Contribution from the Chemistry Division and the Chemical Engineering Division,
Argonne National Laboratory, Argonne, Illinois 60439

Molecular and Crystal Structure of Bis(μ-acetato)-bis(norbornadiene)dirhodium(I): A Catalyst for the Isomerization of Quadricyclane to Norbornadiene[1]

A. H. REIS, JR.,*[2a] C. WILLI,[2a,c] S. SIEGEL,[2b] and B. TANI[2b]

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Bis(μ-acetato)-bis(norbornadiene)dirhodium(I) has been structurally characterized. The compound has been shown to be an active catalyst for the isomerization of quadricyclane to norbornadiene. This material crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with unit cell constants (T = 20 °C) a = 9.7733 (10) Å, b = 15.2859 (15) Å, c = 12.1815 (14) Å, and β = 103.563 (8)°. All 3151 unique reflections were used in the X-ray structure analysis which refined to an R_F of 0.028. The Rh(1)–Rh(2) distance is 3.1050 (7) Å. Each Rh atom is bonded to the two olefin moieties of a norbornadiene ligand and to two oxygen atoms of the bridging acetate ligands. Each Rh coordination sphere has an approximate square-planar configuration with average Rh–olefin and Rh–O distances of 1.975 (4) and 2.106 (7) Å, respectively. The Rh atoms lie 0.098 and 0.157 Å out of their respective coordination planes. The dihedral angle formed between these planes is 50.1°, while the angle between the planes defined only by the Rh and acetate oxygens is 40.2°. Hydrogen atoms on the norbornadiene groups are within van der Waals contact distances, indicative of strong steric interactions between the ligands of the dimer.

Introduction

The photoisomerization of norbornadiene[3] to quadricyclane[4] is promising as a potential solar energy storage system.[5,6] However, the reconversion of quadricyclane to norbornadiene is thermally forbidden according to the Woodward–Hoffmann orbital symmetry rules ($t_{1/2} > 14$ h at 140 °C).[5,7] To compensate for this result, transition-metal complexes may be used as catalysts for reactions involving thermally forbidden olefin rearrangements. For this reason the reaction has been the subject of scrutiny; the isomerization reaction has been the topic of both kinetic and mechanistic studies involving transition-metal catalysis of such "forbidden reactions".[8,9] Bis(μ-acetato)-bis(norbornadiene)dirhodium(I), [Rh(NBD)(AcO)]$_2$, has been studied[10] as a catalyst for the conversion of quadricyclane to norbornadiene. Kinetic studies show [Rh(NBD)(AcO)]$_2$ promotes a reaction rate significantly faster than the corresponding chloride-bridged complex. This paper will describe the molecular and crystal structure of the dimer and relate it to the isomerization mechanism.

Experimental Section

X-ray Data Collection. Red crystals of [Rh(NBD)(AcO)]$_2$ were prepared as described[10] and made available to this study. Preliminary precession photographs showed $2/m$ Laue symmetry. The crystal selected was an approximate rectangular parallelepiped, 0.012 × 0.015 × 0.028 cm. It was attached to the end of a thin glass fiber with epoxy and mounted on a Syntex $P2_1$ automatic diffractometer. The diffractometer is equipped with a molybdenum X-ray tube and a graphite monochromator (λ 0.7107 Å, d = 3.36 Å, 002), at a takeoff angle of ~4°.

The crystal was optically centered in a random orientation. Cell orientation, unit cell parameters, and crystal quality were determined by the following procedure.[11] A rotation photograph was taken with $2\theta = \omega = \chi = 0°$ and a ϕ-axis rotation of 360° for 10 min. The photo was recorded on a flat Polaroid cassette mounted 97.5 mm from the crystal. The separations ($2x_i$,$2y_i$) were measured and fed into a crystal-centering routine.[11] The refined angles were subsequently converted to reciprocal lattice vectors and used to generate real vectors as possible unit cell axes. Axes were chosen on the basis of the preliminary Weissenberg and precession data. Axial photographs were taken. The mirror plane about the b axis was observed, confirming the initial assignment of a monoclinic cell. Indices were assigned via the autoindexing routine.[11] Three intense standard reflections were monitored (every 47 reflections) as a guide to the stability of the system and crystal. These check reflections were found to vary within ±1%, indicating high stability. Intensity data were collected to a 2θ maximum of 50° over four octants. A total of 6286 reflections were collected, 3151 of which were unique. An examination of the data revealed systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, unique to the space group $P2_1/c$. Experimental information is listed in Table I.

Table I. Experimental Details for [Rh(NBD)(AcO)]$_2$

cell constants:[a] a = 9.7733 (10) Å, b = 15.2859 (15) Å, c = 12.1815 (14) Å, β = 103.563 (8)°
cell vol: 1769.1 (3) Å^3
mol wt: 508.18
calcd density: 1.91 g cm^{-3}
measd density: 1.87 (6) g cm^{-3} (water displacement)
$Z = 4$
space group: $P2_1/c$
radiation: Mo Kα, λ 0.710 69 Å
max. 2θ: 50.0° ($\pm h, k, \pm l$)
scan type: θ–2θ coupled
scan width: $[2.4 + \Delta(\alpha_2 - \alpha_1)]°$
scan speed: variable, 1.96–29.30°/min
crystal
  general orientation
  vol 0.42518 × 10^{-4} cm^3 (0.012 × 0.015 × 0.023 cm)
  absorption coeff 18.24 cm^{-1}
  max. transmission factor 0.66
  min. transmission factor 0.37
no. of reflections collected: 6286 (3151 unique)
R_F = 0.028 for all 3151 reflections
R_{wF^2} = 0.063
GOF = 3.165

[a] At T = 20 °C.

