Journal of Organometallic Chemistry, 150 (1978) 171—177

FOURIER TRANSFORM NMR STUDIES OF ORGANOMETALLIC COMPOUNDS

I. ^{199}Hg, ^{29}Si, ^{13}C AND ^{1}H NMR SPECTRA OF ORGANOSILYL AND ORGANOGERMYL MERCURIALS

TERENCE N. MITCHELL and HEINRICH C. MARSMANN

Lehrstuhl für Organische Chemie der Universität Dortmund, D-4600 Dortmund und Fachbereich Chemie der Gesamthochschule Paderborn, D-4790 Paderborn (W. Germany)

(Received November 9th, 1977)

Summary

^{199}Hg, ^{29}Si, ^{13}C and in some cases ^{1}H NMR data are presented for a total of 17 compounds of the type $RHgSiMe_3$, $RHgSiEt_3$ and $RHgGeMe_3$ (R = alkyl, $SiMe_3$, $SiEt_3$ or $GeMe_3$). Except for the symmetrical silylmercurials, the ^{29}Si chemical shift varies only slightly when R is varied, while the coupling constant $^{1}J(^{199}Hg—^{29}Si)$ varies between 957 and 1367 Hz; the magnitude of the coupling depends on the inductive effect of R. A similar dependence is observed for $^{1}J(^{13}C—^{199}Hg)$, which varies between 423 and 716 Hz, a much wider range than is found for the corresponding compounds R_2Hg. The chemical shift of carbons bonded to silicon or germanium shows little dependence on R, while carbons attached to mercury absorb 13—18 ppm downfield of the corresponding carbons in R_2Hg.

Introduction

In recent years, symmetrical organomercurials R_2Hg and compounds of the type RHgX (where X is an electronegative group) have been the object of a number of NMR investigations; though generally only proton NMR data have been obtained, some carbon-13 data have been reported recently [1—3]. Little work has been done on unsymmetrical dialkyls or compounds RHgX in which the electronegativities of mercury and X are comparable. Our interest in the synthesis [4] and synthetic potential [5] of organosilyl- and organogermyl-mercurials prompted us to carry out this study of the NMR spectra of these compounds, the results of which should be useful in helping to rationalise their chemical behaviour, which is in many cases still well from understood [6].

Experimental

Preparation of the compounds studied

Almost all of the compounds investigated are described in the literature, and new compounds were characterised by their spectroscopic data. The following equations describe the preparative methods used:

$2\ Me_3SiCl + Na/Hg\ (amalgam) \rightarrow Na + (Me_3Si)_2Hg$ [7]

$2\ Me_3GeOMe + (Me_3Si)_2Hg \rightarrow (Me_3Ge)_2Hg + 2\ Me_3SiOMe$ [8]

$RHgCl + (Me_3M)_2Hg \rightarrow RHgMMe_3 + Hg + Me_3MCl$ [4, 9]

(M = Si, Ge; R = Me, Et, Pr, Bu, i-Pr, t-Bu)

$(Me_3M)_2Hg + RX \rightarrow RHgMMe_3 + Me_3MX$ [10]

(M = Si, Ge; R = Et, Pr, Bu, CH_2Cl; X = Br, Cl)

Triethylsilyl mercurials were prepared by analogous routes.

Spectroscopic studies

^{199}Hg and ^{29}Si spectra were measured using a Bruker WP 60 DS spectrometer operating at 10.73 MHz (^{199}Hg) or 11.92 MHz (^{29}Si). Samples consisted of neat liquids or concentrated solutions in C_6D_6, which served as internal lock for ^{29}Si; external D_2O was used as lock substance for ^{199}Hg. Carbon-13 measurements were carried out using a Bruker WP 80 operating at 20.155 MHz using neat liquids or concentrated solutions in C_6D_6; TMS was used as internal standard, C_6D_6 as internal lock. Proton spectra were obtained using Varian EM-360 or Perkin—Elmer R24 or R32 spectrometers. The accuracy of the parameters measured is stated as a footnote to the relevant Table.

Results and discussion

The NMR parameters of the compounds studied are listed in Tables 1—4. No sign determinations for coupling constants have been carried out; it is known from the literature that $^1J(Hg—C)$ is generally positive and $^2J(Hg—C)$ generally negative [2]; as far as we are aware, no values for $^1J(Hg—Si)$ have previously been reported. The various features of the spectra will be discussed separately.

