Characterization of Alkyl- and Aryl-mercuric Hydrides by NMR Spectroscopy

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Low-temperature NMR measurements (^1H, ^{13}C, ^{199}Hg) confirm that organomercuric hydrides (RHgH; R = alkyl, cycloalkyl, phenyl) are characterisable species in solution.

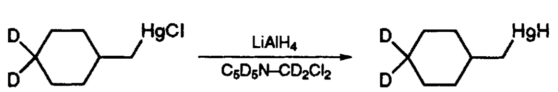
Organomercuric hydrides $(RHgH)_x$, although uncharacterised as a molecular class, are generally assumed to be intermediates in the reduction or organomercury chlorides or acetates by metal hydrides,[1–4] and this reaction (with $NaBH_4$) represents the second stage of the solvomercuration–demercuration route to Markovnikov alcohols, ethers *etc.*[5] Under the conditions normally employed for such reductions (*e.g.* THF–H_2O, THF = tetrahydrofuran), the decomposition of the putative RHgH [eqn. (1)] is very rapid as evidenced by Hg^0 production.

$$RHgX + M\text{-}H \rightarrow [RHgH] \rightarrow R\text{-}H + Hg^0 \quad (1)$$
$$(X = OAc, Cl)$$

Our observations have indicated however, that the rate of decomposition is not so fast as to preclude hope of direct detection of RHgH by low-temperature NMR spectroscopic methods.[6] We now report key NMR parameters for a range of alkyl, cycloalkyl and aryl systems which confirm that $(RHgH)_x$, although relatively unstable, can be characterised by NMR methods.†‡

Our initial experiments were conducted with cyclohexylmethylmercuric chloride, or deuteriated analogues.[7] Thus 4,4-[$^2H_2$]-cyclohexylmethylmercuric chloride **1**, as a [$^2H_5$]pyridine solution (0.5 mmol ml^{-1}) was added very slowly to a suspension of $LiAlH_4$ in CD_2Cl_2 (0.5 mmol ml^{-1}) maintained between −50 and −70 °C. After stirring for 5 min, the solution was transferred through a filter-frit (−78 °C) into a cooled (−70 °C) 5 mm NMR tube, in which finely dispersed Hg^0 accumulated as slow decomposition occurred. NMR measurements were conducted at −70 °C, and the Hg^0 led to line broadening in some cases. $Bu^n{}_3SnH$, in [$^2H_8$]toluene, was also employed as a reducing agent in some experiments.

The ^1H NMR spectrum of the reduction product of **1** [eqn. (2)] exhibited a signal at δ 17.3, which was flanked by satellites



1 **2**

(2)

of the appropriate intensity emanating from molecules containing ^{199}Hg ($I = \frac{1}{2}$, 16.8%), giving $^1J_{^{199}Hg-^1H}$ = 2440 Hz (Fig. 1). Correspondingly, the ^{199}Hg spectrum was a doublet ($^1J_{^{199}Hg-^1H}$ = 2441 Hz) at δ −508 (relative to external Me_2Hg), which collapsed to a singlet when the δ 17.3 region in the ^1H spectrum was irradiated. (The doublet signal in the ^{199}Hg spectrum arises because ^1H decoupling was restricted to the δ 0–10 range, and thus did not perturb Hg–*H*.) A signal at δ 2.20, with $J_{^{199}Hg-^1H}$ ≃ 110 Hz is assigned to –C*H*$_2$HgH. The key signal in the ^{13}C NMR spectrum was that located at δ 47.8 and flanked by ^{199}Hg satellites giving $^1J_{^{13}C-^{199}Hg}$ = 840 Hz and assigned to –*C*H_2HgH. The NMR features described and assigned to **2** [eqn. (2)] were also observed when $Bu^n{}_3SnH$ in [$^2H_8$]toluene was the reducing agent, and hence none of the spectral features requires the presence of Li, Al or Sn alone or in combination. Reduction of **3** provided a ^{199}Hg spectrum consisting of a doublet (δ, −500, J ~ 2400 Hz) bearing fine structure consistent with ^2H-coupling and leading to $^2J_{^{199}Hg-^2H}$ ≃ 15 Hz, consistent with $^2J_{^{199}Hg-^1H}$ ≃ 110 Hz for **2**, as mentioned above. These observations require the attachment of both R and H to Hg for times long on the NMR time-scale, consistent with RHgH in some form.

