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RELATIVE MIGRATORY ABILITIES OF METALS FOR CYCLOPENTADIENYL AND INDENYL LIGANDS

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Summary

The ^1H and $^{13}C—\{^1H\}$ NMR spectra of the fluxional molecules $C_9H_7Si(CH_3)_3$, $C_9H_7Ge(CH_3)_3$, and $C_9H_7Sn(CH_3)_3$ have been studied over a wide range of temperatures The metal atom in the indenylgermane migrates through a 1,2 shift. This is shown by isolation of the Diels—Alder cycloaddition adducts of this compound with the dienophiles tetracyanoethylene, maleic anhydride and acetylene dicarboxylate. The thermodynamic characteristics of metallotropic migration in the Group IVB indenyl derivatives show that the difference between the free energies of activation of indenyl and the corresponding cyclopentadienyl compounds in each case is close to 8.5 kcal/mole. New parameters, μ and r_a, characteristic of the fluxional behaviour of some organometallic compounds have been introduced, and some predictions based on these parameters have been made.

Many papers on organometallic fluxional molecules have dealt with the determination of the mechanism governing the shift of the metal over the organic ligand [1,2]. Some interesting results have been obtained [3,4] from comparison of the fluxional behaviour of cyclopentadienyl and indenyl compounds The investigations showed that indenyl systems, as a rule, undergo migration at temperatures substantially higher than those for the corresponding cyclopentadienyl compounds. This fact may be interpreted, according to Cotton et al. [4], as being due to the 1,2-shift of the metal in indenyl compounds leading to an energetically-unfavourable, short-lived isoindenyl intermediate*, which may be isolated using the Diels—Alder reaction [6,7]. This type of fluxional behaviour in molecules may be termed quasi-degenerate [8].

Earlier, Davison and Rakita [9] studied the temperature-dependent PMR

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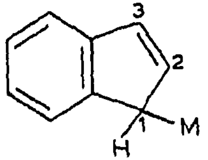
* HMO estimates of the π-electron energy difference between indene and isoindene structures give a value of ca. 9 kcal/mole [5]

TABLE 1

PMR (100 MHz) PARAMETERS OF THE ORGANOMETALLIC INDENYL DERIVATIVES[a]



Organometallic group, M	°C	Solvent	Chemical shifts (δ ppm)					Coupling constants, J_{i-j}(Hz)			
			H_1	H_2	H_3	Ar	CH_3	J_{1-2}	J_{1-3}	J_{2-3}	$\|J_{3-Ar}\|$
$Si(CH_3)_3$	22	neat	3,32	6 49	6 79	7 2	0 24	+2 0	−1 6	+5 4	0 8
	200	neat	b	6 49	b	7 2	0 24	$\|J_{1,3-2}\|$ 4 0 [c]			
$Ge(CH_3)_3$	25	C_6H_{12}	3 52	6 46	6 79	7 3	−0 02	+1 86	−1 26	+5 43	0 72
	200	neat	b	6 46	b	7 3	−0 02	$\|J_{1,3-2}\|$ 3 55			
$Sn(CH_3)_3$	−40	CS_2	3 91	6 58	6 77	7 2	−0 07	+1 8	−0 8	+5 3	0 3
	140	neat	5 34	6 60	5 34	7 2	−0 07	$\|J_{1,3-2}\|$ 3 5			

[a] Chemical shifts are accurate to within ± 0,01 ppm, coupling constants to within ± 0 05 Hz [b] Signal is too broad to be measured [c] $|J_{1,3-2}|=\frac{1}{2}(J_{1-2}+J_{2-3})$

spectra of indenyl compounds of silicon, germanium and tin and showed that these compounds were subject to an intramolecular metallotropic rearrangement proceeding via apparent 1,3-shift. Later [10] they estimated the activation parameters for phenyldimethylsilyl- and phenyldimethylstannyl-indene In our previous paper [11] we used ^{13}C NMR techniques* to study the fluxional behaviour of trimethylstannylindene.

