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Synthesis and ^{13}C, ^{29}Si, ^{199}Hg nuclear magnetic resonance spectroscopy of alkynyl(trimethylsilyl)mercurials

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Abstract—Alkynyl(trimethylsilyl)mercurials are formed by a fast and quantitative reaction between bis(alkynyl)- and bis(trimethylsilyl)mercury in chloroform or benzene at ambient temperature. They decompose slowly in solution to alkynyltrimethylsilanes and mercury. ^{13}C, ^{29}Si, ^{199}Hg NMR data serve for the characterization. The polarizability of the Hg–Si bond and the great polarizing ability of the alkynyl group is clearly reflected by the NMR data.

INTRODUCTION

Alkynyl metal compounds (A) are attractive reagents in organometallic synthesis [1]. Their reactivity is controlled to a large extent by mutual interactions between the alkynyl bonding system and the metal fragment (L_nM). NMR spectroscopy appears to be particularly useful for obtaining information on the M–C≡ and the C≡C bonds. In the case of linear systems L–M–C≡C–R changes in the NMR parameters can be traced to a single L/C≡C–R interaction, mediated by the metal M.

$$L_nM\text{–C≡C–R} \qquad \textbf{A}$$

Our current interest in NMR parameters of alkynes [2–5] led us to study alkynyl(trimethylsilyl)mercurials (2).

$$(CH_3)_3Si\text{–Hg–C≡C–R} \qquad \textbf{2}$$

The NMR data ($\delta^{13}C$, $\delta^{29}Si$, $\delta^{199}Hg$ chemical shifts and various coupling constants) for compounds **2** are of great interest in connection with the large data set available for organyl(alkynyl)mercury [3] and alkyl(trimethylsilyl)mercury compounds [6], and other silylmercury derivatives [7].

EXPERIMENTAL

All NMR spectra have been recorded at 27–28°C from samples (10–15%) in 10 mm (o.d.) tubes with a Bruker WP 200 spectrometer equipped with a multinuclear unit. The ^{29}Si NMR spectra have been obtained with the refocused INEPT pulse sequence [8].

The alkynyl mercurials **1a–c**, **3a–c** [3, 9] and bis(trimethylsilyl)mercury, **4** [10], have been prepared as described. All compounds were carefully handled in an N_2 atmosphere and dissolved in oxygen-free dry solvents. Mixtures of **1** and **4** (1:1 ratio) were made directly in the NMR tubes right before the NMR measurements and kept in the dark.

SYNTHESIS

Various methods are available for the synthesis of unsymmetrical mercury compounds from bis(trimethylsilyl)mercury, **4** [11–13]. Previous results reported for the reaction between **4** and diorganomercurials [12–14] are not encouraging. Either there is no reaction at all in a particular solvent [12, 14] or extensive decomposition is observed. Some ^1H NMR data of the reaction mixtures show that small amounts of the unsymmetrical compounds, $(CH_3)_3Si\text{–Hg–R}$ (e.g. R = CH_3, C_6H_5, $CH{=}CH_2$, C_3H_5), are formed [13]. We found that divinylmercury in $CDCl_3$ does not react with **4** over a period of 24 h. In contrast, a clean and quantitative reaction between the bis(alkynyl)mercury compounds **1** and **4** in $CDCl_3$ or benzene gives the unsymmetrical silylmercury compounds [Eqn. (1)].

$$\underset{\textbf{1}}{Hg(C{\equiv}C\text{–}R)_2} + \underset{\textbf{4}}{Hg[Si(CH_3)_3]_2} \xrightarrow[0\text{–}25^{\circ}C]{CDCl_3\text{ or }C_6H_6} \underset{\textbf{2}}{2\,(CH_3)_3Si\text{–}Hg\text{–}C{\equiv}C\text{–}R} \qquad (1)$$

Attempts to isolate the compounds **2** from the reaction solutions were not successful owing to decomposition of **2** into mercury and alkynyltrimethylsilanes [Eqn. (2)].

$$\underset{\textbf{2}}{(CH_3)_3Si\text{–}Hg\text{–}C{\equiv}C\text{–}R} \rightarrow Hg + \underset{\textbf{6}}{(CH_3)_3Si\text{–}C{\equiv}C\text{–}R} \qquad (2)$$

Again this is a clean reaction which is noticeable in solution at room temperature after several hours. The rate of decomposition increases in the order R = $Si(CH_3)_3 < C_4H_9 < C_6H_5$.

