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Journal of Organometallic Chemistry 515 (1996) 221–232

Journal of Organometallic Chemistry

Organomercury(II) and organotin(IV) compounds with nitrogen-containing substituents

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Received 25 October 1995

Abstract

New compounds of the type ArHgCl, $ArCH_2HgCl$, Ar_2Hg, $(ArCH_2)_2Hg$, $ArSnPh_3$ and $ArCH_2SnPh_3$ are described. The aryl groups carry various substituents, but all have a group in the 2-position which involves a nitrogen atom which could in principle coordinate to the metal atom, e.g. $-NMe_2$, $-CH_2NMe_2$, $-CONH_2$, $-NHCO^tBu$, $-SO_2NMe_2$, –oxaz (oxaz = 4,4-dimethyl-2-oxazoline). Full ^1H and ^{13}C NMR assignments are made for all the compounds; the data provide no evidence for N → Hg coordination in solution. IR data suggest that such interaction is, at most, very weak in the solids.

Keywords: Tin; Mercury; Aminoaryl ligands; Nuclear magnetic resonance

1. Introduction

Organomercury and organotin complexes have been used for many years as intermediates in organic chemistry [1,2] and in the preparation of other organometallics [3]. Their convenience lies in the ease with which they transfer their organic groups to other atoms, usually replacing a halide or other anionic group. In this way, many new cyclometallated complexes otherwise inaccessible by classical Grignard or lithiation reactions have been obtained [3a,3i,4].

We were interested in the development of general routes for the synthesis of aryl–gold(III) compounds in which substituent nitrogen-containing groups would allow chelation. Although several methods have been reported for the formation of gold(III)–carbon bonds [5], the transmetallation reaction between organomercury or organotin compounds and gold(III) salts has been found to be the most suitable method for preparing cyclo-aurated complexes [4,6,7]. We have extended this method to the preparation of derivatives of aryl- and benzyl-amines, aryl-sulphonamides, and aryl-, benzyl- and picolinyl-amides. Since the majority of the intermediate mercury and tin compounds have not been reported previously, we describe here their preparation and characterisation, and examine the possibility of coordination of the nitrogen-bearing group to mercury. Their transmetallation reactions with gold compounds and the characterisation of the cyclometallated gold complexes will be discussed elsewhere [8].

2. Results and discussion

2.1. Preparation of organomercurials and organotin complexes

The preparative methods used and the materials obtained are summarised in Eqs. (1)–(7). The aromatic precursors were prepared by published procedures and their lithiations performed by normal routes (see Table 1 for Refs. [9–19]).

The chloro-organomercury(II) compounds **2a**–**2c**, containing amide substituents, were obtained by direct reaction of the aromatic with mercury(II) acetate followed by lithium chloride (Eq. (1)). All other chloromercury compounds and the triphenyl-organotin(IV) compounds (**2d**–**2u**) were obtained by lithiation of the corresponding aromatics using *n*-butyllithium, followed by the addition of one molar equivalent of mercury(II) chloride or triphenyltin(IV) chloride (Eqs. (2)–(4)). The use of 2:1 ratios gave the bis-aryl mercury derivatives **2v**–**2y** (Eqs. (5)–(7)). Yields were usually reasonably good (50–70%, see Table 2), the major exceptions

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SSDI 0022-328X(95)06081-2

being the bis-arylmercury compounds. All the compounds are new with the exception of **2s**, which is reported here with more detailed NMR data than in the original publication [20].

2.2. Characterisation

Analytical and mass spectrometric data for the mercury and tin compounds are given in Table 2. In the mass spectra, the M + H peaks were usually observed; in some cases the M − H ion was also observed or was the parent ion. All showed the correct isotope distribution patterns.

NMR spectra (Tables 3 and 4) have been fully assigned. For ^{1}H, this could usually be done from the coupling patterns, especially for the less symmetrical molecules. For ^{13}C, DEPT90 and ^{1}H–^{13}C COSY spectra were helpful. C^1, C^2 and C^6 could usually be recognised as having the three highest chemical shifts for the ring carbons [21]. Owing to their low intensity the ^{199}Hg ($I = 1/2$, 19%) satellites were not always seen but those discernible were also useful in making assignments. The direct application of the expectation [21] that $^1J \gg {}^3J > {}^2J > {}^4J$ was often complicated by the presence of the substituents.

