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Steric Blocking of $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ Isomerizations of an η^3-Allylic Ligand. Crystal and Molecular Structures of 1,3-Chloropalladation Products of *cis*-9-Methylenebicyclo[6.1.0]nonane and *cis*-7-Methylenebicyclo[4.1.0]heptane

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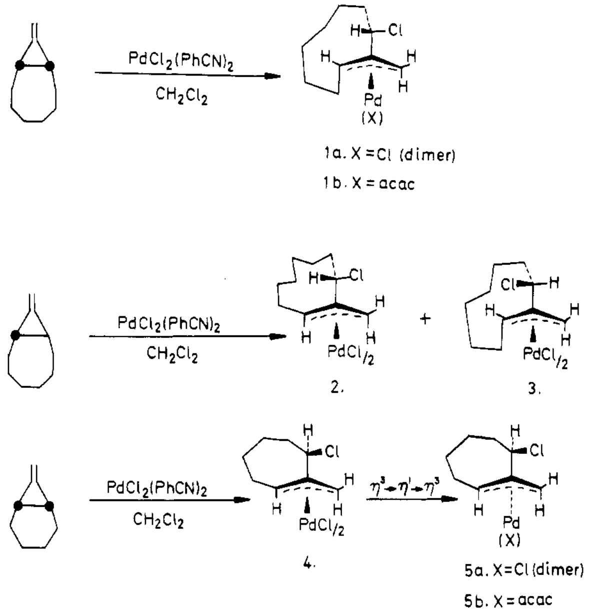
The crystal and molecular structures of $[Pd\{\eta^3\text{-}\overline{CHCl(CH_2)_6\text{-}anti\text{-}CHC}CH_2\}(acac)]$, **1b**, and $[Pd\{\eta^3\text{-}\overline{CHCl(CH_2)_4\text{-}syn\text{-}CHC}CH_2\}(acac)]$, **5b**, were determined by three-dimensional X-ray crystallographic studies. Both compounds crystallize in the monoclinic space group $P2_1/c$—C^5_{2h} (No. 14) with the lattice constants: $a = 19.314$ (5) Å, $b = 5.429$ (1) Å, $c = 15.092$ (3) Å, $\beta = 90.79$ (2)°, and $Z = 4$ for **1b**; $a = 11.325$ (3) Å, $b = 9.659$ (3) Å, $c = 13.838$ (3) Å, $\beta = 110.67$ (2)°, and $Z = 4$ for **5b**. The structures of both compounds were solved by using the "heavy-atom" technique and refined to convergence (R_1(unweighted, based on F) = 0.041 for 3239 independent reflections of **1b** having 2θ(Mo $K\bar{\alpha}$) < 60.4° and $I > 3\sigma(I)$; $R_1 = 0.032$ for 2486 independent reflections of **5b** having 2θ(Mo $K\bar{\alpha}$) < 55° and $I > 3\sigma(I)$) by using empirically weighted full-matrix least-squares techniques. Both **1b** and **5b** exhibit structural features characteristic of η-allyl–Pd bonds. Both molecules show unequal Pd–C distances, but while the allylic C–C bond lengths in **1b** are significantly different, those in **5b** are not. The allyl ligand in **1b** is skewed slightly with respect to the PdO_2 coordination plane. Significantly, the $-CHCl(CH_2)_4-$ chain in **5b** winds almost parallel to the plane of the allylic carbon atoms and does not block either face; in contrast the $-CHCl(CH_2)_6-$ chain in **1b** severely blocks the exo face of the allylic ligand. These structural features provide a rational explanation for the facility of $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ conversion involving **5b** and the high activation energy for an analogous transformation of **1b**.

Introduction

Experimental and theoretical studies on the chloropalladation reactions of alkyl-substituted methylenecyclopropanes indicate that the reaction must occur with suprafacial 1,3 addition of the elements of Pd–Cl to the organic substrate and that opening of the cyclopropane ring occurs by an orbital symmetry-controlled disrotatory process, with the breaking bond bending away from the metal.[2] Similar conclusions have been reached concerning the mechanism of chloropalladation of phenyl-substituted methylenecyclopropanes.[3] A crucial series of experiments which elucidated the intimate stereochemistry of 1,3-chloropalladation involved the reaction of *cis*-9-methylenebicyclo[6.1.0]nonane with $PdCl_2(PhCN)_2$ to give a single product **1a** and the analogous reaction of *trans*-9-methylenebicyclo[6.1.0]nonane to give two isomeric compounds **2** and **3**.[2] Compound **1a** could be converted into its monomeric acetylacetonato derivative **1b**. A most fortunate feature of these two reactions was that the isomeric compounds **1a**, **2**, and **3** did not interconvert via a $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway under chloropalladation conditions or even more vigorous thermal activation, demonstrating that these were indeed the kinetic chloropalladation products. In contrast, chloropalladation of *cis*-7-methylenebicyclo[4.1.0]heptane did not afford the presumed kinetic product **4** but rather the thermodynamic isomer **5a**, which could also be converted into its monomeric acetylacetonato derivative **5b**.



