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Stereochemistry of palladium migration on coordinated cyclooctenyl. Molecular structure and dechloropalladation of tetrakis(.mu.-chloro)bis[1-3-.eta.-6-(.alpha.-chloroethyl)cyclooctenyl]tripalladium(II)

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that the lone pair in each "sandwich" molecule lies beneath several other filled molecular orbitals. This seems to be so in PpMn(CO)$_3$ as well.[9,15]

Although the lone pair apparently is not the frontier orbital, the P atoms in PpFeCp and in Pp$_2$Fe can coordinate to Fe(CO)$_4$,[3,6,7] as classical phosphines do. Our calculations on **2** and **3** give some credence to the proposition that the P atom in the coordinated Pp ligand acts as a π acceptor when **2** and **3** form adducts with Fe(CO)$_4$.[6] Orbital π^*_P presumably can accept electrons from the filled iron orbitals in Fe(CO)$_4$. The observed lengthening of the Fe–Cp and Fe–Pp distances upon formation[6] of the adducts might be caused by the donation of electrons from the Fe(CO)$_4$ group into the two lowest unoccupied molecular orbitals of **2** and **3**; as Figures 1 and 2 show, these molecular orbitals are antibonding between the Fe atom and the rings.

The P atom in the Pp ligand exhibits some electrophilicity and reacts with strong nucleophiles, such as RLi.[5,9] The calculated electronic structures of the complexes 2 and 3 indicate that this weak electrophilicity of the P atom may be caused by orbital and charge effects in concert. Tables I and III show that the LUMO of **2** and the lowest unoccupied molecular orbitals of **3** have appreciable contributions from the phospholyl orbital π_P. This partial localization of the vacant frontier orbitals on the P atom may guide the incoming nucleophile to this atom. Since the phospholyl orbitals π_P and σ_P are essentially orthogonal to each other, the nucleophile directed toward the vacant π_P will largely miss the lone pair in σ_P. Drawings **9** and **13** indicate that the P atom seems to be the most positive one in the ligands. Although its positive charge probably is small, it might contribute to the observed weak electrophilicity of phosphorus.

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Stereochemistry of Palladium Migration on Coordinated Cyclooctenyl. Molecular Structure and Dechloropalladation of Tetrakis(μ-chloro)bis[1–3-η-6-(α-chloroethyl)cyclooctenyl]-tripalladium(II)

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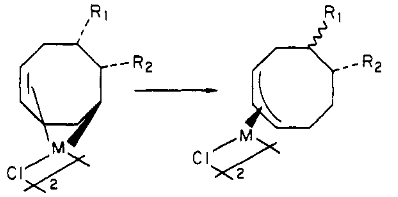
Bis(μ-chloro)bis[1,4,5-η-8-(α-chloroethyl)cyclooctenyl]dipalladium(II), **1c**, is found to undergo palladium migration [via hydrogen shifts(s)] in solution to form π-allylic bis(μ-chloro)bis[1–3-η-6-(α-chloroethyl)-cyclooctenyl]dipalladium(II), **2c**. Attempted growth of **2c** crystals leads to isolation of a tripalladium complex which results from insertion of PdCl$_2$ into the bridge in **2c**, namely, tetrakis(μ-chloro)bis[1–3-η-6-(α-chloroethyl)cyclooctenyl]tripalladium(II)–chloroform (or **2c**·PdCl$_2$·CHCl$_3$). Crystal structure analysis of this latter material shows that palladium migrates such that it stays on the original face of the cyclooctenyl. Thus Pd and α-chloroethyl are mutually trans in both **1c** and **2c**·PdCl$_2$·CHCl$_3$. Reaction of **2c** (or **2c**·PdCl$_2$·CHCl$_3$) with aqueous cyanide leads to the new hydrocarbons *anti*-9-methylbicyclo[4.2.1]non-2-ene, **3a**, and *syn*-9-methylbicyclo[4.2.1]non-2-ene, **3b**, in 78% and 15% yields, respectively. Hydrocarbons **3a** and **3b** result from cyanide-induced dechloropalladation via intramolecular electrophilic attack on what was a terminal π-allyl carbon. The **1c** → **2c** rearrangement is the first reported for a Pd σ,π-cyclooctenyl which bears a substituent trans to palladium on carbon 8.

Introduction

In a previous report from this laboratory,[1] we demonstrated the **1a** → **2a** rearrangement shown in eq 1. This



(1)

1a-d **2a-d**

a, M = Pd, R$_1$ = Cl, R$_2$ = H
b, M = Ni, R$_1$ = R$_2$ = H
c, M = Pd, R$_1$ = H, R$_2$ = α-chloroethyl
d, M = Pd, R$_1$ = H, R$_2$ = H

type of cyclooctenyl isomerization has also been observed by Wilke in a related organonickel system: **1b** → **2b**.[2] Complexes of type 1 (R$_1$ = H, R$_2$ = RO, R$_2$N, R$_3$C, etc.) are readily accessible through nucleophilic attack on coordinated cycloocta-1,5-diene. Although such complexes are potentially valuable precursors to π-allylic rearrangement products, we noted earlier[1] that $\sigma,\pi \rightarrow \pi$-allyl rearrangements had not been reported for any of the large number of complexes of type 1 prepared by the nucleophilic attack route. We now report the first example of $\sigma,\pi \rightarrow \pi$-allyl isomerization in a cyclooctenyl having R$_2$ $\neq$ H, namely, **1c** → **2c**. The rearrangement proceeds with "face retention" (i.e., Pd and α-chloroethyl remain trans). The π-allylic product **2c** reacts readily with cyanide ion to liberate in high yield hydrocarbons **3a** and **3b**. This

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(1) Albelo, G.; Wiger, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510–4518.