Cyclohexylmercuric hydride, if a *bona fide* species, would be anticipated to exhibit NMR signals at *ca.* −70 °C for the *axial* and *equatorial* conformers.[8,9] Treatment of mercurial **4** with $Bu^n{}_3SnH$ at −70 °C ([$^2H_8$]toluene solvent) and immediate acquisition of the 500 MHz ^1H NMR spectrum, provides signals at δ +16.1 ($J_{^{199}Hg-^1H}$ = 2302 Hz) and +17.34 ($J_{^{199}Hg-^1H}$ = 2307 Hz) in a ratio of *ca.* 1:2, respectively. Gradual warming of the sample resulted in signal broadening and coalescence at ca. −20 °C, with δ_H (av.) ≈ 17.1 and $J_{^{199}Hg-^1H}$ ≈ 2300 Hz. On the basis of an *axial* preference for HgH, as has been established for a wide range of mercury groups on cyclohexane,[8,10] the lower field signal (δ +17.34) corresponds to *axial*-cyclohexylmercuric hydride, and that at δ +16.1 to the *equatorial* conformer, providing A_{HgH} ≈ −0.2 kcal mol^{-1}.[10] This interpretation is reinforced by the low-temperature ^{199}Hg NMR spectrum, which consists of *two* doublets, at δ −631.5 ($J_{^{199}H-^1H}$ = 2320 Hz) and δ − 756.3 ($J_{^{199}Hg-^1H}$ = 2310 Hz) with the former signal being considerably more intense, and assigned confidently to the *axial*-conformer on the basis of

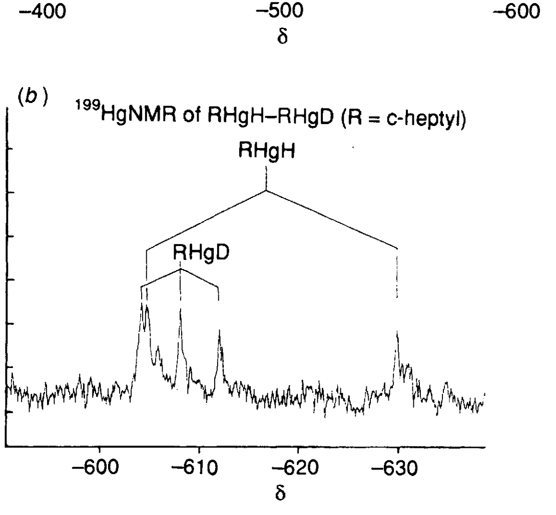
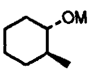
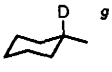
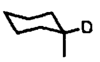
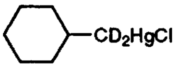


Fig. 1 (*a*) the 89.53 MHz ^{199}Hg NMR spectrum of 4,4-[$^2H_2$]-cyclohexylmethylmercuric hydride with $^1J_{^{199}Hg-^1H}$ being *ca.* 2440 Hz, as measured also from the ^{199}Hg satellites in the 500 MHz ^1H NMR spectrum [solvent: CD_2Cl_2 : C_5D_5N (1:1)]. (*b*) The 89.53 MHz ^{199}Hg NMR spectrum of the RHgH–RHgD mixture (R = cycloheptyl) obtained by reducing RHgCl with a $LiAlH_4$–$LiAlD_4$ mixture (see text for details).

Table 1 NMR parameters[a] for RHgH (−70 °C)

R	δ_{199Hg}[c]	$\delta_{Hg\text{-}H}$[d]	$^1J_{199Hg\text{-}1H}$[e]/Hz	$^2J_{199Hg\text{-}1H}$/Hz	$^1J_{199Hg\text{-}13C}$/Hz
c-Hex-CH$_2$[b]	−508	+17.3	2441	110	840
c-Hex-CD$_2$[b]	−500	+17.6	2409	—	—
c-Hept[b]	−640	+17.1	2308		820[f]
Me[g]	−456	+16.8	2660	100	920[h]
C$_6$H$_5$[g]	−830	+13.3	2936	—	—
 [g]	−725	+17.5	2314	—	—
 [g]	−756	+16.1	2302	—	—
 [g]	−632	+17.3	2307	—	—

[a] Spectra obtained on a Bruker AMX-500 spectrometer with 125 MHz for ^{13}C and 89.53 MHz for ^{199}Hg. [b] Using CD_2Cl_2–C_5D_5N (1:1) solvent and $LiAlH_4$ or $LiAlD_4$ as reducing agent. [c] Relative to external Me_2Hg at 0.0 ppm (80% Me_2Hg in $CDCl_3$). [d] Relative to the lowest field signal of residual C_5H_5N at δ 8.71. [e] Measured from the ^1H NMR spectrum, except for the last entry. [f] ^2J of 86 Hz was measured; $\delta(^{31}C^1)$ = 35.05, $\delta(^{13}C^{2,6})$ = 30.33. [g] Using [$^2H_8$]toluene–C_5D_5N (3:1) solvent and $Bu^n{}_3SnH$ as reducing agent. [h] $\delta(^{13}C)$ = 19.71.



