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Two-dimensional $^{13}C,^{199}Hg$ correlation: a new NMR method for characterisation of organomercury compounds

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Abstract

Two-dimensional $^{13}C,^{199}Hg$ correlation has been used for the first time to facilitate assignments for ^{13}C and ^{199}Hg spins in a dimercury compound. Correlations over more than one bond provide additional information on the constitution of these molecules. Unusual ^{13}C isotope effects on the ^{199}Hg chemical shifts are reported.

Key words: Nuclear magnetic resonance; Mercury; Correlation spectroscopy

1. Introduction

Currently, ^{199}Hg and ^{13}C NMR spectroscopy are the most important techniques used to characterize organomercury compounds [1]. Owing to the relatively high natural abundance of ^{199}Hg, the ^{13}C spectra show satellites from which spin couplings over several bonds can be measured, and these in turn can often be used to assign the carbon spectra. In contrast to ^{13}C, the ^{199}Hg NMR spectra are often difficult to obtain, especially because on modern high-field instruments the ^{199}Hg nucleus relaxes very rapidly and gives very broad signals. In compounds containing more than one chemically distinguishable mercury atom, the analysis of the ^{13}C satellite spectra can become tedious, and sometimes the satellites are obscured by other signals or impurities.

We describe below a new NMR method that has become feasible because of the development of NMR instruments that contain a third independent radio frequency channel and the necessary triple resonance probehead. With these spectrometers a two-dimensional $^{13}C,^{n}X$ correlation with complete proton decoupling can be performed, leading to a very easy assignment of resonances even in otherwise difficult cases. Examples of this new technique were recently communicated for the spin pairs $^{13}C,^{2}H$ [2], $^{13}C,^{6}Li$ [3], $^{13}C,^{15}N$ [4] and $^{13}C,^{31}P$ [5]. In the field of organometallic chemistry we have already shown the possibilities and problems inherent in these methods for the spin pairs $^{13}C,^{29}Si$ [6], $^{13}C,^{119}Sn$ [7] and $^{13}C,^{77}Se$ [8]. However, each new nucleus to be correlated with ^{13}C has its own advantages and difficulties. Here we report on the first example of a $^{13}C,^{199}Hg$ correlation.

2. Results and discussion

To provide a good example for a $^{13}C,^{199}Hg$ correlation we needed a dimercury compound that fulfilled the following requirements: (i) the mercury atoms must be chemically different; (ii) the ^{199}mercury signals should be relatively narrow; and (iii) the compound should be reasonably stable.

We expected that 1,4-bis (methylmercury)-2-methylbutane (**1**) would meet, or come close to meeting, these requirements, and therefore synthesized this new compound. For this task, we adapted the hydroboration and mercuration method developed by Brown and coworkers [9] to obtain the corresponding dimercury chloride of isoprene, which was then methylated with a methyl Grignard reagent. Chromatographic purification was impossible because **1** decomposes at 50°C or on silica gel. However, the ^{199}Hg and ^{13}C NMR spectra confirmed the presence of only one compound, which gave a satisfactory elemental analysis.

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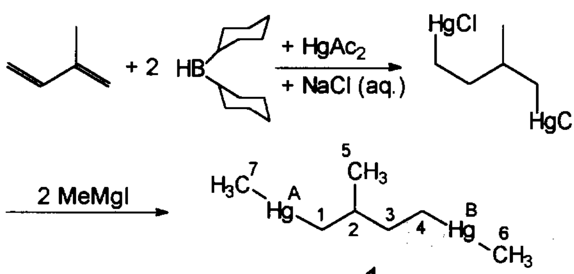

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The ^1H and ^{13}C NMR spectra were assigned by standard methods with, in addition, H,H-COSY and H,C-COSY spectra. The assignments are given in Table 1. In these spectra, we find signals from three methylene groups, two of which show Hg satellites with a large ^1J(Hg,C) spin coupling, thus the starting point of the assignment is the remaining methylene group C-3, from which the other protons and carbon atoms can be identified. Of course, the relative assignment of the methyl groups attached to the mercury atoms and the relative assignment of the mercury atoms remain uncertain.

