

# Allyl- and Allyl-Like-Tin Derivatives. 3. Crystal Structures and Solution Conformations of Some Cyclohex-2-enyl- and Cyclohept-2-enylstannanes

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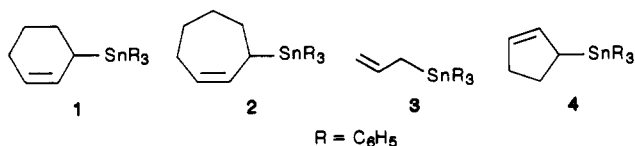
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The crystal structures of the allylic stannanes cyclohex-2-enyl- (1) and cyclohept-2-enyltriphenylstannanes (2) have been determined, and in both, the coordination about tin is tetrahedral, although the enlargement of the  $\angle C(13)-Sn-C(19)$  angle in both 1 ( $114.4^\circ$ ) and 2 ( $117.0^\circ$ ) may be in response to a short intramolecular contact between one phenyl ring and the cycloalkene moiety. The Sn-C(phenyl) bond lengths are normal ( $2.144 \pm 0.005 \text{ \AA}$ ), but the allyl bond ( $Sn-C(19) = 2.185 \pm 0.005 \text{ \AA}$ ) is longer (ca.  $0.04-0.05 \text{ \AA}$ ) than the normal Sn-C(aliphatic) bond length ( $2.13 \pm 0.01 \text{ \AA}$ ) and may be associated with a hyperconjugative  $\sigma_{C-Sn}-\pi$  effect. In 1, the  $(C_6H_5)_3Sn$  group formally occupies a quasi-equatorial orientation with a Sn-C(19)-C(20)-C(21) torsion angle of  $121^\circ$  which permits substantial  $\sigma-\pi$  interaction and may best accommodate other interactions in the crystal. Given the other values of bond and torsion angles, the actual distinction between quasi-axial and quasi-equatorial orientations with respect to double bond interaction with  $\delta_{C-Sn}$  is a fine one. The molecular geometry of 2 is a slightly distorted chair arrangement with the  $(C_6H_5)_3Sn$  group clearly occupying a quasi-axial position with a Sn-C(19)-C(25)-C(24) torsion angle of  $90^\circ$ , the most favored for  $\sigma-\pi$  interaction. However, this "outward splaying" of the C-Sn bond is probably also associated with relief of interactions between  $Sn(C_6H_5)_3$  and the regions of C(21) and C(23). Solid-state (MAS)  $^{13}C$  NMR spectra have been recorded of both 1 and 2, and although only one set of signals was observed for each,  $^{119}Sn-^{13}C$  couplings were not located.  $^1H$  and  $^{13}C$  NMR spectra for 1 and 2 (in solution) have been obtained, and for 1 there is now a preponderance of the conformer with an axially disposed tin group, whereas for 2, the solution conformation is adequately described as a distorted chair arrangement with a quasi-axial  $Sn(C_6H_5)_3$  group, as identified in the crystal.

## Introduction

Unsaturated organotin compounds are of increasing utility in organic synthesis,<sup>1</sup> and our interest in certain synthetic applications<sup>2,3</sup> of allylstannanes required a firm understanding of the stereochemistry of some substitution reactions,<sup>4</sup> which in turn demanded knowledge of the structures and preferred conformations of such allylstannanes.<sup>5</sup> In a previous report,<sup>6</sup> the X-ray structure of allyltriphenylstannane (3) was discussed and the  $Sn(C_6H_5)_3$

independent molecules comprising the asymmetric unit.) These studies were then extended<sup>7</sup> to the cyclic allylic stannanes which incorporate a chiral center and the possibility of either quasi-axial or quasi-equatorial orientation of the tin moiety. In the case of the cyclopent-2-enyl compound 4, the tin group was axially oriented, such arrangement persisting in solution, on the basis of NMR measurements. 1 and 2 are less rigid conformationally than 4, and in view of the extensive mechanistic studies performed on these systems,<sup>4,5</sup> we considered it desirable to determine the crystal structures of these stannanes, and the preferred (solution) conformations by various NMR methods. These endeavors are discussed in this report.



groups were oriented nearly orthogonally to the plane of the allyl system, the preferred arrangement for  $\sigma_{C-Sn}-\pi$  interaction. (Torsion angles of  $97^\circ$  and  $108^\circ$  for the two

## Experimental Section

**Preparation of Cyclohex-2-enyl- and Cyclohept-2-enyltriphenylstannanes.** Cyclohex-2-enyltriphenylstannane (1) was obtained from the reaction of (triphenylstannyl)lithium and cyclohex-2-enyl chloride in tetrahydrofuran (THF) as described previously;<sup>5</sup> mp  $81^\circ C$ . In a similar way, the homologue, cyclohept-2-enyltriphenylstannane (2), mp  $83-85^\circ C$ , was also obtained, and both 1 and 2 were recrystallized from ethanol after (short) column chromatography on Florosil, eluting with pentane. 1 and 2 were characterized by their  $^{119}Sn$ ,  $^1H$ , and  $^{13}C$  NMR spectra, some details of which are discussed in the text. **Compound 1:**

(1) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth Co.: London, 1987.

(2) Young, D.; Kitching, W. *Aust. J. Chem.* **1985**, *38*, 1767.

(3) Tagliavini, G. *Rev. Silicon, Germanium, Tin, Lead Compds.* **1985**, *8*, 237.

(4) (a) Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4848. (b) Wickham, G.; Young, D.; Kitching, W. *Organometallics* **1988**, *7*, 1187.

(5) Kitching, W.; Penman, K. G.; Laycock, B.; Maynard, I. *Tetrahedron*, **1988**, *44*, 3819.

(6) Ganis, P.; Furlani, D.; Marton, D.; Tagliavini, G.; Valle, G. *J. Organomet. Chem.* **1985**, *293*, 207.

(7) Ganis, P.; Valle, G.; Tagliavini, G.; Kitching, W.; Penman, K. G.; Jones, M. A. *J. Organomet. Chem.* **1988**, *349*, 57.

(8) Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4885.

