

An Electron Spin Resonance Study of the Effect of Group IV Substituents in Cyclopentadienyl Radicals

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E.s.r. spectra have been recorded in solution for the substituted cyclopentadienyl radicals $X_3MC_5H_4^{\cdot}$, where $X_3M = Me_3Si, Me_2HSi, Me_2ClSi, Me_2FSi, Ph_2ClSi, Cl_3Si, Me_3Ge, Bu_3Ge, Ph_2ClGe, and Me_3Sn$. The spectra can be interpreted in terms of perturbation of the orbitals ψ_A and ψ_S which are degenerate in the $C_5H_5^{\cdot}$ radical. This allows the substituents to be placed in the following sequence regarding their electronic interactions, compared with that of hydrogen, with the ψ_S MO of the cyclopentadienyl π -system: electron repelling, $Me_3C \gg Bu_3Ge \sim Me_3Ge > H$; electron attracting, $H < Me_3Sn < Me_3Si < Me_2HSi < Me_2ClSi < Ph_2ClGe < Me_2FSi < Ph_2ClSi < Cl_3Si$.

A VARIETY of methods are now available for generating substituted [5]annulene (cyclopentadienyl) radicals under conditions in which their e.s.r. spectra can be recorded in solution.¹⁻⁵ These spectra can be interpreted in terms of the breaking of the degeneracy of the ψ_A and ψ_S MOs by the substituent so that the unpaired electron occupies wholly or principally the upper of these two energy levels and the spectrum reflects the spin distribution in that particular orbital (see Figure 1).¹⁻⁵

substituents stabilise the ψ_S MO by electron attraction, as they do in the substituted benzene radical anions, but the Me_5Si_2 and Me_7Si_3 groups appeared to destabilise the ψ_S MO by electron release,¹ whereas in the benzene radical anions they behave as electron-attracting substituents.⁶

We describe here a study of the e.s.r. spectra of cyclopentadienyl radicals carrying a series of Group IV substituents, $X_3MC_5H_4^{\cdot}$; $M = C, Si, Ge, and Sn$. On

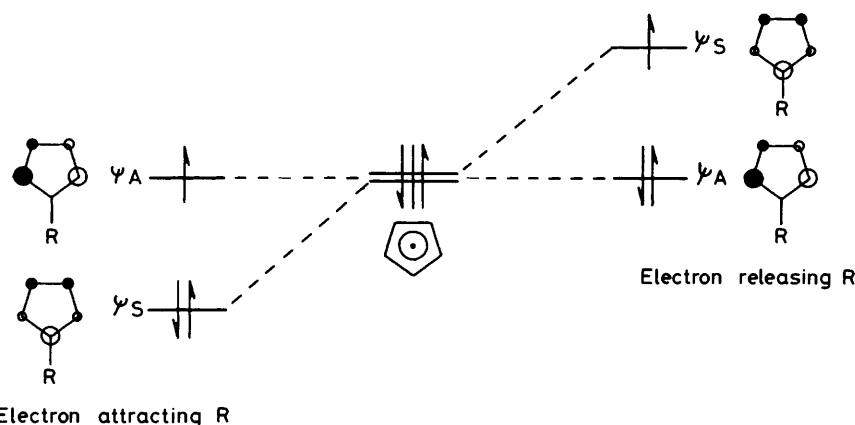


FIGURE 1 Breaking of the degeneracy of the ψ_A and ψ_S molecular orbitals of the $C_5H_5^{\cdot}$ radical by a weakly interacting substituent

With one alkyl substituent present (Me, Et, Prⁱ, or Bu^t), the spectrum shows that the unpaired electron is located in the ψ_S MO, and this has been interpreted as implying that the alkyl groups destabilise the ψ_S MO by electron repulsion, whereas the ψ_A MO, with a node at C(1), is unaffected (Figure 1).^{2,3} The e.s.r. spectra of all the isomeric methylcyclopentadienyl radicals, $Me_n-C_5H_{5-n}^{\cdot}$ ($n = 0-5$) can be interpreted on this model, the effects of polymethylation being approximately additive within the molecule.⁴ A similar analysis of the spectra of the alkyltetramethylcyclopentadienyl radicals, $RMe_4-C_5^{\cdot}$ ($R = Et, Pr, and Bu$), gave a quantitative measure of the interaction of the methyl and alkyl substituents with the π -electron system.⁵

Sakurai reported the e.s.r. spectra of a series of cyclopentadienyl radicals carrying organosilyl substituents, $R_3SiC_5H_4^{\cdot}$ and $R_3Si(R_2Si)_nC_5H_4^{\cdot}$ ($n = 1$ or 2).¹ The results were interpreted to imply that the R_3Si

the model described above, the results can be analysed to show the interaction of the substituents with the π -electron system. In the longer term, they should be useful in helping to decide on the merits of alternative models that are being developed to interpret these systems.