These remaining assignments are most easily obtained by performing a $^{13}C,^{199}Hg$ correlation, and this is shown for the methylene carbon atoms in Fig. 1. Because the assignment of the methylene carbon atoms is known, the attached mercury atoms and, in addition, the corresponding methyl groups can be immediately identified. In Fig. 2 we show that $^{13}C,^{199}Hg$ correlation is also possible over several bonds, and this can lead to an easy assignment of long-range couplings. The usual relationship of $^1J > {}^3J > {}^2J$ is apparently also valid in the spin pair $^{13}C,^{199}Hg$. The sign of these coupling constants can be derived from the two-dimensional H,C COSY spectra from the tilt of the satellite signals, and is in accordance with previous findings [1].

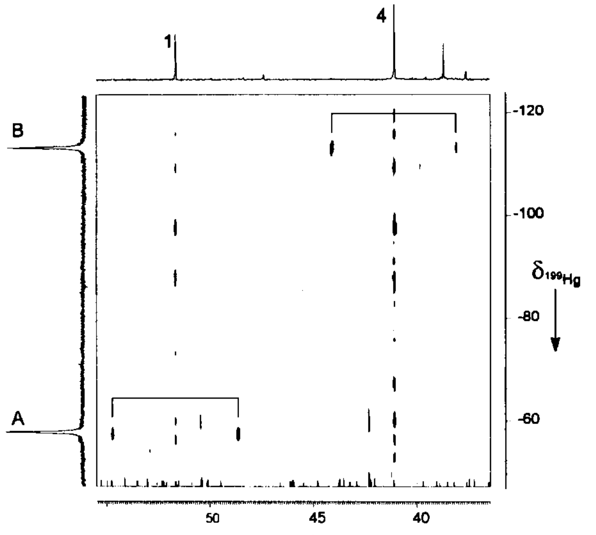

Fig. 1. Two-dimensional $^{13}C,^{199}Hg$ correlation of **1**, using $^1J(^{13}C,^{199}Hg)$; the expansions of the methylene groups C-1 and C-4 are shown.

There are several factors determining the selection of the three possible correlation methods [10], including the T_1 and T_2 relaxation times of the two nuclei, the comparison of the gyromagnetic ratios, and the natural abundance. Empirically, we found that the polarization transfer method with carbon detection, as shown in Fig. 3, is most advantageous for this spin pair.

It is very interesting to note that in dimethylmercury [11], a "wrong sign" isotope effect [12] was found, with the ^{199}Hg spins bound to ^{13}C resonating at lower field

TABLE 1. ^1H, ^{13}C and ^{199}Hg chemical shifts [a] and $^{13}C,^{199}Hg$ spin coupling constants [b] for 1

Atom	δ	J (Hz)	Atom	δ	J (Hz)
C-1	51.7	758 (A)	H-1	1.16–1.24	95(A)
C-2	38.8	98 (B), 35 (A)	H-2	2.48–2.50	
C-3	41.1	80 (A), 29 (B)	H-3	1.73–1.80	
C-4	41.2	749 (B)	H-4	1.05–1.10	95(B)
C-5	25.6	77 (A)	H-5	1.04	
C-6	22.7	596 (B)	H-6	0.33	95(B)
C-7	24.3	600 (A)	H-7	0.345	95(A)
Hg_A	−57.8				
Hg_B	−113.5				

[a] Referred to external $(CH_3)_2Hg$. [b] Coupled Hg atom in parentheses.

