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Nuclear magnetic resonance and mass spectra of organomercury hydrides and deuterides

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A series of new organomercury hydrides, including aromatic and fluoroaromatic compounds, have been characterised by mass and NMR spectroscopy. Unusual features of these compounds included an unusually downfield chemical shift for the Hg–H proton, confirmed by deuterium substitution, and a high value for the ^{199}Hg–H coupling constant. The half-life for dilute solutions of methylmercury hydride was in the region of 1–3 h.

We recently reported the existence and preliminary characterisation of four new organomercury hydrides [HgH(Me), HgH(Et), HgH(Ph) and HgH(C_6F_5)].[1–3] This series of compounds had been thought to be unstable or transient in nature, possibly occurring as intermediates in the reduction of organomercury chlorides or acetates by metal hydrides.[4–6] The reaction with $NaBH_4$ is the second stage of the solvomercuration–demercuration route to Markovnikov alcohols and ethers, *etc.*[7] All workers prior to 1992 had assumed that the organomercury hydride species decomposed rapidly in solution according to equation (1).[1] Furthermore, this reaction had been generally

$$4HgCl(R) + NaBH_4 + 4OH^- \longrightarrow 4RH + 4Hg + 4Cl^- + Na^+ + H_2BO_3^- + H_2O \quad (1)$$

discussed in the context of a reduction in basic media. The only speculation as to the possibility of a greater stability for HgH(Me) was that made by Devaud.[8]

We have investigated the reduction of organometallic species by metal hydrides and similar reagents over many years as part of our work on the volatilisation and derivatisation of organometallics in the environment prior to analysis by interfaced gas chromatography (GC) mass spectroscopy (MS) and similar methods.[9] These reductions (*e.g.* by $NaBH_4$) are normally carried out in acid media, following an acid extraction carried out to remove the organometallic species from a sediment or biological matrix in the natural environment. In the development of a process for the analysis of HgCl(Me) and inorganic Hg^{II} in the environment, we noticed that solutions of reduced methylmercury species were stable enough for characterisation. The precursor mercury compounds [as HgCl(Me) or environmental methylmercury] were reduced at pH 4 in aqueous solution with aqueous $NaBH_4$ and diffused upwards to an interface of a benzene layer on top of the water, where they dissolved and were identified by NMR and MS.[2,3] Alternatively, the hydrides may be purged from solution by helium and condensed in a cold trap prior to direct transfer in a connecting line to a quartz-furnace atomic absorption system where the mercury atoms are detected.[2] The hydride HgH(Me) has also been characterised independently by Baldi and co-workers.[10]

In this paper we report a series of 24 new organomercury hydride and deuteride derivatives and discuss the unusual values observed for the Hg–H chemical shifts and the ^{199}Hg–H coupling constants. These are correlated with the NMR parameters of some alkylmercury hydrides recently reported by Kwetkat and Kitching.[11]

Experimental

Preparations

The hydrides and deuterides were prepared by the reduction of the corresponding organomercury chloride (0.8–1.2 mmol, used as received) with $NaBH_4$ in acid solution as reported for HgH(Me).[2,3] The general procedure was as follows. The chloride HgCl(C_6F_4Me) (2.0 mg, 0.005 mmol) was dissolved in a pH 3.5 acetate buffer (sodium acetate, BDH; acetic acid, Fisons; Millipore Q water) filled to the neck of a 50 cm^3 volumetric flask. To this C_6D_6 (Aldrich, 0.5 cm^3) was added. Sodium tetrahydroborate (Aldrich, 4% in water, 1 cm^3) was added by syringe and was allowed to stand for 15 min, the C_6D_6 layer was then removed, dried over magnesium sulfate and then submitted for NMR and GC–MS analysis.

For the corresponding deuteride, sodium tetradeuterioborate (Aldrich) was used instead of sodium tetrahydroborate.

GC–MS Analysis

A HP5890 gas chromatograph was coupled to a VG-Trio-3 mass spectrometer. Separation was achieved using a Cp.Sil-8 CB capillary column, 10 m in length and 0.23 mm internal diameter with a film thickness of 0.12 mm. The GC operating conditions were as follows: initial column temperature 50 °C, rate of increase 20 °C min^{-1}, final column temperature 220 and injector temperature 100 °C. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV (1.12×10^{-17} J) and mass range of 35–650.

NMR spectroscopy

The NMR spectra were obtained on a Brüker AC250 at 250.13 MHz using C_6D_6 as the solvent at 303.3 K. Chemical shifts were measured relative to residual protons in C_6D_6 at δ 7.16 and are stated in ppm with respect to $SiMe_4$.