Solution and Structure Refinement. Absorption, Lorentz, and polarization corrections were applied to the data, and the data were averaged with the programs DATALIB and DATASORT.[12] The positions of the two rhodium atoms were located from a three-dimensional Patterson map. A three-dimensional Fourier map based on phasing from the Rh atoms provided refined positions for these atoms and determined the positions of the oxygen and carbon atoms. Refinement of the scale factor gave an initial R_F of 0.397. The Rh, C, and O positions were subsequently refined isotropically to an R_F of 0.059. The 22 hydrogen atoms were located on a three-dimensional difference Fourier map. Isotropic thermal parameters were assigned to hydrogen atoms equal to the value of the carbon atoms to which they were attached. Full-matrix least-squares refinement of all atomic positions, scale factor, anisotropic thermal parameters for all atoms except hydrogen, and an extinction correction[13] (g = 0.102 (4)) gave a final R_F of 0.028. A final difference Fourier map was featureless. The quantity minimized during refinement was $\sum w|F_o^2 - F_c^2|^2$, where F_o and F_c are the observed and calculated structure factor amplitudes. Weights were assigned as $w = 1/[\sigma(F_o^2)]^2$, $\sigma(I) = [\mathrm{SC} + \tau^2(B_1 + B_2) + p^2I^2]^{1/2}$. SC is the scan count, τ is the scan to background time ratio, B_1 and B_2 are the background counts on each side of a peak, I is the net intensity, and p is an ignorance factor, set to 0.03. The agreement indices are defined as

$$R_F = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_{wF^2} = [\sum w|F_o^2 - F_c^2|^2/\sum w(F_o^2)^2]^{1/2}$$

$$\mathrm{GOF} = [\sum w|F_o^2 - F_c^2|^2/(N_o - N_R)]^{1/2}$$

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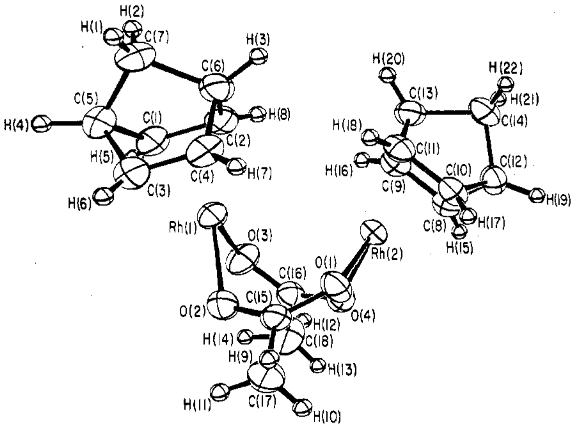

Figure 1. $[Rh(NBD)(AcO)]_2$ dimer showing atom labeling.

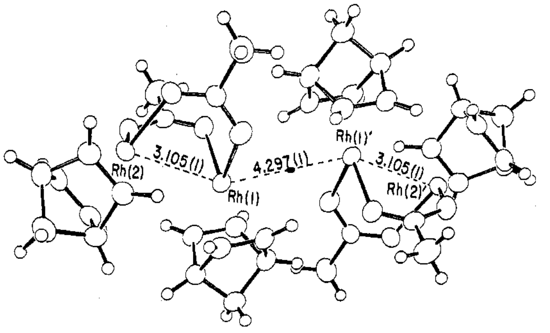

Figure 2. $[Rh(NBD)(AcO)]_2$ molecular interaction across the center of symmetry at 101.

N_o is the number of independent reflections and N_R is the number of parameters varied. The programs S5FOUR[14] and S5XFLS[14] were used for Fourier and least-squares refinement. Bond distances, bond angles, and estimated standard deviations (esd's) were determined by the program S5FFE.[14] LS PLANES[15] was used to determine least-squares planes. Molecular drawings were prepared by using ORTEP.[16] Atomic coordinates are listed in Table II, and the corresponding anisotropic temperature factors are listed in Table III. Scattering factors for the nonhydrogen atoms were taken from the compilation of Cromer and Waber[17] and modified for the real and imaginary components of anomalous dispersion.[18] Hydrogen scattering factors were taken from ref 19. A listing of F_o and F_c is available as supplementary material.

Structure Description

Interatomic distances and angles with estimated standard deviations (esd's) are given in Tables IV and V. Least-squares planes are presented in Table VI. Dihedral angles between least-squares planes are given in Table VII. Figure 1 shows the asymmetric unit of the structure with the numbering system used in this discussion. Figure 2 shows the interaction between two dimers across a center of symmetry. Figure 3 indicates the square-planar geometry around the rhodium atoms. Figure 4 is a stereoview of the packing of the unit cell.