1a. X = Cl (dimer)
1b. X = acac

2.

3.

4.

5a. X = Cl (dimer)
5b. X = acac

In order to establish firmly the structures of the organic ligands in compounds **1** and **5** and to seek information regarding the widely differing proclivities of **1** and **5** toward $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ rearrangements, the crystal and molecular structures of **1b** and **5b** were determined. A preliminary description of the structure of **1b** has appeared.[2b]

Experimental Section

X-ray Crystallographic Studies[4] of $[Pd\{\eta^3\text{-}\overline{CHCl(CH_2)_6\text{-}anti\text{-}CHC}CH_2\}(O_2C_5H_7)]$ (1b) and $[Pd\{\eta^3\text{-}\overline{CHCl(CH_2)_4\text{-}syn\text{-}CHC}CH_2\}(O_2C_5H_7)]$ (5b). Compounds **1b** and **5b** were prepared

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[1] (a) Dartmouth College. (b) Alfred P. Sloan Research Fellow 1980–1984. (c) Crystalytics Co.

[2] (a) Albright, T. A.; Clemens, P. R.; Hughes, R. P.; Hunton, D. E.; Margerum, L. D. *J. Am. Chem. Soc.* **1982**, *104*, 0000. (b) Clemens, P. R.; Hughes, R. P.; Margerum, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 2428–2430.

[3] Dallas, B. K.; Hughes, R. P.; Schumann, K. *J. Am. Chem. Soc.* **1982**, *104*, 0000.

[4] See paragraph at end of paper regarding supplementary material.

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as described previously.[2a] Crystals of each compound suitable for X-ray diffraction studies were grown from CH_2Cl_2/hexanes at −30 °C. Both compounds crystallize in the centrosymmetric monoclinic space group $P2_1/c$—C^5_{2h} (No. 14)[5] with a = 19.314 (5) Å, b = 5.429 (1) Å, c = 15.092 (3) Å, β = 90.79 (2)°, and Z = 4 (d_{calcd} = 1.58 g cm^{-3} and μ_a(Mo K$\bar{\alpha}$)[6a] = 1.31 mm^{-1}) for **1b** and a = 11.325 (3) Å, b = 9.659 (3) Å, β = 110.67 (2)°, and Z = 4 (d_{calcd} = 1.64 g cm^{-3} and μ_a(Mo K$\bar{\alpha}$)[6a] = 1.46 mm^{-1}) for **5b**. Intensity measurements were made on a computer-controlled Nicolet P$\bar{1}$ autodiffractometer for both compounds using 1.0° wide (**1b**) or 1.2° wide (**5b**) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The sample of **1b** was irregularly shaped with minimum and maximum dimensions of 0.56 and 0.88 mm, respectively, while that of **5b** was a rectangular parallelepiped with dimensions of 0.23 × 0.34 × 0.63 mm. For minimization of variable absorption effects, both crystals were mounted with their longest dimensions nearly parallel to the phi axis of the diffractometer. A total of 4715 (**1b**) and 3252 (**5b**) independent reflections having 2θ(Mo K$\bar{\alpha}$) < 60.4° (**1b**) and 2θ(Mo K$\bar{\alpha}$) < 55° (**5b**) were measured for both compounds in concentric shells of increasing 2θ. Scanning rates of 6°/min were employed wiith both compounds for reflections having 2θ(Mo K$\bar{\alpha}$) < 43° and 4°/min for the remaining reflections. The scan for each reflection was between ω settings 0.50° (**1b**) or 0.60° (**5b**) above and below the calculated K$\bar{\alpha}$ (λ = 0.71073 Å) doublet value. Counts were accumulated for 19 equal (time) intervals during each scan, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts for reflections of both compounds, each lasting for one-fourth the total time used for the net scan (13/19 of the total scan time), were measured at ω settings 1.0° (**1b**) or 1.2° (**5b**) above and below the calculated K$\bar{\alpha}$ doublet value for each reflection. The intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

The metal atoms of both compounds were located from Patterson syntheses and the remaining non-hydrogen atoms from difference Fourier syntheses. All chemically anticipated hydrogen atoms for both molecules were located from difference Fourier syntheses calculated from the appropriate full-matrix least-squares refined structural model [R_1 (unweighted, based on F)[7] = 0.052 and 0.040 for **1b** and **5b**, respectively] which incorporated unit weighting and anisotropic thermal parameters for all non-hydrogen atoms. All structure factor calculations for both compounds employed recent tabulations of atomic form factors[6b] and an anomalous dispersion correction[6c] to the scattering factor of the Pd and Cl atoms. The final cycles of empirically weighted[8] full-matrix least-squares refinement which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to values of 0.041 and 0.056 for R_1 and R_2 (weighted, based on F),[7] respectively, for 3239 independent reflections of **1b** having 2θ(Mo K$\bar{\alpha}$) < 60.4° and $I > 3\sigma(I)$.[4] Similar refinement cycles for **5b** gave R_1 = 0.032 and R_2 = 0.039 for 2486 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 55° and $I > 3\sigma(I)$.[4] Since a careful comparison of final F_o and F_c values indicated the absence of extinction effects, extinction corrections were not made.