Results and Discussion

Mass spectroscopy

We have established the identity and existence of the new hydrides or deuterides by MS methods and have studied several in some detail. These identifications depend on the characteristic isotopic distribution within the mercury atom (Table 1). Mercury isotopes range in mass from 196 to 204, but within this distribution there are no isotopes at 197 or 203. Hence, the existence of peaks in the mass spectra at *m*/*z* 197 or

203 suggests the presence of ^{196}Hg–H or ^{202}Hg–H. Similarly a peak at *m*/*z* 205 suggests the occurrence of ^{204}Hg–H and one at *m*/*z* 206 ^{204}Hg–D. The use of characteristic isotope patterns for mercury, and also of characteristic isotope absences, is integral to the identification of the hydrides and deuterides. These arguments are developed further in the following interpretations.

For identification of the presence of HgH(R) and HgD(R) (R = aryl) we chiefly utilised the presence of the highest mercury isotope ^{204}Hg. For each postulated species we observe the HgH(R)$^+$, HgD(R)$^+$, HgH$^+$ and HgD$^+$ as ^{204}HgR + one or + two mass units (Table 2). The compounds from which the HgH(R) or HgD(R) series were made [*i.e.* HgCl(R)] do not show peaks at these *m*/*z* values. Decomposition of the single species HgH(R) [or similarly HgD(R)] produces Hg$^+$R ions as well as the parent HgH(R)$^+$ [or HgD(R)$^+$]. Hence the mass-spectral cluster peaks in these areas are mixed although derived from a single compound. Clearly the existence of HgH(R)$^+$ or HgD(R)$^+$ peaks (Fig. 1) demonstrates the existence of the hydride or deuteride respectively, as does the absence of spaces in the peaks owing to the intervals that would occur if the peaks were caused only by HgR$^+$ or Hg$^+$ (*e.g.* at *m*/*z* 197 or 203 showing HgH$^+$ as ^{197}Hg and ^{203}Hg do not exist). Peaks at *m*/*z* 205 (^{204}HgH$^+$) and 203 (^{202}HgH$^+$), and 206 (^{204}HgD$^+$) and 203 (^{201}HgD$^+$), are especially significant as there would otherwise have been spaces here. The hydrides HgH(C_6H_4Me-*p*) and HgH($C_6H_4NH_2$-*p*) immediately dimerised to the diaryl species in the GC–MS analysis and were observed as HgR_2 derivatives only. The aromatic fragments of the HgH(R) or HgD(R) species appear to fragment conventionally and are not discussed in this context.

Table 1 Mercury isotopes*

Mass	Abundance (%)
196	0.15
198	10.10
199	17.00
200	23.10
201	13.20
202	29.65
204	6.80

* ^{197}Hg and ^{203}Hg do not occur. See text.