Table II. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $[Rh(NBD)(AcO)]_2$ with Estimated Standard Deviations Given in Parentheses[a]

atom	x	y	z	B,[b] Å^2
Rh(1)	0.81697 (3)	0.417474 (10)	0.46494 (2)	
Rh(2)	0.62283 (2)	0.274381 (10)	0.52742 (2)	
C(1)	0.7674 (3)	0.5302 (2)	0.3644 (3)	
C(2)	0.6538 (4)	0.4716 (2)	0.3394 (3)	
C(3)	0.9175 (4)	0.4027 (2)	0.3316 (3)	
C(4)	0.8073 (4)	0.3616 (2)	0.3065 (3)	
C(5)	0.8603 (4)	0.5091 (2)	0.2821 (3)	
C(6)	0.6781 (4)	0.4138 (2)	0.2417 (3)	
C(7)	0.7495 (4)	0.4794 (2)	0.1767 (3)	
C(8)	0.4165 (3)	0.2759 (2)	0.5487 (3)	
C(9)	0.4321 (3)	0.3413 (2)	0.4713 (3)	
C(10)	0.5022 (3)	0.1719 (2)	0.4413 (3)	
C(11)	0.5177 (3)	0.2363 (2)	0.3640 (3)	
C(12)	0.3663 (3)	0.1932 (2)	0.4789 (3)	
C(13)	0.3912 (4)	0.2976 (2)	0.3545 (3)	
C(14)	0.2751 (4)	0.2333 (2)	0.3699 (3)	
C(15)	0.9346 (3)	0.2459 (2)	0.5623 (2)	
C(16)	0.7444 (3)	0.4198 (2)	0.6902 (2)	
C(17)	0.0570 (4)	0.1853 (3)	0.5995 (4)	
C(18)	0.7686 (6)	0.4593 (3)	0.8066 (4)	
O(1)	0.8148 (2)	0.2108 (2)	0.5349 (2)	
O(2)	0.9597 (2)	0.3263 (2)	0.5601 (2)	
O(3)	0.7665 (3)	0.4676 (2)	0.6121 (2)	
O(4)	0.7049 (2)	0.3412 (2)	0.6796 (2)	
H(1)	0.789 (5)	0.451 (3)	0.155 (4)	3.4
H(2)	0.693 (5)	0.522 (3)	0.153 (4)	3.4
H(3)	0.587 (5)	0.383 (3)	0.194 (4)	3.4
H(4)	0.932 (5)	0.555 (3)	0.276 (4)	3.0
H(5)	0.785 (5)	0.578 (3)	0.412 (4)	2.8
H(6)	−0.005 (5)	0.411 (3)	0.343 (4)	3.0
H(7)	0.815 (5)	0.299 (3)	0.310 (3)	2.9
H(8)	0.566 (5)	0.478 (3)	0.360 (3)	3.2
H(9)	0.063 (5)	0.150 (3)	0.535 (4)	3.8
H(10)	0.047 (5)	0.149 (3)	0.656 (4)	3.8
H(11)	0.127 (6)	0.217 (3)	0.617 (4)	3.9
H(12)	0.691 (6)	0.478 (3)	0.814 (4)	4.3
H(13)	0.768 (6)	0.422 (3)	0.869 (4)	4.3
H(14)	0.824 (5)	0.509 (3)	0.813 (4)	4.3
H(15)	0.406 (5)	0.284 (3)	0.625 (4)	2.9
H(16)	0.441 (5)	0.409 (3)	0.486 (3)	3.0
H(17)	0.550 (5)	0.117 (3)	0.454 (4)	3.0
H(18)	0.578 (5)	0.237 (3)	0.312 (4)	2.8
H(19)	0.326 (5)	0.143 (3)	0.511 (3)	2.9
H(20)	0.371 (5)	0.311 (3)	0.288 (4)	3.2
H(21)	0.186 (5)	0.264 (3)	0.382 (4)	3.6
H(22)	0.242 (5)	0.192 (3)	0.304 (4)	3.6

[a] The centers of the olefin bond and norbornadiene groups are as follows.

Center of Olefin Bond

	$(x_1 + x_2)/2$	$(y_1 + y_2)/2$	$(z_1 + z_2)/2$
C(1), C(2)	0.7106	0.5010	0.3519
C(3), C(4)	0.8624	0.3911	0.3190
C(8), C(9)	0.4243	0.3086	0.5100
C(10), C(11)	0.5100	0.2041	0.4026

Center of Norbornadiene Groups

	$\Sigma x_n/n$	$\Sigma y_n/n$	$\Sigma z_n/n$
C(1), C(2), C(3), C(4)	0.7865	0.4460	0.3355
C(8), C(9), C(10), C(11)	0.4671	0.2563	0.4563

[b] Atoms with no isotropic thermal parameters listed were refined anisotropically.