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic, and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Co.

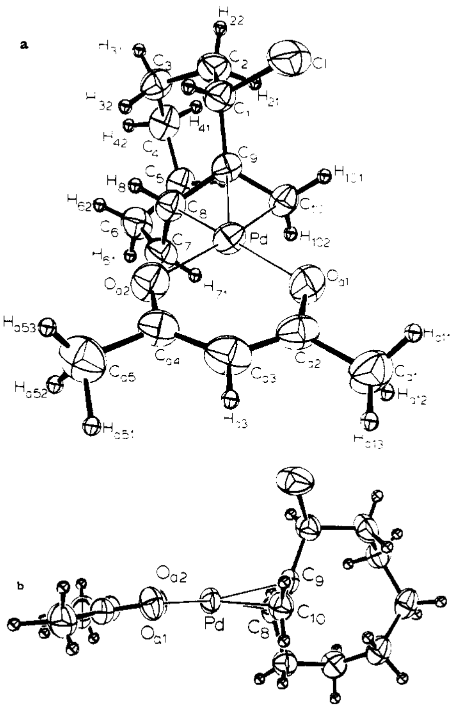

Figure 1. ORTEP drawing of the solid-state structure of $[\mathrm{Pd}\{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_6}\text{-}anti\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})]$, **1b**, viewed from (a) the front and (b) the side. All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

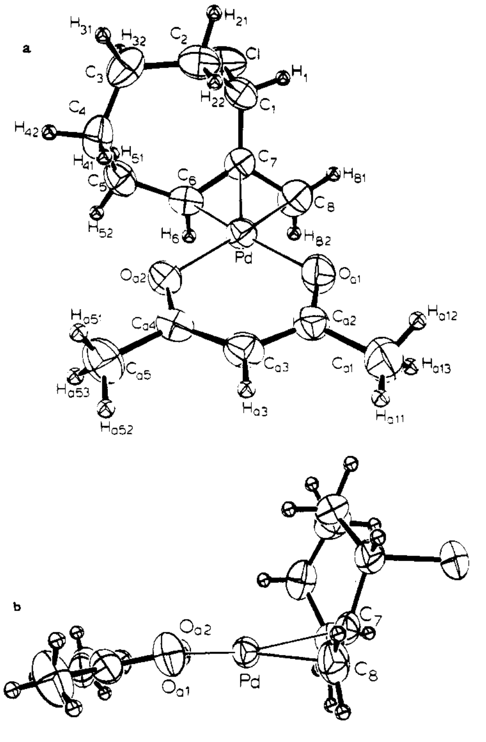

Figure 2. ORTEP drawing of the solid-state structure of $[\mathrm{Pd}\{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_4}\text{-}syn\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})$, **5b**, viewed from (a) the front and (b) the side. Atoms are represented as in Figure 1.

Results and Discussion

Final atomic coordinates for all atoms are given in Table I (compound **1b**) and Table II (compound **5b**). Anisotropic thermal parameters for non-hydrogen atoms are given in Tables III (**1b**)[4] and IV (**5b**).[4] Perspective drawings which

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(5) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

(6) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55–66. (b) *Ibid.*, pp 99–101. (c) *Ibid.*, pp 149–150.

(7) The R values are defined as $R_1 = \{\sum||F_o| - |F_c||/\sum|F_o|\}$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

(8) Empirical weights were calculated from the equation $\sigma = \sum_0^3 a_n|F_o|^n = 1.06 - 1.56 \times 10^{-2}|F_o| + 6.06 \times 10^{-4}|F_o|^2 - 2.45 \times 10^{-6}|F_o|^3$ for **1b** and $0.899 - 1.20 \times 10^{-2}|F_o| + 2.99 \times 10^{-4}|F_o|^2 - 5.86 \times 10^{-7}|F_o|^3$ for **5b**, the a_n being coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = a_n|F_o|^n$, where the F_c values were calulated from the fully refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion.

Table I. Atomic Coordinates in Crystalline Pd $\{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_6}\text{-}\mathit{anti}\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})$**(1b)**[a]

atom[b]	x	y	z	atom[b]	x	y	z
Pd	0.21962 (2)	0.12282 (7)	0.29902 (2)	C_7	0.2225 (3)	−0.0657 (11)	0.1106 (4)
Cl	0.41127 (8)	0.14622 (39)	0.35941 (9)	C_8	0.2618 (2)	0.0998 (9)	0.1726 (3)
O_{a1}	0.1750 (2)	0.0682 (7)	0.4218 (2)	C_9	0.3113 (2)	0.0126 (9)	0.2372 (3)
O_{a2}	0.1515 (2)	0.4100 (6)	0.2730 (2)	C_{10}	0.2891 (3)	−0.1784 (9)	0.2928 (3)
C_1	0.3785 (2)	0.1494 (12)	0.2465 (3)	C_{a1}	0.0938 (4)	0.0833 (16)	0.5344 (4)
C_2	0.4329 (3)	0.0333 (13)	0.1861 (4)	C_{a2}	0.1212 (2)	0.1777 (10)	0.4485 (3)
C_3	0.4179 (3)	0.0717 (10)	0.0860 (3)	C_{a3}	0.0862 (3)	0.3670 (11)	0.4052 (3)
C_4	0.3996 (3)	−0.1566 (11)	0.0326 (4)	$C_{a4'}$	0.1026 (2)	0.4740 (10)	0.3238 (3)
C_5	0.3295 (3)	−0.2760 (11)	0.0501 (4)	C_{a5}	0.0596 (3)	0.6864 (12)	0.2894 (5)
C_6	0.2659 (3)	−0.1175 (13)	0.0280 (3)	C			