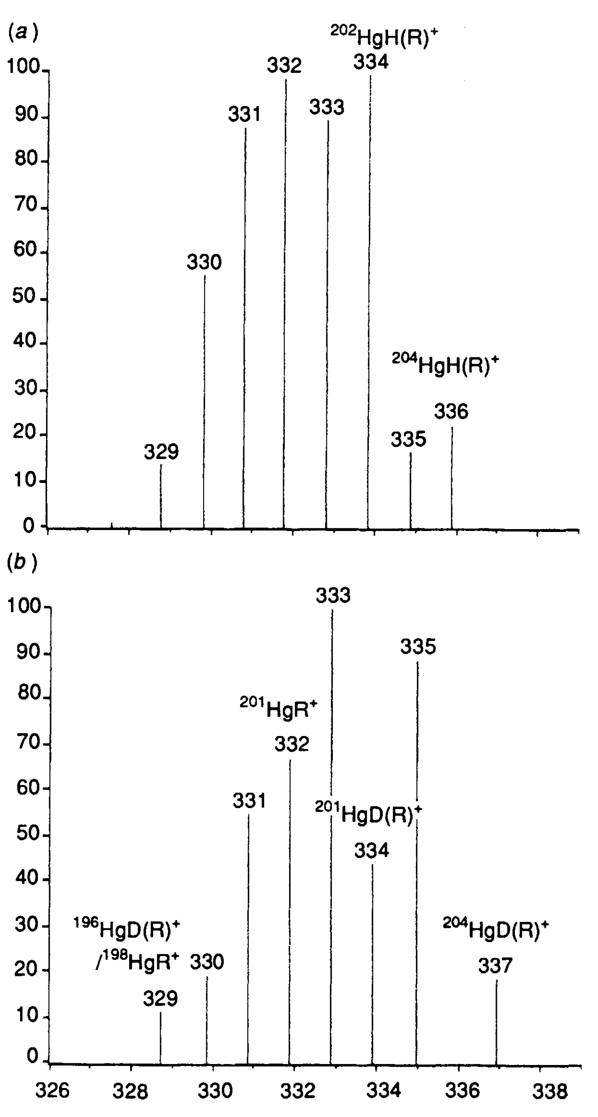

Fig. 1 Mass spectrum of (*a*) HgH($C_6F_3H_2$-3,5) and (*b*) HgD($C_6F_3H_2$-3,5)

NMR spectroscopy

For identification purposes, the ^{1}H NMR spectra are good fingerprints, and confirm the structures of these derivatives (Table 3 and Fig. 2). The downfield chemical shifts are large, with a clear gap between the alkyl and aryl derivatives. The ^{1}H–^{199}Hg coupling constants are also large, increasing as the shifts decrease, with gaps between alkyl and aryl, and between cyclohexyl and perfluoroalkyl ligands. We suggest the shifts depend on direct shielding and a local paramagnetic field from electrons on the mercury. Since the hydrogen ligand is expected to carry a small negative charge rather than a positive charge,[12] direct shielding would be expected to induce an upfield shift. We therefore assign these shifts to the paramagnetic term, with average-induced fields that add to the applied field. These are large because of the large spin–orbit coupling constant for mercury and the very large axial distortion caused by covalent σ bonding.[12] The reduction on going to aryl substituents probably reflects the tendency for these ligands to participate in π bonding, thereby increasing the effective energy gap between the magnetically coupled orbitals.

The spin–spin coupling in this case appears to be induced, in straightforward terms, *via* ^{1}H–(electron)$_1$–(electron)$_2$–^{199}Hg nuclear coupling within the H–Hg σ bond. The isotropic term stems largely from the local s-orbital characters of electrons 1 and 2. In the limit of H$^-$ as a ligand this coupling is minimised. As the local σ-electron density on the HgR unit increases so the coupling increases. Hence, the more the group R removes σ-electron density from mercury, the larger the coupling should become, as indeed is observed. Thus the large coupling is indicative of a strongly covalent HgR bond, whilst the trend to high values shown in Table 3 and Fig. 2 is a result of the increasing electronegativity of the ligands. This is even

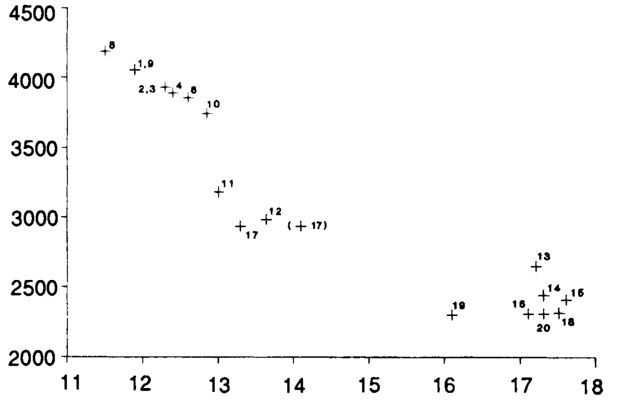

Fig. 2 Correlation of hydride-peak chemical shift and *J*(^{199}Hg–H) in organomercury hydrides

Table 2 Electron-impact mass spectra of organomercury hydrides and deuterides[a]

