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THE STRUCTURE AND CONFORMATION OF STANNYL AND RELATED RADICAL ADDUCTS TO CYCLOPENTADIENE BY ESR

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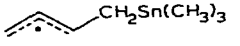
SUMMARY

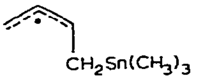
The addition of organostannyl, germyl, silyl and thiyl radicals to cyclopentadiene is examined by electron spin resonance. All of the adducts possess similar basic structures which are related to the cyclopentenyl radical but differ in their conformations. Heteroatoms consisting of tin, germanium and silicon in these adducts occupy an eclipsed position relative to the π-allylic framework, but these radicals do not have symmetrically bridged structures. Sulfur exhibits a smaller conformational effect, and the oxygen adduct is similar to the parent cyclopentenyl radical.

INTRODUCTION

The radical chain addition of trimethylstannane to 1,3-butadiene was reported by Kuivila and co-workers to afford *cis*-crotyltrimethyltin rather than the *trans* isomer as a major product[1]. To explain this unusual result it was suggested that a bridged radical (III) or a π-complex species (IV) exists in equilibrium with the open-chain allylic isomers (I) and (II).



(I)



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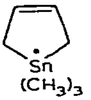

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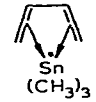
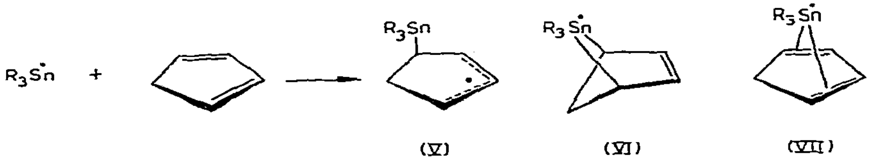


(IV)

In the previous study[2], the electron spin resonance (ESR) spectrum of the adduct of tri-n-butylstannyl radical to butadiene was examined in order to probe this interesting proposal. The results showed: (1) radical additions occurred to the *S-trans* conformation of butadiene to form the open-chain radical (I), (2) the allylic adduct was conformationally stable at least at temperatures between 0° and $-150°$, and (3) the C–Sn bond of the adduct was essentially eclipsed with π orbitals of the allylic moiety similar to the adducts of Group IVB metal- or sulfur-centered radicals to olefins[3–6].

Our inability to obtain any ESR evidence for the *cis*-crotyl radical (II), however, may be due to a relatively high activation barrier for the interconversion of (I) and (II)*. Thus, we sought a diene constrained to a *cisoid* conformation, and we chose cyclopenta-1,3-diene as a model in which the stannyl adduct may exist either as an open, bridged or π-complex species, (V), (VI) or (VII), respectively, without recourse to a prior *cis–trans* isomerization.



(1)

In this paper we report the ESR spectrum of the adduct of tri-n-butylstannyl radical to cyclopentadiene and compare it to the spectra of the adducts of trimethylsilyl, trimethylgermyl, alkoxy and alkylthiyl radicals to cyclopentadiene, in order to relate the structures and the conformations of the adducts.

RESULTS

Adducts of Group IVB metal-centered radicals to cyclopentadiene

Stannyl adducts. A cyclopropane solution of a mixture of tri-n-butylstannane, di-tert-butyl peroxide (DTBP) and cyclopentadiene on photolysis at −90° afforded an ESR spectrum of only one paramagnetic species (Fig. 1A). This spectrum consisted