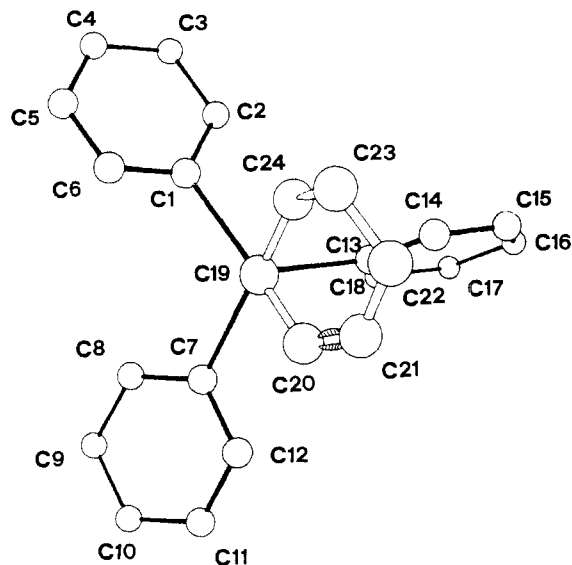


Figure 1. Perspective drawing of cyclohex-2-enyltriphenyltin (1) viewed down the Sn-C(19) axis.

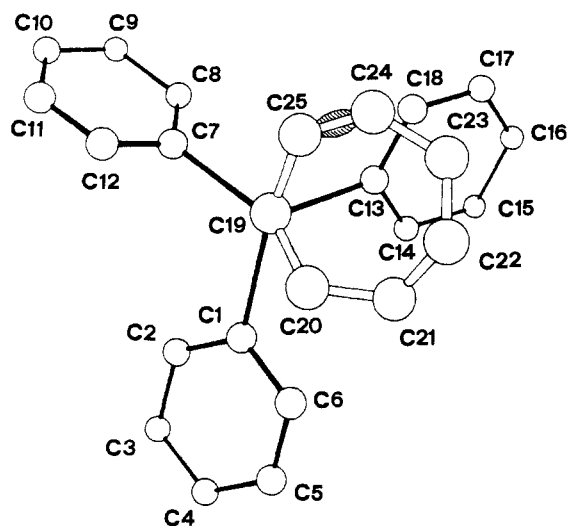


Figure 2. Perspective drawing of cyclohept-2-enyltriphenyltin (2) viewed down the Sn-C(19) axis.

$^{13}\text{C}$  ( $\text{CDCl}_3$ ) 28.88 (389), 129.8 (45.2), 124.24 (48.7), 24.84 (16.1), 23.06 (25.6), 26.69 ppm (19.98);  $^{119}\text{Sn}$  -130.3 ppm (relative ( $\text{C}-\text{H}_3$ ) $_4\text{Sn}$  for  $\text{CDCl}_3$  solvent). **Compound 2:**  $^{13}\text{C}$  ( $\text{CDCl}_3$ ) 35.83 (359, 342), 133.28 (46), 128.35, 32.01 (17), 28.36 (13), 31.82 (25), 29.74 (13);  $^{119}\text{Sn}$  -130.5 ppm. (Values in parentheses are observed  $^{119}\text{Sn}$ - $^{13}\text{C}$  couplings. Aromatic carbon shifts are not listed.) The  $^1\text{H}$  NMR spectra are discussed in the text.

**Nuclear magnetic resonance spectra** ( $^1\text{H}$ ) were recorded at 300 or 400 MHz in the FT mode on Bruker CXP-300 and Jeol JNM-GX400 spectrometers, respectively. Chemical shifts were referenced to internal tetramethylsilane (0.0 ppm) or residual  $\text{CHCl}_3$  (7.24 ppm).  $^{13}\text{C}$  NMR spectra were recorded at 25.05, 75.46, or 100 MHz, and chemical shifts were referenced to the central peak of solvent ( $\text{CDCl}_3$ ) at 77.00 ppm.

**Crystal Data.** Cyclohex-2-enyltriphenyltin (1):  $\text{C}_{24}\text{H}_{24}\text{Sn}$  (mp 81 °C);  $M_r$  431.15; monoclinic; space group  $P2_1/c$ ;  $a = 18.141$  (8),  $b = 15.872$  (7),  $c = 7.067$  (3) Å;  $\beta = 94.38$  (2)°;  $U = 2028.9$  Å $^3$ ;  $Z = 4$ ,  $\rho(\text{calcd}) = 1.41$  g cm $^{-3}$ ;  $\mu(\text{Mo K}\alpha) = 11.51$  cm $^{-1}$ .

Cyclohept-2-enyltriphenyltin (2):  $\text{C}_{25}\text{H}_{26}\text{Sn}$  (mp 83–85 °C);  $M_r$  445.18; triclinic; space group  $P\bar{1}$ ;  $a = 11.653$  (4),  $b = 9.740$  (3),  $c = 10.252$  (4) Å;  $\alpha = 92.82$  (2)°,  $\beta = 111.14$  (4)°,  $\gamma = 99.99$  (3)°;  $U = 1074.86$  Å $^3$ ;  $Z = 2$ ;  $\rho(\text{calcd}) = 1.38$  g cm $^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 10.88$  cm $^{-1}$ .

Diffraction data were collected by using a Philips PW 1000 computer controlled four-circle diffractometer ( $\theta$ - $2\theta$  scan, at 24 °C). The structures were solved by conventional heavy-atom

Table I. Crystal Data and Details of Intensity and Structure Refinement of Cyclohex-2-enyltriphenyltin (1) and Cyclohept-2-enyltriphenyltin (2)

	1	2
mol formula	$\text{C}_{24}\text{H}_{24}\text{Sn}$	$\text{C}_{25}\text{H}_{26}\text{Sn}$
mol wt	431.15	445.18
space group	$P2_1/c$	$P\bar{1}$
cell constants		
$a$ , Å	18.141 (8)	11.653 (4)
$b$ , Å	15.872 (7)	9.740 (3)
$c$ , Å	7.067 (3)	10.252 (4)
$\alpha$ , deg		92.82 (2)
$\beta$ , deg	94.38 (4)	111.14 (4)
$\gamma$ , deg		99.99 (3)
cell vol, Å $^3$	2028.88	1074.86
$Z$	4	2
$\rho$ (calcd), g cm $^{-3}$	1.411	1.375
$\rho$ (measd), g cm $^{-3}$	1.40	1.37
radiatn	Mo $K\alpha$ (0.7107 Å; graphite monochromator)	
cryst dimens, mm	0.3 × 0.4 × 0.4	0.2 × 0.3 × 0.2
$\mu$ , cm $^{-1}$	11.51	10.88
$2\theta$ range, deg		45
decay of std reflectns	±3%	±2%
reflectns collected	3881	3808
reflectns with $I \geq 3\sigma(I)$	2413	3255
$R$ factor	0.048	0.032
$t$ , °C		24