(2) Wilke, G. Belgian Patent 651594, 1963/1965. Cited in the "Gmelin Handbuch der Anorganischen Chemie Band 17, Nickel-Organische Verbindungen, Teil 2"; Springer-Verlag: Berlin, 1974; pp 320–321.

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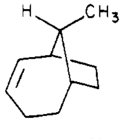
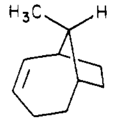


3a (78%)



3b (15%)

is the first reported example of cyanide-induced dechloropalladation where a cyclopropane ring is not formed, with implication for considerable generality for this approach to carbon–carbon bond formation.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were obtained by using a JEOL 200FX instrument (200 MHz, ^1H; 50 MHz, ^{13}C), a Varian EM390 instrument (90 MHz, ^1H), or a Bruker 500 MHz ^1H instrument (the latter located at the California Institute of Technology Regional NMR Center). X-ray intensity data were collected at room temperature by using an Enraf-Nonius CAD-4 diffractometer. Infrared spectra were obtained by using a Perkin-Elmer Model 283 spectrometer. Molecular weight measurements were done by using a Mechrolab vapor pressure osmometer. Mass spectra were obtained by using a Finnegan 1015SL quadrupole mass spectrometer. Microanalysis was performed by Elek Labs, Torrance, CA, or MicAnal, Tuscon, AZ. Abbreviations: d = doublet, t = triplet, q = quartet, s = strong, m = medium, w = weak.

Preparation of Complex 2c. The σ,π complex **1c** (prepared from chloropalladation of *endo*-9-methylbicyclo[6.1.0]non-4-ene, as described earlier[3]) was rearranged as follows: 0.594 g of **1c** was placed in a micro Soxhlet thimble (10 mm × 50 mm) and was extracted for 10 h over 20 mL of refluxing $CDCl_3$. The $CDCl_3$ was evaporated, and the residue was reextracted for 45 min with 10 mL of refluxing $CDCl_3$ (to remove dark residue, possibly $PdCl_2$). To the $CDCl_3$ extract was added 50 mL of pentane, which caused precipitation of a golden brown powder (0.275 g, 46%): IR (NaCl pellet from 6000 to 400 cm^{-1}; polypropylene/Nujol from 600 to 200 cm^{-1}) 3000–2800 (s), 1670–1590 (w), 1490–1400 (m), 1380 (m), 1240 (w), 1015 (w), 905 (w), 795 (w), 725 (w), 660 (w), 620 (w), 340–300 (m) cm^{-1} (ν(PdCl)); ^1H NMR (200 MHz, $CDCl_3$) δ 5.21 (q, 2 H, J = 7.5 Hz, terminal allylic hydrogens), 5.00 (t, 1 H, J = 7.8 Hz, central allylic hydrogen), 3.98 [double quartet, 1 H, J_1 = 6.3 Hz, J_2 = 3.5 Hz, $HC(Cl)(CH_3)$], 2.6–1.1 (11 H, including the δ 1.42 methyl doublet, J = 6.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, broad band and off-resonance decoupled) δ 103.2 (d, C_2), 84.8 (d, C_1 and C_3), 63.4 (d, C_9), 48.5 (d, C_8), 31.7 (t, CH_2), 29.7, 29.4, 29.3 (overlapped triplets, 3 CH_2's), 22.1 (q, C_{10}). Anal. Calcd for $C_{20}H_{32}Cl_4Pd_2$: C, 38.31; H, 5.14; Cl, 22.61; mol. wt, 627.1. Found: C, 38.26, H, 5.22; Cl, 22.73; mol wt, 614 (toluene, 37 °C).

In the preparation of **2c**, it makes no difference whether one ultimately starts from *endo*- or *exo*-9-methylbicyclo[6.1.0]non-4-ene. The **2c** from either precursor has identical spectral chracteristics.

Crystal Growth. The **2c** used for crystal growth was prepared from a sample of **1c**, which was in turn prepared from *exo*-9-methylbicyclo[6.1.0]non-4-ene. The molecular structure of **1c** (from *exo*-9-methylbicyclo[6.1.0]non-4-ene) has been determined by X-ray crystallography.[4]

Single crystals suitable for X-ray analysis were obtained by pentane vapor diffusion into a solution of **2c** in chloroform. The crystals so obtained were either light yellow or orange-red. An orange-red crystal was selected for X-ray analysis. This material was found to have chloroform in the unit cell as well as an extra $PdCl_2$ unit in the bridge. We will refer to the orange-red material as **2c**·$PdCl_2$·$CHCl_3$.

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 (hkl, $h + k = 2n$; $h0l$, $l = 2n$) consistent with the space group $C2/c$ (no. 15). Data reduction and structure solution/refinement was accomplished by using the Enraf-Nonius structure solution programs (version 18.2). The cell constants were based on least-squares refinement of 21 carefully centered high-angle reflections. The atom position and thermal parameters are listed in Table II; a full list of bond distances is presented in Table III, and a list of selected bond angles is found in Table IV.