atom[b]	x	y	z	B,[c] Å^2	atom[b]	x	y	z	B,[c] Å^2
H_1	0.372 (3)	0.302 (12)	0.238 (4)	5 (1)	H_{72}	0.178 (3)	−0.001 (13)	0.097 (4)	5 (1)
H_{21}	0.437 (3)	−0.170 (13)	0.204 (4)	6 (2)	H_8	0.273 (3)	0.236 (12)	0.146 (4)	4 (1)
H_{22}	0.473 (4)	0.090 (12)	0.204 (4)	6 (2)	H_{101}	0.318 (3)	−0.210 (10)	0.348 (4)	4 (1)
H_{31}	0.456 (3)	0.137 (10)	0.060 (4)	4 (1)	H_{102}	0.262 (3)	−0.302 (11)	0.278 (4)	4 (1)
H_{32}	0.377 (2)	0.185 (8)	0.073 (3)	2 (1)	H_{a11}	0.130 (4)	0.083 (15)	0.585 (6)	8 (2)
H_{41}	0.437 (4)	−0.304	0.043 (5)	7 (2)	H_{a12}	0.083 (3)	−0.057 (13)	0.526 (4)	4 (1)
H_{42}	0.397 (3)	−0.122 (9)	−0.035 (4)	4 (1)	H_{a13}	0.046 (6)	0.185 (21)	0.565 (8)	14 (3)
H_{51}	0.335 (3)	−0.317 (12)	0.125 (4)	6 (1)	H_{a3}	0.045 (3)	0.424 (11)	0.436 (4)	5 (1)
H_{52}	0.327 (3)	−0.417 (10)	0.010 (4)	4 (1)	H_{a51}	0.003 (5)	0.674 (17)	0.320 (6)	10 (3)
H_{61}	0.233 (3)	−0.206 (10)	−0.007 (4)	4 (1)	H_{a52}	0.037 (3)	0.640 (12)	0.232 (5)	5 (1)
H_{62}	0.278 (4)	0.012 (16)	−0.011 (5)	7 (2)	H_{a53}	0.078 (4)	0.837 (14)	0.283 (5)	6 (2)
H_{71}	0.207 (3)	−0.199 (11)	0.140 (4)	4 (1)					

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] Isotropic thermal parameter.

Table II. Atomic Coordinates in Crystalline Pd $\{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_4}\text{-}\mathit{syn}\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})$ **(5b)**[a]

atom[b]	x	y	z	atom[b]	x	y	z
Pd	0.43330 (3)	0.30245 (3)	0.31128 (2)	C_6	0.6095 (4)	0.2096 (4)	0.3269 (3)
Cl	0.8541 (1)	0.3159 (1)	0.5377 (1)	C_7	0.6152 (4)	0.2697 (4)	0.4220 (3)
O_{a1}	0.2613 (3)	0.3601 (4)	0.3213 (2)	C_8	0.5215 (4)	0.2212 (6)	0.4595 (4)
O_{a2}	0.3657 (2)	0.3514 (3)	0.1542 (2)	C_{a1}	0.0428 (5)	0.3996 (10)	0.2684 (5)
C_1	0.6978 (4)	0.3898 (5)	0.4739 (3)	C_{a2}	0.1620 (4)	0.3834 (5)	0.2443 (3)
C_2	0.7047 (5)	0.5143 (4)	0.4097 (4)	C_{a3}	0.1536 (4)	0.3951 (5)	0.1414 (3)
C_3	0.7631 (5)	0.4943 (6)	0.3271 (5)	C_{a4}	0.2515 (4)	0.3806 (4)	0.1032 (3)
C_4	0.6901 (5)	0.4014 (6)	0.2375 (4)	C_{a5}	0.2214 (5)	0.4045 (7)	−0.0113 (3)
C_5	0.6865 (5)	0.2512 (5)	0.2628 (4)				