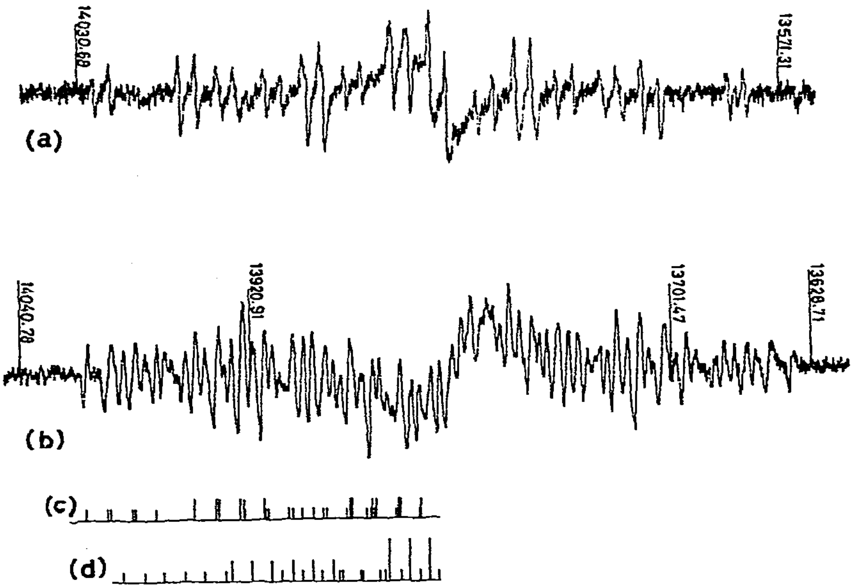


Fig. 1. ESR spectrum of the adduct of tri-n-butylstannyl radical to (a) cyclopenta-1,3-diene and (b) 5-deuteriocyclopenta-1,3-diene. Stick spectra (c) and (d) show the analysis of spectrum (b) (see text). The proton NMR field markers are in kHz.

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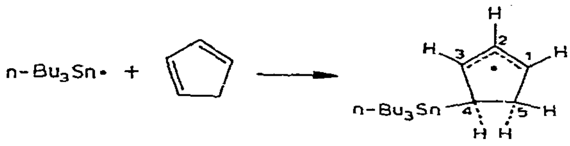
* The chemical experiments were carried out at significantly higher temperatures (100°) than the ESR studies. The activation energy for *cis–trans* isomerization of allyl radical is about 13 kcal/mole[7].

of two sets of triplets (13.1_0 G and 19.1_6 G) split further into two doublets (2.4_7 G and 32.5_0 G) and is assigned to the 4-(tri-n-butylstannyl)-cyclopent-1-en-3-yl radical (VIII). The formation of adduct (VIII) is consistent with the earlier studies in these systems[4], in which tert-butoxy radicals are photochemically generated from DTBP and are further involved by reactions (2) and (3).

$$\text{t-BuO}\cdot + \text{n-Bu}_3\text{SnH} \longrightarrow \text{n-Bu}_3\text{Sn}\cdot + \text{t-BuOH} \qquad (2)$$



(3)

(VIII)

The protons with the hyperfine coupling constants (hfcc's) of 13.1_0 G (two protons) and 2.4_7 G (one proton) are assigned to protons attached to C_1 and C_3 and to C_2 respectively, by comparing them with those reported for the cyclopent-3-en-1-yl radical[8].

The adduct of the organostannyl radical to 5-deuteriocyclopenta-1,3-diene was also examined in order to assign the protons with hfcc's of 19.1_6 G (two protons) and 32.5_0 G (one proton). The ESR spectrum of the radical adduct (Fig. 1B) from deuteriocyclopentadiene indicated the presence of two species in approximately the same concentration. One species had two protons with hfcc in 13.2 G, one proton with 2.5 G, two protons of 19.2 G and one deuterium nucleus with hfcc of 4.9 G.

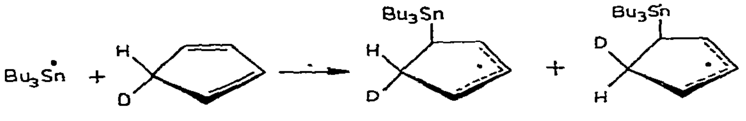
TABLE I

OBSERVED hfcc's OF SUBSTITUTED CYCLOPENT-1-EN-3-YL RADICALS: $\underbrace{\text{CH=CH-}\dot{\text{C}}\text{H-CH}_2\text{-CH}}\text{-MR}_n$