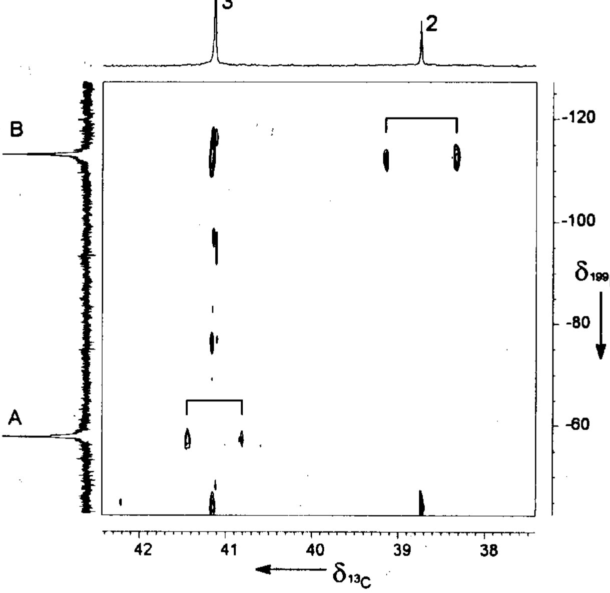

Fig. 2. Two-dimensional $^{13}C,^{199}Hg$ correlation of **1**, using $^3J(^{13}C,^{199}Hg)$; the expansions for carbon atoms C-2 and C-3 are shown.

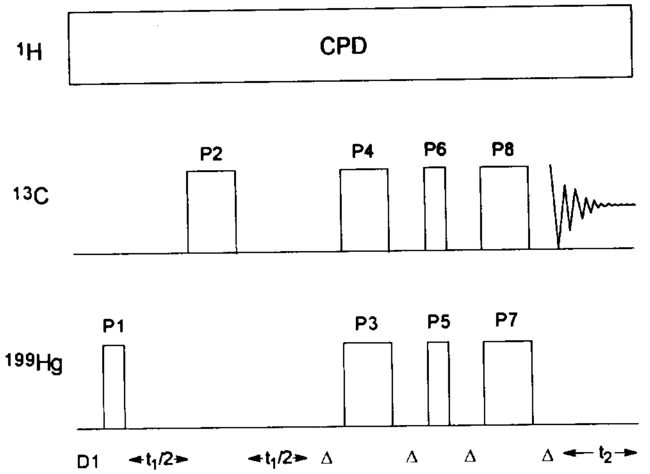

Fig. 3. Pulse sequence used for $^{13}C,^{199}Hg$ correlation. P1, P5 and P6 represent 90° pulses, P2, P3, P4, P7 and P8 180° pulses. Phase Cycles: P1: x; P2, P3, P4, P7: $x, x, -x, -x$; P5: $y, -y$, incremented according to the TPPI method; P6: $(x)_4, (y)_4, (-x)_4, (-y)_4$; P8: $x, x, -x, -x, y, y, -y, -y$; receiver: $(x, -x)_2, (y, -y)_2, (-x, x)_2, (-y, y)_2$. The delay Δ was adjusted to $1/4\ J_{C,Hg}$; composite pulse decoupling (CPD) applying the waltz16 sequence was used on the ^1H channel.

than those bound to ^{12}C. This is not restricted to the linear small molecule dimethylmercury, but is also found for some other alkyl mercury compounds [13]. In **1** we find isotope effects of 262 ppb for the methyl groups C-6 and C-7, and for the methylene groups C-1 and C-4 we find isotope effects of 246 ppb, both downfield with respect to the ^{199}Hg signal bound to ^{12}C. Thus, these positive isotope effects seem to be more general for ^{199}Hg NMR, and warrant theoretical explanation.

3. Experimental details

3.1. Synthesis of 1,4-bis (methylmercury)-2-methylbutane 1

Isoprene (1.02 g, 15 mmol) was added slowly to a mixture of 30 ml of a 1.0 molar borane-THF solution and 4.93 g (60 mmol) cyclohexene at 0°C in a dry nitrogen-flushed flask, and the mixture was then stirred overnight. After addition of 9.56 g mercury(II) acetate, the yellow mixture was stirred for an additional 10 min, and then treated with 100 ml of ice-cold water. Dropwise addition of 30 ml of a 1 molar NaCl solution produced a grey precipitate, which was washed with petroleum ether, and dried in air. A portion (3.0 g, 5.5 mol) of this crude product was added to a Grignard reagent prepared from 3.12 g (22 mmol) of CH_3I in 30 ml of ether at room temperature under dry nitrogen. After 2 h the mixture was hydrolyzed with 20 ml of 1% aqueous H_2SO_4. Extraction was carried out with ether, and the extract was dried over Na_2SO_4; finally the solvent was evaporated off. The resulting yellow oil (0.5 g, 18%) was dried under high vacuum and shown to be analytically and spectroscopically pure. The IR spectrum shows a strong Hg,C vibration band at 521 cm^{-1}. Elemental analysis: ($C_7H_{16}Hg_2$, MW 501.386), C: calc. 16.77%, found 17.05%, H: calc. 3.22%, found 3.30%.

