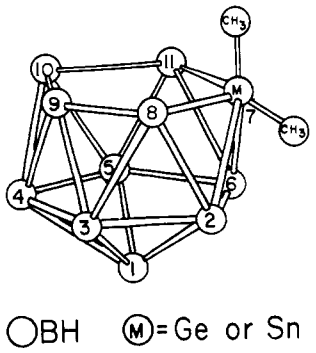

Figure 2. A possible structure for $(CH_3)_2MB_{10}H_{12}$.

2,4 borons of $B_{10}H_{14}$ (and derivatives)[8] suggests that the $(CH_3)_2Ge$ or $(CH_3)_2Sn$ group occupies a cage position such that a plane of symmetry and the equivalence of the 2,4 borons is maintained. The 60.0- and 100-MHz ^1H nmr spectra exhibit broadly spaced peaks due to terminal hydrogens on boron (area 10) and a broad singlet (area 2) at δ 5.4 ppm[9] due to bridge protons. In addition, two sharp singlet peaks of area 3 each at δ -0.46 and -0.27 ppm for $(CH_3)_2GeB_{10}H_{12}$ and δ $+0.13$ and -0.17 ppm for $(CH_3)_2SnB_{10}H_{12}$ are seen. In the latter case, the tin satellite peaks expected for the $(CH_3)_2Sn$ moiety are present, demonstrating conclusively that the methyl groups are bonded to the tin and not to cage boron atoms.

A possible structure for the new germa- and stannaundecaboranes inferred from the above data is shown in Figure 2. Assuming a rearrangement of the boron cage does not occur in the reaction, it seems plausible to describe the compounds as 7-substituted $(CH_3)_2Ge$ or $(CH_3)_2Sn$ undecaboranes. The methyl groups on the group IV element lie on a plane of symmetry in positions exo and endo relative to the open face of the nido 11-atom fragment. Data which allow assignment of the positions of the two bridging hydrogens are not yet available; however, they may reside in 8-9 and 10-11 positions analogous to that suggested for $B_{10}H_{12}$–transition metal complexes.[10,11]

Preliminary reactions of $(CH_3)_2SnB_{10}H_{12}$ have been carried out which support the structure postulated above. Reaction with HCl yields $(CH_3)_2SnCl_2$ and $B_{10}H_{14}$ in >95% yield.

$$(CH_3)_2SnB_{10}H_{12} + 2HCl \longrightarrow (CH_3)_2SnCl_2 + B_{10}H_{14}$$

An analogous reaction using DCl yields μ-$B_{10}H_{12}D_2$. Attempts to deprotonate $(CH_3)_2SnB_{10}H_{12}$ to form the conjugate base anions have so far been unsuccessful. Treatment with aqueous $(CH_3)_4NOH$ solutions results in the formation of mixtures of $(CH_3)_4NB_{10}H_{13}$ and $(CH_3)_4NB_{10}H_{15}$.

Further studies of the mechanism by which the CH_3 group is cleaved from $(CH_3)_3Ge$– and $(CH_3)_3Sn$– moieties in the formation reactions are in progress. The chemistry of the new group IV substituted boranes and other reactions in which they might form are being investigated and will be reported later.

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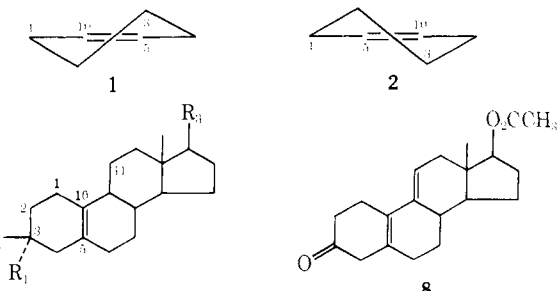
(11) N. N. Greenwood and D. N. Sharrocks, *J. Chem. Soc. A*, 2334 (1969).