MR_n	*Temp* (°C)	$\langle g \rangle$	*Proton hfcc (Gauss)*[a,b]				
			$A(H_1)$[c]	$A(H_2)$	$A(H_4)$	$A(H_5)$	$A(H_5')$
H[d]			14.30	2.77	22.66	22.66	22.66
$Si(CH_3)_3$[e]	−121	2.0027	13.9	2.6	21.9[f]	29.3	22.6[f]
$Ge(CH_3)_3$	−112	2.00271	13.6_6	2.6_3	20.3_5	30.0_2	20.3_5
$Ge(CH_3)_3$[e,g]	−102		13.6	2.8	20.2	29.5	(3.1)
$Ge(CH_3)_3$[3,g]	−102		13.8	2.7	20.5	(4.5)	20.5
$Sn(n\text{-}C_4H_9)_3$	− 88		13.1_0	2.4_7	19.1_6	32.5_0	19.1_6
$Sn(n\text{-}C_4H_9)_3$[e,g]	− 94		13.1	2.5	19.1	32.1	(3.0)
$Sn(n\text{-}C_4H_9)_3$[e,g]	− 94		13.2	2.5	19.2	(4.9)	19.2
$O\text{-}t\text{-}C_4H_9$	−108	2.00253	14.3_9	2.8_0	19.5_6[f]	16.0_9[f]	17.5_3[f]
SCH_3	−102	2.00255	14.3_4	2.6_7	17.0_6	22.5_0	17.8_9
SCH_3[g]	−104		14.3_4	2.6_3	16.9_4	22.4_5	(2.6_3)
SCH_3[g]	−104		14.3_6	2.6_7	17.0_5	(3.3_9)	17.8_9

[a] Numbers in parenthesis show deuterium hfcc. [b] Numbering of protons are similar to that of radical (VIII). [c] $A(H_1)=A(H_3)$ for all the radicals listed in this Table. [d] From ref. 8. [e] Experimental error in the hfcc is ±0.4 G due to the limited quality of the spectrum. [f] Assignments are not definite. See text. [g] The adduct to 5-deuteriocyclopenta-1,3-diene.

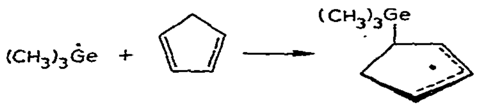
Figure 1D shows the high-field half of the reconstructed stick spectrum of this radical. The absorptions of the other radical consisted of a 1/2/1 triplet (13.1 G) split further into a 1/1/1 triplet of 3.0 G and then further into three sets of doublets (2.5 G, 19.1 G, and 32.1 G) (stick spectrum shown in Fig. 1C). Based on these results, the hfcc of 32.5_0 G is assigned to one of two C_5 protons, and the other C_5 proton is assigned to one of the 19.2 G triplet splittings. The other proton with a splitting of 19.2 G is attached to C_4. The two adducts are shown below in eqn. (4) and the hfcc's are listed in Table 1.



(4)

Germyl adducts. The ESR spectra of the adducts of trimethylgermyl radical to cyclopenta-1,3-diene and 5-deuteriocyclopenta-1;3-diene showed a similar behavior to those of the stannyl radical adducts. Table 1 summarizes the observed hfcc's and the proton assignments for the germyl adducts; *viz.*, 4-(trimethylgermyl)-cyclopent-1-en-3-yl (IX) and 4-(trimethylgermyl)-5-deuteriocyclopent-1-en-3-yl radicals, respectively.

$$(CH_3)_3CO^{\bullet} + (CH_3)_3GeH \longrightarrow (CH_3)_3COH + (CH_3)_3\dot{Ge} \quad (5)$$

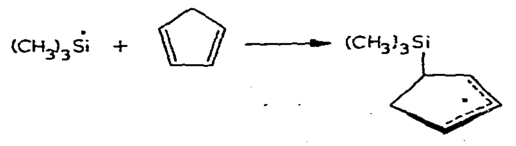


(6)

(IX)