^{199}Hg chemical shifts

Relatively few NMR studies of this nucleus have been carried out until now; although some collections of data are to be found in the literature [11,12]. Within the very large range of mercury shifts, the data reported here are typical for twofold covalently bonded mercury. Although the same chemical shift trends which are found when one alkyl group is exchanged for another in dialkylmercury compounds are also observed in the compounds studied here, the shifts of silicon and germanium derivatives of mercury are generally displaced to lower field with respect to R_2Hg. This is especially true for silylmercurials, as has previously been observed by Ebsworth [13]. In fact, the ^{199}Hg shifts of Me_6Si_2Hg and Et_6Si_2Hg are among the lowest so far observed.

^{29}Si chemical shifts

The substitution of a methyl group in TMS by mercury results in a marked downfield shift of the ^{29}Si resonance. As can be seen from Table 1 and literature data [13], this paramagnetic shift can reach 40 to 60 ppm in disilylmercurials, but is generally around 35 ppm. It may well be due to interactions between the silicon and mercury nuclei involving low-lying mercury orbitals; the Si—Hg bond is known to be considerably shorter than the sum of the covalent radii [14], this bond contraction leading to the yellow colour of the silylmercurials. The electronic structure of Me_6Si_2Hg is discussed in ref. 6. A similar paramagnetic shift is observed in transition metal derivatives of silicon, e.g. $F_3SiCo(CO)_4$ —28.6 ppm compared to F_3SiMe —55.7 ppm [15], so that we can describe this shift as a "heavy metal" effect. The mono- and bis-silylmercurials have a nearly or exactly linear structure [14], and this leads to the production of anisotropy effects, which will also affect the ^{29}Si shift; the structure of the group R also has an affect, increasing carbon chain length causing a low-field shift, while increasing branching causes first a low-field shift which is apparently reversed when R = t-Bu.

^{13}C chemical shifts

These are collected in Table 2; values for the symmetrical mercurials R_2Hg are given in parentheses, and are taken from refs. 1 and 3 (except for $i\text{-}Pr_2Hg$ and $t\text{-}Bu_2Hg$, which have not previously been reported). The values for C(2) and C(3) require no comment, since R_2Hg, $RHgSiMe_3$ and $RHgGeMe_3$ all show similar shifts. However, the C(1) shifts show two salient features: firstly, replacement of one group R in R_2Hg by $SiMe_3$ or $GeMe_3$ causes C(1) of the remaining group R to experience a downfield shift $\Delta\delta$ of 16—18 ppm (Me_3Si) or 13—15 ppm (Me_3Ge). Secondly, the magnitude of $\Delta\delta$ shows no clear dependence on the nature of R. Conversely, on going from $(Me_3M)_2Hg$ to $RHgMMe_3$, the carbons bonded to silicon or germanium are shifted to high field (as is the Si resonance). The chemical shifts of carbons bonded to silicon and germanium are very similar, as are the corresponding proton shifts in the Me_3M groups; this similarity is not

TABLE 1

^{199}Hg AND ^{29}Si CHEMICAL SHIFTS [a] IN COMPOUNDS $RHgSiMe_3$ (in ppm)

Compound	R	$\delta(^{199}Hg)$ [b]	$\delta(^{29}Si)$ [c]
I	Me	[d]	33.0
III	Et	[d,e]	34.0
V	Pr	2527	35.2
VII	Bu	2520	35.0
IX	i-Pr	2312 [f]	34.0
XI	t-Bu	2172 [g]	33.6
XIII	Me_3Si [h]	2927	63.6
XV	CH_2Cl	[d]	30.3
XVII	Et_3Si [i]	3278	35.1

[a] The usual sign convention is used. [b] Relative to a saturated solution of $Hg(NO_3)_2$, ± 2 ppm. [c] Relative to internal TMS, ± 0.3 ppm. [d] Not measured. [e] For $EtHgGeMe_3$ δ = 2272 ppm. [f] For $i\text{-}PrHgGeMe_3$ δ = 2129 ppm. [g] For $t\text{-}BuHgGeMe_3$ δ = 2591 ppm, for $t\text{-}Bu_2Hg$ 1598 ppm. [h] Lit. [13] 64.0 ppm. [i] $(Et_3Si)_2Hg$.