Hydride				Deuteride			
$\mathrm{HgH(R)^+/HgR^+}$ $\mathrm{HgH(C_6F_4Me}$-p) (m/z 360–368 expected)[b]	Assignment	$\mathrm{HgH^+/Hg^+}$	Assignment	$\mathrm{HgD(R)^+/HgR^+}$ $\mathrm{HgD(C_6F_4OMe}$-p) (m/z 361–369 expected)[c]	Assignment	$\mathrm{HgD^+/Hg^+}$	Assignment
362 (47)		198 (33)		361 (5)	$^{196}\mathrm{HgD(R)^+}$	198 (28)	
363 (80)		199 (62)		362 (12)		199 (48)	
364 (92)		200 (85)		363 (47)		200 (75)	
365 (75)		201 (55)		364 (73)		201 (52)	
366 (100)	$^{202}\mathrm{HgH(R)^+}$	202 (100)		365 (98)		202 (100)	
368 (23)	$^{204}\mathrm{HgH(R)^+}$	203 (16)	$^{202}\mathrm{HgH^+}$	366 (63)	$^{201}\mathrm{HgD(R)^+}$	203 (10)	$^{201}\mathrm{HgD^+}$
		204 (23)		367 (100)		204 (45)	
		205 (4)	$^{204}\mathrm{HgH^+}$	369 (24)	$^{204}\mathrm{HgD(R)^+}$	206 (5)	$^{204}\mathrm{HgD^+}$
$\mathrm{HgH(C_6F_4Br}$-p) (m/z 424–434 expected)				$\mathrm{HgD(C_6F_4Br}$-p) (m/z 425–435 expected)			
426 (2)		197 (7)	$^{196}\mathrm{HgH^+}$	425 (4)		198 (38)	
427 (39)		198 (37)		427 (22)		199 (54)	
428 (67)		199 (65)		428 (37)		200 (83)	
429 (68)		200 (84)		429 (67)		201 (50)	
430 (100)	$^{202}\mathrm{Hg^{79}Br(H)(R)^+}$ and $^{200}\mathrm{Hg^{81}Br(H)(R)^+}$	201 (50)		430 (58)		202 (100)	
				431 (100)		203 (5)	$^{201}\mathrm{HgD^+}$
432 (67)	$^{202}\mathrm{Hg^{81}Br(H)(R)^+}$ and $^{204}\mathrm{Hg^{79}Br(H)(R)^+}$	202 (100)		433 (65)	$^{202}\mathrm{Hg^{81}Br(D)(R)^+}$ and $^{204}\mathrm{Hg^{79}Br(D)(R)^+}$	204 (31)	
434 (11)	$^{204}\mathrm{Hg^{81}Br(H)(R)^+}$	203 (6)	$^{202}\mathrm{HgH^+}$				
		204 (22)		435 (12)	$^{204}\mathrm{Hg^{81}Br(D)(R)^+}$	206 (3)	$^{204}\mathrm{HgD^+}$
		205 (2)	$^{204}\mathrm{HgH^+}$			208 (—)	Background
$\mathrm{HgH(C_6F_4H}$-m) (m/z 346–354 expected)				$\mathrm{HgD(C_6F_4H}$-m) (m/z 347–355 expected)			
346 (2)				347 (10)		198 (24)	
347 (13)				348 (15)		199 (37)	
348 (55)	$^{197}\mathrm{HgH(R)^+}$	198 (29)		349 (50)		200 (66)	
349 (84)		199 (66)		350 (69)		201 (52)	
350 (96)		200 (89)		351 (95)		202 (100)	
351 (75)		201 (67)		352 (49)	$^{202}\mathrm{HgD(R)^+}$	203 (17)	$^{201}\mathrm{HgD^+}$
352 (100)	$^{202}\mathrm{HgH(R)^+}$	202 (100)		353 (100)		204 (52)	
354 (23)	$^{204}\mathrm{HgH(R)^+}$	203 (31)	$^{202}\mathrm{HgH^+}$	355 (24)	$^{204}\mathrm{HgD(R)^+}$	206 (8)	$^{204}\mathrm{HgD^+}$
		204 (20)					
		205 (7)	$^{204}\mathrm{HgH^+}$				
$\mathrm{HgH(C_6F_3H_2}$-3,5) (m/z 328–336 expected)				$\mathrm{HgD(C_6F_3H_2}$-3,5) (m/z 329–337 expected)			
328 (2)				329 (12)	$^{196}\mathrm{HgD(R)^+}$ and $^{198}\mathrm{HgR^+}$	198 (24)	
329 (13)		198 (28)					
330 (55)		199 (63)		330 (19)		199 (37)	
331 (88)		200 (88)		331 (55)		200 (68)	
332 (99)		201 (65)		332 (65)			
333 (90)		202 (100)		333 (100)		201 (58)	
334 (100)	$^{202}\mathrm{HgH(R)^+}$	203 (39)	$^{202}\mathrm{HgH^+}$	334 (43)	$^{201}\mathrm{HgD(R)^+}$	202 (100)	
335 (18)		204 (17)		335 (87)		203 (20)	$^{201}\mathrm{HgD^+}$
336 (23)	$^{204}\mathrm{HgH(R)^+}$	205 (7)	$^{204}\mathrm{HgH^+}$	337 (20)	$^{204}\mathrm{HgD(R)^+}$	204 (69)	
						206 (9)	$^{204}\mathrm{HgD^+}$
$\mathrm{HgH(C_6F_4OMe}$-p) (m/z 376–384 expected)				$\mathrm{HgD(C_6F_4OMe}$-p) (m/z 377–385 expected)			
377 (8)		196 (20)		372 (—)	Background	196 (1)	
378 (36)		198 (51)		378 (10)		198 (25)	
379 (60)		199 (90)		379 (72)		199 (39)	
380 (80)		200 (92)		380 (93)		200 (71)	
381 (70)		201 (61)		381 (91)		201 (52)	
382 (100)	$^{202}\mathrm{HgH(R)^+}$	202 (100)		382 (100)	$^{201}\mathrm{HgD(R)^+}$	202 (100)	
384 (25)	$^{204}\mathrm{HgH(R)^+}$	203 (14)	$^{202}\mathrm{HgH^+}$	383 (95)		203 (15)	$^{201}\mathrm{HgD^+}$
		204 (31)				204 (49)	
		205 (2)	$^{204}\mathrm{HgH^+}$	385 (18)	$^{204}\mathrm{HgD(R)^+}$	205 (1)	
						206 (8)	$^{204}\mathrm{HgD^+}$