atom[b]	x	y	z	B,[c] Å^2	atom[b]	x	y	z	B,[c] Å^2
H_1	0.682 (4)	0.419 (5)	0.534 (4)	5 (1)	H_{81}	0.512 (5)	0.276 (5)	0.518 (4)	5 (1)
H_{21}	0.753 (4)	0.586 (5)	0.463 (4)	5 (1)	H_{82}	0.503 (5)	0.120 (6)	0.450 (4)	6 (1)
H_{22}	0.618 (4)	0.547 (5)	0.382 (3)	4 (1)	H_{a11}	−0.020 (6)	0.409 (7)	0.218 (5)	7 (2)
H_{31}	0.769 (5)	0.594 (6)	0.302 (4)	6 (1)	H_{a12}	0.059 (6)	0.463 (8)	0.322 (6)	9 (2)
H_{32}	0.845 (6)	0.453 (6)	0.362 (4)	6 (1)	H_{a13}	0.042 (8)	0.333 (9)	0.313 (7)	10 (3)
H_{41}	0.614 (5)	0.433 (6)	0.208 (4)	5 (1)	H_{a3}	0.074 (4)	0.418 (5)	0.095 (3)	4 (1)
H_{42}	0.731 (6)	0.409 (7)	0.185 (5)	8 (2)	H_{a51}	0.243 (7)	0.484 (8)	−0.026 (5)	8 (2)
H_{51}	0.771 (5)	0.230 (5)	0.295 (4)	5 (1)	H_{a52}	0.136 (5)	0.407 (6)	−0.055 (4)	6 (1)
H_{52}	0.664 (5)	0.191 (5)	0.207 (4)	6 (1)	H_{a52}	0.253 (7)	0.327 (8)	−0.038 (6)	9 (2)
H_6	0.582 (4)	0.119 (5)	0.314 (3)	4 (1)	H_{a53}				

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] Isotropic thermal parameter.

illustrate the numbering schemes and represent the contents of the asymmetric units specified by the atomic coordinates of Tables I and II are depicted in Figures 1 (**1b**) and 2 (**5b**), respectively. Bond lengths for compounds **1b** and **5b** are given with their estimated standard deviations in Tables V and VI, respectively, and covalent bond angles for non-hydrogen atoms in compounds **1b** and **5b** are presented in Tables VII and VIII, respectively. Bond angles involving hydrogen atoms (Tables IX and X) and structure factor tables are included with the supplementary material.[4]

The coordination geometry of the η-allyl–Pd portion of each molecule is quite typical of that found in other η-allylic complexes of palladium[9–19] and of other square-planar metal complexes.[20] In compound **1b** the plane defined[24a] by the allylic carbon atoms C_8,C_9,C_{10} makes a dihedral angle of 119.06° with that[24b] of the Pd,O_{a1},O_{a2}

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Table V. Bond Lengths (Å) in Crystalline

$\mathrm{Pd}\ \{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_6}\text{-}\mathit{anti}\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})\ (\mathbf{1b})^a$

Pd-O$_{a1}$[b]	2.076 (3)	O$_{a1}$···O$_{a2}$	2.944 (5)
Pd-O$_{a2}$	2.074 (4)	O$_{a1}$···C$_{10}$	3.250 (6)
Pd-C$_8$	2.089 (5)	O$_{a2}$···C$_8$	3.125 (6)
Pd-C$_9$	2.100 (4)	C$_8$···C$_{10}$	2.413 (7)
Pd-C$_{10}$	2.119 (5)	C$_{a1}$-H$_{a11}$	1.03 (9)
Cl-C$_1$	1.809 (5)	C$_{a1}$-H$_{a12}$	0.80 (7)
O$_{a1}$-C$_{a2}$	1.268 (6)	C$_{a1}$-H$_{a13}$	1.16 (12)
O$_{a2}$-C$_{a4}$	1.272 (6)	C$_{a3}$-H$_{a3}$	0.98 (6)
C$_{a1}$-C$_{a2}$		C$_{a5}$-H$_{a51}$	1.20 (9)
C$_{a4}$-C$_{a5}$	1.509 (9)	C$_{a5}$-H$_{a52}$	1.00 (7)
C$_1$-C$_9$	1.500 (7)	C$_{a5}$-H$_{a53}$	0.90 (8)
C$_7$-C$_8$	1.498 (7)	C$_1$-H$_1$	0.85 (7)
C$_{a2}$-C$_{a3}$	1.389 (8)	C$_2$-H$_{21}$	1.14 (7)
C$_{a3}$-C$_{a4}$	1.399 (7)	C$_2$-H$_{22}$	0.88 (7)
C$_8$-C$_9$	1.436 (6)	C$_3$-H$_{31}$	0.91 (6)
C$_9$-C$_{10}$	1.404 (7)	C$_3$-H$_{32}$	1.01 (4)
C$_1$-C$_2$	1.537 (8)	C$_4$-H$_{41}$	1.09 (8)
C$_2$-C$_3$	1.548 (7)	C$_4$-H$_{42}$	1.04 (5)
C$_3$-C$_4$	1.517 (8)	C$_5$-H$_{51}$	1.15 (7)
C$_4$-C$_5$	1.528 (8)	C$_5$-H$_{52}$	0.98 (6)
C$_5$-C$_6$	1.532	C$_6$-H$_{61}$	0.95 (6)
C$_6$-C$_7$	1.538 (7)	C$_6$-H$_{62}$	0.95 (8)
		C$_7$-H$_{71}$	0.90 (6)
		C$_7$-H$_{72}$	0.95 (6)
		C$_8$-H$_8$	0.87 (6)
		C$_{10}$-H$_{101}$	1.01 (6)
		C$_{10}$-H$_{102}$	0.87 (6)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