The similarity of fluxional behaviour in the indenyl and cyclopentadienyl series prompts us to attempt the search for a quantitative relationship. We now present results of a comparative analysis of the activation parameters for Group IVB metal migration in each series by using ^{1}H and ^{13}C NMR spectroscopy.

Results and discussion

Table 1 summarises results of PMR investigations on trimethylsilyl- (I), trimethylgermyl- (II) and trimethylstannylindene (III). Although our data are quite close to those given in the literature some newer facts are worth discussing. (i) Above the coalescence temperature (ca. 60°), the temperature-dependent PMR spectrum of (III) exibits unsymmetrical broadening of the ^{117,119}Sn satellites (the high-field satellite broadens substantially faster than the low-field one). This is possibly due to the inequality of the coupling constants· $^2J(^{117,119}\text{Sn—H}_1) > {}^4J(^{117,119}\text{Sn—H}_3)$ It is known that both coupling constants are positive [10]. Analogous spectral patterns have been observed previously for ^{199}Hg [14] and ^{117,119}Sn [8] satellites in the PMR spectra of cyclopentadienyl compounds (ii) Saturation transfer techniques [15] may be used for assignment of the signals It is worthwhile to note that during the irradiation of the methine proton signal (H_1), the signals of both olefinic protons (H_2 and H_3) disappear from the spectrum of indenyltin (III). This may be explained on the basis of mixing the spin states of H_2 and H_3 nuclei owing to their strong spin—sping coupling [16]. (iii) At temperatures above 150° several additional signals appear in the PMR spectrum of (II). These signals may be attributed to the products of hydrogen migration, a process which has been found previously in the silyl compound (I) [6] Integration of the methyl proton signals resulted in the following isomer percentages· (II) (82%), (IIA) (12%), (IIB) (6%) Irreversible changes were found in its PMR spectrum after (III) had been heated for several hours, however, these changes are probably due to Sn—C bond cleavage in (III) rather than to a prototropic rearrangement (iv) Spin—spin coupling constants between H_3 and one of the aromatic protons are readily found in the PMR spectra of (I) - (III)** (Table 1)

We also isolated the Diels—Alder cycloaddition adducts of trimethylgermylindene using tetracyanoethylene, maleic anhydride and acetylene dicarboxylate as dienophiles. This establishes a 1,2-migration of the metal in the compound (Scheme 1). Attempts to isolate an isoindenyl intermediate for (III) were unsuccessful; we found only Sn—indenyl bond cleavage, accompanied by formation of a product containing both dienophile and trimethyltin group.

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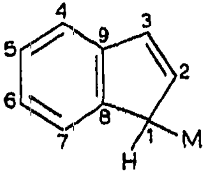
* This technique was found to be quite promising in a study of the various dynamic phenomena [12, 13]

** Complete analysis of the PMR spectrum of the unsubstituted indene gives almost all the possible couplings between protons (the results are now in preparation).

TABLE 2

CARBON CHEMICAL SHIFTS FOR SOME INDENYL COMPOUNDS[a]

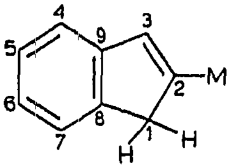


M	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	CH_3	Temperature
H	39 27	133 86	132 43	121 26	126.52	124 88	123 90	143 88	145 17		R.t [b]
$Si(CH_3)_3$ (I)	46 77	135 47	129 39	121.37	125 18	124 05	122 90	145 57	144 49	−2 22	R t
$Ge(CH_3)_3$ (II)	46 18	135 58	128 29	121 36	125 07	124 03	122 35	145 97	143 73	−2 60	R t
$Sn(CH_3)_3$ (III)	45 10	134 74	126 30	121 36	124 60	124 00	121 36	146 60	142 90	−9 21	0°