[a] Percentage abundance is given in parentheses. [b] m/z 196 and 360 are not detected; m/z 163, $\mathrm{C_6F_4Me^+}$. [c] m/z 164, $\mathrm{C_6F_4CH_2D^+}$.

transmitted by the *para* substituents: for example, on going from p-$\mathrm{NH_2}$ to p-$\mathrm{NO_2}$ there is a clear increase in the coupling constant.

It can be seen that coupling of aromatic-ring fluorine atoms to the proton bound to mercury should occur. It is also apparent that for polyfluoro species [*e.g.* $\mathrm{HgH(C_6F_5)}$] whereas $^{19}\mathrm{F}$–$^{1}\mathrm{H}$ coupling should (and does) occur, the situation is complex. The aromatic fluorine peaks in $\mathrm{HgH(C_6F_5)}$ are

Table 3 Proton NMR data for organomercury hydrides

HgH(R)	δ[Hg*H*(R)]	$^{1}J_{(Hg-H)}$/Hz	Partial charge
1 $HgH(C_6F_5)$	11.9	4056	0.182
2 $HgH(C_6F_4Me$-*p*)	12.3	3930	0.176
3 $HgH(C_6F_4OMe$-*p*)	12.3	3930	0.170
4 $HgH(C_6F_4H$-*m*)	12.4	3887	0.176
5 $HgH(C_6H_4Me$-*p*)	*a*	*a*	0.120
6 $HgH(C_6F_4NH_2$-*p*)	12.6	3855	0.176
7 $HgH(C_6F_4OH$-*p*)	12.3	*b*	0.179
8 $HgH(C_6F_4NO_2$-*p*)	11.5	4187	0.189
9 $HgH(C_6F_4Br$-*p*)	11.9	4054	0.181
10 $HgH(C_6F_3H_2$-2,5)	12.85	3743	0.159
11 $HgH(C_6H_4CO_2Me$-*o*)	13.0	3183	0.157
12 $HgH(C_6H_4CO_2Me$-*p*)	13.64	2986	0.136
13 HgH(Me)	17.2	2650	0.067
14 $HgH(CH_2C_6H_{11})^{c}$	17.3	2441	0.072
15 $HgH(CH_2C_6H_{11})^{c}$	17.6	2409	—
16 $HgH(C_7H_{13})^{c}$	17.1	2308	0.074
17 HgH(Ph)	13.3^{d}	2936	0.130
18 $HgH(C_6H_{10}OMe$-*o*)^{c}	17.5	2314	0.090
19 $HgH(C_6H_{10}D$-1)^{c} H_{eq}	16.1	2302	—
20 H_{ax}	17.3	2307	—

[a] Not observed due to rapid decomposition to the HgR_2 derivative. [b] Not observed. [c] Ref. 11. [d] δ 14.1 in ref. 3.