As depicted in Figure 3, the coordination environment of each rhodium atom is a near-square-planar configuration including one oxygen atom from each of the two bridging acetato ligands and the midpoints of the two olefinic bonds of a norbornadiene ligand. This structure is consistent with other d^8 rhodium(I) complexes.[20] The rhodium(1)–rhodium(2) distance of 3.1050 (7) Å is indicative of a weak metal–metal bond.[20] The average Rh–O distance is 2.106 (7) Å, with an average Rh–O–C bond angle of 124.7 (2)°. The norbornadiene (NBD) ligands are symmetrically and approximately perpendicularly bonded to the rhodium atoms via the centers of the olefin bonds. The average Rh–C distance is 2.095 (4) Å, and the average Rh–olefin distance is 1.975 (4) Å. The angle between the two least-squares planes $\overline{\mathrm{C(1)C(2)}}$, $\overline{\mathrm{C(3)C(4)}}$, O(2), O(3) and $\overline{\mathrm{C(8)C(9)}}$, $\overline{\mathrm{C(10)C(11)}}$, O(1), O(4) is 50.1°. The rhodium atoms do not lie precisely in these least-squares planes; Rh(1) and Rh(2) are "popped out" of their respective mean coordinated planes by 0.0985 (2) and 0.1574 (2) Å.

Carbon–carbon single-bond distances and angles within the norbornadiene group agree with those published for nor-

Table III. Anisotropic Thermal Parameters ($\times 10^4$) of $[Rh(NBD)(AcO)]_2$ with Estimated Standard Deviations in Parentheses[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh(1)	79.6 (4)	24.5 (1)	46.4 (2)	1.7 (1)	16.0 (2)	1.4 (1)
Rh(2)	54.4 (3)	27.1 (3)	44.8 (2)	−1.9 (1)	7.9 (2)	−5.2 (1)
C(1)	103 (4)	22.6 (13)	55 (2)	4.2 (19)	23 (2)	1.7 (1)
C(2)	81 (4)	34.9 (15)	58 (2)	9 (2)	17 (2)	6.1 (15)
C(3)	85 (4)	34.5 (15)	56 (2)	8 (2)	25 (2)	0.2 (15)
C(4)	119 (5)	25.0 (14)	52 (2)	6 (2)	27 (3)	1.0 (14)
C(5)	100 (4)	29.5 (14)	59 (2)	−3 (2)	27 (3)	2.5 (15)
C(6)	102 (5)	31.7 (15)	56 (3)	−4 (2)	5 (3)	1.6 (15)
C(7)	128 (5)	34.1 (16)	53 (3)	4 (2)	17 (3)	5.5 (17)
C(8)	67 (4)	37.3 (15)	55 (2)	4.9 (18)	17 (2)	−2.9 (15)
C(9)	69 (4)	30.4 (14)	60 (2)	9.0 (18)	12 (2)	−3.3 (15)
C(10)	60 (3)	28.8 (14)	65 (3)	−0.3 (18)	3 (2)	−8.6 (15)
C(11)	71 (4)	36.7 (15)	45 (2)	−2.2 (19)	11 (2)	−9.7 (15)
C(12)	68 (4)	32.0 (15)	70 (3)	−2.7 (19)	17 (2)	0.9 (16)
C(13)	79 (4)	38.2 (16)	51 (2)	2.8 (20)	6 (2)	2.6 (16)
C(14)	63 (4)	45.2 (18)	74 (3)	−0.3 (21)	1 (3)	−3.2 (19)
C(15)	62 (4)	34.0 (14)	46 (2)	3.3 (18)	11 (2)	5.0 (14)
C(16)	81 (4)	31.5 (15)	47 (2)	−5.1 (18)	13 (2)	−4.3 (14)
C(17)	66 (4)	48 (2)	93 (4)	11 (2)	15 (3)	17 (2)
C(18)	201 (8)	50 (2)	56 (3)	−36 (3)	42 (4)	17 (2)
O(1)	56 (2)	30.9 (10)	78 (2)	1.1 (12)	8.0 (18)	−1.7 (11)
O(2)	79 (3)	31.0 (10)	68.6 (19)	−4.7 (13)	6.8 (18)	6.2 (11)
O(3)	138 (4)	30.7 (10)	54.4 (17)	−1.7 (5)	34 (2)	−0.9 (11)
O(4)	102 (3)	37.1 (11)	46.8 (16)	−17.5 (14)	14.2 (17)	−5.4 (10)

[a] The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

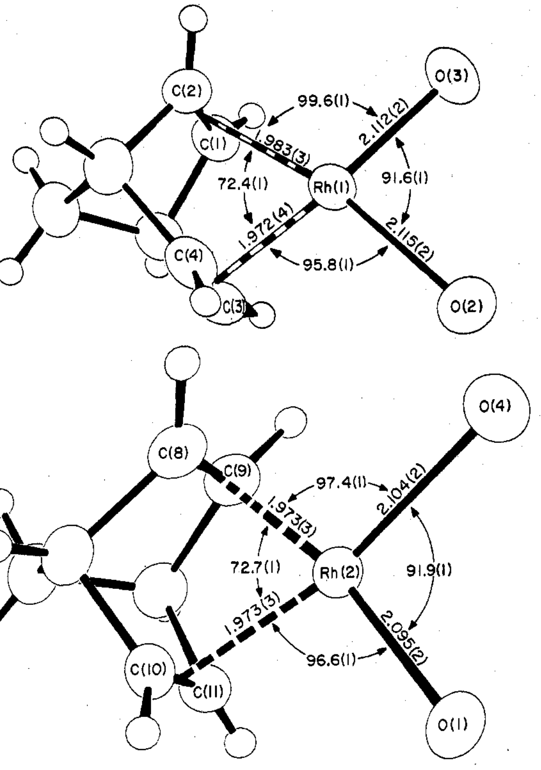

Figure 3. (Top) Rh(1) coordination environment showing an approximate square-planar geometry. (Bottom) Rh(2) coordination environment showing an approximate square-planar geometry.