RESULTS

Most of the radicals $X_3MC_5H_4^{\cdot}$ listed in Table 1 were generated by Sakurai's method of abstracting hydrogen from the corresponding substituted cyclopentadiene in cyclopropane solvent [equations (1) and (2)].

This method failed to generate a radical from silylcyclopentadiene, $H_3SiC_5H_5$, and trichlorogermylcyclopentadiene, $Cl_3GeC_5H_5$, gave mainly the cyclopentadienyl radical resulting from an S_H2 reaction at the germanium centre [equation (3)].

The trimethylstannylcyclopentadienyl radical was pre-

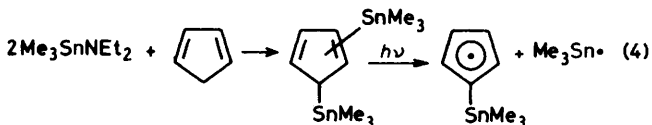
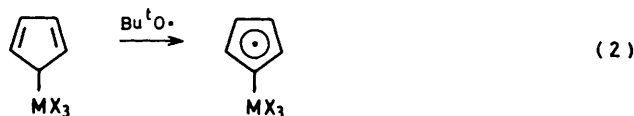
TABLE 1
E.s.r. spectra of substituted cyclopentadienyl radicals, $X_3MC_5H_4^{\cdot}$ ^{a, b}

MX_3	$a_{2,5}/G$	P_A	$a_{3,4}/G$	P_A	\bar{P}_A	a_1^*/G	$T/^\circ C$	g
Me_3C^c	1.45	0.173	7.6	0.202	0.188	11.4	-100	
Me_3Si	8.0	0.642	5.1	0.671	0.657	3.3	-132	
	7.9	0.635	5.2	0.652	0.644	3.5	-100	
	7.3	0.592	5.4	0.615	0.604	4.2	4	
Me_2HSi	8.8	0.700	4.9	0.709	0.704	2.5	-125	2.0025
	8.6	0.685	5.0	0.690	0.688	2.8	-100	
	8.0	0.642	5.0	0.690	0.666	3.1	-35	
Me_2ClSi	10.5	0.821	4.3	0.821	0.821	0.5	-126	2.0025
	10.2	0.800	4.5	0.784	0.792	1.0	-100	
	9.75	0.768	4.5	0.784	0.776	1.5	-28	
Me_2FSi	10.7	0.836	4.2	0.840	0.838	0.2	-126	2.0027
	10.5	0.821	4.1	0.859	0.840	0.15	-100	
	10.1	0.793	4.5	0.784	0.789	1.0	-54	
Ph_2ClSi	10.9	0.850	4.1	0.859	0.854	-0.1	-129	2.0025
	10.9	0.850	4.1	0.859	0.854	-0.1	-100	
	10.6	0.829	4.4	0.803	0.816	0.6	-74	
Cl_3Si	11.5	0.893	3.8	0.915	0.904	-1.0	-100	2.0023
	11.4	0.886	4.0	0.878	0.882	-0.6	-17	
Me_3Ge	5.85	0.488	6.1	0.484	0.486	6.25	-120	2.0024
	5.85	0.488	6.1	0.484	0.486	6.25	-100	
Bu_3Ge	5.6	0.470	6.0	0.502	0.486	6.25	-100	
	5.6	0.470	6.0	0.502	0.486	6.25	-80	
	5.5	0.463	6.0	0.502	0.483	1.5	-35	
Ph_2ClGe	10.5	0.821	4.2	0.840	0.831	0.3	-100	
	10.2	0.800	4.3	0.821	0.811	0.7	-25	
Me_3Sn	6.8	0.556	5.6	0.577	0.567	4.9	-130	
	6.8	0.556	5.6	0.577	0.567	4.9	-100	
	6.7	0.549	5.5	0.596	0.573	4.8	-86	

^a The assignment of $a_{2,5}$ and $a_{3,4}$ was based on the correlation of the observed hyperfine coupling constants with the theoretically calculated values for different populations, as represented by the straight lines in Figure 1. ^b In cyclopropane solvent. ^c Ref. 3.

pared by the photolysis of bis(trimethylstannyl)cyclopentadiene which was obtained from the reaction between trimethylstannyl diethylamide and cyclopentadiene [equation (4)].