Table I. Crystallographic Data and Data Collection Conditions for $C_{21}H_{33}Cl_9Pd_3$

formula	$C_{21}H_{33}Cl_9Pd_3$
space group	$C2/c$ (no. 15)
M_r, daltons	923.77
a, Å	26.754 (2)
b, Å	9.066 (2)
c, Å	14.202 (3)
β, deg	115.34 (1)
V, Å^3	3113.3 (1.8)
Z	8 based on monomer (each dimer sits on a crystallographic center of symmetry)
d_{calcd}, g/cm^3	1.971
d_{obsd}, g/cm^3	1.963[a]
cryst size, mm × mm × mm	0.406 × 0.126 × 0.80
radiation	graphite-monochromated Mo Kα (λ = 0.7107 Å)
scan type	$\omega - 2\theta$
scan width (ΔW), deg	0.75 + 0.35 tan θ
max counting time, s	$2 < 2\theta \leqslant 40°$, 120 s; $40 < 2\theta \leqslant 50°$, 240 s
collectn range	$2 \leqslant 2\theta \leqslant 50°$
no. of unique data	2725
no. of unique data ($I > 3\sigma(I)$)	2064
no. of variables	201
R	0.051[b]
R_w	0.066[c]
esd	2.05[d]
largest parameter shift	1.35[d]
largest peak, e/Å^3	1.537[e]

[a] By flotation in a mixture of CCl_4 and CH_3CHBr_2. [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 $\sigma(I) = [P + (t/20)^2B + (0.045I)^2]^{1/2}$. 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, standard deviation of an observation of unit weight. [e] From final difference Fourier.

NMR Spectral Characteristics of 2c·PdCl$_2$·CHCl$_3$. Subsequent to the structure determination, both ^1H and ^{13}C NMR spectra were obtained for hand-selected (microscope aided) single crystals which were orange-red, i.e., **2c**·$PdCl_2$·$CHCl_3$. Integration of the chloroform proton peak confirmed that 1.0 ± 0.2 $CHCl_3$ molecules are present per dimer unit (residual $CHCl_3$ in the $CDCl_3$ was properly accounted for). Beyond this observation it was found that the NMR spectra of **2c** and **2c**·$PdCl_2$·$CHCl_3$ are nearly identical: ^1H NMR (**2c**·$PdCl_2$·$CHCl_3$, 200 MHz, $CDCl_3$) δ 5.23 (q, 2 H, J = 7.8 Hz, terminal allylic hydrogens), 5.06 (t, 1 H, J = 7.8 Hz, central allylic hydrogen), 3.97 [double quartet, 1 H, J_1 = 6.3 Hz, J_2 = 3.5 Hz, $HC(Cl)(CH_3)$], 2.6–1.1 (11 H, including the δ 1.43 methyl doublet, J = 6.3 Hz). In the 2.6–1.1 region, the complex multiplet patterns are superimposable on the same patterns for **2c**: ^{13}C NMR (**2c**·$PdCl_2$·$CHCl_3$, 50 MHz, $CDCl_3$) δ 103.4 (d, C_2), 85.3 (d, C_1 and C_3), 63.4 (d, C_9), 48.4 (d, C_8), 31.7 (t, CH_2), 29.7, 29.4, 29.3 (overlapped triplets, 3 CH_2's), 22.2 (q, C_{10}). The δ values for C_1–C_3 differ significantly from those for **2c**.

Reaction of Complex 2c with Aqueous Cyanide. Characterization and Hydrogenation of Hydrocarbon Products. In a preparative scale experiment, 0.871 g of **2c** was dissolved in 50 mL of $CHCl_3$ and the solution was placed in a separatory funnel. Sodium cyanide (2.0 g) in 50 mL of H_2O was added and the mixture was shaken for several minutes (color changes over

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(3) Rettig, M. F.; Wilcox, D. E.; Fleischer, R. S. *J. Orgamomet. Chem.* **1981**, *214*, 261–272.