bornadiene.[21] The olefin bonds average 1.397 (5) Å, compared with 1.338 Å for the free molecule. This lengthening is in agreement with the Dewar–Chatt–Duncanson model of olefin–transition-metal bonding, which predicts olefin bond lengthening to 1.40–1.47 Å, depending on the amount of back-donation into the olefin π^* orbitals by the transition metal.[22]

Carbon–carbon, carbon–oxygen, and carbon–hydrogen bond distances within the twin bridging acetate ligands agree with those published for the quadruple acetate bridges in dirhodium(II) tetraacetate dihydrates.[23] The average oxygen–carbon–oxygen bond angle of 125.5 (3)° in $[Rh(NBD)(AcO)]_2$ is also essentially the same. The angle between the least-squares planes defined by the oxygen and carbon atoms of each acetate ligand is 82.49°. Because of the repulsion of the NBD ligands, the rhodium atoms lie well above and below these planes (see Table VI), as compared to the case for the tetraacetate complex in which the Rh atoms lie within their least-squares planes.

The rhodium(1)–rhodium(1) distance across a center of symmetry within the unit cell is 4.296 (1) Å. The shortest rhodium(2)–rhodium(2) distance is 6.136 (1) Å. The rhodium(1)–oxygen–olefin least squares planes are parallel to each other across the center of symmetry (Figures 2 and 4).

Discussion

The "hinged" square-planar configuration is preferred for binuclear chloride-bridged rhodium(I) complexes according to Bonnet.[20a] In these complexes (Table VIII, items 1–5) the preferred Rh–Rh distance is 3.02–3.17 Å, with a corresponding dihedral angle of ~120° between coordination planes. (The stretch of the Rh–Rh bond in the bis(cyclooctadiene) chloride-bridged complex (item 6) and the planarity of this complex are not understood.) In the unbridged dimeric cation (item 8) with bulky phenyl isocyanide ligands the planes are parallel but the Rh–Rh bond is only slightly lengthened. The sulfido bridge (item 7), less sterically demanding, allows the planes to become more nearly parallel. The dihedral angle in $[Rh(NBD)(AcO)]_2$ is less than half of the "preferred" angle. This result is due to the increased width of the bridging acetate ligand compared to that of a chlorine atom. The acetate ligands would prefer a 0° angle between coordination planes with nonbulky ligands. The Rh–Rh separation of 3.1050 (7) Å agrees surprisingly well with the value for both bridged Rh(I) dimers and the unbridged one.

Although the weak metal–metal bond in $[Rh(NBD)(AcO)]_2$ shows only slight lengthening relative to chloride-bridged dimers, indications of strain are nevertheless present. The acetate ligands have twisted, so that they are not perpendicular to each other, as is common in molecules with multiple acetate bridges, but form a dihedral angle of 82.49°. This twist also allows the norbornadiene ligands to avoid an eclipsed configuration (see Figure 1). The average rhodium–oxygen bond length has increased from 2.031 Å for the Rh(II) tetraacetate complex[23] to 2.106 Å. This result is consistent with the change from Rh(II) to Rh(I) and therefore is not entirely an indication

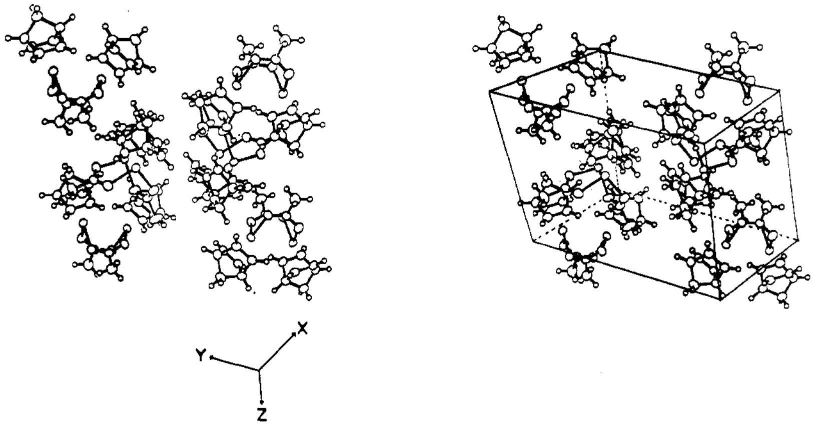

Figure 4. Stereoview of the packing of $[Rh(NBD)(AcO)]_2$ molecules in the unit cell.

