Preparation, spectroscopic properties and thermal stabilities of organomercury compounds containing the bulky ligand $(Me_3Si)_3C$ or $(PhMe_2Si)_3C$

Salih S. Al-Juaid, Colin Eaborn, Paul D. Lickiss, J. David Smith *, Kayumars Tavakkoli, Alexander D. Webb

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Received 29 June 1995

Abstract

Mercury compounds of the types HgR^1R ($R^1 = C(SiMe_3)_3$; R = Me, ^iPr, Bu, ^tBu or Ph) and HgR^2R ($R^2 = C(SiMe_2Ph)_3$; R = Me, Bu, CH_2Ph or Ph) have been prepared. Those containing R^1 were made by reactions of the bromides HgR^1Br with the Grignard reagents MgRX, and those containing R^2 by reaction of HgR^2Cl with LiR or, for R = CH_2Ph, with $Mg(CH_2Ph)Cl$. Replacement of one R group in HgR_2 by the bulky R^1 or R^2 group leads to a large increase in thermal stability, a marked shift in the ^{199}Hg resonance to lower frequency and an increase in the coupling constant $^1J(^{13}C-^{199}Hg)$ for the Hg–R bond. The compound HgR^2Cl does not react further with LiR^2 in tetrahydrofuran, but with LiR^1 gives HgR^1R^2; the arrangement of the $SiMe_2Ph$ groups in the latter in solution in CH_2Cl_2 at low temperature appears to be different from that in the solid.

Keywords: Mercury; Silicon; NMR spectra; Thermal stability; Bulky ligands

1. Introduction

The compound $Hg[C(SiMe_3)_3]_2$, made some years ago [1,2], was found to show remarkable thermal stability for a diorganomercurial [2] but to be sensitive to UV irradiation [1]. In order to examine the effect of a single $(Me_3Si)_3C$ ligand or the related bulky ligand $(PhMe_2Si)_3C$ on the thermal stability and other properties of diorganomercurials we have prepared a range of compounds of the type $Hg\{C(SiMe_3)_3\}R$ or $Hg\{C(SiMe_2Ph)_3\}R$, where R is an alkyl, benzyl or phenyl group. Several unexpected reactions were encountered during these preparations.

Subsequently in this paper the $(Me_3Si)_3C$ and $(PhMe_2Si)_3C$ groups are denoted by R^1 and R^2 respectively.

$(Me_3Si)_3C$ $(PhMe_2Si)_3C$

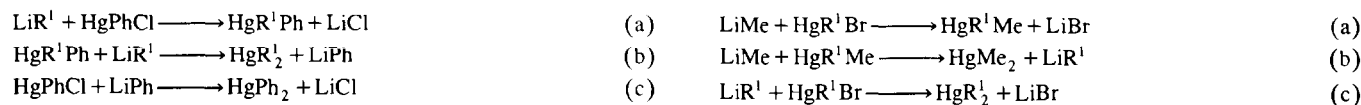R^1 R^2

---

* Corresponding author.
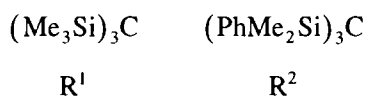
2. Results and discussion

2.1. Syntheses

Reaction of LiR^1 (for the actual nature of the reagent see [3]) with $HgCl_2$ in tetrahydrofuran (THF) gives HgR^1_2 even when the reagents are used in a 1:1 ratio, and HgR^1Cl cannot be satisfactorily obtained in this way. In contrast, the reaction of LiR^2 with $HgCl_2$ in THF was found to give only HgR^2Cl even when a 2:1 ratio of the reagents was used. (The reagent LiR^2 is known to be less reactive than LiR^1 [4].) The HgR^2Cl reacted readily with the reagents LiR, where R = Me, Bu or Ph to give the corresponding HgR^2R, and even with the Grignard reagent $Mg(CH_2Ph)Cl$ to give the benzyl derivative $HgR^2(CH_2Ph)$. The chloride HgR^2Cl also reacted with LiR^1 to give the compound HgR^1R^2 containing both of the bulky ligands, but reaction was slow and the mixture was refluxed for 4 h and then kept overnight. The ^1H NMR spectrum of the solution then showed that no HgR^2Cl remained but that several products were present; one major component was identified as $(PhMe_2Si)_3CH$ and some metallic mercury was also

$$LiR^1 + HgPhCl \longrightarrow HgR^1Ph + LiCl \qquad (a)$$
$$HgR^1Ph + LiR^1 \longrightarrow HgR_2^1 + LiPh \qquad (b)$$
$$HgPhCl + LiPh \longrightarrow HgPh_2 + LiCl \qquad (c)$$

Scheme 1.

$$LiMe + HgR^1Br \longrightarrow HgR^1Me + LiBr \qquad (a)$$
$$LiMe + HgR^1Me \longrightarrow HgMe_2 + LiR^1 \qquad (b)$$
$$LiR^1 + HgR^1Br \longrightarrow HgR_2^1 + LiBr \qquad (c)$$

Scheme 2.

formed. (We suspected from the ^{1}H NMR spectrum that HgR_2^1 was also present but did not confirm that.) Work-up gave the required product HgR^1R^2 in 21% yield. The formation of $(PhMe_2Si)_3CH$ suggests that $(PhMe_2Si)_3C$ radicals may have been generated, possibly as a consequence of photolysis since the refluxing mixture was not protected from light.

Since the chloride HgR^1Cl was not readily available by reaction of $HgCl_2$ with R^1Li (although it has been made by treatment of HgR^1Me with HCl [2]), we initially attempted to make HgR^1Ph from LiR^1 and HgPhCl in THF, but instead obtained HgR_2^1 and $HgPh_2$. It is likely that some HgR^1Ph is first formed but then reacts with LiR^1 to give HgR_2^1 and PhLi (Scheme 1), which then reacts with remaining HgPhCl to give $HgPh_2$. The type of Hg–C bond cleavage shown in step (b) of Scheme 1 occurs in the reaction of HgR^1Br with LiBu in ether to give LiR^1 [5]. Step (b) may in principle be reversible, but any LiPh formed would be rapidly removed by reaction with remaining HgPhCl.