(4) Parra-Hake, M.; Rettig, M. F.; Wing, R. W.; Woolcock, J. C. *Organometallics* **1982**, *1*, 1478–1480.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $C_{21}H_{33}Cl_9Pd_3$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Pd1	0.25000 (0)	0.25000 (0)	0.00000 (0)	4.63 (2)	5.50 (3)	3.94 (2)	0.37 (3)	2.34 (2)	−0.12 (2)
Pd2	0.17574 (2)	0.13742 (8)	0.13339 (4)	5.70 (2)	7.17 (3)	5.21 (2)	0.27 (2)	3.33 (1)	0.45 (2)
Cl1	0.26796 (8)	0.1067 (3)	0.1443 (1)	6.04 (6)	8.7 (1)	5.28 (5)	1.76 (8)	3.26 (4)	1.75 (7)
Cl2	0.16092 (8)	0.2785 (3)	−0.0212 (1)	5.58 (6)	10.9 (1)	7.22 (7)	2.12 (8)	3.85 (5)	2.98 (8)
Cl3	0.05226 (10)	0.1866 (7)	0.4575 (2)	6.45 (9)	31.6 (5)	6.94 (9)	−1.0 (2)	3.57 (6)	3.7 (2)
Cl4	0.51332 (20)	0.1888 (8)	0.1666 (3)	35.2 (2)	23.1 (5)	24.8 (2)	2.9 (3)	25.6 (1)	0.7 (3)
Cl5	0.48199 (37)	0.4322 (9)	0.1877 (7)	13.7 (5)	9.3 (4)	16.5 (6)	2.3 (4)	3.8 (4)	0.7 (4)
C1	0.1779 (3)	0.038 (1)	0.2715 (5)	6.9 (3)	7.0 (4)	6.2 (2)	1.0 (3)	3.9 (2)	1.1 (3)
C2	0.1261 (3)	0.044 (1)	0.1940 (6)	9.0 (3)	7.4 (5)	7.5 (3)	−2.4 (4)	5.3 (2)	−1.1 (3)
C3	0.0999 (3)	0.175 (1)	0.1447 (5)	5.0 (3)	10.4 (6)	5.1 (2)	−1.1 (3)	2.7 (2)	0.6 (3)
C4	0.1033 (3)	0.321 (1)	0.1982 (5)	6.1 (3)	8.8 (5)	5.4 (2)	1.3 (3)	3.2 (2)	1.7 (3)
C5	0.0839 (3)	0.315 (1)	0.2866 (5)	6.3 (3)	10.6 (6)	5.5 (2)	2.3 (4)	3.5 (2)	1.6 (3)
C6	0.1284 (3)	0.296 (1)	0.3951 (5)	4.9 (2)	8.7 (5)	5.3 (2)	1.0 (3)	2.9 (2)	0.9 (3)
C7	0.1630 (3)	0.157 (1)	0.4198 (5)	5.9 (3)	8.8 (5)	4.1 (2)	0.3 (3)	2.2 (2)	0.9 (3)
C8	0.2005 (3)	0.141 (1)	0.3632 (5)	4.9 (3)	7.9 (5)	5.3 (2)	0.6 (3)	2.3 (2)	1.0 (3)
C9	0.1040 (4)	0.320 (2)	0.4750 (6)	6.5 (3)	15.8 (9)	6.1 (3)	0.7 (5)	3.7 (2)	1.3 (5)
C10	0.1470 (3)	0.336 (1)	0.5905 (6)	7.6 (3)	12.3 (7)	6.3 (3)	2.2 (4)	4.6 (2)	0.7 (4)
C11	0.5000 (0)	0.287 (3)	0.2500 (0)	71 (3)	8 (1)	20.5 (9)	0	31.3 (9)	0

atom[b]	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H1	0.196 (2)	−0.041 (7)	0.286 (4)	5.0000 (0)	H7A	0.135 (2)	0.040 (8)	0.415 (4)	5.0000 (0)
H2	0.116 (2)	−0.024 (7)	0.173 (4)	5.0000 (0)	H7B	0.179 (3)	0.147 (7)	0.471 (5)	5.0000 (0)
H3	0.062 (2)	0.175 (7)	0.068 (4)	5.0000 (0)	H8A	0.235 (2)	0.098 (7)	0.412 (4)	5.0000 (0)
H4A	0.087 (2)	0.410 (8)	0.145 (4)	5.0000 (0)	H8B	0.211 (2)	0.233 (8)	0.346 (5)	5.0000 (0)
H4B	0.133 (3)	0.375 (7)	0.222 (4)	5.0000 (0)	H9	0.089 (0)	0.413 (0)	0.447 (0)	5.0000 (0)
H5A	0.067 (3)	0.247 (8)	0.271 (5)	5.0000 (0)	H10A	0.128 (3)	0.369 (7)	0.605 (5)	5.0000 (0)
H5B	0.073 (3)	0.426 (8)	0.284 (4)	5.0000 (0)	H10B	0.173 (2)	0.262 (8)	0.614 (5)	5.0000 (0)
H6	0.159 (2)	0.393 (7)	0.402 (4)	5.0000 (0)	H10C	0.162 (3)	0.388 (7)	0.569 (5)	5.0000 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$ where *a*, *b*, and *c* are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses. [b] None of the H temperature factors were refined. H9's atom coordinates also were not refined.

Table III. Bond Distances (Å) for $C_{21}H_{33}Cl_9Pd_3$

atom 1	atom 2	dist	atom 1	atom 2	dist
Cl3	C9	1.770 (10)	C1	H1	0.84 (6)
C1	C2	1.353 (11)	C2	H2	0.69 (5)
C1	C8	1.503 (10)	C3	H3	1.13 (5)
C2	C3	1.404 (12)	C4	H4A	1.06 (6)
C3	C4	1.507 (11)	C4	H4B	0.88 (6)
C4	C5	1.551 (9)	C5	H5A	0.74 (6)
C5	C6	1.500 (9)	C5	H5B	1.04 (6)
C6	C7	1.516 (9)	C6	H6	1.17 (5)
C6	C9	1.547 (9)	C7	H7A	1.29 (5)
C7	C8	1.537 (8)	C7	H7B	0.67 (6)
C9	C10	1.556 (12)	C8	H8A	0.96 (5)
Pd1	Cl1	2.297 (1)	C8	H8B	0.95 (6)
Pd1	Cl2	2.286 (2)	C9	H9	0.95[a]
Pd2	Cl1	2.421 (2)	C10	H10A	0.70 (6)
Pd2	Cl2	2.422 (2)	C10	H10B	0.92 (6)
Pd2	C1	2.136 (6)	C10	H10C	0.77 (6)
Pd2	C2	2.050 (7)			
Pd2	C3	2.131 (6)			