Table VI. Bond Lengths (Å) in Crystalline

$\mathrm{Pd}\ \{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_4}\text{-}\mathit{syn}\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})^a$

Pd-O$_{a1}$[b]	2.077 (3)	O$_{a1}$···O$_{a2}$	2.946 (4)
Pd-O$_{a2}$	2.087 (3)	O$_{a1}$···C$_8$	3.187 (6)
Pd-C$_6$	2.128 (4)	O$_{a2}$···C$_6$	3.248 (5)
Pd-C$_7$	2.113 (4)	C$_6$···C$_8$	2.379 (7)
Pd-C$_8$	2.091 (5)	C$_{a1}$-H$_{a11}$	0.81 (7)
Cl-C$_1$	1.822 (5)	C$_{a1}$-H$_{a12}$	0.93 (8)
O$_{a1}$-C$_{a2}$	1.267 (5)	C$_{a1}$-H$_{a13}$	0.89 (9)
O$_{a2}$-C$_{a4}$	1.268 (5)	C$_{a3}$-H$_{a3}$	0.93 (5)
C$_{a1}$-C$_{a2}$	1.508 (8)	C$_{a5}$-H$_{a51}$	0.86 (8)
C$_{a4}$-C$_{a5}$	1.516 (6)	C$_{a5}$-H$_{a52}$	0.94 (6)
C$_1$-C$_7$	1.504 (6)	C$_{a5}$-H$_{a53}$	0.96 (8)
C$_5$-C$_6$	1.502 (7)	C$_1$-H$_1$	0.96 (5)
C$_{a2}$-C$_{a3}$	1.399 (6)	C$_2$-H$_{21}$	1.02 (5)
C$_{a3}$-C$_{a4}$	1.393 (6)	C$_2$-H$_{22}$	0.97 (5)
C$_6$-C$_7$	1.418 (5)	C$_3$-H$_{31}$	1.04 (6)
C$_7$-C$_8$	1.416 (7)	C$_3$-H$_{32}$	0.97 (7)
C$_1$-C$_2$	1.514 (6)	C$_4$-H$_{41}$	0.87 (6)
C$_2$-C$_3$	1.521 (8)	C$_4$-H$_{42}$	0.99 (7)
C$_3$-C$_4$	1.516 (8)	C$_5$-H$_{51}$	0.92 (6)
C$_4$-C$_5$	1.496 (8)	C$_5$-H$_{52}$	0.92 (6)
		C$_6$-H$_6$	0.92 (5)
		C$_8$-H$_{81}$	1.00 (5)
		C$_8$-H$_{82}$	1.00 (6)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2.

Table VII. Bond Angles (Deg) Involving Non-Hydrogen Atoms in Crystalline

$\mathrm{Pd}\ \{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_6}\text{-}\mathit{anti}\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})\ (\mathbf{1b})^a$

O$_{a1}$PdO$_{a2}$[b]	90.4 (1)		
O$_{a1}$PdC$_8$	168.2 (2)	O$_{a2}$PdC$_8$	97.3 (2)
O$_{a1}$PdC$_9$	136.0 (2)	O$_{a2}$PdC$_9$	131.8 (2)
O$_{a1}$PdC$_{10}$	101.6 (2)	O$_{a2}$PdC$_{10}$	166.5 (2)
C$_8$PdC$_9$	40.1 (2)		
C$_8$PdC$_{10}$	70.0 (2)		
C$_9$PdC$_{10}$	38.9 (2)		
ClC$_1$C$_2$	108.8 (4)	PdO$_{a1}$C$_{a2}$	124.6 (3)
ClC$_1$C$_9$	112.0 (4)	PdO$_{a2}$C$_{a4}$	124.4 (3)
C$_2$C$_1$C$_9$	109.8 (4)	O$_{a1}$C$_{a2}$C$_{a1}$	115.0 (5)
C$_1$C$_2$C$_3$	113.8 (5)	O$_{a1}$C$_{a2}$C$_{a3}$	126.4 (5)
C$_2$C$_3$C$_4$	116.5 (5)	C$_{a1}$C$_{a2}$C$_{a3}$	118.6 (5)
C$_3$C$_4$C$_5$	117.1 (5)	O$_{a2}$C$_{a4}$C$_{a5}$	114.3 (5)
C$_4$C$_5$C$_6$	115.7 (5)	O$_{a2}$C$_{a4}$C$_{a3}$	126.5 (5)
C$_5$C$_6$C$_7$	111.8 (5)	C$_{a3}$C$_{a4}$C$_{a5}$	119.2 (5)
C$_6$C$_7$C$_8$	109.7 (4)	C$_{a2}$C$_{a3}$C$_{a4}$	127.3 (5)
C$_7$C$_8$C$_9$	123.7 (4)		
PdC$_8$C$_7$	113.9 (3)		
PdC$_8$C$_9$	70.4 (3)		
C$_8$C$_9$C$_{10}$	116.3 (4)		
PdC$_9$C$_8$	69.6 (3)		
PdC$_9$C$_{10}$	71.3 (3)		
PdC$_9$C$_1$	123.4 (3)		
C$_8$C$_9$C$_1$	117.8 (4)		
C$_1$C$_9$C$_{10}$	125.5 (4)		
PdC$_{10}$C$_9$	69.8 (3)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