Later, when it had been shown [5] that the bromide HgR^1Br was readily available from the reaction of LiR^1 with $HgBr_2$, ^{1} we attempted to make HgR^1Me by reaction of the HgR^1Br with LiMe in Et_2O, but the main product was HgR_2^1, together with unchanged HgR^1Br. The possible course of the reaction is shown in Scheme 2. Subsequently we obtained HgR^1Me in 5% yield by

reaction of HgR^1Br with MeLi in 1 : 10 Et_2O : toluene, but it was much more satisfactorily made from HgR^1Br and the Grignard reagent MgMeI. Similar use of the Grignard reagents Mg^iPrCl, MgBuBr, Mg^tBuCl and MgPhBr gave good yields of the expected products HgR^1R with $R = {}^iPr$, Bu, ^tBu or Ph. Surprisingly, in view of the successful preparation of $HgR^2(CH_2Ph)$ from HgR^2Cl and $Mg(CH_2Ph)Cl$ noted above, we found that the reaction of HgR^1Br with $Mg(CH_2Ph)Cl$ did not yield $HgR^1(CH_2Ph)$, only HgR_2^1 and $Hg(CH_2Ph)_2$ being isolated. A similar result was obtained when $LiCH_2Ph$ was used. Apparently even $Mg(CH_2Ph)Cl$ can cleave an $Hg–R^1$ bond, as shown in step (b) of Scheme 3, or can in some other way promote disproportionation of $HgR^1(CH_2Ph)$.

The compound $Hg[C(SiMe_3)_2(SiMe_2H)]_2$ was obtained by treatment of $HgCl_2$ with $LiC(SiMe_3)_2(SiMe_2-H)$. The analogous zinc and cadmium compounds were previously obtained in a similar way [6].

---

^{1} The fact that LiR^1 gives HgR^1Br when treated with $HgBr_2$ but not HgR^1Cl when treated with $HgCl_2$ may be due to the higher solubility of $HgBr_2$ in THF, which means that sufficient $HgBr_2$ is present in solution to trap the LiR^1 before the latter reacts with the HgR^1Br.

Table 1
The ^{199}Hg chemical shifts for compounds HgR^1R, HgR^2R, and HgR_2, with coupling constants $^1J(^{13}C-^{199}Hg)$ for coupling to R ^{a}

Compound	$-\delta(^{199}Hg)$ (ppm)	$^1J(^{13}C-^{199}Hg)$ (Hz)	Compound	$-\delta(^{199}Hg)$ (ppm)	$^1J(^{13}C-^{199}Hg)$ (Hz)
HgR_2^1	499	334	$HgR^{1t}Bu$	612	
HgR^1R^2	609		Hg^tBu_2	844 ^{d}	626 ^{d}
HgR^1Me		800 ^{b,c}	$HgR^2(CH_2Ph)$	515	790
HgR^2Me	203		$Hg(CH_2Ph)_2$	700 ^{d}	633 ^{d}
$HgMe_2$	50 ^{d}	700 ^{d}	HgR^1Ph	535	1263 ^{h}
HgR^1Bu	311	866 ^{e}	HgR^2Ph	500	
HgR^2Bu	316	919	$HgPh_2$	742 ^{d}	1190 ^{d,i}
$HgBu_2$	205 ^{d,f}	659 ^{d}	HgR^1Cl		787 ^{j}
$HgR^{1i}Pr$	507	742 ^{g}	HgR^2Cl	888	
Hg^iPr_2	597 ^{d,f}	634 ^{d}	$HgMeCl$	813 ^{d}	1431 ^{d}

^{a} In C_6D_6 unless otherwise specified.
^{b} In $CDCl_3$ [2].
^{c} Coupling to C of R^1, 264 Hz [2].
^{d} Values from [8]; slightly different values appear in [7], probably because of solvent effects.
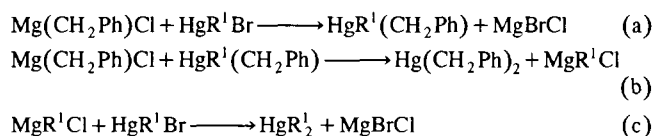^{e} Coupling to C of R^1, 177 Hz.
^{f} In CCl_4.
^{g} Coupling to C of R^1, 193 Hz.
^{h} Coupling to C of R^1, 299 Hz.
^{i} In CH_2Cl_2.
^{j} [2].

$Mg(CH_2Ph)Cl + HgR^1Br \longrightarrow HgR^1(CH_2Ph) + MgBrCl$ (a)

$Mg(CH_2Ph)Cl + HgR^1(CH_2Ph) \longrightarrow Hg(CH_2Ph)_2 + MgR^1Cl$ (b)

$MgR^1Cl + HgR^1Br \longrightarrow HgR^1_2 + MgBrCl$ (c)

Scheme 3.

2.2. ^{199}Mercury NMR spectra

Values for the compounds HgR^1R and HgR^2R of the ^{199}Hg chemical shift, and in some cases of the coupling constants $^1J(^{13}C-^{199}Hg)$ for coupling to the attached carbon of the group R, are shown in Table 1, together with corresponding data [7,8] for the compounds HgR_2.

The features are as follows.

(a) The presence of the R^1 or R^2 ligands gives rise to a substantial shift of the ^{199}Hg resonance to lower frequency. The difference of 110 ppm between the δ values for HgR^1_2 and HgR^1R^2 is larger than might have been expected in the light of the fact that there are not large differences between the shifts for HgR^1Bu and HgR^2Bu or those for HgR^1Ph and HgR^2Ph.

(b) It is sometimes suggested that the larger the ^1J coupling across a single bond the shorter, and so the stronger, is that bond, and we found that there is a surprisingly satisfactory linear relationship (correlation coefficient, 0.98) between the relevant coupling constants and the reported energies D for dissociation of the first Hg–R bond in the dialkyl compounds HgR_2 where R = Me, Et, Pr, ^iPr or Bu. (The values of D [9,10] and $^1J(C-Hg)$ [7,8] are as follows: R = Me, $D = 241$ kJ mol^{-1}, $^1J(C-Hg) = 692$ Hz; R = Et, $D = 191$ kJ mol^{-1}, $^1J(C-Hg) = 647$ Hz, R = Pr, $D = 195$ kJ mol^{-1}, $^1J(C-Hg) = 660$ Hz; R = Bu, $D = 200$ kJ mol^{-1}, $^1J(C-Hg) = 659$ Hz.) In keeping with such a relationship the presence of an R^1 or R^2 group on Hg together with Me, Bu, CH_2Ph or Ph (Table 1) leads to a marked increase in the coupling to the attached carbon

of R over that for the corresponding HgR_2, and at the same time to a large increase in the thermal stability (see Table 3 later). However, the very low value of $^1J(C-Hg)$ for the highly stable HgR^1_2 represents a marked deviation from the suggested relationship.