TABLE 2

^{13}C AND ^{1}H CHEMICAL SHIFTS FOR COMPOUNDS $RHgMMe_3$ (M = Si, Ge) (in ppm; δ(TMS) = 0)
All measurements were carried out using dilute solutions (10—20 vol.%) in C_6H_6 or C_6D_6. Values in parentheses refer to R_2Hg. Shifts measured in this work are accurate to ± 0.05 ppm.

Compound	R	M	δ(C(1))	δ(C(2))	$\delta(\underline{C}\text{—M})$	$\delta(M\underline{Me}_3)$
I	Me	Si	40.08	—	4.76	0.16[a]
			(22.3)	—		
II	Me	Ge	36.66		4.94	0.32[b]
III	Et	Si	53.76	13.17	4.88	0.18
			(35.6)	(12.9)		
IV	Et	Ge	50.53	13.11	5.17	0.30
V	Pr	Si	63.85	22.70[c]	4.82	0.20
			(47.25)	(22.33)[d]		
VI	Pr	Ge	60.57	22.70[e]	5.05	0.31
VII	Bu	Si	60.74	31.56[f]	4.82	0.16
			(44.01)	(31.01)[g]		
VIII	Bu	Ge	57.73	31.56[h]	5.05	0.31
IX	i-Pr	Si	66.41	23.82	4.89	0.15
			(49.72)	(23.46)		
X	i-Pr	Ge	63.69	22.71	5.22	0.30
XI	t-Bu	Si	75.45	30.18	4.94	0.14[i]
			(59.51)	(30.95)[j]		
XII	t-Bu	Ge	73.81	30.32	5.17	0.29[k]
XIII	Me_3Si	Si	—	—	6.55	0.28
XIV	Me_3Ge	Ge	—	—	6.70	0.36
XV	CH_2Cl	Si	83.79	—	4.14	0.23[l]
			(—)			
XVI	CH_2Cl	Ge	79.47	—	4.37	0.23[m]
XVII	Et_3Si	Si[n]	—	—	11.47[o]	—

[a] $\delta(C\underline{H}_3)$ 0.24. [b] $\delta(C\underline{H}_3)$ 0.37. [c] δ(C(3)) 20.27. [d] δ(C(3)) 19.80. [e] δ(C(3)) 20.15. [f] δ(C(3) 28.78, δ(C(4)) 14.08. [g] δ(C(3)) 28.36. δ(C(4)) 13.96. [h] δ(C(3)) 28.89, δ(C(4)) 14.19. [i] $\delta(C\underline{H}_3)$ 1.44. [j] $\delta(C\underline{H}_3)$ 1.23. [k] $\delta(C\underline{H}_3)$ 1.34. [l] $\delta(C\underline{H}_2Cl)$ 3.23. [m] $\delta(C\underline{H}_2Cl)$ 2.93. [n] $SiEt_3$. [o] $\delta(\underline{C}H_3)$ 9.60 ppm.

unexpected, since the (Pauling) electronegativities of Si and Ge are similar.

The chemical shift trends for carbons bonded to mercury and silicon or germanium must have their origin in electronic effects, since the linear structure of the organomercurials precludes steric interaction between R and Me_3M. It has previously been observed [16] that the carbons in Me_2Hg have a chemical shift similar to the methyl groups in neopentane, while the methyl derivatives of Zn, Cd, Si, Ge, Sn and Pb all have shifts similar to that of methane; recent measurements [17,18] show that the difference between δ(C(1)) in R_2Hg and R_4Sn is ca. 35 ppm, although the (Pauling) electronegativities of mercury and tin are similar. The comparison between Me_2Hg (δ 22.3 ppm) and Me_4Pb (δ —4.2 ppm) shows that this difference is not merely a "heavy atom" effect, while the comparison between Me_2Cd (1.2 ppm) and Me_2Hg precludes a large shift dependence on metal hybridisation. It also seems unlikely that hyperconjugation plays an important role for some metals and not for others. Thus it is apparently not possible to identify any one factor which is responsible for the observed δ(C(1)) values, though we must assume that changes in the paramagnetic term play a dominant role; these may at least for the silyl- and germyl-mercurials be connected with changes in ΔE.

