

It is hoped that the work presented here will lead to experimental investigations of a direct mechanism for $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ nucleophilic substitution. Such a mechanism may become more important as the heat of reaction becomes more exothermic. The rotational temperature dependence of the substitution cross section may provide one diagnostic for the direct mechanism.

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Registry No. Cl^- , 16887-00-6; CH_3Cl , 74-87-3.

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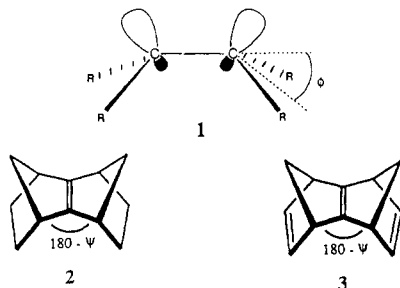
A Shelf-Stable *syn*-Sesquinorbornatriene. An Extreme Example of a Crystallographically Determined π -Pyramidalization Angle¹

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Recent research activity has added considerably to our understanding of alkene pyramidalization and to our ability to prepare molecules having olefin geometries that deviate appreciably from the norm.³ Theoretical calculations indicate the p orbitals of C-C π bonds deformed in this manner to be transformed into hybrid orbitals that are not as well aligned for π bonding as are pure p orbitals.⁴⁻⁶ Accordingly, chemical reactivity increases rapidly in proportion to the extent of structural deformation depicted in **1**. As a consequence, X-ray data have been acquired for only a select few pyramidalized alkenes whose reactivity levels are not overly intensified.⁷⁻⁹



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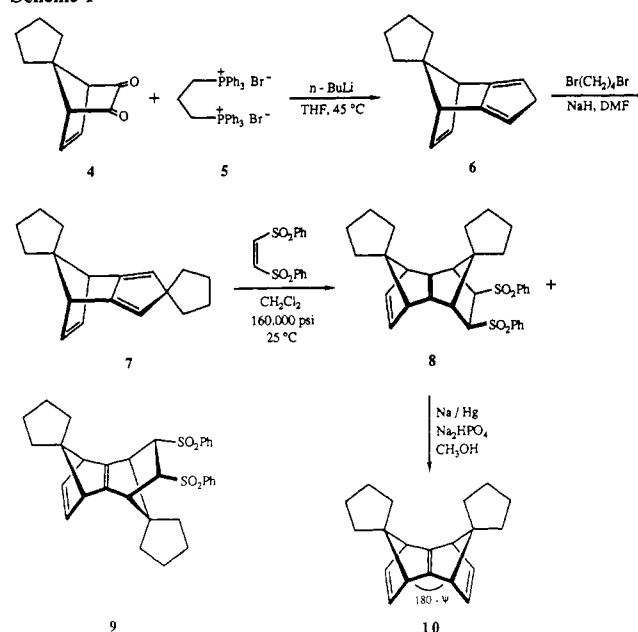
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Scheme I



Our efforts in this area have been directed to *syn*-sesquinorbornene (**2**) and its dehydro analogues. Whereas derivatives of **2** experience substantial hinge-like bending in an endo direction ($\psi = 16-18^\circ$),¹⁰ introduction of a second (peripheral) double bond has the effect of enhancing the level of downward folding to approximately 21° .^{11,12b} Removal of the last two protons to produce *syn*-sesquinorbornatriene (**3**) has been accomplished,¹² and certain of its spectral properties have been determined.¹³ However, the high reactivity of **3** has so far precluded experimental definition of the extent of π -pyramidalization at its central double bond, conjectured to be the most extreme attainable under normal circumstances within a norbornadiene skeleton.¹²

We describe herein the preparation and crystallographic analysis of the first stable *syn*-sesquinorbornatriene (**10**). Since **3** is particularly subject to exo attack by atmospheric oxygen at its internal unsaturated linkage, approach from this face had to be sterically impeded. However, the intent was not to encumber the target molecule to such an extent that structural deformation beyond that already embodied in **3** would materialize concurrently.

To this end, bis-Wittig condensation of the known diketone **4**¹⁴ with the double phosphonium salt **5** according to precedent^{10c,15} afforded **6** (30%). This colorless oil¹⁶ was spiroalkylated with 1,4-dibromobutane and sodium hydride in DMF¹⁷ to give **7** (40%). Diels-Alder addition of (Z)-1,2-bis(phenylsulfonyl)ethylene¹⁸ to

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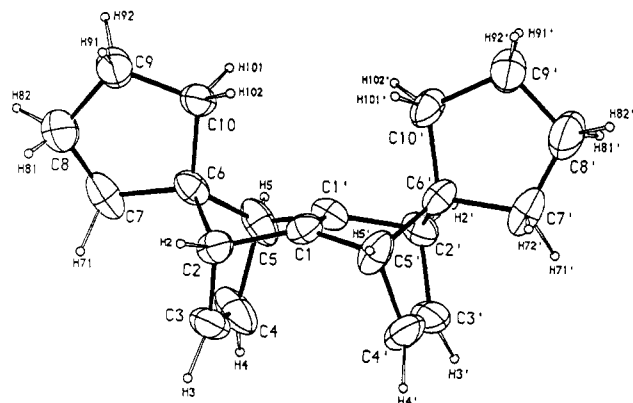


Figure 1. Computer-generated perspective drawing of the final X-ray model of **10**. The non-hydrogen atoms are represented by 30% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