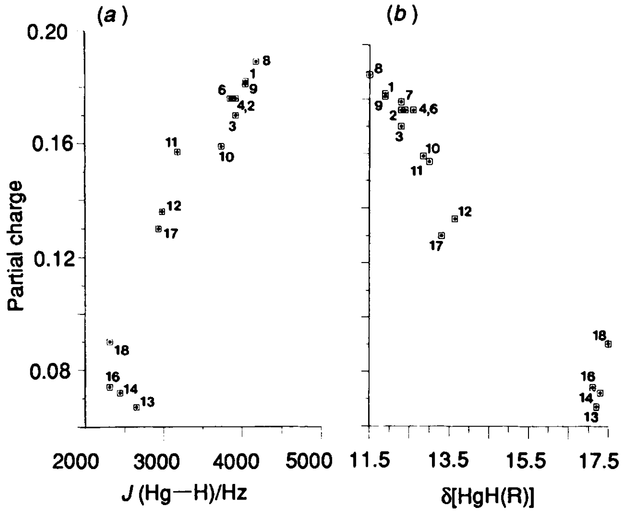

Fig. 3 Correlation of the electron-withdrawing nature of the R group of HgH(R) [measured by partial charge (relative to *e* = 1 ≈1.602 × 10^{-19} C) on H of R–H] with (*a*) *J*(Hg–H) and (*b*) δ[Hg*H*(R)]

compressed, with couplings existing for a given fluorine from two further adjacent fluorine nuclei, the proton bound to mercury and also ^{199}Hg. With regard to the ^{1}H NMR spectra, in all cases the proton occurs as a complex multiplet (demonstrating coupling with the organic group), with coupling occurring within a maximum band width of 20 Hz. For $HgH(C_6F_5)$ this multiplet appears to be an overlapping triplet of triplet of doublets system. Further investigations on the ^{13}C and ^{199}Hg NMR spectra are in progress and will be reported at a later date. At present the small differences in the chemical shifts of the aromatic nuclei and the complexity and overlapping of the predicted couplings makes deconvolutions of the spectroscopic data somewhat intractable, although chemical shifts are as expected for the appropriate organofluorine or aromatic grouping. The $^{19}F-^{1}H$ coupling constants are of the order of 1.1 Hz. This coupling, through at least two intervening atoms compares to much larger values for F–X–H of 50 Hz for some metalloidal elements.[13] We note that the presence of complex coupling between the organic group and the proton bound to mercury demonstrates the interactions between these species within the molecule, and among other things, the existence of the HgH(R) molecule as postulated.

The electronegativity of the organic ligands of HgH(R) can be deduced from the partial charge that they induce on a substituent. The partial charge on the hydrogen atom of R–H was used as a model. This was determined through molecular-orbital calculations using the AM1 semi-empirical Hamiltonian.[14] The partial charges are reported in Table 3 and are found to correlate well with both H–Hg coupling constants and the hydride chemical shift (Fig. 3).

Continued NMR spectroscopic observation of the hydride peak at 20 °C in C_6D_6 gave a half-life of 120 min for HgH(Me) in good agreement with ref. 10.

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References

1 P. J. Craig, D. Mennie, N. Ostah, O. F. X. Donard and F. Martin, *Analyst*, 1992, **117**, 823.
2 P. J. Craig, D. Mennie, M. Needham, N. Ostah, O. F. X. Donard and F. Martin, *J. Organomet. Chem.*, 1993, **447**, 5.
3 P. J. Craig, H. Garraud, S. H. Laurie, D. Mennie and G. H. Stojak, *J. Organomet. Chem.*, 1994, **468**, 7.
4 J. L. Wardell, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 2, p. 966.
5 W. Kitching, A. R. Atkins, G. Wiekham and V. Alberts, *J. Org. Chem.*, 1981, **46**, 563.
6 C. L. Hill and G. M. Whitsides, *J. Am. Chem. Soc.*, 1974, **96**, 870.
7 R. L. Larock, in *Solvomercuration–Demercuration Reactions in Organic Synthesis*, Springer, Berlin, 1986.
8 M. Devaud, *J. Organomet. Chem.*, 1981, **220**, C27.
9 J. R. Ashby and P. J. Craig, *Sci. Total Environ.*, 1989, **78**, 219.
10 M. B. Filipelli, F. Baldi, F. E. Brinckman and G. J. Olson, *Environ. Sci. Technol.*, 1992, **26**, 1457.
11 K. Kwetkat and W. Kitching, *J. Chem. Soc., Chem. Commun.*, 1994, 345.
12 M. J. Almond, D. A. Rice, L. A. Sheridan, P. J. Craig, G. Stojak, M. C. R. Symons and U. S. Rai, *J. Chem. Soc., Faraday Trans.*, 1994, 3153.
13 C. J. Jameson, in *Multinuclear NMR*, ed. J. Mason, Plenum, New York, 1987, p. 437.
14 M. J. S. Dewar, E. G. Zoebisch, E. F. Healey and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

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