We were unable to prepare bis(trimethylplumbyl)cyclopentadiene by a similar method, and as yet we have



found no route to the trialkylplumbylcyclopentadienyl radicals.

Measured values of the hyperfine coupling constants $a_{2,5}$, $a_{3,4}$, and a_1^* [see equation (10)] at $-100^\circ C$ and at the extremes of the temperature range which could be studied for each radical are given in Table 1. The assignments are based on the correlation with the theoretically calculated values (Figure 2) as explained below. A thorough study was carried out of the temperature dependence of the spectrum of the radical $Me_3SiC_5H_4^{\cdot}$ from -130 to $0^\circ C$, and the results agreed closely with those reported by Sakurai.¹

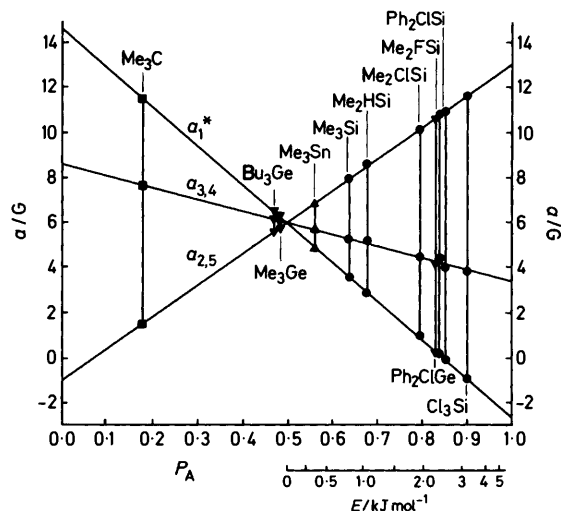


FIGURE 2 Correlation between observed and predicted proton hyperfine coupling constants for the radicals $X_3MC_5H_4^{\cdot}$ at $-100^\circ C$

DISCUSSION

Treatment of the Data.—The data have been analysed in the same way that we followed for the methylated cyclopentadienyl⁴ and alkyltetramethylcyclopentadienyl⁵ radicals. The McLachlan equation (5) has been used to calculate the spin densities, ρ_i , in the pure ψ_A and ψ_S MOs using the Hückel coefficients in equations (6) and (7). We have assumed a value of λ of 0.75, as justified previously;⁴ a minimum value of 0.6 would be

needed to accommodate the hyperfine coupling constants of the $\text{Cl}_3\text{SiC}_5\text{H}_4^\cdot$ radical. Equation (8), with a Q_{H} value of $(-)\text{30.00 G}$, then gives the predicted hyperfine coupling constants for the radical $\text{C}_5\text{H}_5^\cdot$ in the ψ_{A} and the ψ_{S} configurations.

$$\rho_{\text{I}} = c_{\text{I}}^2 + \lambda \sum_{r=1}^5 \pi_{\text{I}r} c_r^2 \quad (5)$$

$$\psi_{\text{A}} = 0.602(\phi_2 - \phi_5) + 0.372(\phi_3 - \phi_4) \quad (6)$$

$$\psi_{\text{S}} = 0.632\phi_1 + 0.195(\phi_2 + \phi_5) - 0.512(\phi_3 + \phi_4) \quad (7)$$

$$a_{\text{I}} = Q_{\text{H}}\rho_{\text{I}} \quad (8)$$

The concept of the hyperfine coupling to an imaginary proton at C(1), a_{I}^* , is a useful one (because it permits the specific site of one of the interactions to be assigned directly, whence the others can be inferred); it is usually calculated by equation (9), but this is incorrect if, as we maintain,⁴ the overall width of the spectrum of the $\text{C}_5\text{H}_5^\cdot$ radical in the pure ψ_{A} or pure ψ_{S} configuration is greater than Q_{H} .

