6B)	118.1 (68)	H(10A)-C(10)-H(10B)	124.1 (95)
C(2)-C(3)-H(3B)	116.7 (38)	C(8)-C(7)-C(6)	114.0 (8)	H(10A)-C(10)-H(10C)	103.7 (86)
C(4)-C(3)-H(3A)	109.8 (39)	C(8)-C(7)-H(7A)	103.8 (44)	H(10B)-C(10)-H(10C)	120.6 (86)
C(4)-C(3)-H(3B)	106.2 (38)	C(8)-C(7)-H(7B)	114.0 (55)	Cl(1)-Pd(1)-C(1)	91.4 (3)
H(3A)-C(3)-H(3B)	107.7 (52)	C(6)-C(7)-H(7A)	100.2 (44)	Cl(1)-Pd(1)-C(5)	150.27 (25)
Pd(1)-C(4)-C(3)	108.2 (7)	C(6)-C(7)-H(7B)	106.2 (55)	Cl(1)-Pd(1)-C(4)	170.9 (3)
Pd(1)-C(4)-C(5)	70.5 (6)	H(7A)-C(7)-H(7B)	118.1 (68)	C(1)-Pd(1)-C(5)	90.0 (4)
Pd(1)-C(4)-H(4)	102.1 (62)	C(1)-C(8)-C(7)	113.2 (8)	C(1)-Pd(1)-C(4)	81.6 (4)
C(3)-C(4)-C(5)	127.3 (9)	C(1)-C(8)-C(9)	112.0 (7)	C(5)-Pd(1)-C(4)	36.4 (3)

by palladium(II) and (ii) the sequence ordering of atoms on C(9), which indicates inversion at C(9) on nucleophilic attack by Cl(2).

As was previously reported,[4] complex **3** reacts with cyanide ion to liberate the trans-9-methyl epimer **5** in



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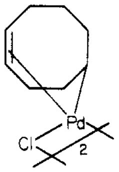
quantitative yield. Thus the observed carbon inversion in the $\mathbf{1a} \xrightarrow{PdCl_2} \mathbf{3} \xrightarrow{CN^-} \mathbf{5}$ process clearly occurs in the first step, in which palladium attacks with inversion at carbon.

In a related investigation, we have determined the structure of complex **4** by X-ray crystallography.[8] Ex-



4

cepting the equatorial α-chloroethyl group in **3**, the cyclooctenyl conformations, dimensions, and bonding to palladium are essentially identical in **3** and **4**. Reaction of a $CDCl_3$ solution of complex **4** with CN^-/D_2O leads to removal of all hydrocarbon residue from the $CDCl_3$ and appearance of an organopalladium species in the D_2O layer that has ^1H and ^{13}C NMR spectra (Experimental Section) consistent with $[(CN)_x Pd(\sigma\text{-cyclooctenyl})]^{(-x+1)}$. This σ-cyclooctenyl is stable for days in the aqueous medium—an initially surprising result in view of the four β-hydrogens available for elimination. However, the strongly bound cyanides no doubt effectively inhibit the expected β-hydride decomposition by blocking coordination sites.

Clearly, complexes **3** and **4** differ in that **3** has a chlorine leaving group. On the basis of the cyanide reaction with **4**, we believe that complex **3** reacts with cyanide to form a σ-[(chloroethyl)cyclooctenyl]; however in this case the very polar Pd → C σ electron pair readily displaces chlorine from α-chloroethyl to form a new carbon–carbon bond with retention at C(1), resulting in hydrocarbon **5**.

In our initial report[4] of the chloropalladation of the 9-methylbicyclo[6.1.0]non-4-ene systems, we discussed the possibility that the reactions take place via a corner-palladated cyclopropane intermediate which, on attack of C(9) by chloride, would lead to the C(1) inverted product which we now verify. The formation of the corner-palladated intermediates is no doubt facilitated by the expected relatively stable twist-tub conformations of the bicyclo[6.1.0]non-4-enes.[9] Our system undergoes chloropalladation with inversion at C(1) in both $CDCl_3$ and benzene, in contrast to the (+)-car-2-ene system noted above.[5] In the chloropalladation of (+)-car-2-ene in benzene an oxidative addition path was suggested for the predominant retention path.[5] We note, however, that a corner-palladated intermediate analogous to that suggested by us earlier would equally well accommodate the observation of the two chloropalladation products of (+)-car-2-ene.[10] Finally, based on the results published earlier,[4] we conclude that the endo **1b** also inverts at carbon on attack by palladium.

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Registry No. **1a**, 79181-18-3; **3**, 79188-47-9; **4**, 59419-85-1.

Supplementary Material Available: Tables of observed and calculated structure factors, least-squares planes, and torsion angles (8 pages). Ordering information is given on any current masthead page.

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(8) Woolcock, J.; Rettig, M. F.; Wing, R. M., in preparation.

(9) For discussion of conformational changes on diene coordination, see: Rettig, M. F.; Wing, R. M.; Wiger, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 2980.

(10) A corner-palladated (+)-car-2-ene would nicely account for the trans relative stereochemistry of palladium and chlorine in the π-allyl product formed with carbon retention.[5]