[a] Note: H9 was not refined so in fact the C9–H9 distance is fixed.

in seconds) to liberate hydrocarbons from **2c**. The $CHCl_3$ layer was passed through a short column of 3 g of $MgSO_4$ (anhydrous), followed by evaporation to a volume of 3.85 mL. Analysis of the 3.85-mL solution by gas chromatography led to the conclusion that 100 ± 2% of the expected mass of hydrocarbon was contained in the 3.85 mL (6 ft × 0.25 in. Apiezon L on Chromosorb W, 138 °C, single broad peak from 19 to 25 min, internal standard was *exo*-9-methylbicyclo[6.1.0]non-4-ene). The 3.85-mL solution was microdistilled to 0.5 mL, and this residue (containing ~0.38 g $C_{10}H_{16}$ hydrocarbons, 78% **3a** and 15% **3b**) was concentrated in portions by preparative gas chromatography (above conditions). We have found no satisfactory conditions for separation of these hydrocarbons by gas chromatography.

The reaction can be conducted on an NMR tube scale by simply scaling it down appropriately and allowing the layers to separate. The hydrocarbon NMR can then be observed in the lower layer ($CDCl_3$). The ^1H NMR obtained in this way is virtually identical with the ^1H NMR obtained for the hydrocarbon mixture collected from the gas chromatograph.

The following characterization experiments were performed on the hydrocarbon mixture collected from the chromatograph as described above: mass spectrum, *m/e* (% total intensity) 136 (2), 121 (3), 107, (3), 94 (8), 79 (10), 67 (9), 53 (3), 39 (5). Anal. (olefinic mixture) Calcd for $C_{10}H_{16}$: C, 88.18; H, 11.82. Found: C, 88.18; H, 12.13. At 500 MHz the important features for **3a** and **3b** are resolved in the ^1H NMR of the olefinic mixture: ^1H NMR (500 MHz, **3a**) δ 6.05–5.97 [seven lines (4 doublets, overlapped center line), vinyl H, J_1 = 11.3 Hz (olefin H–olefin H), J_2 = 8.2 Hz, J_3 = 3.0 Hz], 5.48–5.56 [seven lines (4 doublets, overlapped center line), vinyl H, J_1 = 11.3 Hz (olefin H–olefin H), J_2 = 8.0 Hz, J_3 = 3.5 Hz], 2.25–1.85 (complex multiplet), 1.80 (quartet, 1 H, (*H*CCH_3, syn to double bond, unresolved coupling of ~0.8 Hz to each bridgehead H), *J* = 7.0 Hz), 1.65–1.25 (complex multiplet), 0.86 (doublet, 3 H (methyl), *J* = 7.0 Hz); ^1H NMR (500 MHz, **3b**) δ 5.75–5.67 [seven lines (4 doublets, overlapped center line), vinyl H, J_1 = 12.0 Hz, J_2 = 8.5 Hz, J_3 = 3.0 Hz], 5.65–5.57 [seven lines (4 doublets, overlapped center line), vinyl H, J_1 = 12.0 Hz, J_2 = 8.5 Hz, J_3 = 3.0 Hz], 2.3–1.3 obscured by major epimer **3a**, 0.97 (doublet, methyl, *J* = 7.0 Hz); ^{13}C NMR (**3a**, 50 MHz, $CDCl_3$, both broad-band and off-resonance decoupled) δ 139.4 (olefinic CH), 128.6 (olefinic CH), 48.1 (CH), 46.0 (CH), 45.5 (CH), 32.6 (CH_2), 31.5 (CH_2), 27.3 (CH_2), 24.4 (CH_2), 21.3 (CH_3). The 500-MHz spectra were done in $CDCl_3$.

Analysis of the integrals in the ^1H NMR (500 MHz) of the $C_{10}H_{16}$ mixture led to the conclusion that the mixture is 78% **3a**, 15% **3b**, and 7% "other". The same mixture is obtained on cyanation of **2c**·$PdCl_2$·$CHCl_3$.

The 78/15/7 mixture was hydrogenated (pentane, Pd/C, 1 atm H_2, 25 °C, stir overnight, filter, remove pentane). The hydrogenated material has the following spectral characteristics: ^1H NMR ($CDCl_3$, 90 MHz) δ 2.6–0.95 (15 H), 0.9 (3 H, d, *J* = 7.0 Hz, methyl); ^{13}C NMR ($CDCl_3$, 50 MHz, broad-band and off-resonance decoupled) δ 44.8 (2 CH), 41.9 (1 CH), 34.7 (2 CH_2), 31.2 (2 CH_2), 25.3 (2 CH_2), 22.3 (CH_3).

Discussion

Description of Structure. The structure of **2c**·

$PdCl_2$·$CHCl_3$ (Figure 1) is that of a $PdCl_2$ inserted, planar-bridged centrosymmetric dimer, with each cyclooctenyl in a boat–chair conformation and with palladium and α-chloroethyl mutually trans on the cyclooctenyl rings.