The unsymmetrical mercury compounds **5a–c** were studied by NMR in the reaction solution (Eqn. (3) [11, 12]) in order to have more data for comparison.

$$RHgCl + \underset{\textbf{4}}{Hg[Si(CH_3)_3]_2} \rightarrow \underset{\textbf{5}}{(CH_3)_3Si\text{–}Hg\text{–}R} + Hg + (CH_3)_3SiCl \qquad (3)$$

If R = $CH{=}CH_2$ the reaction according to Eqn. (3) leads to divinylmercury and hexamethyldisilane instead of $(CH_3)_3Si\text{–}Hg\text{–}CH{=}CH_2$. This reminds one somewhat of the result reported for the reaction between C_6H_5HgCl and bis(triethylgermyl)mercury [11].

Table 1. ^{13}C, ^{29}Si, ^{199}Hg NMR data*† of organomercury(II) and silylmercury(II) compounds

No.	Compound	$\delta^{13}C^{\alpha}$	$\delta^{13}C^{\beta}$	$\delta^{13}C$ (other)	$\delta^{199}Hg$	$\delta^{29}Si$	Solvent
1a	$Hg(C\equiv C\text{-}C_4H_9)_2$	110.9 [2391.0]	106.3 [628.0]	19.2, 31.3, 22.0, 13.5 (C_4H_9) [41.7] [13.0]	−859	—	$CDCl_3$
1b	$Hg(C\equiv C\text{-}C_6H_5)_2$	122.8 [2526.0]	107.0 [648.0]	123.8 (i) 132.8 (o) 128.3 (m) 128.3 (p) (C_6H_5) [52.4] [17.2]	−863	—	C_6D_6
1c	$Hg[C\equiv C\text{-}Si(CH_3)_3]_2$‡	138.1 [2358.0]	115.9 [538.5]	0.1 ($SiCH_3$) [—]	−1004	−19.3	C_6D_6
2a	$(CH_3)_3Si\text{-}Hg\text{-}C\equiv C\text{-}C_4H_9$§	156.4 [660.0]	110.7 [200.0]	19.0, 31.3, 21.9, 13.5 (C_4H_9) [13.0] 3.6 ($SiCH_3$) [156.2]	−404	+15.7 [1950]	$CDCl_3$
2b	$(CH_3)_3Si\text{-}Hg\text{-}C\equiv C\text{-}C_6H_5$‖	167.6	108.8	123.6 (i) 132.1 (o) 128.2 (m) 127.7 (p) (C_6H_5) 3.6 ($SiCH_3$) [169.0]	−417	+15.3 [2001]	C_6D_6
2c	$(CH_3)_3Si\text{-}Hg\text{-}C\equiv C\text{-}Si(CH_3)_3$¶	186.4 [650.0]	113.4 [190.0]	0.6 (C-SiCH_3), 3.5 ($HgSiCH_3$) [—] [157.3]	−446	+15.4 (SiHg) [1946] −21.9 (SiC)	C_6D_6
3a	$CH_3\text{-}Hg\text{-}C\equiv C\text{-}C_4H_9$	131.6 [1400.3]	108.2 [403.8]	19.2, 31.2, 22.0, 13.9 (C_4H_9) [26.0] 7.0 [1132]	−450	—	$CDCl_3$
3b	$(CH_3)_3C\text{-}Hg\text{-}C\equiv C\text{-}C_6H_5$	144.0 [916.0]	106.0 [294.0]	124.9 (i) 132.5 (o) 128.3 (m) 129.3 (p) (C_6H_5) [19.0] 50.1, 31.4 ($C(CH_3)_3$) [1294] [n.o.]	−822	—	C_6D_6

3c	CH_3-Hg-C≡C-Si$(CH_3)_3$**	160.9 [1319.1]	112.8 [334.3]	0.6 ($SiCH_3$) 7.4 (CH_3Hg) [—] [1138.0]	−503	−21.2 [29.0]	C_6D_6
4	Hg[Si$(CH_3)_3$]$_2$‡‡	—	—	6.6 [93.8]	+485	+63.6 [981]	C_6D_6
5a	$(CH_3)_3$Si-Hg-CH_3‡‡	—	—	39.9 (CH_3) 4.6 ($SiCH_3$) [423.0] [118.4]	+153	−32.5 [1393]	$CDCl_3$
5b	$(CH_3)_3$Si-Hg-C_2H_5‡‡	—	—	53.5, 13.1 (C_2H_5), 4.6 ($SiCH_3$) [493.2] [18.3] [109.8]	+7	+33.8 [1227]	$CDCl_3$
5c	$(CH_3)_3$Si-Hg-$CH_2C(CH_3)_3$‡‡	—	—	78.0, 29.7, 36.5 ($CH_2C(CH_3)_3$) [512.7] [35.3] [61.0] 4.6 [113.5]	+121	+36.2 [1245]	$CDCl_3$
5d	$(CH_3)_3$Si-Hg-$C(CH_3)_3$§§	—	—	75.5, 30.2 ($C(CH_3)_3$) [612.0] [26.6] 4.9 ($SiCH_3$) [109.9]	−259	33.6 [995.6]	C_6D_6