The low value of $^1J(C-Hg)$ for HgR^1_2 has been attributed, at least in part, to the large $Me_3Si-C-SiMe_3$ angles, which result in a low degree of s character in the C–Hg bond [2]. (A similar effect has been considered in the case of the corresponding $^1J(^{13}C-^1H)$ coupling in R^1H [11].) Our results suggest that in the unsymmetrical compounds R^1HgR or R^2HgR a reduction in s character in the R^1–Hg or R^2–Hg bond is accompanied by an increase in that of the Hg–R bond relative to that in the Hg–R bonds in HgR_2.

2.3. Vibrational spectra

The compounds R^2HgX (X = Cl, Me, Bu, Ph or CH_2Ph) provide a fingerprint of the IR frequencies associated with C–H, C–C and C–Si vibrations of the group R^2. All show absorptions at 2900–2910vs (ν(CH)), 1426–1428w, 1250–1256m (δ(CH$_3$)), 1105m (Ph), 841–850s, 807–823w, 784–792m (ρ(CH$_3$)), 723–729m, 700–705m, 668–677w, 639–641w, 472–478w, 277–283w, 233–246w (δ(SiC$_3$)) cm^{-1}. Peaks due to the other organic groups are usually obscured, but there are windows in which absorption ascribed mainly to Hg–C stretching is observed. Table 2 (which includes data from [12–15]) shows that for symmetrical mercurials the frequencies asssociated with asymmetric and symmetric Hg–C stretching lie between those, at about 620 and 395 cm^{-1}, observed for the compounds HgR^2R.

Glockling et al. [2] showed that the substantial lowering of the Hg–C stretching frequencies for HgR^1_2 (and found by us for HgR^1R^2) is observed only when all three hydrogen atoms of the methylmercury fragment

Table 2
IR absorptions for compounds HgR_2 and HgR^2R in the Hg–C stretching region

ν (cm^{-1}) for following R in HgR_2				
Me [a]	Et [b]	Ph [c]	CH$_2$Ph [b]	R^1 [d,e]
540	562	660	571	365
518	486	464	560	

ν (cm^{-1}) for following R in HgR^2R					
Me	Bu	Ph	CH$_2$Ph	R^1 [f]	Cl
619	618	620	616	417	
396	395	397	394	398	391

[a] [12].
[b] [13].
[c] [14].
[d] [15], 360 cm^{-1} in [2].
[e] 368 cm^{-1} in Raman spectrum of solid; cf. 367 (Raman) and 368 cm^{-1} (IR) in CdR^1_2.
[f] 416, 365 cm^{-1} in Raman spectrum of solid (δ(CHgC) = 200 cm^{-1}).

are replaced by bulky organosilyl groups: the frequencies are 530 cm^{-1} in $Hg(CH_2SiMe_3)_2$ [16] and 510 cm^{-1} in $Hg[CH(SiMe_3)_2]_2$ [2]. The values of $\nu(Zn-C)$ [17] and $\nu(Hg-C)$ in MR_2^1 are similar to one another, as they are in the methyl derivatives MMe_2 [12]. The low frequencies observed in the IR and Raman spectra of HgR_2^1 and HgR^1R^2 appear to reflect substantial coupling of the symmetric and asymmetric vibrations of the C–Hg–C skeleton with those of the CSi_3 fragments. They do not, however, mean that the Hg–C bonds are readily broken by homolytic dissociation, as the thermal stabilities of these compounds show.

The compound HgR^1R^2 gives bands at 417 and 398 cm^{-1} in the IR and at 416 and 365 cm^{-1} in the Raman spectrum. The value of the corresponding frequency in the Raman spectrum of HgR_2^1 is 368 cm^{-1}, and very similar values (364 and 367 cm^{-1} respectively) were observed for ZnR_2^1 and CdR_2^1 [15].

2.4. Decomposition temperatures

For a range of compounds HgR^1R and HgR^2R and for $Hg(CH_2Ph)_2$ the temperatures of onset of decomposition observed for samples in sealed melting-point (m.p.) tubes are shown in Table 3. In a few cases the decomposition temperatures were also determined by differential scanning calorimetry (DSC) and there was reasonable agreement with those found for the samples in m.p. tubes. The table also includes a value for the decomposition temperature of Hg^tBu_2; this is actually the temperature at which rapid decomposition was found to occur in solution in cyclodecane [18], but it has been shown in the case of $Hg(CH_2Ph)_2$ that the decomposition temperature for the melt is similar to that for a solution in toluene [19,20].

We plan to discuss elsewhere the possible implications of these results (for a preliminary account see [21]), but note here the marked increase in stability on going from Hg^tBu_2 to $HgR^{1t}Bu$ and from $Hg(CH_2Ph)_2$

Table 3
Approximate temperatures of onset of decomposition for some diorganomercury compounds

Compound	Decomposition temperature [a] (°C)	
	In m.p. tube [b]	By DSC
HgR^1Me	325	
HgR^2Me	307	
$HgR^{1t}Pr$	233	
HgR^1Bu	280	290
HgR^2Bu	285	
$HgR^{1t}Bu$	220	
Hg^tBu_2	(140) [c]	
HgR^1Ph	268	
HgR^2Ph	280	280
$HgPh_2$	213	215
HgR^2CH_2Ph	240	275
$Hg(CH_2Ph)_2$	155	
HgR_2^1	300	330
HgR^1R^2	322	
HgR^2Cl	272	

[a] To within about ± 10°C.
[b] Unless otherwise indicated.
[c] In solution [18].

to $HgR^1(CH_2Ph)$. (Monitoring by ^1H NMR spectroscopy has shown that only at about 245°C does HgR^1CH_2Ph decompose in solution at approximately the same rate as $Hg(CH_2Ph)_2$ at 150°C [20].) In the the usually accepted mechanism of thermal decomposition of a diorganomercurial HgR_2 the rate of the reaction is that of the dissociation of one Hg–R bond or of both such bonds simultaneously [18,19,22,23]. The stabilization by the R^1 or R^2 group indicates either (a) that, as suggested previously [15], this mechanism is incorrect (for evidence that a chain mechanism is involved in photostimulated decomposition of $Hg(CH_2Ph)_2$ see [24]) or (b) that the presence of the R^1 or R^2 group really does reduce the ease of dissociation of the Hg–R bond [21].
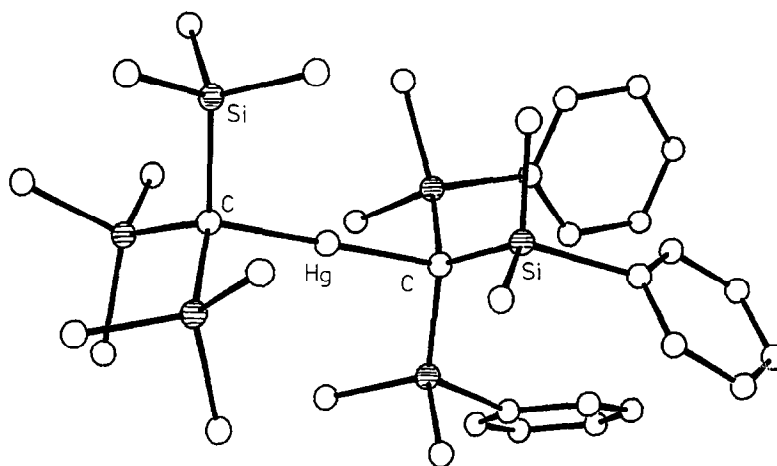

Fig. 1. The structure of $(Me_3Si)_3CHgC(SiMe_2Ph)_3$ in the crystal.