Table VIII. Bond Angles (Deg) Involving Non-Hydrogen Atoms in Crystalline

$\mathrm{Pd}\ \{\eta^3\text{-}\overline{\mathrm{CHCl(CH_2)_4}\text{-}\mathit{syn}\text{-}\mathit{CHC}}\mathit{CH_2}\}(\mathrm{O_2C_5H_7})^a$

O$_{a1}$PdO$_{a2}$[b]	90.1 (1)	C$_6$PdC$_7$	39.1 (2)
		C$_7$PdC$_8$	39.4 (2)
		C$_6$PdC$_8$	68.7 (2)
O$_{a1}$PdO$_6$	166.9 (1)	O$_{a2}$PdC$_6$	100.8 (1)
O$_{a1}$PdC$_7$	133.6 (1)	O$_{a2}$PdC$_7$	133.9 (1)
O$_{a1}$PdC$_8$	99.8 (2)	O$_{a2}$PdC$_8$	168.1 (2)
ClC$_1$C$_2$	110.7 (3)	PdO$_{a1}$C$_{a2}$	124.5 (3)
ClC$_1$C$_7$	105.2 (3)	PdO$_{a2}$C$_{a4}$	123.9 (3)
C$_2$C$_1$C$_7$	119.0 (4)	O$_{a1}$C$_{a2}$C$_{a1}$	115.6 (4)
C$_1$C$_2$C$_3$	117.8 (4)	O$_{a1}$C$_{a2}$C$_{a3}$	126.3 (4)
C$_2$C$_3$C$_4$	115.7 (5)	C$_{a1}$C$_{a2}$C$_{a3}$	118.2 (5)
C$_3$C$_4$C$_5$	115.8 (5)	O$_{a2}$C$_{a4}$C$_{a5}$	115.1 (4)
C$_4$C$_5$C$_6$	117.8 (4)	O$_{a2}$C$_{a4}$C$_{a3}$	127.1 (4)
C$_5$C$_6$C$_7$	126.3 (4)	C$_{a3}$C$_{a4}$C$_{a5}$	117.8 (4)
PdC$_6$C$_5$	123.1 (3)	C$_{a2}$C$_{a3}$C$_{a4}$	127.0 (4)
PdC$_6$C$_7$	69.9 (2)		
C$_6$C$_7$C$_8$	114.2 (4)		
PdC$_7$C$_6$	71.0 (2)	PdC$_8$C$_7$	71.2 (3)
PdC$_7$C$_8$	69.5 (3)		
PdC$_7$C$_1$	120.9 (3)		
C$_6$C$_7$C$_1$	125.2 (4)		
C$_8$C$_7$C$_1$	120.0 (4)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2.

system. A similar feature is found in **5b** where the corresponding dihedral angle between the C$_6$,C$_7$C$_8$[24a] and Pd,O$_{a1}$,O$_{a2}$[24b] planes is 116.56°.[21] As observed in the structures of other η-allyl compounds[9-20] the two carbon atoms which occupy the terminal positions of the allylic ligand lie below the square plane of coordination, as defined by the Pd,O$_{a1}$,O$_{a2}$ plane. In **1b**, C$_8$ lies 0.323 Å and C$_{10}$ lies 0.229 Å below this plane, while in **5b**, C$_6$ is 0.267 Å and C$_8$ is 0.241 Å below the corresponding coordination plane; it is clear that the allylic ligand in **1b** is slightly skewed compared to that in **5b**. This aditional skewing in **1b** is presumably the result of intramolecular nonbonded repulsion between Pd and C$_7$ (Pd···C$_7$ separation is 3.024 (5) Å). Those hydrogen and carbon atoms directly bound

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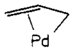
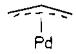
(21) Similar dihedral angles are found in other η-allyl complexes.[9-20]

to the η-allyl framework are not coplanar with the allylic moiety. In **1b**, C_1 is displaced toward Pd by 0.152 Å from the C_8,C_9,C_{10} plane, while in **5b** the corresponding displacement of C_1 from the C_6,C_7,C_8 plane is 0.195 Å. Similar distortions are observed at the terminal allylic carbon atoms. In **1b** the anti-carbon C_7 is displaced by 0.965 Å from the C_8,C_9,C_{10} plane away from Pd, and the corresponding anti-hydrogen H_{102} is displaced by 0.42 Å in the same direction; the syn-hydrogen atoms H_8 and H_{101} are displaced by 0.16 and 0.25 Å toward the Pd. Similarly in **5b** the anti-hydrogen atoms H_6 and H_{82} are displaced from the C_6,C_7,C_8 plane away from Pd by 0.44 and 0.58 Å, respectively, while the syn atoms C_5 and H_{81} ocupy positions which are displaced by 0.150 and 0.19 Å toward the metal atom. Very similar distortions have been noted in other palladium complexes of this type; in general, distortions of anti groups away from the metal are more severe than the corresponding displacements of syn groups toward the metal.[10,14–16,18–20]