The Crystal Structure of a 5(10)-Unsaturated 3-Keto Steroid. The Conformation of Ring A[1]

Sir:

The half-chair cyclohexene[2] conformation **1** has been proposed[3] as the low-energy form of ring A in 5(10)-unsaturated steroids in order to account for (a) the stereoselective LiAl(*O-tert*-Bu)$_3$H reduction of the 3-ketone **3** leading to the 3α- and 3β-alcohols **6** and **7** in 7:1 molar ratio and (b) the nmr spectral characteristics of the epimeric 3-alcohols and 3-azides in the respective C-3 proton regions.[4] On the other hand, similar



3, $R_1 = R_2 = O$; $R_3 = O_2CC_2H_5$
4, $R_1 = R_2 = O$; $R_3 = O_2CCH_2I$
5, $R_1 = R_2 = O$; $R_3 = OH$
6, $R_1 = OH$; $R_2 = H$; $R_3 = O_2CC_2H_5$
7, $R_1 = H$; $R_2 = OH$; $R_3 = O_2CC_2H_5$

experiments[5] starting with the estra-5(10),9(11)-dien-3-one (**8**) have led to the conclusion that conformational preference in ring A of this system is very weak, though in the same direction. These results have recently provided a testing ground for semiempirical calculations of equilibrium geometry employing advanced computer methods.[6] It was calculated that ketone **3** should exist in the half-chair form **1**, favored by 0.9 kcal/mol over the alternative half-chair **2**. Ketone **8** was predicted to favor conformer **2**, but by only 0.3 kcal/mol. We have now found that the conformation of the 5(10)-unsaturated 3-ketone **4** *in the crystalline state* entails not a half-chair but a *semiplanar*[2] form of

(1) This work was supported by the U. S. Public Health Service under Grant No. AMO9279.
(2) For a resumé of the current status of conformational analysis of cyclohexene and its derivatives, see: F. R. Jensen and C. H. Bushweller, *J. Amer. Chem. Soc.*, **91**, 5774 (1969).
(3) (a) S. G. Levine, N. H. Eudy, and E. C. Farthing, *Tetrahedron Lett.*, 1517 (1963); (b) S. G. Levine, N. H. Eudy, and C. F. Leffer, *J. Org. Chem.*, **31**, 3995 (1966).
(4) Additional evidence for the preferred half-chair **1** was obtained in a study of 5(10)-estrene-2,3-*cis*-diols: S. G. Levine, D. M. Feigl, and N. H. Eudy, *Tetrahedron Lett.*, 4615 (1967).
(5) S. G. Levine and N. H. Eudy, *J. Org. Chem.*, **35**, 549 (1970).
(6) N. C. Cohen, *Tetrahedron*, 27, 789 (1971).

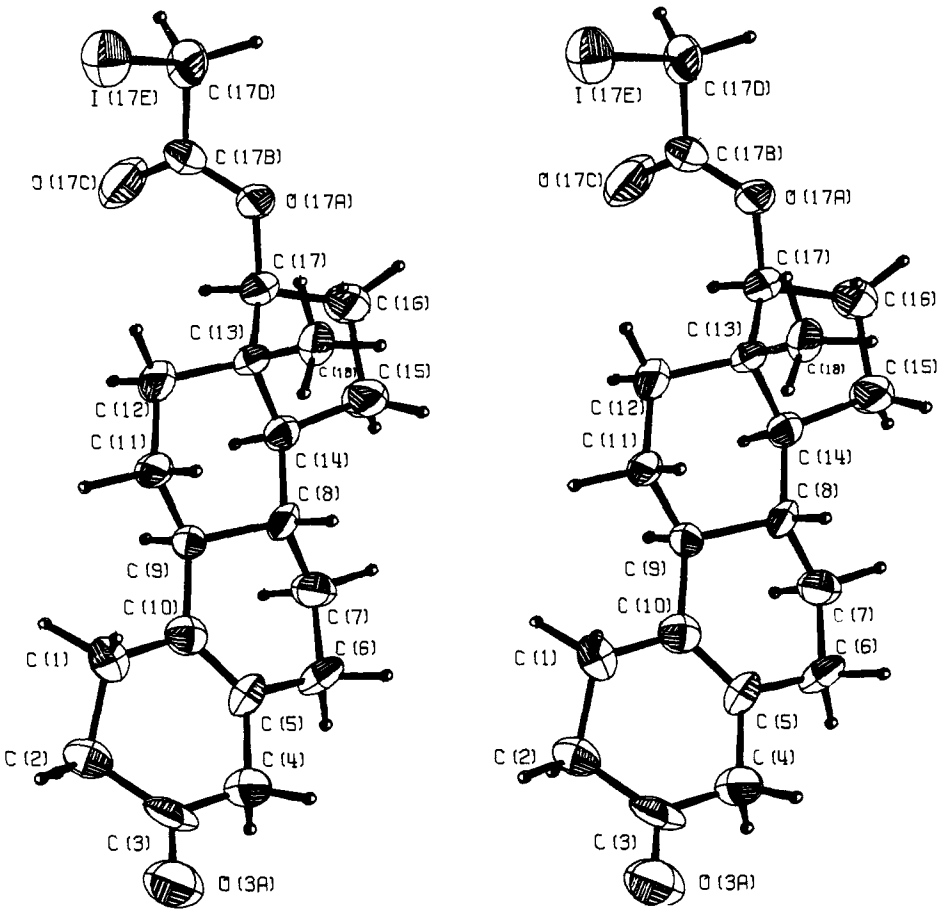
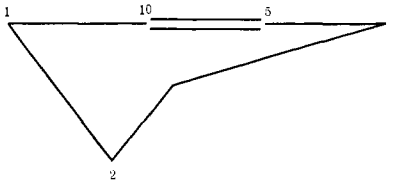