Table II. Cyclohex-2-enyltriphenyltin (1): Fractional Atomic Coordinates ( $\times 10^4$ ) for Non-Hydrogen Atoms<sup>a</sup>

atom	$x/a$	$y/b$	$z/c$
Sn	2367 (0)	4830 (1)	2121 (1)
C(1)	1684 (3)	5579 (3)	3798 (8)
C(2)	1193 (3)	5183 (3)	4937 (8)
C(3)	754 (3)	5665 (3)	6063 (8)
C(4)	807 (3)	6542 (3)	6049 (8)
C(5)	1299 (3)	6937 (3)	4911 (8)
C(6)	1737 (3)	6455 (3)	3785 (8)
C(7)	1657 (3)	4117 (4)	130 (8)
C(8)	1964 (3)	3578 (4)	-1158 (8)
C(9)	1504 (3)	3096 (4)	-2405 (8)
C(10)	738 (3)	3152 (4)	-2364 (8)
C(11)	432 (3)	3691 (4)	-1077 (8)
C(12)	891 (3)	4174 (4)	170 (8)
C(13)	3043 (2)	5652 (4)	586 (8)
C(14)	3793 (2)	5764 (4)	1122 (8)
C(15)	4213 (2)	6317 (4)	109 (8)
C(16)	3883 (2)	6758 (4)	-1441 (8)
C(17)	3134 (2)	6646 (4)	-1977 (8)
C(18)	2713 (2)	6093 (4)	-964 (8)
C(19)	2986 (5)	3945 (6)	4011 (14)
C(20)	3453 (7)	3353 (7)	2991 (18)
C(21)	4137 (7)	3296 (11)	3326 (27)
C(22)	4585 (6)	3725 (8)	4791 (22)
C(23)	4130 (7)	4185 (7)	6306 (19)
C(24)	3418 (8)	4483 (6)	5309 (20)

<sup>a</sup>Standard deviations in parentheses.

methods. Least-squares refinement (with the phenyl rings assumed as regular rigid hexagons: C-C = 1.395, C-H = 0.96 Å,  $\angle\text{C}-\text{C}-\text{C} = \angle\text{C}-\text{C}-\text{H} = 120^\circ$ ) using anisotropic thermal parameters for all the non-hydrogen atoms converged at  $R$  values of 0.048 (for 2413 independent reflections [ $I \geq 3\sigma(I)$ ]) for 1 and 0.032 (for 3255 independent reflections [ $I \geq 3\sigma(I)$ ]) for 2, respectively. Scattering factors for the atoms were taken from Cromer and Waber,<sup>9</sup> the scattering factor for tin atoms was corrected for the real and imaginary parts of anomalous dispersion by using Cromer's values.<sup>10</sup>

A summary of collection parameters is given in Table I. Figures 1 and 2 show a perspective drawing of 1 and 2, respectively, as viewed down their Sn-C(19) bonds; atom labels are reported except for hydrogen atoms. The final positional parameters of the non-hydrogen atoms for 1 and 2 are given in Tables II and

(9) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(10) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

Table III. Cyclohept-2-enyltriphenyltin (2): Fractional Atomic Coordinates ( $\times 10^4$ ) for Non-Hydrogen Atoms<sup>a</sup>

atom	x/a	y/b	z/c
Sn	1353 (0)	1284 (0)	3192 (0)
C(1)	862 (4)	-909 (4)	2972 (5)
C(2)	-327 (5)	-1421 (5)	2208 (5)
C(3)	-664 (5)	-2818 (6)	2062 (6)
C(4)	207 (7)	-3714 (5)	2698 (7)
C(5)	1414 (6)	-3237 (5)	3482 (7)
C(6)	1765 (6)	-1826 (5)	3648 (6)
C(7)	-3339 (4)	2256 (4)	2197 (5)
C(8)	-661 (5)	2727 (5)	859 (5)
C(9)	-1768 (6)	3339 (6)	236 (6)
C(10)	-2550 (6)	3498 (6)	951 (8)
C(11)	-2244 (5)	3036 (7)	2261 (8)
C(12)	-1148 (5)	2430 (5)	2896 (6)
C(13)	2535 (4)	1657 (5)	2051 (5)
C(14)	2743 (5)	571 (5)	1254 (5)
C(15)	3500 (5)	765 (7)	496 (6)
C(16)	4091 (6)	2029 (8)	564 (7)
C(17)	3893 (6)	3121 (7)	1327 (7)
C(18)	3117 (6)	2941 (6)	2068 (6)
C(19)	2072 (5)	2021 (5)	5415 (5)
C(20)	2884 (6)	1005 (6)	6366 (6)
C(21)	4126 (6)	826 (6)	6308 (7)
C(22)	5068 (6)	2020 (8)	6849 (8)
C(23)	4851 (7)	3276 (8)	6058 (8)
C(24)	3714 (6)	3995 (6)	5835 (7)
C(25)	2577 (6)	3489 (6)	5610 (6)

<sup>a</sup>Standard deviations in parentheses.Table IV. Cyclohex-2-enyltriphenyltin (1): Selected Structural Parameters<sup>a</sup>