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*$\delta^{13}C$ (±0.1), $\delta^{29}Si$ (±0.1) relative to $(CH_3)_4$ Si, $\delta^{199}Hg$ (±0.5) relative to $HgMe_2$ (neat) ($\Xi_{(^{199}Hg)}$ = 17 910 670 Hz.

†Coupling constants $J(^{199}Hg^{13}C)$ and $J(^{199}Hg^{29}Si)$ are given in square brackets.

‡$J(^{29}Si^{13}C\equiv) = 77.1$, $^2J(^{29}Si\equiv^{13}C) = 10.7$, $^1J(^{29}Si^{13}CH_3) = 56.2$ Hz.

§$^1J(^{29}Si^{13}C) = 47.0$ Hz.

‖$^1J(^{29}Si^{13}C) = 47.0$ Hz.

¶$^1J(^{29}Si^{13}C\equiv) = 76.0$, $^2J(^{29}Si\equiv^{13}C) = 10.5$, $^1J(^{29}Si^{13}C) = 56.0$, $^1J[^{29}Si(Hg)C] = 46.1$ Hz.

**$^1J(^{29}Si^{13}CH_3) = 55.7$ Hz.

††See also Refs [6, 7].

‡‡$^1J(^{29}Si^{13}C) = 46.1$ Hz.

§§Data from Ref. [6].

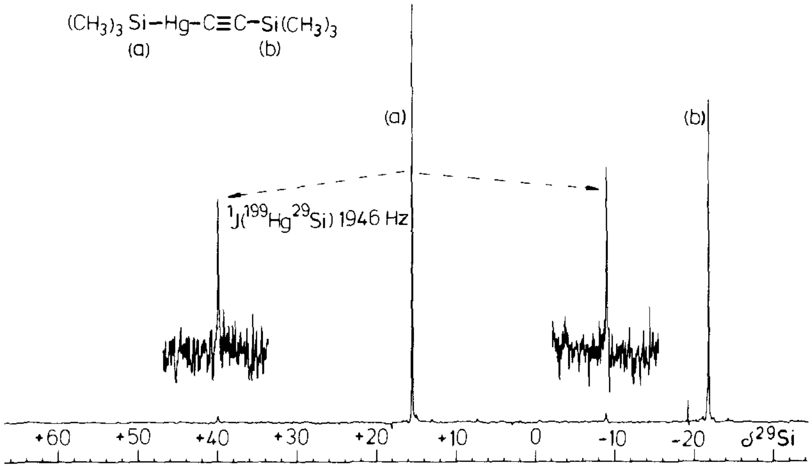

Fig. 1. ^{29}Si NMR (39.76 MHz) (refocused INEPT [8] with ^{1}H-decoupling) of the reaction solution containing the compound **2c**. The assignment is based on the δ^{29}Si values and on the coupling constant $^1J(^{199}Hg^{29}Si)$, as measured from the ^{199}Hg satellites. The ^{199}Hg satellites are slightly broadened owing to efficient chemical shift anisotropy relaxation of the ^{199}Hg nucleus [3, 24, 25] which prevents the observation of ^{199}Hg satellites for $^3J(^{199}Hg^{29}Si)$.

All reactions [Eqns (1–3)] are readily monitored by ^{199}Hg or ^{29}Si NMR (see Fig. 1). The new compounds **2** are fully characterized by their ^{13}C, ^{29}Si, ^{199}Hg NMR data and the decomposition products **6** [Eqn. (2)] are identified by ^{13}C and/or ^{29}Si NMR. NMR data are given in Table 1, together with some data for other mercury compounds for comparison.