Figure 1. Stereoplot of **4**.

ring A (**9**) with only C-2 appreciably out of the average plane of the 5(10)-double bond.



9

Treatment of 17β-hydroxyestr-5(10)-en-3-one (**5**) with chloroacetic anhydride gave the 17-chloroacetate,[7] mp 126–128°; subsequent reaction with sodium iodide in acetone provided the 17-iodoacetate (**4**),[7] mp 123–126°. The structure and conformation of **4** were established by a single-crystal X-ray analysis. Crystals were grown by a slow evaporation technique and cut to an appropriate size (Table I). The crystal was surveyed and 1-Å intensity data (maximum sin θ/λ = 0.5) collected on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator and copper radiation. The trial structure was derived by the usual Patterson and Fourier techniques. This trial structure refined smoothly to a final R index of 0.051. A difference Fourier was used to locate the hydrogen positions. A final difference Fourier indicated no missing or misplaced atoms. The final cycles of full-matrix least-squares refinement contained all atomic coordinates, scale factor, and anisotropic temperature factors for non-hydrogen atoms. The temperature factors for the hydrogen atoms were not refined. Crystal and data collection parameters are presented in Table I.

(7) All new compounds gave spectral and elemental analyses in agreement with the assigned structures.

Table I. Crystal and Data Collection Parameters

Crystallization medium	Acetone
Crystal size	0.2 × 0.2 × 0.3 mm
Space group	$P2_1$
Cell dimensions	a = 12.93 ± 0.01; b = 7.00 ± 0.01; c = 10.65 ± 0.01 Å; β = 95.14 ± 0.03°
Density obsd	1.50 g/cm^3
Density calcd	1.526 g/cm^3
Scan mode	$\theta/2\theta$
Scan rate	2°/min in 2θ
Background count time	Peak scan time/2 (at both ends of scan)
No. of reflections	1094
Nonzero reflections	1065

The structure obtained in the analysis was stereographically plotted using the ORTEP computer program of C. K. Johnson[8] (Figure 1). Bond distances and angles are summarized in Figure 2. Standard deviations[9] in coordinates are: I, 0.001 Å; C, 0.020 Å; O, 0.015 Å. Uncertainties in bond lengths are about 0.03 Å. Uncertainties in bond angles are 1.8°. Deviations from the least-squares plane defined by

(8) C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tenn.

(9) Standard deviations in the coordinates were derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle.

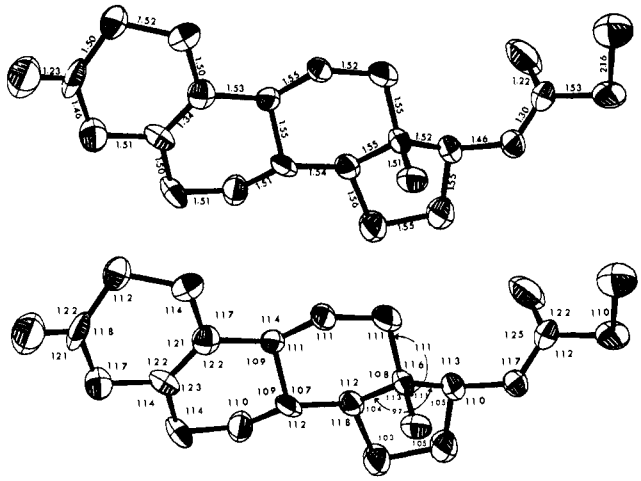


Figure 2. Plot of bond distances and angles for **4**.