2.5. Structure of HgR^1R^2

An X-ray diffraction study of a crystal of $Hg\{C(SiMe_3)_3\}\{C(SiMe_2Ph)_3\}$ showed that there were three independent molecules with very similar geometries in the trigonal unit cell. All three have linear C–Hg–C linkages parallel to the threefold crystallographic axis, with two pointing one way and one the other. Possibly because of the large number of parameters involved, the quality of the data was too low to justify a detailed report ($R = 0.138$, $R' = 0.148$ for 2912 reflections with $|F| > \sigma(F^2)$), but there was no doubt about the overall form of the molecule, which is that shown in Fig. 1 [25].

The features of relevance are as follows.

(a) In the $(Me_3Si)_3C$ ligand, one Me of each $SiMe_3$ group points in towards the mercury atom and two away from it, as observed in various compounds of the type $M\{C(SiMe_3)_3\}_2$, where M = Hg [2], Zn [17], Mg [26] or Mn [27]. (In contrast, in the anions $[M\{C(SiMe_3)_3\}_2]^-$ with M = Li [3], Na [28], Cu [29] or Ag [30], two of the Me groups of each $SiMe_3$ point slightly inwards and one outwards in such a way as to leave the metal atom much more exposed.)

(b) In the $(PhMe_2Si)_3C$ ligand the planes of the phenyl groups are almost parallel to the C–Hg–C axis and one ortho-proton of each Ph group lies over the face of another such group. This type of arrangement is found in other compounds of the type $(PhMe_2Si)_3CX$ where X is a bulky ligand (e.g. $SiCl_3$ [31] or $SnCl_3$ [32]), whereas in those in which X is small (e.g. H [33] or Br) the Ph groups lie well apart and are separated by Me groups [31].

In the light of the observation described under (b) the results of a low temperature ^1H NMR study of a solution of HgR^1R^2 in CD_2Cl_2 are of interest. At −100°C the resonance pattern for the protons of the Ph groups at $\delta = 7.25–7.67$ ppm is little different from that at $\delta = 7.16–7.32$ ppm at room temperature. However, the signal from the $SiMe_2$ protons, which is a singlet at $\delta = 0.31$ ppm at room temperature, is split into two well-separated signals, at $\delta = 0.44$ and $−0.55$ ppm, at −100°C. (The singlet from the $SiMe_3$ protons of R^1 at $\delta = 0.35$ ppm remains unchanged down to $−100°C$, as does that from the ^{199}Hg nucleus down to $−60°C$.) This behaviour is of the type observed previously for $(PhMe_2Si)_3CBr$, for which the splitting of the Me signal is attributed to the fact that at low temperatures the structure adopted has the Ph groups well separated, with $SiMe_2$ groups between them in such a position that some Me groups lie above Ph rings [31]. Such an arrangement is observed in the crystal structure of $(PhMe_2Si)_3CH$ [33], and so probably also in that of $(PhMe_2Si)_3CBr$ [31]. In contrast, for $(PhMe_2Si)_3CSiCl_3$, in which the arrangement of the $(PhMe_2Si)_3C$ group in the crystal is similar to that in HgR^1R^2, the signals from

the $SiMe_2$ protons are only slightly split (by 0.2 ppm) at −100°C but those from half of the ortho-protons have moved upfield by 2.8 ppm, and the implication is that one ortho-proton in each phenyl group lies over the face of another such group, as is the case in the crystal structure. It thus appears that, whereas for $(PhMe_2Si)_3$-$CSiCl_3$ and $(PhMe_2Si)_3CBr$ the respective structures in solution at low temperature are closely similar to those in the solid [30], in the case of HgR^1R^2 the arrangement of the $(PhMe_2Si)_3C$ ligand resembles that in $(PhMe_2Si)_3CSiCl_3$ in the crystal but that in $(PhMe_2Si)_3CBr$ in solution at low temperature. This may be related to the fact that the effective bulk of the $HgC(SiMe_3)_3$ ligand is smaller than that of the $SiCl_3$ ligand but somewhat larger than that of the Br ligand, so that there is little difference between the energies for the two conformations of the R^2 group.

Since the compound HgR^1R^2 (i) is colourless, (ii) contains a heavy atom and (iii) crystallizes in a non-centrosymmetrical space group, we thought that it might show useful non-linear optical properties but, when crystals were examined by the Kurtz method, the effects were found to be small [34].

3. Experimental details

Reactions involving chlorosilanes, lithium metal, organolithium compounds or Grignard reagents were conducted under dry argon. Solvents were dried by standard methods. The ^1H NMR spectra were recorded at 80 MHz on a Bruker WP80 FT spectrometer, and ^{13}C and ^{29}Si NMR spectra at 90.5 and 71.5 MHz respectively on a Bruker WM360 spectrometer (with $SiMe_4$ as internal reference in each case). The ^{199}Hg NMR spectra were recorded at 64.4 MHz on the latter instrument with $HgMe_2$ as external reference. Mass spectroscopy (MS) was carried out by electron impact at 70 eV unless otherwise stated. Where relevant the m/z values refer to ions containing ^{35}Cl, ^{79}Br or ^{202}Hg; the form used to suggest identities of the ions is not meant to indicate fragmentation patterns. The IR spectra were recorded as Nujol mulls between CsI plates or, where indicated, as solutions in CCl_4, on a Perkin–Elmer 1720 FT spectrometer. Solutions of LiMe and LiBu were purchased from Aldrich. M.p.s. of samples in sealed capillaries were determined with an Electrothermal apparatus. The chloride HgR^2Cl was made as previously described [35].