Silyl adducts. During the photolysis of a cyclopropane solution containing DTBP, trimethylsilane and cyclopenta-1,3-diene, the ESR spectra of three species were observed. Two of these species were also observed during photolysis of the mixture of DTBP and cyclopentadiene, and were identified as the tert-butoxy radical adduct (X) to cyclopentadiene and the cyclopentadienyl radical (XI)[9] (*vide infra*). The remaining absorptions consisted of a triplet of 13.9 G split further into four sets of doublets (2.6 G, 29.3 G, 22.6 G, and 21.9 G). The third spectrum is assigned to the 4-(trimethylsilyl)-cyclopent-1-en-3-yl radical (XII), *i.e.*, the adduct of trimethylsilyl radical to cyclopentadiene. The two protons showing a triplet splitting of 13.9 G are assigned to the C_1 and C_3 protons, in analogy with the hfcc's of radicals (VIII) and (IX) for the stannyl and germyl analogs. The proton splitting of 2.6 G is assigned to the

$$(CH_3)_3C\dot{O} + (CH_3)_3SiH \longrightarrow (CH_3)_3COH + (CH_3)_3\dot{Si} \quad (7)$$



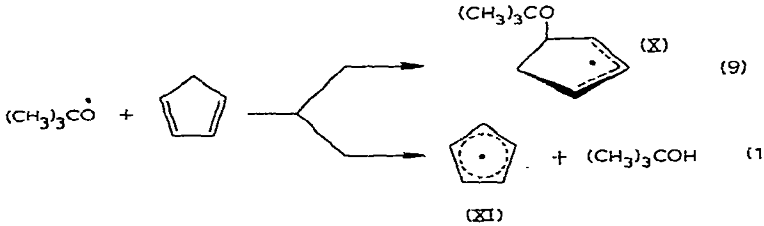
(8)

(XII)

C_2 proton, and the 29.3 G splitting to one of two C_5 protons. The proton hfcc's of 22.6 G and 21.9 G are tentatively listed in Table 1 under $A(H'_5)$ and $A(H_4)$ but these assignments may be interchanged.

Reaction of tert-butoxy radical with cyclopentadiene

Photolysis of a mixture of DTBP and cyclopentadiene in cyclopropane solutions afforded a spectrum consisting of a superposition of the ESR spectra of cyclopentadienyl (XI) and 4-tert-butoxycyclopent-1-en-3-yl (X) radicals[9]. The ESR parameters of (XI) consisted of $\langle g \rangle = 2.0025$ and $A(H) = 6.0_6$ G (5 protons) at $-108°$. The spectrum of radical (X) consisted of a 1/2/1 triplet (14.3_9 G) further split into four sets of doublets (2.8_0 G, 16.0_9 G, 19.5_6 G, and 17.5_3 G) with g 2.0025 at $-108°$. The tentative assignments of these hfcc's are listed in Table 1. The proton assignments of the hfcc's whose values are 16.0_9 G, 19.5_6 G and 17.5_3 G are not certain*, although it is clear that these hfcc's should be assigned to the two C_5 protons and the C_4 proton.

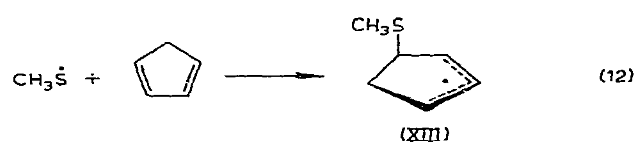


The presence of both cyclopentadienyl (XI) and the tert-butoxycyclopentenyl radicals (X) during the generation of the silyl adduct (XII) presented above, is also related to the relatively high steady state concentration of tert-butoxy radical under these conditions. On the other hand, the absence of (XI) and (X) in significant amounts during reactions involving the stannane and germane analogs (VIII) and (IX) under comparable conditions is probably due to their faster rate of hydrogen transfer [eqns. (2) and (5)] compared to that involving the silane [eqn. (7)].