Palladium–Allyl Interaction. The palladium–allyl interaction is very similar to related π-allyl systems. Thus in the present structure the range of palladium to allylic carbon bond lengths (2.050–2.136 Å) and the inclination of the allylic carbon best plane to the Pd1Pd2Cl1Cl2 best plane, which is 115.0°, agree well with the values found for bis(μ-chloro)bis(1–3-η-allyl)palladium(II) (2.108–2.123 Å and 111.5°),[5] for bis(μ-chloro)bis[4–6-η-(1-chlorocyclooctatrienyl)dipalladium(II) (2.104–2.134 Å and 119.8°),[6] for tetrakis(μ-chloro)bis(1–3-η-2-methylallyl)tripalladium(II) (2.05–2.14 Å and 113°),[7] and for bis(μ-chloro)bis(1–3-η-1,1,3,3-tetramethylallyl)palladium(II)[8] (2.12–2.14 Å and 121.5°). In the coordinated cyclooctenyl, carbons 4 and 8 are decidedly noncoplanar with the allyl carbons. Thus the C4C3C1C8/C1C2C3 dihedral angle is 34.4°. The distortion of anti substituents out of the allyl plane has been observed also in the previously cited structures, where analogous dihedral angles of 32°[6] and 28.5°[8] are reported.

The C1C2 and C2C3 bond distances [1.353 (11) and 1.404 (12) Å, respectively] are typical[6] of literature values for palladium allyls. The relatively large trans influence of the allyl moiety is seen in the Pd2Cl1 and Pd2Cl2 distances of 2.421 (1) and 2.422 (2) Å, respectively. These distances again are typical of analogous distances in related π-allyls,[5-8] where a range of 2.41–2.43 Å is reported.

The Pd_3Cl_4 Bridge. We have reported the structure of the σ,π precursor **1c**.[4] In that structure, the bridging chloride trans to olefin has a Pd–Cl distance of 2.396 (3) Å, while that trans to alkyl has a Pd–Cl distance of 2.516 (3) Å. Thus, the π-allyl moiety exerts a trans influence comparable to olefin in these related cyclooctenyl systems.

The bridging chlorine to Pd(1) distances are significantly shorter than those to Pd(2). Thus we find that the Pd1Cl1 distance is 2.297 (1) Å and the $Pd1Cl_2$ distance is 2.286 (2) Å. These distances are quite similar to the analogous distances in the only other X-ray characterized tripalladium bridge (ref 7, 2.313 (9) and 2.297 (9) Å). It was pointed out[7] that the central palladium in the bridge has distances to chlorine similar to the palladium–chlorine distances in $(NH_4)_2PdCl_4$ [2.299 (4) Å].[9] We further note that the central palladium to chlorine distances in both structures are similar to those found in $[PdCl_2]_n$ (2.31 Å)[10a] and very recently in *trans*-dichlorobis(triphenylphosphine)palladium(II) [2.290 (1) Å].[10b] The range 2.29–2.31 Å is thus found for chlorine trans to chlorine on Pd(II).

Although the Pd–Cl distances in **2c**·$PdCl_2$·$CHCl_3$ are quite similar to the analogous ones in the (2-methylallyl)tripalladium complex,[7] the near planarity of the Pd_3Cl_4 unit in the present structure contrasts with the "flat rippled" arrangement reported.[7] In the 2-methylallyl structure, the "central" $PdCl_4$ unit makes dihedral angles of 158° to the "terminal" Cl_2Pd planes (with preservation of the center of symmetry).[7] In our system, the analogous dihedral angle is 177.2°. Since there are a number of (noncentrosymmetric) palladium π-allyls which are "bent" at the bridging halogens,[11] it appears that the "flat" vs. "bent" structures are probably energetically similar. Thus, the "bent" vs. "flat" structures in the two tripalladium bridges may result from crystal packing forces.

The Cyclooctenyl Ring. The cyclooctenyl ring is coordinated in a boat–chair conformation. Each of the other eight-membered ring π-allyls of which we are aware occur in boat–boat conformations.[6,12,13] In the present case, the α-chloroethyl group on C6 rules out the possibility of a stable boat–boat.

The palladium and the α-chloroethyl substituents are situated in a trans arrangement on the cyclooctenyl ring. The trans relationship of palladium and α-chloroethyl was found also in precursor **1c**[4] (as a result of carbon inversion accompanying Pd(II) attack on the cyclopropane ring of 9-methylbicyclo[6.1.0]non-4-ene).

The σ,π → π-Allyl Rearrangement. The palladium–hydrogen interchange which constitutes this cyclooctenyl rearrangement was first noted for the **1a** → **2a** transformation.[1] In view of the relatively large number of known complexes of structure 1 (noted above), it is surprising that no further reports of this rearrangement have appeared until now. Complex **1c** is formally quite similar to the other σ,π-cyclooctenyls which have substituents trans and beta to the palladium–carbon σ bond. Thus, the facile rearrangement of **1c** → **2c** suggests that many similar rearrangements may open a new path to cyclic and acyclic palladium(II) π-allyls, which have become important synthetic intermediates.[14]

In the earlier work with **1a** and now with **1c** we have shown that the allyl function results not from double bond migration but rather from net allylic C–H, Pd–C interchange. We now find that the interchange is such that palladium remains on the original cyclooctenyl face, trans to the α-chloroethyl substituent. Such a process could occur by one of several pathways, such as sequential β-hydride elimination, oxidative addition of allylic C–H to Pd(II) followed by reductive elimination, or allylic deprotonation followed by protonolysis of the palladium–carbon σ bond. Studies are currently underway[13] with **1d** and its derivatives to further narrow the mechanistic possibilities for this type of rearrangement.