Bond Lengths (Å)			
Sn-C(1)	2.139 (5)	C(19)-C(20)	1.49 (2)
Sn-C(7)	2.154 (5)	C(20)-C(21)	1.26 (2)
Sn-C(13)	2.142 (6)	C(21)-C(22)	1.44 (2)
Sn-C(19)	2.189 (5)	C(22)-C(23)	1.58 (1)
		C(24)-C(19)	1.44 (1)
Bond Angles (deg)			
C(1)-Sn-C(7)	108.1 (2)	C(20)-C(19)-C(24)	112 (1)
C(1)-Sn-C(13)	108.7 (2)	C(19)-C(20)-C(21)	123 (1)
C(1)-Sn-C(19)	108.1 (3)	C(20)-C(21)-C(22)	127 (1)
C(7)-Sn-C(13)	109.0 (2)	C(21)-C(22)-C(23)	114 (1)
C(7)-Sn-C(19)	108.3 (3)	C(22)-C(23)-C(24)	107 (1)
C(13)-Sn-C(19)	114.4 (3)	C(23)-C(24)-C(19)	121 (1)
Sn-C(19)-C(20)	113.2 (7)		
Sn-C(19)-C(24)	103.7 (5)		
Torsion Angles (deg)			
C(6)-C(1)-Sn-C(19)	-55	C(19)-C(24)-C(23)-C(22)	45
C(12)-C(7)-Sn-C(19)	-63	C(24)-C(23)-C(22)-C(21)	-32
C(18)-S(13)-Sn-C(19)	-16	C(23)-C(22)-C(21)-C(20)	11
Sn-C(19)-C(20)-C(21)	121	C(22)-C(21)-C(20)-C(19)	5
		C(21)-C(20)-C(19)-C(24)	4
		C(20)-C(19)-C(24)-C(23)	-32

<sup>a</sup>Estimated standard deviations in parentheses.

III, respectively. Selected molecular geometrical parameters of 1 and 2 are reported in Tables IV and V, respectively.

All computations were carried out on a CDC Cyber 76 computer using the programmes of Sheldrick.<sup>11</sup> Thermal factors (Tables VI and VII), hydrogen atom coordinates with their thermal parameters (Tables VIII and IX), and listings of the structure factors (Tables X and XI) are deposited as supplementary material and are available from the authors on request.

## Results and Discussion

**Solid-State Structures:** Consideration of the previously obtained data<sup>6,7</sup> on 3 and 4 with the present information permits the following observations. The coordination about tin is tetrahedral (see Tables IV and V),

Table V. Cyclohept-2-enyltriphenyltin (2): Selected Structural Parameters<sup>a</sup>

Bond Lengths (Å)			
Sn-C(1)	2.162 (4)	C(25)-C(19)	1.492 (7)
Sn-C(7)	2.147 (4)	C(19)-C(20)	1.526 (7)
Sn-C(13)	2.142 (6)	C(20)-C(21)	1.489 (11)
Sn-C(19)	2.182 (5)	C(21)-C(22)	1.488 (9)
		C(22)-C(23)	1.482 (11)
		C(23)-C(24)	1.478 (11)
Bond Angles (deg)			
C(1)-Sn-C(7)	106.8 (2)	C(20)-C(19)-C(25)	117.4 (4)
S(1)-Sn-C(13)	107.6 (2)	C(19)-C(20)-C(21)	117.9 (6)
C(1)-Sn-C(19)	109.7 (2)	C(20)-C(21)-C(22)	117.1 (6)
C(7)-Sn-C(13)	108.7 (2)	C(21)-C(22)-C(23)	118.1 (5)
C(7)-Sn-C(19)	106.6 (2)	C(22)-C(23)-C(24)	119.8 (7)
C(13)-Sn-C(19)	117.0 (2)	C(23)-C(24)-C(25)	129.9 (6)
Sn-C(19)-C(20)	112.6 (4)	C(24)-C(25)-C(19)	129.2 (6)
Sn-C(19)-C(25)	110.9 (4)		
Torsion Angles (deg)			
C(6)-C(1)-Sn-C(19)	-59	C(19)-C(25)-C(24)-C(23)	-4
C(12)-C(7)-Sn-C(19)	-50	C(25)-C(24)-C(23)-C(22)	-36
C(18)-C(13)-Sn-C(19)	-39	C(24)-C(23)-C(22)-C(21)	58
Sn-C(19)-C(25)-C(24)	-90	C(23)-C(22)-C(21)-C(20)	-67
		C(22)-C(21)-C(20)-C(19)	67
		C(21)-C(20)-C(19)-C(25)	-60
		C(20)-C(19)-C(25)-C(24)	41

<sup>a</sup>Estimated standard deviations in parentheses.

although the enlargement of the  $\angle C(13)-Sn-C(19)$  angle in both 1 ( $114.4^\circ$ ) and 2 ( $117^\circ$ ) may be in response to short intramolecular contact between one phenyl ring and the cycloalkene moiety (see Figures 1 and 2). The Sn-C(phenyl) bond lengths are normal ( $2.144 \pm 0.005$  Å), but the Sn-C(allyl) bond has a value ( $2.185 \pm 0.005$  Å) which is longer than the normal average value<sup>12</sup> for Sn-C(aliphatic) ( $2.13 \pm 0.01$  Å) by ca.  $0.04-0.05$  Å. This may be associated with the operation of  $\sigma_{C-Sn}-\pi$  hyperconjugative interaction, and it is striking that in the four allyltin compounds examined structurally, the torsion angle (Sn-CH-CH=CH) lies between  $90^\circ$  and  $120^\circ$  (Tables IV and V), such angles permitting essentially the maximum conjugative mixing. In 2, the angle of  $90^\circ$  may, in part, however, result from an "outward splaying" of the C-Sn bond to relieve interactions between  $Sn(C_6H_5)_3$  and the C(21) and C(23) regions. In 4 and 2, the Sn moiety is clearly quasi-axially oriented (torsion angles above) but in 1 occupies a formal quasi-equatorial position (torsion angle of  $121^\circ$  for Sn-C(19)-C(20)-C(21), still permitting substantial conjugation but presumably best accommodating other crystal interactions. Given the other values of bond and torsion angles (e.g. C(20)-C(21)-C(22)-C(23) =  $11^\circ$  and C(21)-C(20)-C(19)-C(24) =  $4^\circ$ ), the actual distinction between quasi-axial and quasi-equatorial orientations with respect to any double bond interaction with  $\sigma_{C-Sn}$  is a fine one. However, the torsion angle Sn-C(19)-C(24)-C(23) in 2 differs drastically from the two orientations, and this is relevant to the magnitude of  $^3J_{Sn-C(23)}$  for example, to be discussed later. Definite manifestations of the  $\sigma-\pi$  effect in the acyclic 3<sup>6</sup> were associated with a widening of the  $\angle C-C=C$  angle ( $\sim 140^\circ$ ) and a shortening of the C-C ( $1.37$  Å) and C=C ( $1.26$  Å) bonds. For cyclic analogues, the suggestion has been made that structural consequences of such conjugation could be masked by "ring closure effects",<sup>13,14</sup> and no similar bond

(12) This value is estimated from X-ray structural data of tetrahedral organostannanes of the last 10 years as quoted in: *Dictionary of Organometallic Compounds*; Chapman and Hall: London, 1984; supplements 1 and 2. See also; Cusack, P. A.; Smith, P. J.; Donaldson, J. D.; Grimes, S. M. *Bibliography of X-ray Crystal Structures of Tin Compounds*; I.T.R.I. Publication No. 588, 1980.