Adducts of alkylthiyl radicals to cyclopentadiene

The photolysis of the mixture of methanethiol, DTBP and cyclopentadiene formed the adduct of methanethiyl radical to cyclopentadiene, 4-methanethiylcyclopent-1-en-3-yl radical (XIII). The ESR spectrum consisted of a single species showing a 1/2/1 triplet (14.3_4 G) split further into four sets of doublets (2.6_7 G, 22.5_0 G, 17.8_9 G, and 17.0_6 G) with the g-factor of 2.00255 at $-102°$. The addition of the thiyl radical to

$$CH_3SH + (CH_3)_3C\dot{O} \longrightarrow (CH_3)_3COH + CH_3\dot{S} \qquad (11)$$



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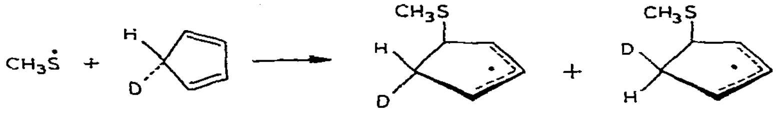
* The quality of the spectrum was insufficient to allow a more rigorous assignment using deuteriocyclopentadiene.

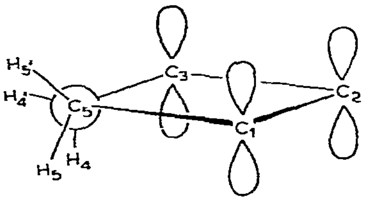
5-deuteriocyclopenta-1,3-diene resulted in two magnetically inequivalent adducts. One species showed an hfcc of 2.6_3 G due to splitting by a deuterium nucleus and the 17.8_9 G proton doublet in the spectrum of radical (XIII) was absent. The spectrum of the other species had a 1/1/1 triplet of 3.3_9 G due to a deuterium nucleus in place of the missing 22.5_0 G doublet of the spectrum of the non-deuterated radical (XIII). Thus, the proton hfcc's of 22.5_0 G and 17.8_9 G of radical (XIII) are assigned to the pair of magnetically inequivalent protons bonded to C_5. The assignments of the other proton hfcc's then follow and are also listed in Table 1.



(13)

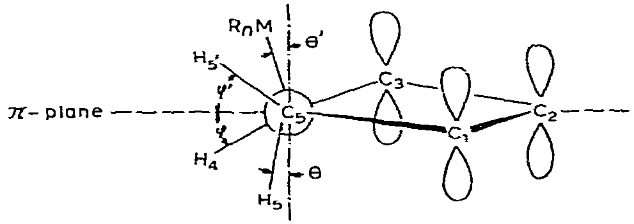
DISCUSSION

The ESR spectra of the adducts of Group IVB metal-centered radicals to cyclopentadiene, as well as the alkoxy and alkylthiyl analogs show no evidence for the presence of any bridged or π-complex species analogous to (VI) and (VII). All of the adducts can be described in the open form as derivatives of the cyclopentenyl radical. The stable conformation (XIV) of the cyclopentenyl radical must be one in which all four β-protons are (nearly) equivalent as shown by the quintet splitting for H_4, H'_4, H_5 and H'_5 in the ESR spectrum[8].



(XIV)

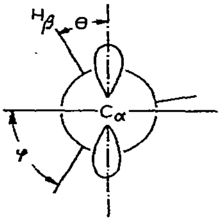
The adduct radicals (XV) listed in Table 1 [$MR_n = (n\text{-}C_4H_9)_3Sn$, $(CH_3)_3Ge$, $(CH_3)_3Si$, $(CH_3)_3CO$, CH_3S] are all structurally related to the cyclopentenyl radical. The principal differences among the ESR spectra of these adducts lie in the magnitudes



(XV)

of the hfcc's of the two protons attached to C_5 and the single proton attached to C_4 bearing the heteroatom substituent. All three protons are formally located in β-position relative to the radical center(s) and their hfcc's should be approximated by the usual $\cos^2\theta$ dependence given in eqn. (14)[10], where θ is the dihedral angle between the C–H bond and the π orbital which bears the odd electron density, ρ.