$$\sum_{r=1}^5 a_{\text{I}} = Q_{\text{H}} \quad (9)$$

We have therefore used equation (10), in the rearranged form (11), to calculate the populations P_{A} from the observed hyperfine coupling constants $a_{2,5}$ and $a_{3,4}$.

$$a_{\text{I}} = (P_{\text{A}}\rho_{\text{IA}} + P_{\text{S}}\rho_{\text{IS}})Q_{\text{H}} \quad (10)$$

$$P_{\text{A}} = \frac{a_{\text{I}} - \rho_{\text{IS}}Q_{\text{H}}}{Q_{\text{H}}(\rho_{\text{A}} - \rho_{\text{S}})} \quad (11)$$

The average of these two values of P_{A} , which corresponded closely, was then put back into equation (10) to calculate the values of a_{I}^* which are given in Table 1.

If there is no perturbation of the degenerate MOs by the substituent R, $P_{\text{A}} = P_{\text{S}} = 0.5$, and $a_{\text{I}}^* = 6.00 \text{ G}$. If R releases electrons, $P_{\text{S}} > 0.5$ (Figure 1), and a_{I}^* will increase up to a limit of 14.61 G ; similarly, if R attracts electrons, $P_{\text{A}} > 0.5$, and a_{I}^* will decrease below 6.00 G , reaching zero at $P_{\text{A}} \text{ ca. } 0.84$, then increasing again in absolute magnitude until $a_{\text{I}}^* = 2.61 \text{ G}$ at $P_{\text{A}} = 1.0$.†

The relationship between orbital populations and the three predicted and observed hyperfine coupling constants is illustrated in Figure 2.

The diagonal lines intersecting at the coupling constant of the $\text{C}_5\text{H}_5^\cdot$ radical ($a_{1-5} = 6.00 \text{ G}$, $P_{\text{A}} = P_{\text{S}} = 0.5$) represent the values calculated for the coupling constants when the ψ_{A} and ψ_{S} MOs are populated by the unpaired electron with the probabilities P_{A} and P_{S} [equation (12)].

$$a_{\text{I}} = P_{\text{A}}a_{\text{IA}} + P_{\text{S}}a_{\text{IS}} \quad (12)$$

† The McConnell constant Q_{H} will be negative as coupling to an α -proton is by spin polarisation of the C-H σ bond. Values of a_{I}^* , $a_{2,5}$, and $a_{3,4}$ will therefore actually usually be negative, but a_{I}^* and $a_{2,5}$ will become positive as $P_{\text{A}} \rightarrow 1$ and $P_{\text{S}} \rightarrow 1$ respectively, and the spin densities assume small negative values. This change in sign of a^* and $a_{2,5}$ is apparent in Figure 2, where, however, values of $-a_{\text{I}}$ rather than a_{I} are plotted to correlate with the diagram for $a_{\text{I}}(\text{H})$ and $a_{\text{I}}(\text{Me})$ for the methylated cyclopentadienyl radicals in ref. 4.

These populations are assumed to be related to the energy separation, ΔE , between the two orbitals, according to the Boltzmann equation (13).

$$P_{\text{A}}/P_{\text{S}} = \exp \Delta E/RT \quad (13)$$

The divergence of the lines to the right of the centre indicates an increasing population of the ψ_{A} orbital by the unpaired electron as the ψ_{S} orbital is stabilised by an electron-attracting substituent (Figure 1), and ΔE increases. Conversely, the divergence of the lines to the left of the centre reflect the increasing occupancy by the unpaired electron of the ψ_{S} MO as it is increasingly destabilised by an electron-repelling group.

Experimental values of the hyperfine coupling constants at -100°C for the cyclopentadienyl radicals of Table 1 have been added to the graph to give the best fit with these calculated lines. The correlation between the experimental points and the theoretical lines is very satisfactory. An indication of the magnitudes of ΔE which the derived populations represent [equation (13)] is given by the scale on the x -axis.