Table IV. Interatomic Distances in $[Rh(NBD)(AcO)]_2$ with Estimated Standard Deviations Given in Parentheses (Å)

(A) Distances around the Rh Atoms

Rh(1)-Rh(2)	3.1050 (7)	Rh(2)-O(1)	2.095 (2)
Rh(1)-O(2)	2.115 (2)	Rh(2)-O(4)	2.104 (2)
Rh(1)-O(3)	2.112 (2)	Rh(2)-C(8)	2.093 (4)
Rh(1)-C(1)	2.104 (3)	Rh(2)-C(9)	2.095 (3)
Rh(1)-C(2)	2.103 (3)	Rh(2)-C(10)	2.088 (3)
Rh(1)-C(3)	2.087 (4)	Rh(2)-C(11)	2.096 (3)
Rh(1)-C(4)	2.092 (3)	Rh(2)-Rh(2)	6.1362 (7)
Rh(1)-Rh(1)	4.296 (1)		

(B) Distances within the Norbornadiene Groups

C(3)-C(4)	1.384 (5)	C(8)-C(9)	1.406 (5)
C(1)-C(2)	1.403 (5)	C(10)-C(11)	1.394 (5)
C(1)-C(5)	1.531 (5)	C(8)-C(12)	1.538 (5)
C(2)-C(6)	1.545 (5)	C(9)-C(13)	1.537 (5)
C(3)-C(5)	1.528 (5)	C(10)-C(12)	1.538 (5)
C(4)-C(6)	1.545 (5)	C(11)-C(13)	1.535 (5)
C(6)-C(7)	1.543 (6)	C(12)-C(14)	1.541 (5)
C(5)-C(7)	1.545 (5)	C(13)-C(14)	1.546 (5)
C(1)-H(5)	0.93 (4)	C(8)-H(15)	0.97 (5)
C(2)-H(8)	0.95 (5)	C(9)-H(16)	1.06 (4)
C(3)-H(6)	0.75 (5)	C(10)-H(17)	0.94 (5)
C(4)-H(7)	0.94 (5)	C(11)-H(18)	0.96 (5)
C(5)-H(4)	1.00 (5)	C(12)-H(19)	0.98 (5)
C(6)-H(3)	1.04 (4)	C(13)-H(20)	0.93 (4)
C(7)-H(1)	1.02 (5)	C(14)-H(21)	1.04 (5)
C(7)-H(2)	0.86 (5)	C(14)-H(22)	1.01 (5)
C(2)-C(4)	2.350 (5)	C(8)-C(10)	2.335 (5)
C(1)-C(3)	2.322 (5)	C(9)-C(11)	2.345 (5)

(C) Distances within the Acetate Groups

C(15)-O(1)	1.259 (4)	C(16)-O(3)	1.257 (4)
C(15)-O(2)	1.255 (4)	C(16)-O(4)	1.259 (4)
C(15)-C(17)	1.496 (5)	C(16)-C(18)	1.507 (5)
C(17)-H(9)	0.96 (5)	C(18)-H(12)	0.83 (6)
C(17)-H(10)	0.90 (5)	C(18)-H(13)	0.95 (5)
C(17)-H(11)	0.84(5)	C(18)-H(14)	0.93 (5)
O(1)-O(2)	2.238 (3)	O(1)-O(4)	3.019 (3)
O(2)-O(3)	3.031 (3)	O(4)-O(3)	2.237 (3)
O(3)-O(1)	4.089 (3)	O(4)-O(2)	3.173 (4)

(D) Hydrogen-Hydrogen Interactions (2.6 Å)

Norbornadiene(1) Hydrogens

H(4)-H(6)[a]	2.37 (7)	H(7)-H(18)	2.51 (6)
H(6)-H(7)[a]	2.41 (7)	H(8)-H(16)	2.42 (7)
H(6)-H(10)[a]	2.60 (7)	H(8)-H(16)[a]	2.54 (6)

Norbornadiene(2) Hydrogens

H(16)-H(8)	2.42 (7)	H(18)-H(7)	2.51 (6)
H(16)-H(8)[a]	2.54 (6)	H(18)-H(15)[a]	2.50 (7)

(E) Acetate Hydrogens

H(10)-H(14)[a]	2.46 (7)	H(10)-H(6)[a]	2.60 (7)

[a] Neighboring dimer group.

Table V. Interatomic Angles for $[Rh(NBD)(AcO)]_2$ with Estimated Standard Deviations Given in Parentheses

(A) Angles around the Rh Atoms

O(2)-Rh(1)-O(3)	91.63 (9)	O(1)-Rh(2)-O(4)	91.94 (9)
C(4)-Rh(1)-C(2)	68.14 (14)	C(9)-Rh(2)-C(11)	68.03 (13)
C(3)-Rh(1)-C(1)	67.29 (14)	C(8)-Rh(2)-C(10)	67.91 (13)
C(3)-Rh(1)-C(4)	38.68 (14)	C(11)-Rh(2)-C(10)	38.91 (13)
C(1)-Rh(1)-C(2)	38.96 (13)	C(9)-Rh(2)-C(8)	39.22 (13)
C(1)-Rh(1)-C(4)	80.98 (13)	C(9)-Rh(2)-C(10)	81.26 (12)
C(2)-Rh(1)-C(3)	80.79 (14)	C(11)-Rh(2)-C(8)	81.31 (13)
C(3)-Rh(1)-O(2)	94.12 (12)	C(11)-Rh(2)-O(1)	98.44 (11)
C(4)-Rh(1)-O(2)	96.80 (11)	C(10)-Rh(2)-O(1)	93.93 (11)
C(1)-Rh(1)-O(3)	97.40 (11)	C(9)-Rh(2)-O(4)	100.17 (11)
C(2)-Rh(1)-O(3)	100.73 (12)	C(8)-Rh(2)-O(4)	93.73 (11)
C(4)-Rh(1)-O(3)	164.22 (12)	C(11)-Rh(2)-O(4)	166.40 (11)
C(3)-Rh(1)-O(3)	153.94 (11)	C(10)-Rh(2)-O(4)	149.35 (12)
C(1)-Rh(1)-O(2)	152.98 (12)	C(9)-Rh(2)-O(1)	163.60 (11)
C(2)-Rh(1)-O(2)	161.50 (10)	C(8)-Rh(2)-O(1)	151.52 (10)