Reaction of 2c with Cyanide. We have reported previously[1,3,4] that complexes of type 1 which have a leaving group on the cyclooctenyl ring react quantitatively with aqueous cyanide solutions to produce $Pd(CN)_4^{2-}$ and hydrocarbons. In our laboratory prior to this communication, each derived hydrocarbon involved formation of a cyclopropane ring via a cyanide-induced 1,3-Pd,Cl elimination. We now find that even when the palladium migrates to a "remote" position (1,6 with respect to chlorine), the reaction with cyanide leads to nearly quantitative Pd,Cl elimination to form bicyclics **3a** and **3b** in 78% and 15% yields, respectively. The structure proofs for **3a** and **3b** were primarily accomplished via ^1H and ^{13}C NMR, which allowed us to rule out competing structures of formula $C_{10}H_{16}$.[15] We have also confirmed our conclusions

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[5] Smith, A. E. *Acta Crystallogr.* **1965**, *18*, 331–340.

[6] Baenziger, N. C.; Goebel, C. V.; Foster, B. A.; Doyle, J. R. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1681–1684. Note: this paper summarizes earlier palladium–π-allyl structures.

[7] Bailey, P. M.; Kelley, E. A.; Maitlis, P. M. *J. Organomet. Chem.* **1978**, *144*, C52–C56.

[8] Mason, R.; Wheeler, A. G. *J. Chem. Soc. A.* **1968**, 2543–2549.

[9] Bell, J. D.; Hall, D.; Waters, T. N. *Acta Crystallogr.* **1966**, *21*, 440.

[10] (a) Wells, A. F. *Z. Krist* **1939**, **100**, 189. (b) Ferguson, G.; McCrindle, R.; McAlees, A. J.; Parvez, M. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2679–81.

[11] (a) For leading references, see: Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; DeBoer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167–77; (b) Kilbourn, B. T.; Mais, R. H. B.; Owston, P. G. *J. Chem. Soc. Chem. Commun.* **1968**, 1438–1440.

[12] Brown, R. K.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 981–987: $[Fe(P(OCH_3)_3)_3(\mu_3\text{-}C_8H_{13})][BF_4]$.

[13] Woolcock, J.; Rettig, M. F.; Wing, R. M., in preparation: **2d**, $[ClPd(1\text{-}3\text{-}\eta\text{-}C_8H_{13})]_2$.

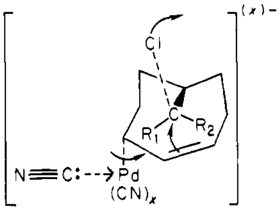
[14] Trost, B. M. *Acc Chem. Res.* **1980**, *13*, 385–393.

Table IV. Bond Angles (deg) for $C_{21}H_{33}Cl_9Pd_3$

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C2	C1	C8	124.9 (7)	Cl1	Pd1	Cl2	89.39 (6)
C1	C2	C3	124.0 (7)	Cl1	Pd2	Cl2	83.44 (5)
C2	C3	C4	125.4 (6)	Pd1	Cl1	Pd2	93.42 (5)
C3	C4	C5	114.3 (6)	Pd1	Cl2	Pd2	93.68 (6)
C4	C5	C6	116.2 (6)	C1	Pd2	C2	37.6 (3)
C5	C6	C7	118.1 (6)	C2	Pd2	C3	39.2 (3)
C5	C6	C9	109.8 (5)	H4A	C4	H4B	83 (4)
C7	C6	C9	110.5 (6)	H5A	C5	H5B	132 (7)
C6	C7	C8	115.3 (5)	H7A	C7	H7B	92 (5)
C1	C8	C7	113.7 (6)	H8A	C8	H8B	105 (5)
Cl3	C9	C6	110.8 (6)	H10A	C10	H10B	137 (6)
Cl3	C9	C10	113.2 (6)	H10A	C10	H10C	117 (8)
C6	C9	C10	115.6 (6)	H10B	C10	H10C	98 (6)

through careful comparison of our spectral results to those of Keese and co-workers, who recently synthesized the parent bicyclo[4.2.1]non-3-ene,[16] and also by comparison of our spectra for the reduction products of **3a**,**3b** to those of bicyclo[4.2.1]nonane.[17]

We suggest that **3a** and **3b** arise from an intermediate anion such as **4**. Anion **4** involves a σ palladium interaction, with the cyclooctenyl ring in a "boat–boat" conformation to bring the electrophilic carbon in proximity to the allyl moiety. The sketched (**4**) process would lead to **3a** if R_1 = H and to **3b** if R_1 = CH_3. It is interesting to note that the **4** ⟶ **3a**, **3b** transformations involve activation of a former π-allyl terminus to *electrophilic* attack, which is the "inverse" of the usual approach to π-allyl activation.[14]