Substituent Effects.—Figure 2 shows that on the model outlined above, the Me_3C group (like Me_2CH , MeCH_2 , and CH_3) is strongly electron repelling, and places the unpaired electron predominantly in the ψ_{S} orbital ($P_{\text{S}} = 0.82$). The Me_3Si group, on the other hand, as Sakurai showed, is electron attracting, with $P_{\text{A}} = 0.63$. The Me_3Ge group is almost electronically neutral, repelling electrons very weakly so that $P_{\text{S}} = 0.52$, but Me_3Sn is weakly electron attracting, giving $P_{\text{A}} = 0.56$.

If one methyl ligand of the Me_3Si substituent is replaced by hydrogen, the electron-attracting character is increased ($P_{\text{A}} = 0.68$). The introduction of chloro- or fluoro-ligands causes the group to attract electrons much more strongly, and $\text{Cl}_3\text{SiC}_5\text{H}_4^\cdot$ shows a set of proton hyperfine coupling constants which lie beyond the theoretical limits permitted by the simple Hückel treatment for the ψ_{A} MO ($a_{\text{I}}^* 0.00$, $a_{2,5} 10.85$, $a_{3,4} 4.15 \text{ G}$), and approach those ($P_{\text{A}} = 0.90$) calculated by the McLachlan equation with $\lambda = 0.75$. From the comparison between the groups Me_2ClSi and Ph_2ClSi , phenyl ligands appear to be more effective than methyl ligands in causing the group to attract electrons. The same effect was observed by Sakurai, the electron attracting power increasing in the sequence $\text{Me}_3\text{Si} < \text{Me}_2\text{PhSi} < \text{MePh}_2\text{Si}$.¹

The Bu_3Ge group is perhaps slightly more electron repelling than Me_3Ge , but Ph_2ClGe is relatively strongly electron attracting, though slightly less so than Ph_2ClSi .

Many studies have been carried out on the interaction of Group IV substituents with π -electron systems.^{7,8} The overall effect can be broken down into four modes of interaction, *viz.* the inductive effect, σ - π hyperconjugation, σ^* - π hyperconjugation, and d - π conjugation.

The inductive effect represents the polarity of the σ -bond between the sp^2 hybridised carbon of the ring and the sp^3 hybridised atom M of the substituent MX_3 , which, when $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{or Sn}$, will involve a transfer of electrons towards the π -system. This could break

the degeneracy of the orbital energy levels by modifying the coulomb integrals,⁷ but any such effect appears to be small.

The perturbation energy δE_p resulting from a combination of the ψ_S MO with either the σ or σ^* M-X orbitals, or a d -orbital on M of appropriate symmetry, will be proportional to the square of the coefficients of the atomic orbitals concerned [c_C for the C(1) atom of the ring and c_M for the atom M] and inversely proportional to the difference in energy of these orbitals [equation (14)]; in this simplified equation, P is the perturbation integral.

$$\delta E_p = \pm c_C^2 c_M^2 P / \Delta \epsilon \quad (14)$$

Since the energy level of ψ_S probably lies between that of the orbital σ_{M-X} and σ^*_{M-X} , both types of interaction $\sigma-\pi$ and $\sigma^*-\pi$ are possible. The interaction diagram

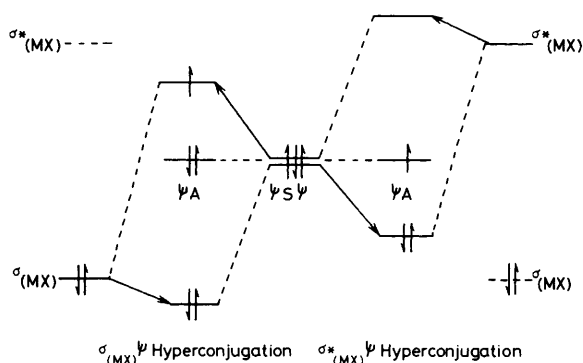


FIGURE 3 Hyperconjugative interaction in the radicals $X_3MC_6H_4\cdot$

(Figure 3) shows that the $\sigma-\pi$ combination has the effect of destabilising ψ_S , and consequently the unpaired electron. The $\sigma^*-\pi$ combination stabilises ψ_S below ψ_A ; two electrons are stabilised, and the third remains at the original energy level. The net effect of the two interactions will depend on both the energy separation between the different orbitals, and the electron density at atom M, according to equation (14).