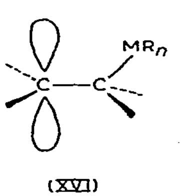
$$A(\text{H}) = B\cdot\rho\cdot\cos^2\theta \tag{14}$$



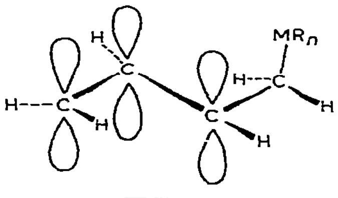
The inequivalence of the hfcc's of the pair of protons on C_5 for the radicals listed in Table 1, thus, indicates that H_5 and H'_5 are "frozen" in different locations relative to the π-plane (described by carbon atoms C_1, C_2 and C_3)*. Furthermore, in radicals (VIII), (IX), (XII) and (XIII), the hfcc of H_4 is equal or nearly equal to the hfcc of H'_5 (which is the proton on C_5 with the smaller value of hfcc). Stated alternatively, the dihedral angles φ and φ', *i.e.*, the angles which H_4 and H'_5, respectively, make with the π-plane [see (XV)], are nearly equal. If the tetrahedral configuration is maintained about C_4 and C_5, it follows that θ and θ' are also equal and the heteroatom is as far displaced as H_5 from the nodal plane.

A study of other allyl and cycloallyl radicals, particularly cyclohexenyl and *cis*-1-methallyl radicals, suggests that a β-proton occupying an axial position in a cycloallyl radical [(*i.e.*, $\theta = 0°$ in (XV)] would exhibit a splitting of approximately 26 G[12]. Values of this magnitude are indeed shown by H_5 in the silicon and sulfur adducts. The higher values for the hfcc of H_5 in the germanium and tin adducts suggest some distortion of C_5 (and C_4) from the tetrahedral configuration**,***. The precise magnitude of this distortion must await more rigorous calculations on the electronic structure of these adducts. The latter notwithstanding, the trend towards greater distortion in the order: Sn > Ge > Si > S ≫ O is nonetheless inescapable. Such distortions also place the heteroatoms closer to an eclipsing position relative to the π-orbitals.

Similar conformational effects of Sn, Ge, Si and S have been observed previous-



(XVI)



(XVII)

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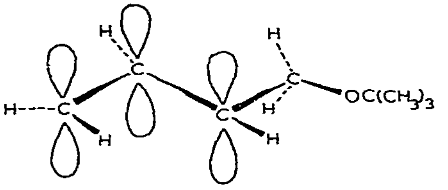
* Temperature dependent and selective line broadening effects are minor in these adducts. (*Cf.* ref. 2, 4 and 11).

** The lower value of $A(\text{H}_1)$ in these radicals, however, indicates that ρ in eqn. (14) may not be the same.

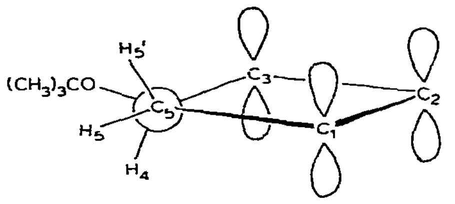
*** The origin of such distortions is discussed in refs. 5 and 15. See also refs. 4, 8, 13 and 14 for other examples.

ly in *acyclic* radicals[2,4]. Thus, in both the β-substituted ethyl and allyl radicals (XVI) and (XVII) generated by the addition of the $R_nM\cdot$ radical to ethylene and butadiene, respectively, the heteroatom occupies an eclipsed position relative to the π orbital[2,4,8].

On the other hand, the adduct of tert-butoxy radical to butadiene differs from the others, and it was shown[8,15] to have a stable conformation (XVIII) in which the oxygen atom lies close to the nodal plane of the π orbital. Similarly, the adduct of tert-butoxy radical to cyclopentadiene differs from the others listed in Table 1 in that none of the β-hfcc's is as large as that for H_5 in the other adducts, and there is a possibility that the oxygen substituent lies toward the nodal plane as indicated in (XIX)*.