4

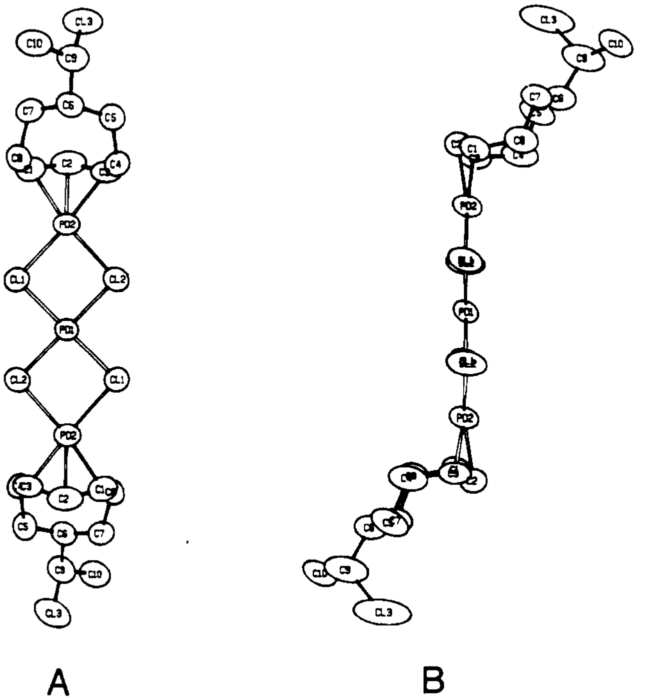


Figure 1. (A) Drawing of molecular structure of $2c\cdot PdCl_2$ ($CHCl_3$ excluded, looking perpendicular to coordination plane, hydrogens omitted for clarity). (B) Rotation of A by 90°. The Pd_3 organometallic unit sits on special site 4d which has 1 bar symmetry; the $CHCl_3$ associated with each $2c\cdot PdCl_2$ unit is disordered on site 4e which has twofold symmetry and is associated with one α-chloroethyl group.

We finally note that formation of **3a**,**b** from the cyanide-induced dechloropalladation indicates considerable generality and synthetic utility for this mode of carbon–carbon bond formation.

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Registry No. **1c**, 79188-47-9; **2c**, 85613-20-3; $2c\cdot PdCl_2\cdot CHCl_3$, 85629-00-1; **3a**, 85613-21-4; **3b**, 85613-22-5.

Supplementary Material Available: Observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(15) (a) The ^{13}C NMR spectra of **3a** and hydrogenated **3a**, along with the observation of the small bridgehead couplings to $HCCH_3$ in **3a**, allowed exclusion of all competing hydrocarbon structures for **3a**. The repetition of the olefinic hydrogen J pattern of **3a** by the minor (15%) epimer at δ 5.75–5.67 indicates the retention of the bicyclo[4.2.1]non-2-ene structure in the minor epimer. (b) The cyanation produced hydrocarbon mixture containing **3a** (78%), **3b** (15%), and 7% unidentified hydrocarbons (total mole balance 100 ± 2%) was concentrated and collected by GLC, as described in the Experimental Section. The 7% "unidentified" material is strongly suspected to be epimeric 9-methylbicyclo[4.2.1]non-3-enes, based on the known Pt(0)-catalyzed rearrangement of the parent bicyclo[4.2.1]non-2-ene (see: Stamm, E.; Becker, K. B.; Engel, P.; Keese, R. *Helv. Chim. Acta* **1979**, *62*, (FASC. 7) 2181–2185) and on our observation of a Pd/C catalyzed double bond shift to form a symmetric olefin during hydrogenation of the 78/15/7 olefinic mixture.

(16) The ^1H and ^{13}C NMR parameters for bicyclo[4.2.1]non-2-ene have been reported and are in excellent agreement with our results for **3a**,**b**; see: Stamm, E.; Leu, H.-R.; Keese, R. *Helv. Chim. Acta* **1979**, 62 (FASC. 7), 2174–2180. Note: in this latter paper, the ^1H NMR of bicyclo[4.2.1]non-2-ene is incorrectly reported. Professor Keese has provided us with the original spectra (in two solvents) from which we report the ^1H NMR of bicyclo[4.2.1]non-2-ene as follows: (i) (in $CFCl_3$ at −20 °C, Bruker 80 MHz) δ 5.9–5.5 (complex multiplet, vinyl H), 5.45–5.1 (complex multiplet, vinyl H), 2.5–2.0 (br, 2 H), 2.1–1.7 (complex multiplet, 2 H), 1.7–1.1 (complex multiplet, 8 H); (ii) (in toluene-d_8 at −60 °C, Varian XL100, 100 MHz) δ 6.3–6.0 [seven lines (4 doublets, overlapped center line), vinyl H, J_1 = 11.8 Hz (olefin H–olefin H), J_2 = 7.6 Hz, J_3 = 2.4 Hz], 5.75–5.5 [seven lines (4 doublets, overlapped center line), vinyl H, J_1 = 11.8 Hz, J_2 = 7.4 Hz, J_3 = 3.8 Hz], 2.6–2.2 (br, 2 H), 2.2–1.8 (obscured by $-CD_2H$), 1.8–1.3, complex multiplet, 8 H).

(17) The published ^1H and ^{13}C NMR for bicyclo[4.2.1]nonane agree well with our results for the hydrogenated mixture. See: Schuster, D. I.; Lee, F.-T. *Tetrahedron Lett* **1965**, *46*, 4119–4127. Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, (FASC. 1), 81–93.