(B) Angles within the Norbornadiene Groups

C(5)-C(1)-C(2)	106.5 (3)	C(12)-C(8)-C(9)	106.5 (3)
C(1)-C(2)-C(6)	106.0 (3)	C(8)-C(9)-C(13)	105.4 (3)
C(5)-C(3)-C(4)	107.2 (3)	C(11)-C(10)-C(12)	106.9 (3)
C(3)-C(4)-C(6)	106.0 (3)	C(10)-C(11)-C(13)	105.6 (3)
C(7)-C(6)-C(4)	100.5 (3)	C(10)-C(12)-C(14)	101.0 (3)
C(7)-C(6)-C(2)	101.1 (3)	C(8)-C(12)-C(14)	101.1 (3)
C(4)-C(6)-C(2)	99.0 (2)	C(10)-C(12)-C(8)	98.7 (2)
C(3)-C(5)-C(1)	98.7 (3)	C(11)-C(13)-C(14)	101.7 (3)
C(3)-C(5)-C(7)	100.7 (2)	C(9)-C(13)-C(14)	101;7 (3)
C(1)-C(5)-C(7)	101.4 (3)	C(9)-C(13)-C(11)	99.5 (2)
C(5)-C(7)-C(6)	94.3 (2)	C(13)-C(14)-C(12)	93.7 (2)

(C) Angles within the Acetate Groups

Rh(2)-O(1)-C(15)	125.6 (2)	Rh(2)-O(4)-C(16)	126.7 (2)
Rh(1)-O(2)-C(15)	123.4 (2)	Rh(1)-O(3)-C(16)	123.2 (2)
O(2)-C(15)-O(1)	125.7 (3)	O(3)-C(16)-O(4)	125.4 (3)
O(2)-C(15)-C(17)	117.8 (3)	O(3)-C(16)-C(18)	117.5 (3)
O(1)-C(15)-C(17)	116.4 (3)	O(4)-C(16)-C(18)	117.0 (3)

of strain. The average Rh–O–C bond angle has increased from 119.5° for the tetraacetate complex[23] to 124.7 (2)°. The source of the strain is most likely the steric interactions of the bulky norbornadiene ligands. The hydrogen atoms of the two norbornadiene ligands of a dimeric unit are within van der Waals contact distances, e.g., H(8)–H(16) = 2.42 (7) Å (see Table IV(D)). A contact of 2.37 (7) Å occurs between dimeric units (H(4)–H(6)′). The following distortions from idealized symmetry tend to decrease the van der Waals overlap of hydrogen atoms. The dihedral angle between the centroid of [C(1), C(2), C(3), C(4)], Rh(1), Rh(2) and the centroid of [C(8), C(9), C(10), C(11)] is 64.9° indicative of the distortion of the NBD ligands from an eclipsed geometry (0°). Each norbornadiene moiety is bent back from the nearest O, Rh, O plane, leading to an observed dihedral angle between the O(2), Rh(1), O(3) plane and the $\overline{C(3)C(4)}$, $\overline{C(1)C(3)}$, O(2), O(3) plane of 3.83° and between the O(1), Rh(2), O(4) plane and the $\overline{C(8)C(9)}$, $\overline{C(10)C(11)}$, O(1), O(4) plane of 6.22°. The bond angles Rh(1)–O(2)–C(15) = 123.4 (2)°, Rh(1)–O(3)–C(16) = 123.2 (2)°, Rh(2)–O(1)–C(15) = 125.6 (2)°, and Rh(2)–O(4)–C(16) = 126.7 (2)° are all above the

Table VI. Least-Squares Planes of $[Rh(NBD)(AcO)]_2$

atom	dev	wt	atom	dev	wt
Oxygen–Norbornadiene Plane 1					
$-0.7395x - 0.6546y - 0.1572z + 10.067 = 0$					
$\chi^2 = 3.7456$					
O(2)	0.002 (2)	1.0	C(3),C(4) bond center	−0.003 (4)	1.0
O(3)	−0.002 (2)	1.0			
C(1),C(2) bond center	0.003 (4)	1.0	Rh(1)	0.0985 (2)	0.0
Oxygen–Norbornadiene Plane 2					
$0.3387x + 0.7372y - 0.5846z - 0.8351 = 0$					
$\chi^2 = 238.7672$					
O(1)	0.018 (2)	1.0	C(10),C(11) bond center	−0.024 (3)	1.0
O(4)	−0.018 (2)	1.0			
C(8),C(9) bond center	0.024 (3)	1.0	Rh(2)	0.1574	0.0
Acetate Plane 1					
$0.3169x - 0.811y - 0.09450z + 4.2084 = 0$					
$\chi^2 = 1.4823$					
O(1)	0.001 (2)	1.0	C(17)	0.001 (5)	1.0
O(2)	0.001 (2)	1.0	Rh(1)	0.5979 (2)	0.0
C(15)	−0.003 (3)	1.0	Rh(2)	−0.5819 (2)	0.0
Acetate Plane 2					
$-0.9324x + 0.03009y - 0.2002z + 4.6551 = 0$					
$\chi^2 = 1.7118$					
O(3)	−0.001 (2)	1.0	C(18)	−0.001 (6)	1.0
O(4)	−0.001 (2)	1.0	Rh(1)	−0.7340 (3)	0.0
C(16)	0.004 (3)	1.0	Rh(2)	0.3953 (2)	0.0