atoms 1, 4, 5, 10, 9, 6 are as follows: 1, −0.04 Å; 2, −0.61 Å; 3, −0.06 Å; 4, 0.03 Å; 5, 0.00 Å; 6, −0.03 Å; 9, 0.03 Å; 10, 0.02 Å; 18, 2.80 Å. Atomic coordinates are given in Tables II and III. The observed and calculated structure factors appear in Table IV.[10]

The semiplanar conformation 9 of ring A defined[11] by these data places C-2 out of the double bond plane in the α direction and is in that sense related to the half-chair conformation **1**. The most severe nonbonded interaction in the structure occurs between the 1α- and 11α-hydrogen substituents whose interatomic distance was found to be 2.18 Å, corresponding to a destabilization energy of 0.4–0.5 kcal/mol. Any variation of the semiplanar form toward the half-chair **1** would effect an increase in this interatomic distance and a decrease in repulsion energy.[12] This suggests that preference for a semiplanar form may be intrinsic to β,γ-cyclohexenones and we plan to pursue this question by the study of additional cases.

(10) Tables II–IV (listings of coordinates and structure factors) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(11) While the presence of the iodine atom gives rise to rather large positional standard deviations for the carbon atoms, these deviations could not appreciably alter the conformation of ring A. An analysis of the 17-alcohol **5**, now in progress, should lead to more accurate data.

(12) The semiplanar enantiomeric with **9** would place the 1β- and 11α-hydrogen substituents 1.79 Å apart, corresponding to a repulsion interaction of approximately 2.0 kcal/mol.

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Photochemical Isomerization of a Dicyanoacetylene Complex of Platinum and the Structure of Cyano-(cyanoacetylido)bis(triphenylphosphine)platinum(II)[1,2]

Sir:

We report the first example of the isomerization of an acetylenic complex to the corresponding acetylido complex and describe the structure of the product which contains the novel cyanoacetylido group, N≡C—C≡C–, as a ligand. Thermal isomerizations of olefin complexes of platinum to σ-vinyl complexes have been previously reported,[3,4] but the analogous reaction in the case of acetylenic complexes had not been directly observed, although it is of interest that a mechanism proposed for the linear and cyclic polymerization of acetylenes catalyzed by $Ni(CO)_2(PPh_3)_2$ includes such a step.[5]

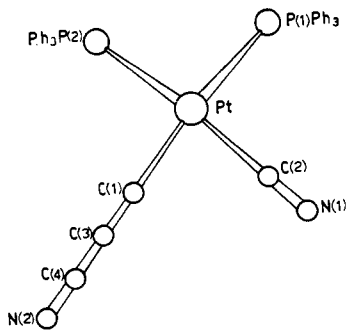
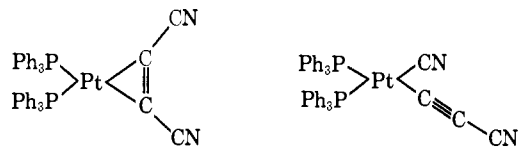


Figure 1. A drawing of the inner coordination sphere about platinum in $Pt(CN)(-C{\equiv}CCN)(PPh_3)_2$.

Infrared spectra in the 1600–2300-cm^{-1} region of some dicyanoacetylene complexes of noble metals[2,6] were remeasured recently (3–5 years after the preparation of the compounds) and were found in several instances to be different from the spectra that were originally recorded. For example, the mull spectrum



1 2

of orange crystals believed to have structure **1** included bands at 1683 (m) ($\nu_{C=C}$), 2177 (m), 2185 (s), and 2196 (m) ($\nu_{C\equiv N}$) in the original spectrum, but an aged sample shows not only these bands but also additional bands at 2070 (w), 2140 (w), and 2235 (vs). Refluxing of an aged sample in various solvents causes no significant changes in the spectrum, but irradiation of an acetone solution of aged sample with a sun lamp for 3 hr, followed by removal of solvent, gives a residue of white crystals whose spectrum in the 1600–2300-cm^{-1} region contains only the bands at 2070, 2140, and 2235 cm^{-1}. We believe these changes are a result of a photochemical reaction wherein **1** undergoes isomerization to **2**.

A crystallographic study of an aged sample shows that the title compound crystallizes in the orthorhombic system *Pbca* with unit cell parameters a = 21.43, b = 21.90, c = 14.50 Å, M = 795.7, U = 6805.1 Å^3, Z = 8, D_c = 1.553, and D_m = 1.56 g cm^{-3} (by flotation in *sym*-dichloroethane and *sym*-tetrabromoethane).

(1) Part X of the series Metal Complexes of Cyanocarbons; ref 2 is part IX.

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