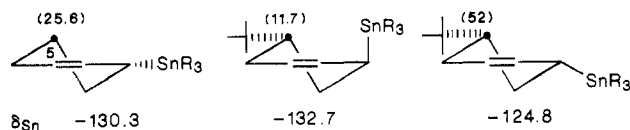
(11) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination; Cambridge University: Cambridge, England, 1975.

or angle alterations were in fact observed for 4. However, as ring size increases, it is reasonable to suppose that such closure requirements will be less severe and in 2  $\angle C(19)-C(25)=C(24)$  is nearly  $130^\circ$ , as is  $\angle C(25)=C(24)-C(23)$ . The lengthening of the Sn-C(19) allyl bond may be a more reliable indicator of the effect of hyperconjugation<sup>13-15</sup> on these structures, and this occurs in 1, 2, and 3 but was not obvious for 4 which, besides being a less rigid molecule, had the highest level of indetermination due to thermal disorder. Such an effect has, however, been noted for  $(C_6H_5)_3Sn-CH_2-C(CH_3)=CH_2$ .<sup>16</sup>

Comparing the structural data of 1 and 2 with those of 3 and 4,<sup>6,7</sup> it is clear that the average thermal factors of the carbon atoms of the allyl group and the cycloalkenyl group decrease sensibly and regularly with their increasing bulkiness, i.e.  $U_{eq} = 0.18, 0.16, 0.12,$  and  $0.08 \text{ \AA}^2$ , for 3, 4, 1, and 2, respectively, showing that the higher the steric encumbrance, the lower the libration about the Sn-C(allyl) bond. Such increasing bulkiness will presumably stabilize one of the two paddlewheel (left- and right-handed) configurations of the  $(C_6H_5)_3Sn$  groups, explaining the absence of two diastereomeric molecular forms in the same crystal for 1 and 2 but presence<sup>6,7</sup> in 3 and 4.

**Solid-State  $^{13}C$  NMR (MAS) Measurements.** The finding that the tin moiety in 1 was formally quasi-equatorial (given the caveats expressed above) prompted the acquisition of solid-state  $^{13}C$  NMR spectra, in the hope that observation of  $^3J_{Sn-C}$  (i.e. vicinal Sn-C coupling, known to have a strong dihedral angle dependence)<sup>17</sup> in the solid could be compared with similar values from solution spectra. Satisfactorily resolved  $^{13}C$  spectra were obtained from 1, 2, and 4 but regrettably we could not identify any Sn-C coupling. There was no duplication of resonances for either the cycloalkenyl ring or the phenyl groups in any of the three stannanes. Harris and Sebal<sup>18</sup> have reported the CP MAS solid-state  $^{119}Sn$  and  $^{13}C$  NMR spectra of 3, and two  $^{119}Sn$  signals ( $\Delta\delta = 17.9$  ppm) were observed, presumably corresponding to the two crystallographically independent molecules. However, the solid-state  $^{13}C$  spectrum of 3 (overnight accumulation) did not allow the identification of any  $^nJ_{Sn-^{13}C}$ , a situation we encountered for 1, 2, and 4. However, solid-state  $^{119}Sn$  measurements for these latter compounds may be worthwhile.

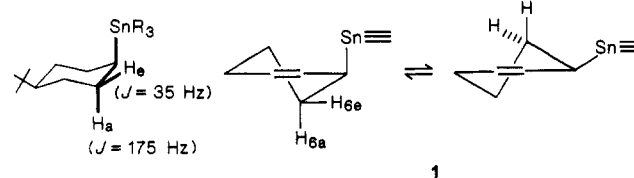
**Solution NMR Measurements. Cyclohex-2-enyltriphenylstannane (1).** The first indication that the tin moiety in 1 (in solution) was preferentially quasi-axial resulted from  $^{119}Sn$  chemical shifts (ppm) which are shown below



(relative to internal  $(CH_3)_4Sn$ ;  $CDCl_3$  solvent;  $R = C_6H_5$ ). On the basis that the *trans* 5-*tert*-butyl compound overwhelmingly must have a quasi-axial tin group and the *cis* 5-*tert*-butyl a quasi-equatorial group and that no serious deformations are present; 1 appears to prefer the quasi-axial orientation for  $SnR_3$  (ca. 70%).  $^{13}C$  NMR measurements supported this conclusion, and in particular

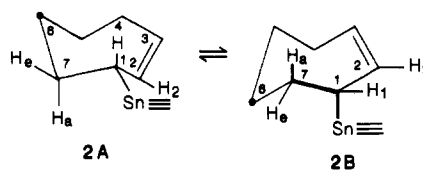
$^3J_{Sn-C} = 25.6$  Hz (to  $C_5$ ) required<sup>8,17</sup> a quasi-axial preference when the indicated values of 11.7 and 52 Hz are considered for the *cis* and *trans* 5-*tert*-butyl compounds.