Table VII. Dihedral Angles between Planes in $[Rh(NBD)(AcO)]_2$ (deg)

1. Rh(1), $\overline{C(1)C(2)}$ bond center, $\overline{C(3)C(4)}$ bond center with Rh(2), $\overline{C(8)C(9)}$ bond center, $\overline{C(10)C(11)}$ bond center	−59.31
2. Rh(1), O(2), O(3) with Rh(2), O(1), O(4)	−40.22
3. $\overline{C(1)C(2)}$ bond center, $\overline{C(3)C(4)}$ bond center, O(2), O(3) with $\overline{C(8)C(9)}$ bond center, $\overline{C(10)C(11)}$ bond center, O(1), O(4)	−50.12
4. O(1), O(2), C(15), C(17) with O(3), O(4), C(16), C(18)	−82.49
5. Centroid of [C(1), C(2), C(3), C(4)], Rh(1), Rh(2) with centroid of [C(8), C(9), C(10), C(11)]	64.9 (1)

Table VIII. Dihedral Angles, ω, between Coordination Planes and Metal–Metal Distances, d, for Dimeric Rh(I) Compounds

	compd	ω, deg	d_{M-M}, Å	ref
(1)	$[RhCl(CO)_2]_2$	124	3.12	20b
(2)	$[RhCl(C_2H_4)_2]_2$	115.8	3.02	20d
(3)	$[RhCl(C_6H_{10})_2]_2$	115.8	3.090	20e
(4)	$[RhCl(CO)(PMe_2Ph)]_2$	123.0	3.167	20g
(5)	$(\eta\text{-}1,5\text{-}C_8H_{12})Rh_2Cl_2(P(OPh)_3)_2$	122.6	3.138	20f
(6)	$(\eta\text{-}1,5\text{-}C_8H_{12})Rh_2Cl_2(P(OPh)_3)_2$	180	3.50	20c
(7)	$[Rh(SPh)(CO)(PMe_3)]_2$	113.0	3.061	20a
(8)	$[Rh_2(CNPH)_8][BPH_4]_2$	0	3.193	20h
(9)	$[Rh(NBD)(AcO)]_2$	50.1	3.105	this work
(10)	$[Rh(PPh_3)_2Cl]_2$	180	3.662	24

expected 120° showing the extent of the steric repulsion of the norbornadiene ligands. The amount of the distortion is, however, asymmetric as can be seen in the difference in the magnitudes of the above angles.

Hydrogen–hydrogen interactions between NBD ligands of the same dimer and those of NBD ligands and acetate ligands of different dimers are not equal. The hydrogen atoms of NBD(1) (H(4), H(5), and H(6)) are closer to hydrogen atoms of *neighboring dimers* than those of corresponding NBD(2), (H(15), H(17), and H(19)). See Figures 1, 2, and 4 and Table IV(D). NBD(1) has hydrogen–hydrogen interactions at 2.37 (7) and 2.41 (7) Å (H(6)–H(4)′ and H(6)–H(7)′). The shortest hydrogen interaction of NBD(2) is 2.64 (6) Å (H(17)–H(13)′). The hydrogen atoms of NBD(1) and NBD(2) of the same dimer are also within van der Waals radii contact (H(7)–H(18) = 2.51 (6) Å, H(8)–H(16) = 2.42 (7) Å). These interactions have given rise to the unequal distortion of the NBD ligands relative to the coordination sphere.

Conclusion

The isomerization of quadricyclane to norbornadiene is catalyzed by $[Rh(NBD)(AcO)]_2$. On the basis of ^{13}C NMR measurements[10] a rhodocyclobutane intermediate is formed which is consistent with a stepwise mechanism involving insertion of Rh(I) into a cyclopropyl ring. The formation of such an intermediate may be assisted by the scission of one of the acetate bridges, therefore decreasing the strain brought about by the interaction of the bulky norbornadiene ligands. Manassen suggested[9b] that for the transition metal catalyzed isomerization of quadricyclane to norbornadiene, distortions from square-planar coordination impaired the catalytic ability. Since $[Rh(NBD)(AcO)]_2$ is strained and each Rh is shielded by the surrounding ligands, the formation of an unstrained complex would be appropriate for catalytic activity. The details of the isomerization are discussed in the accompanying paper.[10]

Registry No. $[Rh(NBD)(AcO)]_2$, 36570-53-3.

Supplementary Material Available: A listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) (a) Chemistry Division, Argonne National Laboratory. (b) Chemical Engineering Division, Argonne National Laboratory. (c) Undergraduate research participant sponsored by the Argonne Center for Educational Affairs; from Luther College, Decorah, Iowa.

(3) Bicyclo[2.2.1]hepta-2,5-diene.

(4) Tetracyclo[$3.2.0.0^{2,7}.0^{4,6}$]heptane.

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