The $d-\pi$ interaction is stabilising, like the $\sigma^*-\pi$ interaction, since the d -orbital is empty. This interaction is often analysed separately and regarded as the dominant effect, but it is difficult to separate it from the $\sigma^*-\pi$ hyperconjugation because the d and σ^* orbitals are probably close in energy and combine, when it is better to speak of a $[d, \sigma^*]-\pi$ interaction.⁷

When $X_3M = Me_3C$, the orbital σ^*_{C-C} is very high in energy, and the interaction $\sigma_{C-C}-\pi$ dominates, so that the unpaired electron is found almost exclusively in the orbital ψ_S .

On passing from Me_3C to Me_3Si , one notes two essential differences: first, the separation in energy between ψ_S and σ^*_{Si-C} is much smaller (in part because σ^* is stabilised by combination with the d -orbital), and, second, as a result of the polarity of the $Si^{\delta+}-Me^{\delta-}$ bond, the coefficient c_{Si} is smaller in the orbital σ_{Si-C} , but it is important in the antibonding orbital σ^*_{Si-C} . The interaction of ψ_S with the vacant orbitals σ^* and d

outweighs the $\sigma-\psi_S$ interaction, and thus Me_3Si behaves as an electron-attracting substituent.

Although they are less important, these stabilising interactions also operate with the substituents Me_3Ge and Me_3Sn , making them weaker electron acceptors or very weak electron donors.

The replacement of a CH_3 ligand by H, Ph, or Cl has the effect of increasing the positive charge on M ($M = Si$ or Ge), and of lowering the energy levels of the orbitals σ and σ^* . This reduces further the destabilising $\sigma-\pi$ interaction, and increases the $[d, \sigma^*]-\pi$ stabilising interaction.

The effects observed here of the interaction of the substituents with the [5]annulene π -system can be compared with the results reported for the interaction of the same substituents with other π -systems.

The most direct comparison is with the e.s.r. studies of the substituted benzene radical anions, $X_3MC_6H_5\cdot^-$. In their classic paper of 1963, Bedford *et al.*⁹ showed that, in $Me_3SiC_6H_5\cdot^-$, the Me_3Si group was electron attracting, as we observe [$Me_3SiC_6H_5\cdot^-$: $a(H\ ortho)$ 2.66, $a(H\ meta)$ 1.06, $a(H\ para)$ 8.13 G. Cf. $C_6H_6\cdot^-$: $a(6H)$ 3.75 G].⁶ The spectra, however, cannot be analysed in terms of the simple Hückel treatment of the benzene ring, and the organometallic substituent has to be treated as a heteroatom which brings about a small redistribution of spin density in the ψ_S MO.¹⁰ The correlation between the experimental points and the theoretical lines in Figure 2 shows that this refinement is unnecessary for $Me_3SiC_6H_5\cdot^-$.

The e.s.r. spectra of the radical anions $Me_{3-n}H_nSiC_6H_5\cdot^-$ similarly show that the electron-attracting power of the substituent increases as n increases:¹¹ this is parallel to the effect which we find in the cyclopentadienyl derivatives.

In $Me_3GeC_6H_5\cdot^-$, the Me_3Ge group is overall electron-attracting [$a(H\ ortho)$ 2.33, $a(H\ meta)$ 1.46, $a(H\ para)$ 7.61 G], whereas in $Me_3GeC_5H_4\cdot^-$ we find it to be very weakly electron repelling.⁹ This may be because, compared with the SOMO of the benzene ring, the SOMO of the cyclopentadienyl ring is further from σ^*_{Ge-Me} and closer to σ_{Ge-Me} , reducing hyperconjugative release into the Me_3Ge group. The solvation of the aromatic radical anion, and the presence of a counterion, may also be important, as it appears to be in the toluene radical anion.¹²

The only reference to the e.s.r. spectra of stannyl-substituted annulenes appears to be Solodovnikov and Prokof'ev's report that the radical anion $Me_3SnC_6H_5\cdot^-$ shown $a(H\ ortho)$ 4.0 and $a(H\ para)$ 8.2 G,¹³ so that, in this situation, the Me_3Sn group exerts an electron-attracting effect similar to that of the Me_3Si group, and not unlike the effect which we observe in the cyclopentadienyl radical. The individual contributions of the various terms which result in similar overall effects in the two systems, may however be quite different.