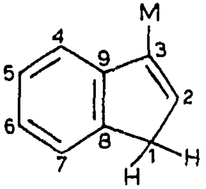
[a] The shifts are in ppm relative to TMS with an accuracy of ± 0 05 ppm [b] R.t = room temperature

TABLE 3

CARBON CHEMICAL SHIFTS FOR VINYLIC ISOMERS OF TRIMETHYLSILYL AND TRIMETHYLGERMYL INDENE[a]



(A)

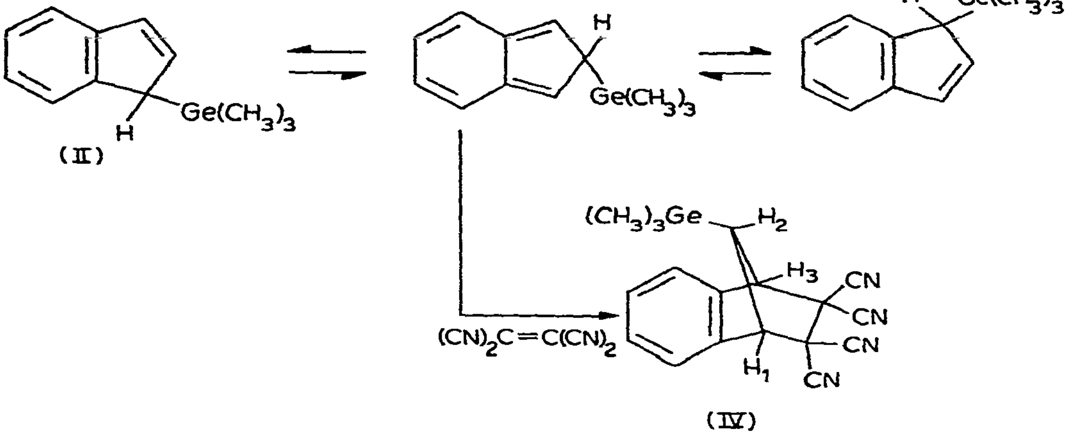


(B)

M	Isomer	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	CH_3
$Si(CH_3)_3$	(IA)	42 60 (42 80)	148 64 (148 50)	141 20 (141 70)	121 17	126 54	125 09	123 89	145 95	146 95	−0 65
	(IB)	41 06 (39 40)	144 02 (143 50)	148.22 (147 20)	122 21	126 46	124 63	123 95	144 80	145.39	−0 65
$Ge(CH_3)_3$	(IIA)	42 96	150 27	139 32	120 88	126 56	124 77	123 81	145 82	146 62	−1 35
	(IIB)	40 81	141 28	148 27	121 95	126 53	124.70	124 08	144 60	146 24	−1 26

[a] Shifts are in ppm relative to TMS with an accuracy of ± 0 05 ppm The values of carbon chemical shifts expected on the additive scheme (SiR_3 group increments) are given in parentheses

SCHEME 1



Exact determination of the activation parameters of the exchange processes requires total line shape analysis or even the more elaborate density-matrix methods (in the case of the strong spin—spin coupling) to be used [17] These difficulties may be overcome by using temperature-dependent ^{13}C NMR spectra (completely proton decoupled) in the manner already demonstrated for compound (III) [11].

Similar measurements were made for the compounds (I) and (II). Carbon chemical shifts for both $C_9H_7M(CH_3)_3$ (M = Si, Ge, Sn) under stereochemically rigid conditions, and unsubstituted indene, are listed in Table 2.

Line shape analysis was performed by use of a 620/*f* Varian computer with a program written for the equations given previously for the two-site exchange [18].

The carbon-13 spectra of (I) and (II) also showed additional signals when these compounds were heated at temperatures above 150°; the signals should be attributed to the vinylic isomers. The assignment of the signals to the individual isomers (see Table 3) is based on the following: (i) off-resonance techniques, (ii) deshielding effect of the metal group on the olefinic carbons, and (iii) comparison of the data with that established for allylic isomers and unsubstituted indene.