3.1. Preparation of $LiC(SiMe_3)_3$ (LiR^1)

A 1.2 mol dm^{-3} solution of LiMe in diethyl ether (19.7 cm^3; 10% excess) was placed in a three-necked flask (100 cm^3) equipped with a water condenser, pressure-equalizing funnel and stirrer. A solution of

$(Me_3Si)_3CH$ (5.0 g, 21.5 mmol) in THF (30 cm^3) was added dropwise with stirring, the ether was distilled off, and the remaining solution heated under reflux for 4 h, after which the ^{1}H NMR spectrum showed that $LiC(SiMe_3)_3$ had been formed in 95-100% yield.

3.2. Preparations of the compounds HgR^2R $(R^2 = C(SiMe_2Ph)_3)$

3.2.1. R = Me.

A solution of 1.53 mol dm^{-3} LiMe in Et$_2$O (1.0 cm^3, 1.53 mmol) was added dropwise to one of HgR^2Cl (1 g, 1.53 mmol) in toluene (20 cm^3). The mixture was stirred for 2 h and the solvent then removed under vacuum to leave a white solid, which was extracted with warm heptane (60 cm^3). The extract was filtered, concentrated, and kept at $-10°C$ to give crystals of HgR^2Me (yield, 0.72 g (74%); m.p., 131-132°C). Anal. Found: C, 49.0; H, 5.9. $C_{26}H_{36}HgSi_3$ Calc.: C, 49.3; H, 5.7% ^{1}H NMR (C_6D_6): δ 0.35 (18H, s, SiMe$_2$), 0.69 (3H, s, Me), 6.90-7.29, 7.33-7.6 (15H, m, Ph) ppm. ^{13}C NMR (C_6D_6): δ 4.5 (SiMe$_2$), 18.4 (Me), 143.1 (ipso-C of Ph), 134.3 (o-C), 127.9 (m-C), 128.6 (p-C) ppm. ^{29}Si NMR (C_6D_6): δ -6.86 ppm. MS: m/z 634 (M$^+$, 2%), 619 (M $-$ Me, 8), 541 (M $-$ Me $-$ PhH, 7), 402 [(Me$_2$PhSi)$_3$C $-$ Me, 73], 387 (11), 340 (16), 325 (38), 309 (70), 267 (11), 247 (12), 217 (11), 202 (12), 197 (29), 175 (28), 135 (100), 121 (13), 105 (20).

3.2.2. R = Bu.

A 3.2 mol dm^{-3} solution of LiBu in Et$_2$O (0.48 cm^3, 1.53 mmol) was added dropwise to one of HgR^2Cl (1.0 g, 1.53 mmol) in toluene (20 cm^3) at 0°C. The solution was allowed to warm to room temperature and then stirred for a further 2 h. Solvent was then removed to leave a white solid, which was extracted with warm heptane. The extract was filtered, concentrated and kept at $-10°C$ to give white crystals of HgR^2Bu (yield, 0.84 g (81%); m.p., 137-139°C). Anal. Found: C, 51.4; H, 6.3. $C_{29}H_{42}HgSi_3$ Calc.: C, 51.6; H, 6.3%. ^{1}H NMR (C_6D_6): δ 0.42 (18H, s, SiMe$_2$), 0.90-2.47 (9H, m, Bu), 6.90-7.32, 7.37-7.75 (15H, m, Ph) ppm. ^{13}C NMR (C_6D_6): δ 4.6 (SiMe$_2$), 14.0 (CH$_2$), 28.5 (CH$_2$), 31.6 (CH$_2$), 40.9 (CH$_3$ of Bu), 134.4 (o-C), 128.1 (m-C), 128.6 (p-C) ppm. ^{29}Si NMR (C_6D_6): δ -6.9 ppm. MS: m/z 676 (M$^+$, 11%), 661 (M $-$ Me, 16), 402 (98), 387 (20), 384 (20), 340 (26), 325 (47), 309 (100), 267 (17), 247 (18), 202 (20), 197 (43), 175 (29), 135 (98), 121 (12), 105 (8).

3.2.3. R = Ph.

A solution of HgR^2Cl (1.0 g, 1.53 mmol) in toluene (20 cm^3) was treated with one of 1.27 mol dm^{-3} LiPh in Et$_2$O (1.2 cm^3, 1.53 mmol). The mixture was stirred for 1 h at room temperature and the solvent then removed under vacuum. The solid residue was extracted

with warm heptane, and the extract was filtered, concentrated and cooled to give white crystals of HgR^2Ph (yield, 0.78 g (77%); m.p., 119-121°C). Anal. Found: C, 53.4; H, 5.8. $C_{31}H_{38}HgSi_3$ Calc.: C, 53.5; H, 5.5%. ^{1}H NMR (C_6D_6): δ 0.45 (18H, s, SiMe$_2$), 6.95-7.32, 7.41-7.72 (m, PhHg and PhSi) ppm. ^{13}C NMR (C_6D_6): δ 4.52 (SiMe$_2$), 173.1 (ipso-C of PhHg); 143.1 (ipso-C of PhSi in R^2) DEPT CH only, 134.4 (o-C of PhSi), 128.2 (m-C of PhSi), 128.7 (p-C of PhSi), 136.8 (o-C of PhHg), 129.6 (m-C of PhHg), 130.8 (p-C of PhHg) ppm. ^{29}Si NMR (C_6D_6): δ -6.1 ppm. MS: m/z 696 (M$^+$, 3%), 681 (11), 402 (61), 387 (11), 340 (20), 325 (35), 309 (78), 267 (11), 247 (16), 202 (15), 197 (30), 175 (25), 135 (100), 121 (13), 105 (10), 77 (28).