EXPERIMENTAL

Most cyclopentadienylmetallic compounds were prepared by the reaction of (a) cyclopentadienyl-lithium, or (b)

cyclopentadienylsodium, or (c) cyclopentadienylpotassium with the appropriate metallic chloride. One example is given of each method, and the ^1H n.m.r. spectra of all the products are listed in Table 2.

TABLE 2

^1H N.m.r. spectra at 37 °C of cyclopentadienylmetallic compounds, $\text{R}_n\text{X}_{3-n}\text{M}-\text{CH}$

Compound $\text{R}_n\text{X}_{3-n}\text{M}$	$\delta(\text{CCl}_4)$		Other ring protons
	R	CH	
Me_3Si	0.02	3.25	6.4—6.8
Me_2HSi	0.95	2.65—2.90 ^a	6.3—6.7
Me_2ClSi	0.14	3.47—3.74	6.56—6.83
Me_2FSi	0.03, 0.12	2.95—3.15	6.4—6.9
Ph_2ClSi	7.1—7.9	2.7—3.2	6.4—6.8
Cl_3Si		3.77—3.85	6.50—6.70, 6.82—6.03
H_3Si	3.4	2.9	5.7—6.2
Me_3Ge	0.02	2.8	5.6—6.3
Bu_3Ge	0.6—1.4	2.9	5.6—6.1
Ph_2ClGe^b	7.2—7.9		5.8—6.4
Cl_3Ge^c		2.7	5.7—6.7
$(\text{Me}_3\text{Sn})_2\text{C}_5\text{H}_4$	0.15, 0.2		6.3—6.5, 6.55—6.8
Me_3Pb	0.2		6.05
Et_3Pb	0.9		5.55

^a Includes SiH. ^b Photolysis in the absence of peroxide showed the e.s.r. spectrum of the $\text{C}_5\text{H}_5^{\cdot}$ radical; when ethyl bromide was added, no spectrum of the ethyl radical was observed. ^c Photolysis in the presence of di-*t*-butyl peroxide showed also the spectrum of the $\text{C}_5\text{H}_5^{\cdot}$ radical. When di-*t*-butyl peroxide was photolysed in the presence of tributylchlorogermane, no spectrum of the butyl radical could be detected.

Method (a).—Cyclopentadiene (1.65 cm³) in ether (10 cm³) was added at 0 °C to butyl-lithium (13.5 cm³ of 1.6M solution in hexane), yielding a suspension of cyclopentadienyl-lithium. After 45 min, a solution of tributylchlorogermane (5.58 g) in ether (10 cm³) was added, and the mixture was heated under reflux for 6 h. Lithium chloride was filtered off, and the filtrate was distilled, yielding tributylcyclopentadienylgermane,¹⁴ b.p. 93 °C at 0.3 mmHg.

Method (b).—Sodium (1.0 g) was dissolved by stirring it for 2 h in a solution of cyclopentadiene (4.3 cm³) in tetrahydrofuran (10 cm³). Dichlorodiphenylsilane (10.12 g), was then added. Next day, the solvent was removed under reduced pressure, and cyclopentadienyldiphenylchlorosilane was recovered by repeated trap-to-trap distillation.

Method (c).—Tetrachlorosilane (14 cm³) was condensed onto solid cyclopentadienylpotassium¹⁵ (78 mmol) at -196 °C on a vacuum line, then kept at room temperature for 3 h. Volatile material was collected in a trap at -196 °C, then cyclopentadienyltrichlorosilane¹⁶ was isolated by repeated trap-to-trap distillation.

Cyclopentadienyldimethylsilane.—Chlorodimethylsilyl-cyclopentadiene (7.0 g) in ether (10 cm³) was added slowly to lithium aluminium hydride (2.0 g) suspended in ether. The excess of lithium aluminium hydride was hydrolysed with water, and the product was distilled, b.p. 120 °C at 18 mmHg.

Cyclopentadienyldimethylfluorosilane.—Chlorodimethylsilylcyclopentadiene (0.8 g) was condensed at -78 °C onto antimony trifluoride (ca. 1 g) on a vacuum line, and allowed to warm to room temperature. The product was condensed out of, then back into, the reaction flask three times. The n.m.r. spectrum of the product showed that exchange was not complete, but the residual chlorosilane did not complicate the e.s.r. experiment.