Temperature-dependent PMR spectra were also used in the calculation of the activation parameters; approximate formulae were applied in this case [compounds (II) and (III)] Spin—spin coupling effects were taken into account by the effective spin—spin relaxation time constant, T_2.

The thermodynamic parameters of the metallotropic rearrangements in the σ-indenyl and σ-cyclopentadienyl compounds of silicon, germanium and tin are listed in Table 4.

It is worth emphasizing that the difference between the free energies of activation of indenyl and the respective cyclopentadienyl compound in each case is close to 8.5 kcal/mole, which is quite similar to the HMO-estimate This strikingly constant value prompts us to introduce a new parameter μ, the *migratory aptitude* of a metal as follows:

$$\mu = \lg k_M^{300}/k_H^{300} = 0.43/RT\ (\Delta G_H^\ddagger - \Delta G_M^\ddagger)$$

where $\Delta G^{\ddagger}_{M}$ and $\Delta G^{\ddagger}_{H}$ are the free energies of activation for metal and hydrogen migration in cyclopentadienyl compounds, respectively; k^{300}_{M} and k^{300}_{H} refer to the corresponding rate constants at 300 K. We have used the value 24.2 kcal/mole for hydrogen migration in C_5H_6 taken from the data of Roth [19], and corrected for the primary isotope effect. The data available (see Table 4) lead to values of migratory aptitudes which vary from +12.4 (tin) to −12.6 (carbon) (Table 5) and increase over the series. $\mu_C < \mu_H = 0.00 < \mu_{Si} < \mu_{Ge} < \mu_{Sn}$ It is very interesting to note that the same tendency may be established by quantitative analysis of keto—enol tautomerism studied for Group IVB elements (see, for example, ref. 20 for a review), even in non-degenerate cases.

We may also introduce a parameter to account for the relative ability of a ligand to facilitate metal migration, for example:

$$r_a = -0.43/RT\,[\Delta G^{\ddagger}_{M}\,(\text{ligand}) - \Delta G^{\ddagger}_{M}\,(\text{cyclopentadienyl})]$$

TABLE 4

CHARACTERISTICS OF THE METALLOTROPIC REARRANGEMENT IN δ-CYCLOPENTADIENYL AND δ-INDENYL DERIVATIVES OF THE GROUP IVB METALS

Compound	Parameters					Note
	E_a (kcal/mole)	log A	$\Delta S^{\ddagger}_{300}$ (cal/mole·K)	$\Delta G^{\ddagger}_{300}$ (kcal/mole)	T_r[a] (°C)	
$C_5H_5Si(CH_3)_3$	13 0 ± 1 0	11 3 ± 1 0	− 9 2 ± 4	15 2 ± 0 2	− 23	^{1}H [b]
$C_5H_5Ge(CH_3)_3$	9 2 ± 1 0	9 9 ± 1 0	−15 8 ± 4 0	13 3 ± 1 0	− 73	^{1}H [c]
	10 7 ± 0 9	10 9	−11 0	13 4 ± 0 9	− 62	^{13}C [d]
$C_5H_5Sn(CH_3)_3$	7 8 ± 1 0	13 8 ± 1 0	+ 2 ± 4	6 6 ± 1 0	−152	^{1}H [c]
	6 8 ± 0 7	12 6	− 2 7	7 1 ± 0 7	−157	^{13}C [d]
$C_9H_7Si(CH_3)_3$	22 4 ± 1 0	11 7 ± 0 5	− 6 9 ± 2 1	23 8 ± 0 1	142	^{13}C
$C_9H_7Ge(CH_3)_3$	18 2 ± 0 5	10 3 ± 0 2	−13 7 ± 1 1	21 6 ± 0 1	110	^{1}H(100 MHz)
	18 4 ± 0 4	10 3 ± 0 2	−13 7 ± 0 9	21 8 ± 0 1	115	^{13}C
$C_9H_7Sn(CH_3)_3$	12 0 ± 0 3	10 4 ± 0 2	−13 2 ± 0 8	15 3 ± 0 1	− 22	^{1}H(100 MHz)
	12 1 ± 0 2	10 6 ± 0 2	−12 2 ± 0 8	15 1 ± 0 1	− 25	^{1}H(60 MHz)
	12 7 ± 0 4	11 0 ± 0 3	−10 5 ± 1 3	15 2 ± 0 1	− 22	^{13}C