High-field  $^1H$  NMR measurements completely support the conclusion that the equilibrium content at ca.  $300^\circ C$  is ca. 2-4 in favor of the axial form. The easily located  $>CHSn$  signal ( $\delta$  2.89 ( $^2J_{Sn-H} = 87.5$  Hz)) exhibited  $W_{1/2} \approx 13.5$  Hz, closer to that for the *trans* (11.3 Hz) than the *cis* (22.9 Hz) 5-*tert*-butyl derivatives. Nevertheless, the generally compressed nature of the high-field part of the spectrum (with, for example, little chemical shift difference between  $H_{ax}$  and  $H_{eq}$  at  $\delta$  1.65) suggests comparable populations of two (or more) conformations. Irradiation at  $\delta$  1.65 ( $H_{5eq}$ ) reveals two "AB" patterns associated with the allylic protons ( $H_{4a}, H_{4e}$ ) and ( $H_{6a}, H_{6e}$ ), the latter being vicinal to tin and therefore, in principle, being accompanied by satellites due to  $^3J_{Sn-H}$ , known to have a strong dihedral angle dependence,<sup>19</sup> as shown below for



(*cis*-4-*tert*-butylcyclohexyl)triphenylstannane.<sup>20</sup> Thus, in the conformational equilibrium of 1,  $H_6$ , when *trans* diaxial to Sn, would experience a large coupling ( $\sim 165$  Hz), whereas in the alternative conformer with equatorial Sn- $(C_6H_5)_3$ , both  $H_6$ , with small dihedral angles relative to C(1)-Sn, would have  $^3J \approx 30$  Hz. (These values have been reduced from those of the cyclohexylstannane because of the different angles). The largest measured coupling to  $H_6$  is ca. 100-110 Hz, indicating  $K \approx 1$  for the above equilibrium. Hence, solution NMR measurements confirm that for 1, there is a definite axial preference for  $Sn(C_6H_5)_3$ , although this represents a small energy difference ( $\sim 400$  cal at 300 K) between the two conformations. The change in preferred orientation of the tin group in the crystal (formal quasi-equatorial) from that in solution is thus easily acceptable.

**Cyclohept-2-enyltriphenylstannane (2).** Information available for cycloheptenyl derivatives suggested that the general chair geometry was favored,<sup>21</sup> and we based our early considerations of 2 in terms of the following:



In the  $^{13}C$  NMR spectrum, C(6) resonated at 31.8 ppm with  $^3J_{Sn-C} = 25$  Hz, a value inconsistent<sup>17</sup> with a predominance of 2a but more or less consistent with 2B, on the basis of the known<sup>17</sup> angular dependence of  $^3J_{Sn-C}$ . Although 2b has one formal 1,3-diaxial Sn-H6a interaction, it escapes the severe 1,2 interaction between Sn and  $H_2$  in 2a, in which the C-Sn and  $C_2H_2$  bonds are virtually eclipsed, and also gains from any  $\sigma_{C-Sn}-\pi$  conjugation, now a recognized and crucial feature affecting conformations and geometry in ( $\sigma$ -allyl)metal compounds.<sup>15</sup> That the general features of 2B describe the preferred conformation

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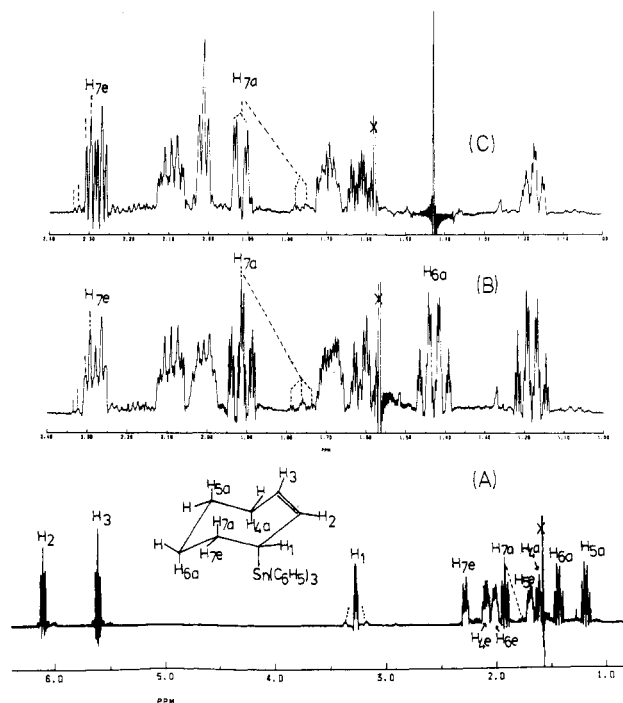
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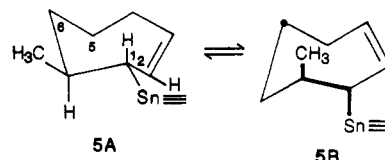
**Figure 3.** (A) The 500-MHz  $^1\text{H}$  NMR spectrum of cyclohept-2-enyltriphenylstannane ( $\text{CDCl}_3$  solvent) showing assignments based on decoupling experiments.  $^{117,119}\text{Sn}$  couplings to  $\text{H}_1$  and  $\text{H}_{7a}$  (high-field side) are indicated. (Aromatic resonances have been omitted.) (B) Expansion of high-field region of spectrum, with  $^{117,119}\text{Sn}$  couplings to  $\text{H}_{7e}$  and  $\text{H}_{7a}$  indicated. (Some resolution of the separate  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  couplings to  $\text{H}_{7a}$  is evident.) (c) Irradiation of  $\text{H}_{6a}$  and the effect on  $\text{H}_{7a}$  and  $\text{H}_{7e}$  and their attendant  $^{117,119}\text{Sn}$  satellites.

of 2 was confirmed by 400-MHz (and later 500-MHz)  $^1\text{H}$  NMR studies. The general "spread" of the high-field protons (from  $\delta$  1.0 to  $\delta$  2.4) was not indicative of interconversion between conformations of comparable populations but rather of an extremely lopsided conformational profile. Straightforward decoupling experiments and consideration of chemical shifts and coupling constants required a structure approximating to 2B to be heavily predominant if not virtually exclusive in solution. The  $^1\text{H}$  spectrum was completely assigned and reproduced in Figure 3. The chief aspects requiring 2B are as follows: (i)  $J_{\text{H}_1-\text{H}_2} \approx 8$  Hz is consistent with the almost eclipsed arrangement of  $\text{H}_1$  and  $\text{H}_2$  in 2B whereas in 2A a much smaller  $J$  value would be expected; (ii) irradiation of  $\text{H}_1$  ( $\delta$  3.25 ( $J_{\text{Sn}-\text{H}} = 96$  Hz)) removes a very small coupling only from  $\text{H}_{7a}$ , showing these protons have not a *trans*-diaxial arrangement as present in 2A; (iii)  $\text{H}_{7a}$  is a triplet ( $J \approx 13.5$  Hz with superimposed smaller couplings as required by 2B, whereas in 2A,  $\text{H}_{7a}$  would experience three large couplings ( $\text{H}_{7e}$ ,  $\text{H}_1$ ,  $\text{H}_{6a}$ ).