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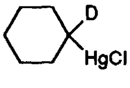

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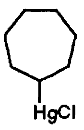

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MeHgCl

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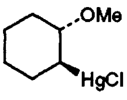

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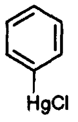

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^{199}Hg shifts for other *axial-equatorial* conformers of cyclohexylmercury systems.[10]

Reduction of mercurial **5** with a mixture of $LiAlH_4$ and $LiAlD_4$ (*ca.* 30:70) provided the expected RHgH–RHgD mixture, the ^{199}Hg NMR spectrum of which consisted of a doublet at δ −617.3 ($^1J_{199Hg\text{-}1H}$ = 2317 Hz) for the hydride and a triplet at δ −608.2 ($^1J_{199Hg\text{-}2H}$ = 356 Hz) for the deuteride. These results provide a ^2H isotope effect ($^1\Delta$) on the ^{199}Hg chemical shift of δ +9.1, and this large value reflects the responsiveness of ^{199}Hg chemical shifts to the mercury environment.[10,11] Replacement of H with D in $Bu^n{}_3SnH$ leads to a high field shift of −1.6 ppm in the ^{119}Sn resonance.[12] The NMR parameters for the organomercuric hydrides examined are located in Table 1.

With respect to stability of the derived RHgH, that from the oxymercurial **7** is very unstable, as is phenylmercuric hydride, formed from chloride **8**. The chief decomposition product from phenylmercuric hydride is diphenylmercury, identified by its ^{199}Hg signal at δ −766.[11] Decomposition of these hydrides is accompanied by gas formation (hydrogen?) and may involve a species akin to RHgHgR, consistent with our observation of greater longevity of RHgH at low concentrations.† Trends in the coupling constants to ^{199}Hg (Table 1) are consistent with hydride resembling alkyl as a ligand on mercury, on the basis that $^1J_{199Hg\text{-}13C}$ are approximately halved for the change $RHgX \rightarrow R_2Hg$.[10,11,13] Thus $^1J_{199Hg\text{-}13C}$ values for Me_2Hg, MeHgH and MeHgCl are 692, 920 and 1665 Hz, respectively.§ The large value of $^1J_{Hg\text{-}H}$ = 2936 Hz in phenylmercuric hydride, compared with the lower values for the alkyl derivatives, is consistent with known trends in similar organometallic compounds *e.g* of Sn. ^{199}Hg chemical shifts are very dependent on concentration and solvent,[10,11] but the shifts in Table 1 for the various hydrides are nicely in accord with effects of branching within alkyl groups on such shifts, and the more pronounced shielding of Hg attached to a phenyl ring is expected.[11] The changes in coupling constants to ^{199}Hg, with changing solvent, indicate RHgH possess little Lewis acceptor character, as is generally the case for dialkylmercurials. The degree of aggregation and geometry of RHgH are unknown, but measurements of $^3J_{H\text{-}H}$ across H–C–Hg–H may be informative.

The most characteristic feature of the spectra of RHgH is the signal for δ_{HgH} at *ca.* +17, with attendant satellites, giving $^1J_{Hg\text{-}H}$ of 2300–2900 Hz. This chemical shift is intriguing and in stark contrast to the shielded nature of hydridic transition metal bound protons.[14] At this time, we merely note that in Me_3SnH, δ_H is +5.37,[15] and for a range of complexed organozinc hydrides, δ_{ZnH} is between δ +4 and +5.[16] This work describing NMR measurements of the three nuclei present in organomercuric hydrides removes them from the category of presumed but elusive intermediates.

The authors are grateful to the Australian Research Council for support of this work, and to The University of Queensland Centre for Magnetic Resonance (Director: Professor D. Doddrell) for access to the Bruker AMX-500 spectrometer, and to Dr I. Brereton for help and advice. Dr Adam P. Wells kindly donated some organomercury compounds.

Received, 9th August 1993; Com. 3/04810A

Footnotes

† The very recent report (P. J. Craig, D. Mennie, M. Needham, N. Oshah, O. F. X. Donnard and F. Martin, *J. Organometal. Chem.*, 1993, **447**, 5) describing the ^1H NMR and mass spectra of the reduction product of MeHgCl under very dilute conditions is noteworthy. We utilized different solvent system (for low temperature observations) and more concentrated solutions so that the species could be characterised by ^{13}C and ^{199}Hg NMR spectra, as well as ^1H NMR. However, the deposition of Hg^0 during spectral acquisition sometimes led to poorer resolution. The experiences of Craig and coworkers with MeHgH, and ours with a wider range of systems

indicate that the decomposition rates are influenced by concentration and solvent. We thank Professor Craig for a valuable exchange of information.

‡ Mass spectral evidence for MeHgH has also been obtained. Extraction of tuna fish with HCl, derivatisation with $NaBH_4$, and purge and trap procedures *etc.* permitted acquisition of mass spectra consistent with MeHgH. The halflife of MeHgH in water at *ca.* 20 °C was estimated to be 2 h (M. B. Filippell, F. Baldi, F. E. Briackman and G. J. Olson, *Environ. Sci. Technol.*, 1992, **26**, 1457).

§ In cyclohexylmethylmercuric chloride, $-CH_2HgCl$ is located at δ 42.7 with $^1J_{^{199}Hg-^{13}C} = 1400$ Hz, and δ 2.2 with $^2J_{^{199}Hg-^{13}C} = 200$ Hz.

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