[a] T_r = temperature at which migration rate k is equal to 1 sec^{-1} [b] Ref 24 [c] Ref 8 [d] Ref 26

TABLE 5

MIGRATORY APTITUDES OF THE ELEMENTS[a]

Compound	μ (300 K)	$\Delta(\Delta G^{\ddagger}_{300})$ (kcal/mole)	Ref
Cyclopentadiene-d_5	− 0 7		19
5 5-Dimethylcyclopentadiene	−12 6		21
$C_5H_5Si(CH_3)_3$	+ 6 5	8 6	24
$C_5H_5Ge(CH_3)_3$	+ 7 8	8 4	8, 26
$C_5H_5Sn(CH_3)_3$	+12 4	8 4	8 26
$(\pi\text{-}C_5H_5)Fe(CO)_2(\delta\text{-}C_5H_5)$	+ 9 2		22, 23, 13
$(\pi\text{-}C_5H_5)Ru(CO)_2(\delta\text{-}C_5H_5)$	+ 7 5		22, 23

[a] For calculation of μ and $\Delta(\Delta G^{\ddagger}_{300})$ we used the average values of the literature and our present data $\Delta(\Delta G^{\ddagger}_{300}) = \Delta G^{\ddagger}_{300}(\text{indenyl}) - \Delta G^{\ddagger}_{300}(\text{cyclopentadienyl})$

The previous analysis with indenyl as the ligand showed that the r_a factor was constant and equal to −6.0 indicating the more limited non-rigidity of the indenyl series. This approach allows some predictions to be made. For example, the free energy of activation of mercury migration in the cyclopentadienyl ligand may be expected to be ca. 5 kcal/mole, which may be correlated with the low-temperature measurements by West et al. [14]. Another test is the prediction of the free energy of activation for the iron indenyl which should be more than 20 kcal/mole, and this agrees with the data of Cotton et al. [3].

One rather novel example of the fluxional behaviour is presented by Group IVB pyrazole derivatives. Data recently obtained in this laboratory [25] allows the estimation of the pyrazole ligand r_a factor. This is found to be −4 0, thus the pyrazole ligand may be considered to support metal migration more than indenyl but less than cyclopentadienyl.

Experimental

PMR spectra of (I), (II) and (III) were measured on JNM - C - 60HL (JEOL), HA - 100D (Varian) and XL - 100 - 15 (Varian) spectrometers. The $^{13}C-\{^{1}H\}$-FT spectra of these compounds were measured on an XL - 100 - 15 (Varian) instrument at 25.2 MHz for carbon nuclei, 12 mm o.d. sample tubes were used. The temperature was controlled to within ± 1°. Spectra were measured on neat liquids.

The PMR spectrum (100 MHz) of (IV) is characterized by the following data: δ 7 52 (multiplet, AA′BB′, aromatic); and 4 85 ppm (doublet, H_1 and H_3), $J_{(HH)}$ 1.17 ± 0.05 Hz, δ 2.33 ppm (triplet, H_2), $J_{(HH)}$ 1.17 ± 0.05 Hz; δ 0.00 ppm (singlet, CH_3). (Found: C, 60.10, H, 4.49; Ge, 20.29, N, 15.42 $C_{18}H_{16}N_4Ge$ calcd.. C, 60 00; H, 4 67; Ge, 20.11, N, 15.52%.)

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