The conclusion that 2B is overwhelmingly preferred in solution has the consequence that  $^{119}\text{Sn}$  coupling (i.e.  $^3J_{\text{Sn}-\text{H}}$ ) should be quite large<sup>19</sup> to one of the 7-protons, whereas in 2A both 7-protons would exhibit relatively small couplings. (Estimated dihedral angle for  $\text{Sn}-\text{C}(1)-\text{C}(7)-\text{H}(7a) \approx 165-170^\circ$  and for  $\text{Sn}-\text{C}(1)-\text{C}(7)-\text{H}(7e) \approx 85^\circ$  for an undistorted chair). In the 400-MHz  $^1\text{H}$  spectrum (particularly when  $\text{H}_{6a}$  or  $\text{H}_{7e}$  are decoupled) tentative identification of  $^{119,117}\text{Sn}$  satellites about  $\text{H}_{7a}$  (on the high-field side) was made, providing  $^3J_{\text{Sn}-\text{H}} = 150-160$  Hz. The spectrum was also obtained at 500 MHz (Figure 3), and the greater dispersion allowed unambiguous identification of the high-field set of  $^{119,117}\text{Sn}$  satellites, which change from a general "triplet" appearance to a "doublet"

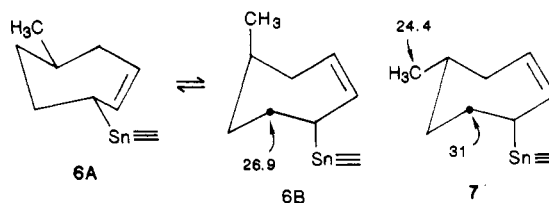
on irradiation of  $\text{H}_{6a}$ . The value of  $^3J_{\text{Sn}-\text{H}_{7a}} \approx 155$  Hz and indicates a dihedral angle of  $\sim 180^\circ$ , based on values of  $^3J_{\text{Sn}-\text{D}} \approx 20-22$  Hz for  $\sigma = 180^\circ$  for trialkylstannanes.<sup>19</sup> For an undistorted chair cycloheptene, the relevant  $\phi \approx 160^\circ$ , and the large value of  $^3J_{\text{Sn}-\text{H}}$  observed suggests an outward "splaying" of the Sn group which increases this angle toward  $180^\circ$  and places the C-Sn bond nearly orthogonal to the double bond, as in the crystal.  $^3J_{\text{Sn}-\text{H}_{7a}}$  is ca. 30-32 Hz, a value also indicating some outward splaying of the tin group, for otherwise  $\text{Sn}-\text{C}(1)-\text{C}(7)-\text{H}(e) \approx 90^\circ$ , with an expected much smaller value for this coupling. Thus the highly preferred, if not exclusive, conformation incorporates a quasi-axial tin group in a slightly distorted chair arrangement.

Similar NMR examinations show cyclohept-2-enyltrimethylstannane to prefer an arrangement with a quasi-axial tin group also. For example,  $^3J_{\text{Sn}-\text{H}_{7a}} \approx 130$  Hz, which was consistent with the  $^1\text{H}$ -coupled  $^{119}\text{Sn}$  spectrum (with decoupling of the methyl groups). This strong preference appears to be necessary to explain some NMR features of certain methyl-substituted cyclohept-2-enyltrimethylstannanes.<sup>5,22</sup> For example, the *trans* 7-methyl derivative 5 has spectral properties that cannot be reconciled with a predominantly diequatorial conformation below.



The DEPT spectrum revealed the C- $\text{CH}_3$  (21.06 ppm) and one  $\text{CH}_2$  group (22.16 ppm) to be at unusually high field (in other isomers of this series, predominantly equatorial C- $\text{CH}_3$  have  $\delta$  24.0) suggesting a significant role for 5B with axial C- $\text{CH}_3$  and steric  $\gamma$ -shielding of C(5). That 5B was predominant was confirmed by the large  $^3J_{\text{Sn}-\text{C}}$  to C- $\text{CH}_3$  (48 Hz), requiring a large average dihedral angle. The lower energy of 5B is explicable in terms of gauche (or nearly eclipsing) interactions between  $\text{Sn}(\text{CH}_3)_3$  and  $\text{CH}_3$  and also  $\text{H}_2$  in 5A. These are relieved in 5B which gains from  $\sigma-\pi$  conjugation but has a destabilizing gauche-butane fragment.

Similar considerations apply to the *trans* 5-methyl isomer 6 shown below:



The C- $\text{CH}_3$  shift of 21.1 ppm is to higher field of that for the *cis* isomer 7 (24.4 ppm) and also the C(7) shift (26.9 ppm) when compared with C(7) (31.0 ppm) in 7 which can be adequately described in terms of the conformation drawn. These are the expected consequences of a substantial intervention by 6B in the equilibrium.

These studies demonstrate that tin moieties in both cyclohex-2-enyl and particularly cyclohept-2-enyl systems prefer a quasi-axial orientation in solution and also clearly in the crystal for cyclohept-2-enyltriphenylstannane. These findings are relevant to the highly preferred  $\gamma$ -anti mode of electrophile delivery in cyclohept-2-enyl systems,<sup>5,22</sup> as  $\sigma-\pi$  activation of the  $\gamma$ -anti site operates most

efficiently when the C-Sn bond is orthogonal to the  $\pi$ -system.<sup>15</sup> Studies of medium ring systems incorporating metal substituents are currently being examined structurally and mechanistically, and these will be reported at a later date.

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to Professor David St. C. Black, University of New South Wales, for the acquisition of the 500-MHz NMR spectrum.

**Registry No.** 1, 14540-08-0; 2, 118893-17-7; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnLi, 4167-90-2; cyclohept-2-enyl chloride, 35021-99-9.