3.2.4. R = CH$_2$Ph.

A solution of HgR^2Cl (0.84 g, 1.28 mmol) in THF (20 cm^3) was added dropwise to one of $Mg(CH_2Ph)Cl$ in Et$_2$O (25 cm^3) prepared from benzyl chloride (0.2 g, 1.58 mmol) and magnesium turnings (0.04 g, 1.69 mmol). During the addition a white precipitate separated from the solution but slowly redissolved as the proportion of THF increased. When the addition was complete the solution was heated under reflux at 75°C for 15 min and the solvent was then removed under vacuum. The solid residue was extracted with warm heptane and the extract was filtered, concentrated and kept at $-10°C$ to give white crystals of HgR^2CH_2Ph (yield, 0.55 g (60%); m.p., 142-144°C). Anal. Found: C, 54.3; H, 5.3. $C_{32}H_{40}HgSi_3$ Calc.: C, 54.2; H, 5.7%. ^{1}H NMR (C_6H_6): δ 0.24 (18H, s, SiMe$_2$), 2.55 (2H, s, CH$_2$, ^2J (^{1}H$-^{199}$Hg) = 154 Hz), 6.86-7.20, 7.23-7.51 (m, CH$_2$Ph and PhSi) ppm. ^{13}C NMR (C_6D_6): δ 4.4 (SiMe$_2$), 46.9 (CH$_2$), 143.3 (ipso-C of CH$_2$Ph), 143.0 (ipso-C of Ph in R^2) DEPT CH only; 127.8 (o-C of CH$_2$Ph), 128.9 (m-C of CH$_2$Ph), 124.0 (p-C of CH$_2$Ph), 134.4 (o-C of Ph in R^2), 128.2 (m-C), 128.6 (p-C) ppm. ^{29}Si NMR (C_6D_6): δ -6.7 ppm. MS: m/z 710 (M$^+$, 10%), 695 (M $-$ Me, 2), 418 (9), 403 (26), 339 (64), 325 (39), 309 (45), 267 (12), 237 (10), 202 (20), 197 (47), 175 (20), 135 (100), 121 (11), 105 (8).

3.2.5. R = C(SiMe$_3$)$_3$.

A solution of HgR^2Cl (1.52 g, 2.32 mmol) in THF (20 cm^3) was added to one of $LiC(SiMe_3)_3$ (0.89 g, 2.32 mmol) in THF (25 cm^3) over a period of 30 min, during which the colour of the mixture turned from orange to yellow. The progress of the reaction was monitored by withdrawal of samples at intervals for ^{1}H NMR spectroscopy. The solution was heated under reflux for 4 h and stirred overnight after which some decomposition had taken place, as shown by the presence of a small mercury droplet at the bottom of the flask. The ^{1}H spectrum showed four signals in the SiMe$_2$ region but none from the starting materials; one of the major

components was identified as $(Me_2PhSi)_3CH$ by enhancement of its signals in the ^1H NMR spectrum upon addition of an authentic sample. The solvent was then removed under vacuum, the residual solid extracted with warm heptane, and the extract concentrated and kept at $-10°C$ to give white crystals, which were recrystallized from $CHCl_3$ to give HgR^1R^2 (yield, 0.41 g (21%); m.p., 262–264°C). Anal. Found: C, 49.4; H, 6.8 $C_{35}H_{60}HgSi_6$ Calc.: C, 49.5; H, 7.1%. ^1H NMR (C_6D_6): δ 0.44 (27H, s, $SiMe_3$), 0.48 (18H, s, $SiMe_2$), 6.93–7.38 (15H, m, Ph) ppm. ^{13}C NMR (C_6D_6): δ 5.89 $(SiMe_3)$, 6.86 $(SiMe_2)$, 142.2 (ipso-C of Ph), 135.4 (o-C), 128.3 (m-C), 129.0 (p-C) ppm. ^{29}Si NMR (C_6D_6): δ -7.7 $(SiMe_2)$, -3.4 $(SiMe_3)$ ppm. MS: m/z 850 $(M^+, 0.5\%)$, 446 (0.2), 433 $[(Me_3Si)_3CHg]$, 0.2], 402 (15), 325 (5), 309 (10), 231 (15, $Me_3Si)_3C)$, 217 (5), 201, (18), 197 (5), 175 (5), 135 (24), 111 (10), 105 (9), 83 (30), 73 (52), 43 (MeSi, 100).

Crystal data: $C_{35}H_{60}HgSi_6$; $M = 850.0$; trigonal; $P3$; $a = 15.512(8)$ and $c = 14.649(6)$ Å; $U = 3052.6$ Å^3; $Z = 3$; $D_c = 1.39$ g cm^{-3}; $F(000) = 1302$; Mo Kα radiation; $\lambda = 0.71069$ Å; $\mu = 39.8$ cm^{-1}.

3.3. Preparation of $Hg\{C(SiMe_3)_3\}Br$ (HgR^1Br) (cf. [5])

A solution of LiR^1 (4.2 g, 1.85 mmol) in THF (about 40 cm^3) was added slowly with stirring to one of $HgBr_2$ (7.63 g, 2.1 mmol) in diethyl ether maintained at $-10°C$. When addition was complete, the mixture was stirred for 2 h at room temperature, the solvent then removed, and the residue extracted (Soxhlet apparatus) with light petroleum (b.p., 60–80°C). The ^1H NMR spectrum showed that the extract contained HgR^1Br along with some HgR^1_2. Column chromatography (Kieselgel 60 (70–230 mesh) ASTM). with light petroleum (b.p., 60–80°C) as eluent gave HgR^1Br (yield, 6.4 g (62%); m.p., 228–230°C (229°C [5]). ^1H NMR $(CDCl_3)$: δ 0.07 (0.07 [5]).

3.4. Preparation of the compounds $Hg\{C(SiMe_3)_3\}R$ (HgR^1R)

3.4.1. R = Me.
The Grignard reagent MgMeI was made from MeI (0.56 g, 4.0 mmol) and magnesium turnings (0.10 g, 4.2 mmol) in diethyl ether (100 cm^3). The solution was added dropwise to one of HgR^1Br (2.0 g, 3.9 mmol) in THF (100 cm^3) maintained at $-40°C$. When the addition was complete, the mixture was allowed to warm slowly to 0°C (ice bath) and then stirred overnight. The solvent was removed under vacuum and the product extracted with light petroleum (b.p., 40–60°C). The extract was filtered, the solvent removed, and the residual solid subjected to column chromatography (condi-

tions as above) to give white crystals of HgR^1Me (yield, 0.54 g (31%); m.p., 184–185°C). ^1H NMR $(CDCl_3)$: δ 0.22 (27H, s, Me_3Si), 0.43 (3H, s, Me) ppm. $(^1H$ NMR (C_6D_6): δ 0.21, 0.41 ppm [2].)

3.4.2. R = ^iPr.
The procedure described in Section 3.4.1 (including the chromatography) was used, but starting from ^iPrCl (7 mmol). The product was obtained as a colourless oil (yield, 81%). Anal. Found: C, 31.0; H, 6.1. $C_{13}H_{34}HgSi_3$ Calc.: C, 32.9; H, 7.2%. ^1H NMR $(CDCl_3)$: δ 0.21 (27H, s, Me_3Si), 1.46 (6H, d, Me of ^iPr), 1.60 (1H, m, CH of ^iPr) ppm. ^{13}C NMR $(CDCl_3)$: δ 6.1 (Me_3Si) 22.8 (Me, ^iPr), 33.1 $(CSi_3$, 48.6 ppm (CH of ^iPr) ppm. ^{29}Si NMR $(CDCl_3)$: δ -3.75 ppm. MS: m/z 476 $(M^+, 10\%)$, 461 $(M - Me, 7)$, 419 (5), 231 $[(Me_3Si)_3C, 41]$, 216 (27), 201 (45), 157 (20), 143 (18), 131 (22), 73 (100), 43 (38).