CHEMICAL SHIFTS δ^{13}C, δ^{29}Si, δ^{199}Hg

The electropositive character of the $(CH_3)_3$ Si group is clearly reflected by the decrease in the shielding of $^{13}C^{\alpha}$ in **2** with respect to **1** and also to **3**. In contrast there is only a very small shift to higher frequency of the $^{13}C^{\beta}$–resonance in **2** compared to **1** and **3**. This shows that the π-system of the C≡C bond is hardly involved in any interactions with the mercury [15]. The data show the increasing electronegativity, as expected, with $(CH_3)_3Si < (CH_3)_3C$ (alkyl) $<$ C≡C–R. This follows from the δ^{13}C(Hg–C) values for the tert-butyl derivatives **5d**, **3b** (δ^{13}C 75.5 and 50.1, respectively) and also from the δ^{29}Si values for **4**, **5d**, **2** (δ^{29}Si 63.6, 33.6 and 15.7, 15.3, 15.4, respectively). As the changes in the nuclear shielding of ^{13}C, ^{29}Si and ^{199}Hg are governed mainly by changes in the local paramagnetic term (within POPLE's MO treatment of nuclear shielding [16]) B_0-induced mixing of excited states with the ground state has to be considered. This will be more important in the case of weak Hg–X (X $= {}^{29}$Si, ^{13}C) σ-bonds.

The mercury atom mediates all mutual ligand effects. Thus, the shielding of the ^{199}Hg nucleus will be affected both by the release of electron density, e.g. from the $(CH_3)_3$ Si group, and by the charge withdrawing ability of the alkynyl group. The former effect destabilizes Si–Hg–X σ-orbitals with respect to all other unoccupied orbitals at the mercury atom, and it also destabilizes the occupied mercury 5*d*-orbitals. Such influences are expected to cause deshielding of the ^{199}Hg nucleus. This is evident from the correlation between δ^{199}Hg and the lowest observed u.v. absorption of some silylmercurials [7]. The shielding effect observed for the ^{199}Hg nucleus in the presence of electron withdrawing groups [3, 7] provides an indirect proof for these assumptions. In the case of compounds **2** the electronegative alkynyl group compensates part of the deshielding effect of the $(CH_3)_3Si$ group. The great difference in the bond polarity of Hg–C and Hg–Si bonds is reflected by the non-additivity of ligand contributions to ^{199}Hg-nuclear shielding. It was shown that δ^{199}Hg values of the compounds R–Hg–C≡C–X correspond almost exactly to the mean value of $\delta^{199}Hg(R_2Hg)$ and $\delta^{199}Hg[Hg(C{\equiv}C{-}X)_2]$ [3] (see also the δ^{199}Hg values of compounds **1**, **3** in Table 1). Considering the δ^{199}Hg values for $(CH_3)_3Si$–Hg–R (see Ref. [6] and compounds **4**, **5** in Table 1) a similar impression may be formed at first sight. However, there is a noticeable shift of the δ^{199}Hg values of **5** towards $\delta^{199}Hg(HgR_2)$, and this trend is much more amplified in the case of the alkynyl(trimethylsilyl)mercurials **2** (with respect to $\delta^{199}Hg[Hg(C{\equiv}C{-}X)_2]$).

COUPLING CONSTANTS, $J(^{199}Hg^{13}C)$, $J(^{199}Hg^{29}Si)$

The numerous values of $J(^{199}Hg^{13}C{\equiv})$ available [3] show that the decrease in $^1J(^{199}Hg^{13}C{\equiv})$ is accompanied by a decrease in $^2J(^{199}Hg^{13}C{\equiv})$ (both coupling constants are > 0 [17]). Furthermore, it was found that in most cases a decrease in shielding of $^{13}C^{\alpha}$ is connected with a smaller value of $^1J(^{199}Hg^{13}C{\equiv})$ [3]. These features have also been observed for a series of isobutylmercury compounds [8] and they are evident for $^1J(^{199}Hg^{13}C)$ (alkyl) (*cf.* Table 1) and $^1J(^{199}Hg^{29}Si)$ values (Table 1, [6, 7]).

As for other alkynylmercury compounds [3], the most striking fact is the large range found for $^1J(^{199}Hg^{13}C\equiv)$. The coupling constant $^1J(^{199}Hg^{13}C\equiv)$ in **2c** (650 Hz) has the smallest value observed so far. This extends the range of $^1J(^{199}Hg^{13}C\equiv)$ values to ca 2300 Hz ($^1J(^{199}Hg^{13}C\equiv)$ in $Hg(C\equiv C\text{–}Cl)_2$ 2991 Hz [3]). As pointed out previously [3] this range appears to be too large to be accommodated in the average excitation energy (ΔE) approach (a simplification of POPLE and SANTRY's MO treatment [9, 20], assuming the Fermi-contact term to be dominant). The new data available reinforce this conclusion. Indeed, it may be advisable to include the influence of relativistic effects [21] on the Hg-6*s* electrons, for a more quantitative understanding of $^1J(^{199}HgX)$.