7 was conducted in dichloromethane solution at ambient temperature in a high pressure reactor at 160000 psi for 6 days. These conditions furnished a chromatographically separable mixture of **8** (77%) and **9** (11%), the relative stereochemistries of which were distinguished by ^1H NMR spectroscopy.¹² Reductive desulfonylation¹⁹ of syn adduct **8** gave rise to **10** (47%). Following recrystallization of this hydrocarbon from methanol in open vessels, large clear crystals were obtained that melted at 86 °C. The C_{2v} symmetry of this molecule is clearly apparent from its ^1H [CDCl_3 δ 6.29 (t, J = 1.7 Hz, 4 H), 3.19 (t, J = 1.7 Hz, 4 H), 1.84–1.44 (m, 16 H)] and ^{13}C NMR spectra [CDCl_3 172.00, 141.31, 90.46, 59.94, 34.23 (2C), 26.10, 25.40 ppm]. Of particular note is the highly deshielded chemical shift of the central olefinic carbons (172.00 ppm), which falls within experimental error of the value recorded for the same atoms in **3** (172.14 ppm).¹² On this basis, the two molecules seemingly share a close conformational relationship.

Examination of the X-ray diffraction pattern for **10** obtained at -45 °C indicated it to be monoclinic [space group $C2/c$ (no. 15)] and to have a 2-fold crystallographic axis. The unit cell parameters are a = 21.004 (7) Å, b = 7.782 (2) Å, c = 9.970 (2) Å, and β = 114.28 (2)°. The structure was solved by MULTAN 11/82,²⁰ the final refinement cycle for 730 unique reflections with $I > 3\sigma(I)$ resulting in 91 variable parameters (the non-hydrogen atoms were refined anisotropically). A clear disorder of the atoms C3, C4, and C8 was apparent. The final X-ray model shown in Figure 1 is the result of agreement indices R_f 0.083 and R_w 0.116. The dihedral angle and nonbonded contacts were determined by CHEM-X.

These results show that **10** has a central flap angle of 157.3 (4)° (ψ = 22.7 (5)°), a record deformation level for these systems.²¹ The relevant pyramidalization angle ϕ (see **1**) is 32.4°.²² Adoption of this equilibrium geometry has the effect of positioning the key methylene protons on the exo surface (H101–H102') at a closer distance (3.001 Å) than either the trigonal carbons (C3–C4' and C3'–C4 = 3.442 Å) or the vinylic hydrogens (H3–H4' and H4–H3' = 3.790 Å) present on the endo surface. The relatively small size of the "hole" extant above the π system clearly contributes in a significant way to the greatly attenuated reactivity of this triene.

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(22) As defined in ref 3: $\cos \phi = -\cos(R-C-C)/\cos \frac{1}{2}(R-C-R)$.

Noteworthy, **10** exhibits no sensitivity to atmospheric oxygen under normal circumstances. Nor is reaction seen between **10** and buffered (NaHCO_3) *m*-chloroperbenzoic acid in dichloromethane at room temperature during 24 h.²³ The unreactivity of the triene is further reflected in its total inertness to both phenyl azide (CH_2Cl_2 , room temperature, 2 days) and diazomethane (Et_2O , 0 °C/4 h $\rightarrow$ room temperature/16 h).

At 32.4°, the ϕ value for **10** is seen to exceed that of 9,9',10,10'-tetrahydrodianthracene (19.7°),⁷ tricyclo-[4.2.2.2^{2,5}]dodeca-1(2),5(6)-diene (**11**, 27.3°),⁸ and the methiodide of 10-selenatricyclo[3.3.3.0^{3,7}]undec-3(7)-ene (20.3° and 12.3°).⁹ Molecules such as **11** do indeed have larger ψ values (e.g., 35.6°) which are however counteracted by a markedly widened C–C–(sp²)–C angle.

In light of the kinetic stability of **10**, prospects for the utilization of steric screening to gain access to chemically persistent alkenes having still greater levels of pyramidalization seem bright.

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Supplementary Material Available: Tables of crystallographic data, bond distances and angles, positional parameters, and anisotropic thermal parameters for **10** (6 pages); tables of observed and calculated structure factors for **10** (8 pages). Ordering information is given on any current masthead page.

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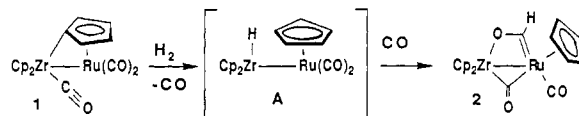
A New Synthesis of Rhenium–Carbene Complexes from the Reaction of $\text{Cp}(\text{CO})_2\text{ReH}^-$ with $\text{Cp}_2\text{Zr}(\eta^2\text{-COR})\text{Cl}$

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Previously we had discovered that the reaction of the zirconium–ruthenium compound **1** with H_2 led to the reduction of coordinated CO and formation of the zirconoxycarbene complex of ruthenium **2**.¹ The reaction was suggested to proceed by hydrogenolysis of the strained Zr–C₃H₄ bond of **1** to give a reactive zirconium hydride intermediate A. The product ruthenium–carbene complex **2** was inert to further reduction by H_2 .



Since the rearrangement of metal–carbene–hydride complexes to metal–alkyl complexes is a facile and well-studied process,² it seemed likely that a zirconoxycarbene–metal complex might be further reduced if a hydride were present on the same metal as the carbene ligand. In an effort to prepare such a complex, we have studied the reaction of the η^2 -acylzirconium compounds $\text{Cp}_2\text{Zr}(\eta^2\text{-COR})\text{Cl}$ (**3**, R = CH₃; **4**, R = CH₂CH₂CMe₃) with the rhenium hydride anion $\text{K}^+\text{Cp}(\text{CO})_2\text{ReH}^-$ **5**. It appeared plausible that formation of a Re–Zr bond in intermediate B might occur and that acyl migration from zirconium to rhenium might

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