**Supplementary Material Available:** Tables of thermal parameters and hydrogen atom coordinates for 1 and 2 (4 pages); listings of structure factors for 1 and 2 (35 pages). Ordering information is given on any current masthead page.

## Preparation, Characterization, and Structural Analyses of [Rh(chp)(NBD)]<sub>2</sub> and [Rh(chp)(NBD)]<sub>2</sub>(PF<sub>6</sub>). Isolation of a Paramagnetic d<sup>7</sup>-d<sup>8</sup> Binuclear Radical and Its d<sup>8</sup>-d<sup>8</sup> Precursor

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Single-crystal X-ray studies of [Rh(chp)(NBD)]<sub>2</sub> and its one-electron oxidation product [Rh(chp)(NBD)]<sub>2</sub>PF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub> (chp = 6-chloro-2-hydroxypyridinate; NBD = norbornadiene) have been completed. Crystal data for [Rh(chp)(NBD)]<sub>2</sub> at 22 °C: space group *P*2<sub>1</sub>/*c*; *Z* = 4; *a* = 14.639 (2) Å, *b* = 10.483 (3) Å, *c* = 15.271 (3) Å,  $\beta$  = 103.04 (2)°, *V* = 2283 (2) Å<sup>3</sup>; *R* = 0.024, *R*<sub>w</sub> = 0.034 for 3784 reflections with *F*<sub>o</sub><sup>2</sup> >  $\sigma$ (*F*<sub>o</sub><sup>2</sup>). Crystal data for [Rh(chp)(NBD)]<sub>2</sub>PF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub> at -72 °C: space group *P* $\bar{1}$ ; *Z* = 2; *a* = 10.160 (4) Å, *b* = 12.770 (5) Å, *c* = 13.129 (7) Å,  $\alpha$  = 75.70 (4)°,  $\beta$  = 68.39 (4)°,  $\gamma$  = 67.94 (3)°, *V* = 1456.0 (1.1) Å<sup>3</sup>; *R* = 0.061, *R*<sub>w</sub> = 0.060 for 3237 reflections with *F*<sub>o</sub><sup>2</sup> >  $\sigma$ (*F*<sub>o</sub><sup>2</sup>). [Rh(chp)(NBD)]<sub>2</sub> contains two square-planar Rh(I) units that intersect with a dihedral angle of 49° bridged by two hydroxypyridinate ligands. The molecule is structurally similar to the previously characterized [Rh(mhp)(COD)]<sub>2</sub> (mhp = 6-methyl-2-hydroxypyridinate; COD = 1,5-cyclooctadiene). The Rh-Rh distance is relatively short (3.040 (1) Å) for d<sup>8</sup>d<sup>8</sup> complexes, which is consistent with our observations of a low-energy d $\sigma^*$  → p $\sigma$  electronic spectral band and its ease of oxidation. Addition of AgPF<sub>6</sub> to CH<sub>2</sub>Cl<sub>2</sub> solutions produces the stable d<sup>8</sup>d<sup>7</sup>, mixed-valence complex [Rh(chp)(NBD)]<sub>2</sub>PF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>. This complex is paramagnetic ( $\mu_{\text{eff}}$  = 1.76  $\mu_{\text{B}}$ ; EPR *g*<sub>1</sub> = 2.08, *g*<sub>2</sub> = 2.21, and *g*<sub>3</sub> = 2.25) and shows a broad signal for *g*<sub>1</sub> that is consistent with two equivalent Rh(I<sup>1/2</sup>) atoms. The crystal structure of the d<sup>8</sup>d<sup>7</sup> radical indicates that its geometry is similar to the d<sup>8</sup>d<sup>8</sup> parent, but the Rh-Rh distance is considerably shorter (2.819 (1) Å). The shortening of the Rh-Rh distance is consistent with the 1/2 bond order expected for a (d $\sigma$ )<sub>2</sub>(d $\sigma^*$ )<sup>1</sup> electronic configuration in the radical.

### Introduction

Binuclear complexes of rhodium and iridium undergo facile redox reactions that implicate them as catalytic electron-transfer agents.<sup>1</sup> Binuclear systems previously studied are capable of one- or two-electron oxidations that generate d<sup>7</sup>-d<sup>8</sup> radical species,<sup>2,3</sup> or d<sup>7</sup>-d<sup>7</sup> binuclear complexes.<sup>4-6</sup> Our previous studies have demonstrated that the thermodynamics of electron transfer are sensitive to factors such as structural changes and medium effects,<sup>7</sup> but the precise nature of these effects is largely unexplored.

Previous work<sup>8-11</sup> has centered on the properties of the d<sup>8</sup>-d<sup>8</sup> complexes rather than the less stable, radical reaction intermediates. The combination of chp (chp = 6-chloro-2-hydroxypyridinate) as the bridging ligand and NBD (NBD = norbornadiene) has allowed the synthesis and structural examination of a reduced d<sup>8</sup>-d<sup>8</sup> binuclear and the corresponding oxidized d<sup>8</sup>-d<sup>7</sup> radical with identical ligation. This pair of complexes allows the influence of oxidation state on the metal-metal and metal-ligand interactions to be investigated.

### Experimental Section

**General Considerations.** All synthetic procedures were carried out under an atmosphere of purified N<sub>2</sub> by using standard

Schlenk techniques. Solvents used were of spectroscopic grade and used without further purification unless otherwise noted. Protonated hydroxypyridinates, cyclooctadiene, norbornadiene, AgPF<sub>6</sub>, and AgBF<sub>4</sub> were purchased from Aldrich Chemical Co. The hydroxypyridines were converted to their corresponding sodium salts with sodium methoxide in methanol. [Rh(NBD)Cl]<sub>2</sub> was prepared by a published procedure.<sup>12</sup> NMR spectra were recorded on a Nicolet NT-300 WB instrument. Proton chemical shifts are reported relative to Si(CH<sub>3</sub>)<sub>4</sub>. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ).

**Synthesis.** [Rh(chp)(NBD)]<sub>2</sub>. A solution of 0.5454 g of AgBF<sub>4</sub> (2.80 × 10<sup>-3</sup> mol) and 0.6460 g (1.40 × 10<sup>-3</sup> mol) of [Rh-

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