3.4.3. R = Bu.
The procedure described in Section 3.4.1 was used but starting from BuBr (7.0 mmol). The product was a colourless oil (yield, 76%). Anal. Found: C, 34.0, Hg, 7.1. $C_{14}H_{36}HgSi_3$ Calc.: C, 34.4; H, 7.4%. ^1H NMR $(CDCl_3)$: δ 0.22 (27H, s, Me_3Si) ppm. ^{13}C NMR $(CDCl_3)$: δ 6.1 (Me_3Si), 13.8 (Me of Bu), 28.1 $(CH_2$ of Bu), 30.6 $(CH_2$ of Bu) 34.4 (CSi_3), 42.2 $(CH_2$ of Bu) ppm. ^{29}Si NMR $(CDCl_3)$: δ -3.78 ppm. MS: m/z 490 $(M^+, 7\%)$, 475 $(M - Me, 20)$, 231 (8), 216, 201 (55), 143 (12), 85 (10), 73 (100).

3.4.4. R = ^tBu.
The Grignard reagent Mg^tBuCl was prepared from ^tBuCl (0.96 g, 7.0 mmol) and Mg turnings (0.17 g, 7.0 mmol) in diethyl ether (50 cm^3) with iodine initiation. Subsequent procedure as described in Section 3.4.2 above gave a colourless oil that was shown to be $HgR^{1t}Bu$ (yield, 2.40 g (83%). Anal. Found: C, 34.6, H, 7.3. $C_{14}H_{36}HgSi_3$ Calc.: C, 34.4, H, 7.4%) ^1H NMR $(CDCl_3)$: δ 0.18 (27H, s, Me_3Si), 1.36 (9H, s, ^tBu) ppm. ^{29}Si NMR $(CDCl_3)$: δ -3.80 ppm. MS. m/z 490 $(M^+, 5)$, 475 $(M - Me, 5)$, 217 (45), 202 (42), 129 (10), 73 (6), 57 (Bu, 100).

3.4.5. R = Ph.
The procedure described under Section 3.4.1 was used but starting from PhBr (7.0 mmol), and gave crystals of HgR^1Ph (yield, 1.72 g (57%); m.p. 39–40°C). Anal. Found: C, 37.7; H, 6.2. $C_{16}H_{32}HgSi_3$ Calc.: C, 37.7; H, 6.3%. ^1H NMR $(CDCl_3)$: δ 0.20 (27H, s, Me_3Si), 7.40 (5H, m, Ph) ppm. ^{13}C NMR $(CDCl_3)$: δ 6.1 (Me_3Si), 28.9 (CSi_3), 128.4 (p-C of Ph), 128.9 (m-C), 136.1 (o-C), 175.1 (ipso-C) ppm. ^{29}Si NMR $(CDCl_3)$: δ -2.70 ppm. MS: m/z 495 $(M - Me, 25)$, 216 (10), 201 (80), 85 (18), 73 (100).

3.5. The reaction between HgR^{1}Br and MeLi

A 1.0 mol dm^{-3} solution of LiMe in Et$_2$O (5.9 cm^3, 5.9 mmol) was added dropwise from a syringe to a stirred solution of HgR^{1}Br (5.9 mmol) in diethyl ether (40 cm^3) maintained at − 10°C. The mixture was allowed to warm to room temperature and stirred for a further 2 h. The ^{1}H NMR spectrum of the mixture showed that it contained roughly equal amounts of HgR$^1_2$ and unchanged HgR^{1}Br (confirmed by addition of authentic samples).

3.6. Reaction of HgR^{1}Br with Mg(CH$_2$Ph)Cl

The Grignard reagent was made from PhCH$_2$Cl (0.89 g, 7.0 mmol) and Mg (0.17 g, 7.0 mmol) in diethyl ether (50 cm^3) and added dropwise to a stirred solution of HgR^{1}Br (3.0 g, 5.9 mmol) in THF (100 cm^{-3}) maintained at − 40°C. The stirred mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed under vacuum and the residue extracted with light petroleum (b.p., 40–60°C). The extract was concentrated and kept at − 20°C to yield crystals of Hg(CH$_2$Ph)$_2$ (m.p., 109–110°C (111°C [20])). ^{1}H NMR (CCl$_4$): δ 2.3 (2H, s, CH$_2$), 7.0 and 7.1 (5H, m, Ph) ppm. The mother liquor was further concentrated and kept at − 20°C to give crystals of HgR$^1_2$ (m.p., 264–265°C 263–265°C [2]). ^{1}H NMR (CCl$_4$–CH$_2$Cl$_2$): δ 0.30 ppm.

3.7. Reaction of Hg(CH$_2$Ph)Cl with LiR^1

A solution of LiR^1 (16.5 mmol) in THF (about 40 cm^3) was added dropwise with stirring to one of Hg(CH$_2$Ph)Cl (14.0 mmol) in THF (40 cm^3). The mixture was boiled under reflux for 3 h, allowed to cool to room temperature and added to ice–water. Extraction with diethyl ether, followed by drying (MgSO$_4$) of the extract and removal of the solvent left a solid, which was recrystallized from hot heptane and shown to be Hg(CH$_2$Ph)$_2$ (m.p. and δ(^{1}H NMR) as above). The mother liquor was concentrated and kept at − 20°C, and the crystals that separated were shown to be HgR$^1_2$ (m.p. and δ(^{1}H NMR) as above).