Coupling constants

Mercury—carbon and mercury—silicon coupling constants are listed in Table 3, mercury—proton coupling constants in Table 4. The latter have been discussed in a previous publication [19]; the complex proton spectra of the alkyl groups allow determination of ^2J(Hg—C—H) and ^3J(Hg—C—C—H) in only a limited number of cases.

It can be seen from the Tables that replacement of R in R_2Hg by Me_3M causes a decrease in ^1J(Hg—C(1)), ^2J(Hg—C—H) and ^3J(Hg—C—C—H); similarly, replacement of Me_3M in $(Me_3M)_2Hg$ by R causes an increase in ^1J(Hg—Si), ^2J(Hg—M—C) and ^3J(Hg—M—C—H). The magnitude of the one-bond coupling constants in the unsymmetric compounds $RHgMMe_3$ show good (^1J(Hg—C), $r = 0.979$ (Si) or 0.986 (Ge); ^1J(Hg—Si), $r = 0.981$) correlations with the Taft σ^* value for the alkyl group R; in R_2Hg, the corresponding correlation for ^1J(Hg—C) is 0.885. Correlations between direct and long-range coupling constants are also good (for ^1J(Hg—Si) and ^2J(Hg—Si—C) $r = 0.990$; for ^2J(Hg—Si—C) and ^3J(Hg—M—C—H) $r = 0.971$). The third main feature is that when we compare compounds $RHgMMe_3$ ^1J(Hg—C(1) is generally larger for M = Ge while ^2J(Hg—M—C) is generally smaller.

These features can be rationalised on the basis of rehybridisation (as postulated by Bent [20]) on going from R_2Hg or $(Me_3M)_2Hg$ to $RHgMMe_3$, electron

TABLE 3

MERCURY—CARBON AND MERCURY—SILICON COUPLING CONSTANTS IN COMPOUNDS $RHgMMe_3$ (M = Si, Ge) (in Hz). Values in parentheses refer to R_2Hg. Coupling constant values are generally accurate to ±0.5 Hz.

Compound	R	M	^1J(Hg—C(1))	^2J(Hg—C(2))	^2J(Hg—M—C)	^1J(Hg—Si)
I	Me	Si	423.4	—	116.8	1367.0
			(689)			
II	Me	Ge	524.3	—	117.9	—
III	Et	Si	495.5	18.3	109.9	1213.0
			(648)	(25)		
IV	Et	Ge	601.5	25.3	105.3	—
V	Pr	Si	497.8	18.3[a]	112.1	1234.1
			(658)	(26)[b]		
VI	Pr	Ge	597.4	24.1[c]	106.4	—
VII	Bu	Si	496.8	18.0[d]	112.1	1225.9
			(656)	(26)[e]		
VIII	Bu	Ge	593.3	25.3[f]	109.9	—
IX	i-Pr	Si	564.7	[g]	104.4	1084.9
			(633.6)	(32)		—
X	i-Pr	Ge	666.0	[g]	97.3	—
XI	t-Bu	Si	611.9	26.6	101.5	995.6
			(631)	(30)		
XII	t-Bu	Ge	716.4	22.9	92.7	—
XIII	Me_3Si	Si	—	—	93.8	989.6[h]
XIV	Me_3Ge	Ge	—	—	96.3	—
XV	CH_2Cl	Si	446.3	—	132.8	1137.0
			(—)			
XVI	CH_2Cl	Ge	573.4	—	132.8	—
XVII	Et_3Si	Si[i]	(—)	—	58.0[j]	957.0[h]
			(—)			

[a] ^3J(Hg—C(3)) 91.5. [b] ^3J(Hg—C(3)) 103. [c] ^3J(Hg—C(3)) 103.0. [d] ^3J(Hg—C(3)) 89.3. [e] ^3J(Hg—C(3)) 100. [f] ^3J(Hg—C(3)) 103.5. [g] No coupling observed. [h] ±2 Hz. [i] $(Et_3Si)_2Hg$. [j] ^3J(Hg—C) 37.8 Hz.

TABLE 4

MERCURY—PROTON COUPLING CONSTANTS IN COMPOUNDS $RHgMMe_3$ (M = Si, Ge) (in Hz)

All measurements were carried out using dilute solutions in benzene. Values in parentheses are literature values for R_2Hg.