The qualitative expectations for changes in $^1J(^{199}Hg^{13}C)$ or $^1J(^{199}Hg^{29}Si)$ based on rehybridization [22] are fulfilled. Valiant attempts have been made to use the simple hybrid orbital model for the quantitative prediction of $^1J(^{199}Hg^{13}C\equiv)$ values but the results are not very accurate [23]. The same authors also have claimed a quantitative relationship between $^1J(^{199}Hg^{13}C)$ and $^1J(^{199}Hg^{29}Si)$ in organyl(silyl)mercurials [19]. This relationship holds for the alkyl(trimethylsilyl)mercurials but it breaks down completely if the data for compounds **2a, c** or **1a, c** are inserted. Obviously, these simple concepts are useful and work well if the ligand properties are not too different. This guarantees that most factors influencing the magnitude of $^1J(^{199}Hg^{13}C)$ or $^1J(^{199}Hg^{29}Si)$ remain fairly constant except for the changes in the "*s*-character" of the Hg–C or Hg–Si hydrid orbitals. However, the introduction of strongly polarizing groups, like the alkynyl group, together with the presence of a readily polarizable Hg–Si bond, breaks up this concept.

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REFERENCES

[1] (a) R. NAST, *Coord. Chem. Rev.* **47**, 89 (1982); (b) B. WRACKMEYER, *Rev. Silicon, Germanium, Tin, Lead Compds* **6**, 75 (1982).

[2] B. WRACKMEYER, *J. Magn. Reson.* **42**, 287 (1981).

[3] A. SEBALD and B. WRACKMEYER, *Spectrochim. Acta* **38A**, 163 (1982).

[4] A. SEBALD, B. WRACKMEYER and W. BECK, *Z. Naturforsch. Teil B* **38**, 45 (1983).

[5] A. SEBALD, P. FRITZ and B. WRACKMEYER, *Spectrochim. Acta* **41A**, 1405 (1985).

[6] T. N. MITCHELL and H. C. MARSMANN, *J. Organomet. Chem.* **150**, 171 (1978).

[7] M. J. ALBRIGHT, T. F. SCHAAF, A. K. HOVLAND and J. P. OLIVER, *J. Organomet. Chem.* **259**, 37 (1983).

[8] (a) D. P. BURUM and R. R. ERNST, *J. Magn. Reson.* **39**, 163 (1980); (b) G. A. MORRIS, *J. Magn. Reson.* **41**, 185 (1980).

[9] L. G. MAKAROVA and A. N. NESMEYANOV, *The Organic Compounds of Mercury.* Worth-Holland, Amsterdam (1967).

[10] E. WIBERG, O. STECHER and E. STAUDE, *Angew. Chem.* **75**, 516 (1963).

[11] N. S. VYAZANKIN, E. N. GLADYSHEV, E. A. ARKHANGEL'SKAYA and G. A. RAZUVAEV, *J. Organomet. Chem.* **17**, 340 (1969).

[12] T. N. MITCHELL, *J. Organomet. Chem.* **71**, 27 (1974).

[13] T. F. SCHAAF and J. P. OLIVER, *Inorg. Chem.* **10**, 1521 (1971).

[14] A. G. LEE, *J. Organomet. Chem.* **16**, 321 (1969).

[15] C. CAULETTI, C. FURLANI, M. N. PIANCASTELLI, A. SEBALD and B. WRACKMEYER, *Inorg. Chem.* **23**, 1113 (1984).

[16] J. A. POPLE, *Molec. Phys.* **7**, 301 (1964) and references cited therein.

[17] W. MCFARLANE, A. SEBALD and B. WRACKMEYER, to be published.

[18] D. STEINBORN, R. TAUBE, R. RADEGLIA and W. HÖBOLD, *J. Organomet. Chem.* **210**, 139 (1981).

[19] J. A. POPLE and D. P. SANTRY, *Molec. Phys.* **8**, 1 (1964).

[20] H. M. MCCONNELL, *J. chem. Phys.* **24**, 460 (1956).

[21] (a) P. PYKKÖ, *Chem. Phys.* **22**, 289 (1977); (b) P. PYKKÖ, *J. Organomet. Chem.* **232**, 21 (1982).

[22] H. A. BENT, *Chem. Rev.* **61**, 275 (1961).

[23] R. RADEGLIA, D. STEINBORN and R. TAUBE, *Spectrochim. Acta* **39A**, 843 (1983).

[24] A. SEBALD and B. WRACKMEYER, *J. Magn. Reson.* **63**, 397 (1985).

[25] D. G. GILLIES, L. P. BLAAUW, G. R. HAYS, R. HUIS and A. D. H. CLAGUE, *J. Magn. Reson.* **42**, 420 (1981).