3.8. Preparation of Hg{C(SiMe$_3$)$_2$(SiMe$_2$H)}$_2$

A 1.2 mol dm^{-3} solution of LiBu in hexane (7.3 cm^3, 8.8 mmol) cooled to − 80°C was added during 15 min with stirring to a solution of (Me$_3$Si)$_2$(HMe$_2$Si)-CCl (2.0 g, 7.9 mmol) in a mixture of THF (25 cm^3), Et$_2$O (4 cm^3) and pentane (1.5 cm^3). The solution was stirred at − 110°C for 2 h, then transferred to a dropping funnel surrounded by solid carbon dioxide and added dropwise to a stirred solution of HgCl$_2$ (1.05 g, 3.86 mmol) in THF (20 cm^3) at − 110°C. The mixture

was stirred for a further 1 h and then allowed to warm to room temperature. The solvents were removed under reduced pressure and the residue extracted with pentane. The extract was filtered and the solvent evaporated, to leave a solid, which was recrystallized from MeOH to give Hg{C(SiMe$_3$)$_2$(SiMe$_2$H)}$_2$ (yield, 0.83 g (16.5%); m.p., 130°C). Anal. Found: C, 35.2; H, 8.4. C$_{18}$H$_{48}$HgSi$_6$ Calc.: C, 34.9; H, 7.9%. ^{1}H NMR (CCl$_4$–CDCl$_3$): δ 0.18 (18H, s, SiMe$_3$), 0.25 (6H, d, SiMe$_2$), 4.21 (1H, m, SiH) ppm. ^{13}C NMR (CCl$_4$–CDCl$_3$): δ 2.7 (SiMe$_2$), 5.6 (SiMe$_3$) ppm. ^{29}Si NMR (CCl$_4$–CDCl$_3$): δ − 2.95 and − 2.06 ppm. IR: ν(Si–H) 2089 (m) cm^{-1}, MS: m/z 635 (M − H, 2%, 621 (M − Me, 3), 417 (7), 329 (8), 273 (25), 257 (18), 217 (100), 201 (90), 129 (72), 73 (90), 59 (32), 45 (15).

References

[1] A.R. Bassindale, A.J. Bowles, M.A. Cook. C. Eaborn, A. Hudson, R.A. Jackson and A.E. Jukes, J. Chem. Soc., Chem. Commun., (1970) 559.

[2] F. Glockling, N.S. Hosmane, V.B. Mahale, J.J. Swindall, L. Magos and T.J. King, J. Chem. Res., (1977) (S) 116; (M) 1201.

[3] C. Eaborn, P.B. Hitchcock, J.D. Smith and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1983) 827; A.G. Avent, C. Eaborn, P.B. Hitchcock, P.D. Lickiss, M. Mallien, J.D. Smith, A.D. Webb and B. Wrackmeyer, J. Chem. Soc., Dalton Trans., (1993) 3259.

[4] C. Eaborn and A.I. Mansour, J. Chem. Soc., Perkin Trans. II, (1985) 729.

[5] W. Hiller, M. Layh and W. Uhl, Angew Chem., Int. Edn. Engl., 30 (1991) 324.

[6] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock and J.D. Smith, J. Organomet. Chem., 437 (1992) 41.

[7] J. Browning, P.L. Goggin, R.J. Goodfellow, N.W. Hurst, L.G. Mallinson and M. Murray, J. Chem. Soc., Dalton Trans., (1978) 872.

[8] B. Wrackmeyer and R. Contreras, Annu. Rep. NMR Spectrosc., 24 (1992) 267.

[9] R.J. Kominar and S.J. Price, Can. J. Chem., 47 (1969) 991; H.V. Carter, E.I. Chappell and E. Warhurst, J. Chem. Soc., (1956) 106.

[10] H.T.J. Chilton and B.G. Gowenlock, Trans. Faraday Soc., 50 (1954) 824; B.H.M. Billinge and B.G. Gowenlock, Trans. Faraday Soc., 59 (1963) 690.

[11] B. Beagley, R.G. Pritchard, C. Eaborn and S.S. Washburne, *J. Chem. Soc., Chem. Commun.*, (1981) 710.

[12] I.S. Butler and M.L. Newbury, *Spectrochim. Acta, Part A, 33* (1977) 669.

[13] J.H.S. Green, *Spectrochim. Acta, Part A, 24* (1968) 863.

[14] P.L. Goggin and D.M. McEwan, *J. Chem. Res.*, (1978) (S) 171; (M) 2253.

[15] C. Eaborn, N. Retta and J.D. Smith, *J. Organomet. Chem., 190* (1980) 101.

[16] F. Glockling, S.R. Stobart and J.J. Sweeney, *J. Chem. Soc., Dalton Trans.*, (1973) 2029.

[17] M. Westerhausen, B. Rademacher and W. Poll, *J. Organomet. Chem., 421* (1991) 175.

[18] R. Benn, *Chem. Phys., 15* (1976) 369.

[19] R.A. Jackson and D.W. O'Neill, *J. Chem. Soc., Perkin Trans. 2*, (1978) 509, and references cited therein.

[20] K.C. Bass and G.M. Taylor, *J. Chem. Soc. B*, (1970) 1615.

[21] C. Eaborn, K.L. Jones, J.D. Smith and K. Tavakkoli, *J. Chem. Soc., Chem. Commun.*, (1989) 1201.

[22] S.J.W. Price, in C.H. Bamford and C.F.H. Tipper (eds.), *Comprehensive Chemical Kinetics*, Vol. 4, Elsevier, Amsterdam, 1972, pp. 197–257.

[23] J.L. Wardell, in G. Wilkinson, F.G.A. Stone and E.A. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon, Oxford, 1982, pp. 953–956.

[24] G.A. Russell, *Adv. Free Radical Chem., 1* (1990) 12; G.A. Russell, P. Ngoviwatchai, H.I. Tashtoush, A. Pla-Dalmau and R.J. Khanna, *J. Am. Chem. Soc., 110* (1988) 3530.

[25] K. Tavakkoli, *D.Phil. Thesis*, University of Sussex, 1989.

[26] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, C.A. McGeary and J.D. Smith, *J. Chem. Soc., Chem. Commun.*, (1989) 273.

[27] N.H. Buttrus, C. Eaborn, P.B. Hitchcock, J.D. Smith and A.C. Sullivan, *J. Chem. Soc., Chem. Commun.*, (1985) 1380.

[28] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, K. Izod, M. Mallien and J.D. Smith, *Angew. Chem., Int. Edn. Engl., 33* (1994) 1268.

[29] C. Eaborn, P.B. Hitchcock, J.D. Smith and A.C. Sullivan, *J. Organomet. Chem., 263* (1984) C23.

[30] C. Eaborn, P.B. Hitchcock, J.D. Smith and A.C. Sullivan, *J. Chem. Soc., Chem. Commun.*, (1984) 870.

[31] A.G. Avent, S.G. Bott, J.A. Ladd, P.D. Lickiss and A. Pidcock, *J. Organomet. Chem., 427* (1992) 9.

[32] M. Al-Rawi, *D. Phil. Thesis*, University of Sussex, 1995.

[33] C. Eaborn, P.B. Hitchcock and P.D. Lickiss, *J. Organomet. Chem., 269* (1984) 235.

[34] A.J. McCaffery, personal communication, 1990.

[35] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, K. Tavakkoli and A.D. Webb, *J. Organomet. Chem., 462* (1993) 45.