Compound	R	M	^2J(Hg—C—H)	^3J(Hg—C—C—H)	^3J(Hg—M—C—H)
I	Me	Si	74.0 (101.4)	—	51.8
II	Me	Ge	84.5	—	42.0
III	Et	Si		96	48.5
IV	Et	Ge	(91)	(120)	38.5
V	Pr	Si	75.0 (90)	91 (108)	48.5
VI	Pr	Ge			38.9
VII	Bu	Si			48.0
VIII	Bu	Ge	(—)	(—)	38.5
IX	i-Pr	Si	 (78)	106 (126)	46.0
X	i-Pr	Ge			35.5
XI	t-Bu	Si	—	93 (104)	45.0
XII	t-Bu	Ge	—	109.5	34.8
XIII	Me_3Si	Si	—	—	40.8
XIV	Me_3Ge	Ge	—	—	37.5
XV	CH_2Cl	Si	28.5 (—)	—	60.4
XVI	CH_2Cl	Ge	33.0	—	50.5

density being highest in the bond between mercury and the least electronegative group (MMe_3), and changes in ^1J reflecting electronegativity changes (σ^*) in R. This corresponds to a polarisation, though small, in the sense $R^{\delta-}$—Hg—$^{\delta+}MMe_3$. Since Me_3Ge is (on the grounds of electronegativity) probably a slightly better electron donor than Me_3Si, ^1J(Hg—C) is larger in $RHgGeMe_3$ than in $RHgSiMe_3$.

The situation is somewhat different for compounds XV and XVI, in which R is a strongly electronegative group. Since the effective nuclear charge on mercury is increased, we can expect larger values for both direct coupling constants (in comparison with $MeHgMMe_3$); rehybridisation will also be important.

Acknowledgement

We thank Miss Christel Kummetat for preparing a number of the compounds studied, and the Deutsche Forschungsgemeinschaft for supporting this work.

References

1 L.A. Fedorov, Z.A. Stumbrevichute and E.I. Fedin, J. Struct. Chem. (U.S.S.R.), 15 (1974) 943; and refs. therein.
2 F.J. Weigert and J.D. Roberts, Inorg. Chem., 12 (1973) 313.
3 J. Casanova, H.R. Rogers and K.L. Servis, Org. Magn. Res., 7 (1975) 57.
4 T.N. Mitchell, J. Organometal. Chem., 71 (1974) 27.
5 T.N. Mitchell, J. Organometal. Chem., 71 (1974) 39.
6 W.P. Neumann and K. Reuter, Accounts Chem. Res., in press.
7 E. Wiberg, O. Stecher, H.J. Andrascheck, L. Kreuzbichler and E. Staude, Angew. Chem., 75 (1963) 516.

8 T.N. Mitchell, J. Organometal. Chem., 38 (1972) 17.
9 N.S. Vyazankin, E.N. Gladyshev, E.A. Archangel'skaya and G.A. Razuvaev, J. Organometal. Chem., 17 (1969) 340.
10 F. Werner, Dissertation, Dortmund 1974.
11 M.A. Sens, N.K. Wilson, P.D. Ellis and J.D. Odon, J. Magn. Resonance, 19 (1975) 322.
12 G.E. Maciel in T. Axenrod and G.A. Webb (Eds.), Nuclear Magnetic Resonance Spectroscopy of Nuclei other than Protons, Wiley, New York, 1974.
13 S. Cradock, E.A.V. Ebsworth, N.S. Hosmane and K.M. Mackay, Augew. Chem., 87 (1975) 207.
14 P. Bleckmann, M.S. Soliman, K. Reuter and W.P. Neumann, J. Organometal. Chem., 108 (1976) C18.
15 R.B. Johanesen, F.E. Brinckman and T.D. Coyle, J. Phys. Chem., 72 (1968) 660.
16 F.J. Weigert, M. Winokur and J.D. Roberts, J. Amer. Chem. Soc., 90 (1968) 1566.
17 H.G. Kuivila, J.C. Considine, R.H. Sarma and R.J. Mynott, J. Organometal. Chem., 111 (1976) 179.
18 T.N. Mitchell and G. Walter, J. Organometal. Chem., 121 (1976) 177.
19 T.N. Mitchell, J. Organometal. Chem., 71 (1974) 27.
20 H.A. Bent, Chem. Revs., 61 (1961) 275.