Cyclopentadienylsilane.—Freshly prepared cyclopentadienyltrichlorosilane (1.5 g) in ether (10 cm³) was added dropwise during 30 min to a solution of lithium aluminium hydride (0.3 g) in ether (40 cm³) under nitrogen. The mixture was then heated under reflux for 2 h. The ether was removed under reduced pressure, and the product¹⁴ was purified by trap-to-trap distillation.

Photolysis of di-*t*-butyl peroxide in the presence of the silane did not show any spectrum which might be assigned to the radical $\text{H}_3\text{SiC}_5\text{H}_4^{\cdot}$, but did give a spectrum of the radical $\text{C}_2\text{H}_5\text{OCHCH}_3$, from the abstraction of hydrogen from residual traces of ether. It seems then that the SiH_3 substituent may deactivate the cyclopentadienyl ring towards abstraction of hydrogen.

Bis(trimethylstannyl)cyclopentadiene.—A mixture of freshly distilled cyclopentadiene and diethylaminotrimethyltin (1 : 2 molar ratio) was maintained at 40 °C in a distillation apparatus under nitrogen for 2 h. The diethylamine which was formed was removed under reduced pressure, and the product was distilled as a yellow liquid, b.p. 80 °C at 3 mmHg.

Cyclopentadienyltrimethyl-lead.—In an attempt to prepare bis(trimethylplumbyl)cyclopentadiene, a mixture of cyclopentadiene and diethylaminotrimethyl-lead (1 : 5 molar ratio) was stirred at 0—5 °C under nitrogen, but only trimethylplumbylcyclopentadiene was obtained, which gave the cyclopentadienyl radical on photolysis. Attempts to plumblylate this further through the sodium or lithium derivatives with trimethyl-lead chloride, were unsuccessful. Similarly an attempt was made to prepare the compound $(\text{Me}_3\text{PbC}_5\text{H}_4)_2\text{Hg}$ by treating the lithium derivative with mercury(II) chloride, but photolysis of the product did not show any spectrum which could be ascribed to the radical $\text{Me}_3\text{PbC}_5\text{H}_4^{\cdot}$.

E.s.r. Experiments.—Solutions in cyclopropane were photolysed in the cavity of a Varian E4 spectrometer by the technique which has been described previously.⁴

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REFERENCES

- M. Kira, M. Watanabe, and H. Sakurai, *J. Am. Chem. Soc.*, **1977**, **99**, 7780.
- M. Kira, M. Watanabe, and H. Sakurai, *J. Am. Chem. Soc.*, **1980**, **102**, 5202.
- P. J. Barker, A. G. Davies, and M.-W. Tse, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 946.
- A. G. Davies, E. Luszytk, and J. Luszytk, *J. Chem. Soc.*, **1982**, 729.
- A. G. Davies, J. P. Goddard, E. Luszytk, and J. Luszytk, preceding paper.
- F. Gerson, J. Heinzer, H. Bock, A. Alt, and H. Seidl, *Helv. Chim. Acta*, **1968**, **51**, 707.
- C. G. Pitt, *J. Organomet. Chem.*, **1973**, **61**, 49.
- H. Kwart and K. G. King, 'd-Orbitals in the Chemistry of Silicon, Phosphorus, and Sulphur,' Springer-Verlag, Berlin, **1977**.
- J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **1963**, **59**, 53.

- ¹⁰ H. J. Sipe and R. West, *J. Organomet. Chem.*, 1974, **70**, 367.
¹¹ J. Reffy, *J. Organomet. Chem.*, 1975, **96**, 187.
¹² K. D. Jordan, J. A. Michejda, and P. D. Burrow, *J. Am. Chem. Soc.*, 1976, **98**, 1295.
¹³ S. P. Solodovnikov and A. K. Prokof'ev, *Russ. Chem. Rev.*, 1970, **39**, 591.
¹⁴ M. Lesbre, P. Mazerolles, and G. Manuel, *Compt. Rend.*, 1962, **255**, 544.
¹⁵ A. P. Hagan and P. J. Russo, *Inorg. Synth.*, 1977, **17**, 172.
¹⁶ I. M. Shologon, M. K. Romantsevich, and S. V. Kul'kova, *Zh. Obshch. Khim.*, 1967, **37**, 2315.