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 NaBH₄) 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–H₂O, THF = tetrahydrofuran), the decomposition of the putative RHgH [eqn. (1)] is very rapid as evidenced by Hg⁰ production.

$$RHgX + M-H \rightarrow [RHgH] \rightarrow R-H + Hg^{0}$$
(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-[²H₂]-cyclohexylmethylmercuric chloride 1, as a [²H₃]pyridine solution (0.5 mmol ml⁻¹) was added very slowly to a suspension of LiAlH₄ in CD₂Cl₂ (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 Hg⁰ accumulated as slow decomposition occurred. NMR measurements were conducted at -70 °C, and the Hg⁰ led to line broadening in some cases. Bun₃SnH, in [²H₈]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



of the appropriate intensity emanating from molecules containing ¹⁹⁹Hg $(I = \frac{1}{2}, 16.8\%)$, giving ¹ $J_{199Hg-1H} = 2440$ Hz (Fig. 1). Correspondingly, the ¹⁹⁹Hg spectrum was a doublet (¹ $J_{199Hg-1H} = 2441$ 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 ¹⁹⁹Hg 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 $J_{199Hg=1H} \simeq 110$ Hz is assigned to $-CH_2$ HgH. The key signal in the ¹³C NMR spectrum was that located at δ 47.8 and flanked by ¹⁹⁹Hg satellites giving ${}^{1}J_{13C-199Hg} = 840$ Hz and assigned to -CH2HgH. The NMR features described and assigned to 2 [eqn. (2)] were also observed when Buⁿ₃SnH in [²H₈]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 ¹⁹⁹Hg spectrum consisting of a doublet (δ , -500, $J \sim 2400$ Hz) bearing fine structure consistent with ²H-coupling and leading to ${}^{2}J_{199Hg-2H}$ \simeq 15 Hz, consistent with ${}^{2}J_{199Hg-1H} \simeq$ 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 Bun₃SnH at -70 °C ([2H₈]toluene solvent) and immediate acquisition of the 500 MHz ¹H NMR spectrum, provides signals at δ +16.1 ($J_{199Hg-1H}$ = 2302 Hz) and +17.34 ($\hat{J}_{199Hg-1H}$ = 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 $\delta_{\rm H}$ (av.) ≈ 17.1 and $J_{199{\rm Hg}-1{\rm H}}$ \approx 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 $A_{HgH} \approx -0.2$ kcal mol^{-1.10} This interpretation is reinforced by the low-temperature ¹⁹⁹Hg NMR spectrum, which consists of *two* doublets, at δ -631.5 $(J_{199H-1H} = 2320 \text{ Hz})$ and $\delta - 756.3 (J_{199Hg-1H} = 2310 \text{ Hz})$ 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 ¹⁹⁹Hg NMR spectrum of 4,4-[²H₂]cyclohexylmethylmercuric hydride with ¹J_{199Hg-1H} being ca. 2440 Hz, as measured also from the ¹⁹⁹Hg satellites in the 500 MHz ¹H NMR spectrum [solvent: $CD_2Cl_2:C_5D_5N$ (1:1)]. (b) The 89.53 MHz ¹⁹⁹Hg NMR spectrum of the RHgH–RHgD mixture (R = cycloheptyl) obtained by reducing RHgCl with a LiAlH₄-LiAlD₄ mixture (see text for details).

Table 1 NMR parameters^a for RHgH (-70 °C)

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| R | δ _{199Hg} ^c | $\delta_{\mathrm{Hg-H}}{}^{d}$ | ¹ J _{199Hg-1H} ^e /Hz | ² J _{199Hg-1H} /Нz | ¹ J _{199Hg-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 | | 820f |
| Me ^g | -456 | +16.8 | 2660 | 100 | 920 ^h |
| $C_6H_5^g$ | -830 | +13.3 | 2936 | | _ |
| OMe ^g | -725 | +17.5 | 2314 | | — |
| | -756 | +16.1 | 2302 | - | |
| mpo ° | -632 | +17.3 | 2307 | | |

^{*a*} Spectra obtained on a Bruker AMX-500 spectrometer with 125 MHz for ¹³C and 89.53 MHz for ¹⁹⁹Hg. ^{*b*} Using CD₂Cl₂-C₅D₅N (1:1) solvent and LiAlH₄ or LiAlD₄ as reducing agent. ^{*c*} Relative to external Me₂Hg at 0.0 ppm (80% Me₂Hg in CDCl₃). ^{*d*} Relative to the lowest field signal of residual C₅H₅N at δ 8.71. ^{*e*} Measured from the ¹H NMR spectrum, except for the last entry. ^{*f*} ²J of 86 Hz was measured; δ (³¹C¹) = 35.05, δ (¹³C^{2.6}) = 30.33. ^{*s*} Using [²H₈]toluene-C₅D₅N (3:1) solvent and Buⁿ₃SnH as reducing agent. ^{*h*} δ (¹³C) = 19.71.



¹⁹⁹Hg shifts for other *axial-equatorial* conformers of cyclohexylmercury systems.¹⁰

Reduction of mercurial 5 with a mixture of LiAlH₄ and LiAlD₄ (*ca.* 30:70) provided the expected RHgH-RHgD mixture, the ¹⁹⁹Hg NMR spectrum of which consisted of a doublet at δ -617.3 (¹J_{199Hg-1H} = 2317 Hz) for the hydride and a triplet at δ -608.2 (¹J_{199Hg-2H} = 356 Hz) for the deuteride. These results provide a ²H isotope effect (¹ Δ) on the ¹⁹⁹Hg chemical shift of δ +9.1, and this large value reflects the responsiveness of ¹⁹⁹Hg chemical shifts to the mercury environment.^{10,11} Replacement of H with D in Buⁿ₃SnH leads to a high field shift of -1.6 ppm in the ¹¹⁹Sn 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 ¹⁹⁹Hg 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 ¹⁹⁹Hg (Table 1) are consistent with hydride resembling alkyl as a ligand on mercury, on the basis that ¹J_{199Hg-13C} are approximately halved for the change RHgX \rightarrow R₂Hg.^{10,11,13} Thus ¹J_{199Hg-13C} values for Me₂Hg, MeHgH and MeHgCl are 692, 920 and 1665 Hz, respectively.§ The large value of ¹J_{Hg-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. ¹⁹⁹Hg 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 ¹⁹⁹Hg, 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-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 ${}^{1}J_{\text{Hg-H}}$ 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 Me₃SnH, 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.

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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 ¹³C and ¹⁹⁹Hg NMR spectra, as well as ¹H NMR. However, the deposition of Hg⁰ 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 NaBH₄, 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, -CH2HgCl is located at δ 42.7 with ${}^{1}J_{199Hg-13C} = 1400$ Hz, and δ 2.2 with ${}^{2}J_{199Hg-13C} = 200$ Hz.

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347