(XVIII)



(XIX)

The latter represents a conformation which is closer to the parent cyclopentenyl radical (XIV) than the other adducts.

CONCLUSIONS

The ESR study of a series of radical adducts to cyclopentadiene indicates an *allylic* (cyclopentenyl) structure, the conformation of which depends on the heteroatom substituent. The Group IVB metal adducts (Sn, Ge and Si) exist largely in a conformation (XV) in which the metal atom resides in an eclipsed position relative to the π orbitals**. These adducts, however, are not symmetrically bridged but exist in a frozen conformation which could allow for the control of stereochemistry. The adduct with a sulfur substituent shows similar behavior but of reduced magnitude, and an oxygen substituent is the closest to the symmetrical parent cyclopentenyl radical (XIV). The conformational dependence of these adducts on the heteroatom

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* The assignments of the hfcc's in Table 1 are based on conformation (XIX). If conformation (XV) $[MR_n = OC(CH_3)_3]$ pertains, the assignments would be $A(H_4) = 16.0_5G$, $A(H_5) = 19.5_6G$ and $A(H_5') = 17.5_3G$.

** Strictly speaking, this conclusion of course only applies to radicals generated under these experimental conditions.

is no doubt related to the electronic interaction between orbitals on the metal and the radical center*. Hyperconjugative and homoconjugative mechanisms have been described[5,15], but the magnitudes of the interactions are insufficient to allow for a stable non-classical structure.

EXPERIMENTAL SECTION

ESR measurement

The ESR spectrometer and the photolysis equipment are the same as that reported earlier[16]. To determine the *g*-factor, the X-band microwave frequency was measured with a Hewlett–Packard 5248A frequency counter equipped with 5255A frequency converter. The magnetic field strength was measured with a Harvey–Wells NMR Precision Gaussmeter G-502. The magnetic field difference between the ESR sample position and the point of the NMR probe was repeatedly calibrated daily by measuring the field difference with the perylene cation-radical as a standard. The *g*-factor of perylene cation in concentrated sulfuric acid is reported as 2.002583 (before the second-order corrections)[17]. With this method, *g*-factors could be determined within an experimental error of ±0.00003.

The ESR sample was cooled by a stream of cold nitrogen gas and the temperature was measured by a copper–constantan thermocouple at the point just before the gas enters the cavity. The temperature difference between the sample during photolysis and the nitrogen gas was calibrated by measuring the temperature of n-pentane, liquid cyclopropane or liquid ethane in a sample tube irradiated with the UV lamp and the temperature of the flowing gas. The correction due to the heating by radiation ranged from 2° to 13° depending on the temperature of the flowing cold nitrogen. The probable maximum error in the determination of the temperature of the sample is ±5°.

Materials

DTBP was obtained from Shell Chemical Co., washed with acidic aqueous solution of potassium iodate and then water, dried over anhydrous magnesium sulfate and distilled at reduced pressure. Trimethylgermanium hydride was prepared by $NaBH_4$ reduction of trimethylgermanium bromide (Alfa Inorganics Co.)[18]. Tri-n-butyltin hydride was obtained from tri-n-butyltin oxide and methyl hydrogen polysiloxane[19]. All other chemicals were obtained commercially; triethylsilane (Columbia), trimethylsilane (Columbia) and methanethiol (Eastman).

Cyclopentadiene was prepared by pyrolysis of dicyclopentadiene and purified by a fractional distillation and kept at dry-ice temperatures. 5-Deuteriocyclopenta-1,3-diene was prepared by treatment of cyclopentadienylmagnesium bromide with D_2O and kept at dry-ice temperatures. To avoid the deuterium migration the deuterated cyclopentadiene was transferred to sample tubes by vacuum distillation at temperatures below −10°.

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* The smaller values of the hfcc for H_1 and H_3 listed in Table 1 for adducts with Group IVB substituents also suggest that the perturbations exerted by these groups are different from those by oxygen, carbon and hydrogen.

ACKNOWLEDGEMENT

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