There are some interesting differences in the Pd–C, and C–C, distances for the allyl ligand in these two compounds. Compound **1b** has a significantly shorter (0.030 Å) distance from Pd to the substituted allylic carbon C_8 than to the unsubstituted carbon C_{10}. It could be argued that this corresponds to a greater contribution from the σ,π-bonding mode **6a** rather than the symmetrically bonded form **6b**;[20] this appears to be supported by the observation that the C_9–C_{10} distance is significantly shorter (0.32 Å) than the corresponding C_8–C_9 distance. However, it is not clear why such asymmetry in bonding should occur in this system; previous examples of the bonding mode shown as **6a** have involved compounds in which the two ends of the allylic ligand are opposite atoms of differing trans influence.[12,14,16–18] This is clearly not the case here, and the asymmetry in the η-allyl–Pd bonding is not reflected by any variation in the Pd–O distances opposite the allyl ligand. Furthermore, in asymmetrically bonded allyl ligands it is usually the σ-bonding carbon atom which is displaced less from the square plane of coordination;[18] the opposite is true for **1b**, in which C_8 lies further below the coordination plane than does C_{10} (vide supra). As mentioned earlier, the skewing of the allyl ligand in **1b** probably occurs to minimize steric interactions of the anti-carbon C_7 with the metal; it is difficult to anticipate what effects such skewing would have on the Pd–C and C–C distances involved.



6a.



6b.

In contrast, **5b** exhibits a shorter distance from Pd to the unsubstituted allylic carbon atom C_8 (2.091 Å) than to the substituted carbon C_6 (2.128 Å). The dissimilar Pd–C distances are not reflected within the allylic ligand, however, where the C–C distances are identical (1.418 Å), but the Pd–O_{a2} distance (2.087 Å) is slightly longer than the Pd–O_{a1} separation (2.077 Å). The longer Pd–C_6 and Pd–O_{a2} distances are probably a manifestation of steric interactions between the methylene hydrogen H_{41} (which is tipped toward the metal) and O_{a2} ($H_{41}\cdots O_{a2}$ = 2.76 (6) Å).

Bond lengths and angles within the acetylacetonato[13] and organic ligand ring systems[15,16] appear to be normal.

The gross features of the conformation of the organic ring systems in **1b** and **5b** also serve to explain the different facilities with which **1a** and **5a** undergo the dynamic $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformation in the presence of donor ligands in solution.[2a] It is quite clear from the structure of **5b** that the $-(CH_2)_4CHCl-$ chain winds essentially parallel to the plane of the allylic carbon atoms.[22] The $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformation, preferentially forming the σ bond at the unsubstituted carbon atom, requires that the metal transfer from one face of the allyl ligand to the other, and such a process in **5a** or its immediate kinetic precursor **4**, would meet with minimal steric interference from the ring.[23] Isomer **5a** is thermodynamically preferred, probably because the Pd and the Cl atoms reside on opposite faces of the ligand. In **1b**, the situation is markedly different, since the $-(CH_2)_6CHCl-$ chain effectively blocks the back-face of the allyl ligand. Any $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization of **1a** would require severe conformational changes in the ring to accommodate the migrating metal atom. Presumably this factor raises the activation energy for this process sufficiently to preclude such isomerization.[23]

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Registry No. 1b, 77773-12-7; **5b**, 82495-27-0.

Supplementary Material Available: Anisotropic thermal parameters for non-hydrogen atoms (Tables III and IV), bond angles involving hydrogen atoms (Tables IX and X), and observed and calculated structure factors from the final cycles of refinement (compound **1b**, Table XI: compound **5b**, Table XII) (29 pages). Ordering information is given on any current masthead page.

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(22) A similar conformational feature is observed for the organic ligand in $[PdCl\{\eta^3\text{-}\overline{CH(Me)(CH_2)_3\text{-}syn\text{-}CHC}CH_2\}]_2$.[15]

(23) See discussion in ref 2a.

(24) The least-squares mean planes for the following groups of atoms in **1b** and **5b** are defined by the equation: $aX + bY + cZ = d$, where X, Y, Z are orthogonal coordinates measured along $\vec{\mathbf{a}}$, $\vec{\mathbf{b}}$, $\vec{\mathbf{c}}^*$, respectively, of the crystal system. (a) C_8, C_9, and C_{10} for **1b**: $a = 0.340$, $b = -0.674$, $c = -0.656$, $d = -0.366$. C_6, C_7, and C_8 for **5b**: $a = -0.468$, $b = 0.731$, $c = -0.500$, $d = -3.11$. (b) Pd, O_{a1}, and O_{a2} for **1b** and **5b**: for **1b**, $a = 0.644$, $b = -0.645$, $c = -0.411$, $d = -4.98$; for **5b**; $a = -0.275$, $b = 0.936$, $c = 0.218$, $d = -4.55$.