3.2. NMR spectroscopy

All spectra were recorded on a Bruker AMX-500 spectrometer at 300 K using a half-concentrated sample of **1** in C_6D_6. A triple-resonance probe head with a ^1H coil in inverse geometry was used; this coil was double tuned to ^{13}C at 125.76 MHz. A second multinuclear tunable coil was adjusted to ^{199}Hg at 89.56 MHz. The two-dimensional spectra were taken on 2048 data points in F_2 and with 64 time increments in F_1 using relaxation delays of 5 s and 200 scans for each FID in the case of the correlation over one bond. An exponential window in F_2 and a $\pi/2$-shifted, squared sinebell window in F_1 were applied. δ_{Hg} values are referred to external Me_2Hg, δ_C values were measured *vs.* C_6D_6, and calculated with $\delta(TMS) - \delta(C_6D_6) = 128.0$.

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References

1 B. Wrackmeyer and R. Contreras, *Ann. Rep. NMR Spectrosc.*, *24* (1992) 267.
2 J.R. Wesener, P. Schmitt and H. Günther, *Org. Magn. Reson.*, *22* (1984) 468; J.R. Wesener, and H. Günther, *J. Am. Chem. Soc.*, *107* (1985) 1537.
3 D. Moskau, F. Brauers, H. Günther and A. Maercker, *J. Am. Chem. Soc.*, *109* (1987) 5532; H.-J. Gais, J. Vollhardt, H. Günther, D. Moskau, H.J. Lindner and S. Braun, *J. Am. Chem. Soc.*, *110* (1988) 978.
4 R.E. Moore, V. Bornemann, W.P. Niemczura, J.M. Gregson, J.-L. Chen, T.R. Norton, G.M.L. Patterson and G.L. Helms, *J. Am. Chem. Soc.*, *111* (1989) 6128.
5 L.D. Sims, L.R. Soltero and G.E. Martin, *Magn. Reson. Chem.*, *27* (1989) 599; G. Grossmann and H. Kornber, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, *61* (1991) 269; H. Beckmann, G. Grossmann and G. Ohms, *Magn. Reson. Chem.*, *30* (1992) 860.
6 S. Berger, *J. Magn. Reson. Ser. A*, *101* (1993) 329.
7 S. Berger and T.N. Mitchell, *Organometallics*, *11* (1992) 3481.
8 T. Fäcke, R. Wagner and S. Berger, *J. Org. Chem.*, *58* (1993) 5475.
9 R.C. Larock and H.C. Brown, *J. Am. Chem. Soc.*, *92* (1970) 2467; G. Zweifel, N.R. Ayyangar and H.C. Brown, *J. Am. Chem. Soc.*,

85 (1963) 2072; G. Zweifel, K. Nagase and H.C. Brown, *J. Am. Chem. Soc.*, *84* (1962) 190.
10 P. Bast, S. Berger and H. Günther, *Magn. Reson. Chem.*, *30* (1992) 587.
11 J. Jokisaari and K. Räisänen, *Mol. Phys.*,*36* (1978) 113.
12 S. Berger, in P. Diehl, E. Fluck, H. Günther and R. Kosfeld (eds.) *NMR – Basic Principles and Progress*, Vol. 22, Springer, Berlin, 1990, p. 1.
13 Yu.K. Grishin and Yu.A. Ustynyuk, *Zh. Strukt. Khim.*, *23* (1982) 163.