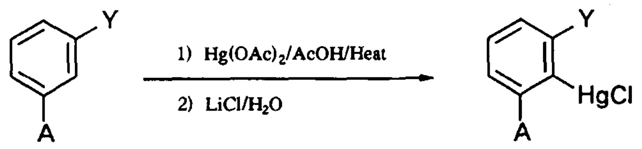
Coupling between ^{199}Hg and the directly bonded carbon atom is always substantial, being 1735–2603 Hz for ArHgCl and 830–943 Hz for Ar_2Hg, which are the normal ranges [21–23]. The difference between the mono- and bis-aryl derivatives is usually explained on the assumption that the Hg–C bonds have high (Hg)6s-character; in the case of the bis-aryl compounds, the 6s-orbital is shared between the two groups, reducing the s-character per bond and hence the Fermi-contact contribution to the coupling [24].

Coupling is also seen to the tin isotopes (^{117}Sn, $I = 1/2$, 7.6%; ^{119}Sn, $I = 1/2$, 8.6%), and the ^1J values indicate that the tin is, as expected, four-coordinate (^1J(C–^{119}Sn) = 543, 596 Hz for the aromatic carbon atoms). Coordination of additional ligands is not known for tetra-organotin(IV) compounds; if it occurred it would result in two sets of couplings, both lower than those observed [25].

For the mercury derivatives, chelation by the C–N ligand is not expected for Ar_2Hg but is, in principle, possible in ArHgCl. Unfortunately, its presence or absence is not revealed by the coupling constants. However, the chemical shifts of the nitrogen-containing groups are very close to those of the uncoordinated aromatic molecules. For gold(III) complexes containing the same ligands, substantial positive (downfield) coordination chemical shifts (ccs) are seen when the substituents are coordinated [8,23]. Evidence has been presented for chelation in ArHgX (Ar = o-$C_6H_4CH(CH_3)$-NMe_2; X = Cl, OAc), in which the benzylic carbon atoms are chiral [26]: at low temperature (210 K) the signal for the NMe groups splits into two (see **B** and **C** in Table 4). This was attributed to blocking by coordination of inversion at the nitrogen atom, rendering the methyl groups diasteroscopic. However, the ccs values remain very small whereas, in the gold(III) complexes of the damp ligand (damp = o-$C_6H_4CH_2NMe_2$) [23], the NMe groups show a ccs of about +9 ppm when the NMe_2 group is coordinated but only about +0.4 ppm when it is definitely not coordinated (cf. data for (damp)HgCl, **A** in Table 4). The benzylic CH_2 group similarly shows a ccs of 14–16 ppm in gold(III) complexes [23]. It must therefore be concluded that, for ArHgCl in solution, any association between the nitrogen atoms of any of the present ligands and mercury is very weak and certainly highly fluxional.

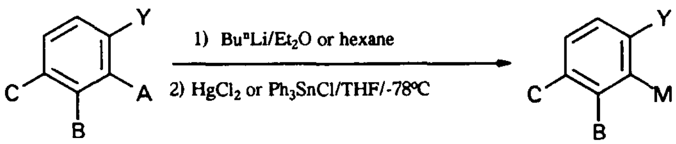
The ccs values of the mercury-bound carbon atoms are substantial (ca. 20 ppm) and positive (downfield shift). The adjacent carbon atom (C^6) also shows a positive ccs, but much smaller: 8–10 ppm. The effect on C^2 is usually much smaller, being offset by the effects of the substituents. The ^{1}H ccs values are all very small.

The solid state IR spectra of ArHgCl show absorptions corresponding to the substituted aryl groups. They

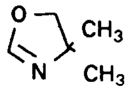


(1)

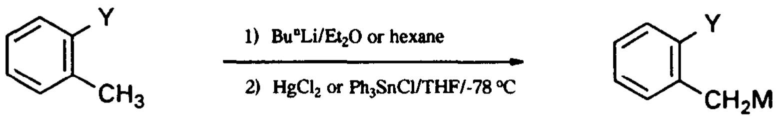
	Y	A	
1a	$CONH_2$	H	2a
1b	CONHEt	H	2b
1c	$CONEt_2$	$CONEt_2$	2c



(2)

	Y	A	B	C	M = HgCl	M = SnPh$_3$
1d	CH$_2$NMe$_2$	H	H	OMe	2d	
1e		H	OMe	OMe	2e	
1f		H	H	NMe$_2$	2f	
1g		H	OMe	H	2g	
1h		H	NMe$_2$	H	2h	
1i		H	H	CH$_2$NMe$_2$	2i	
1j	CH$_2$NHMe	H	OMe	H	2j	
1k	SO$_2$NMe$_2$	H	H	H	2k	2l
1m		Br	H	H	2m	2n
1o		H	H	OMe	2o	
1p		H	H	NMe$_2$	2p	

also have very similar patterns of bands in the 500–300 cm^{-1} region: a relatively strong absorption band between 350 and 323 cm^{-1} (Table 5), and a weaker band between 470 and 450 cm^{-1}; these are assigned to ν(Hg–Cl) and ν(Hg–C) respectively. The bis(organo)mercury(II) compounds display only a band corresponding to the mercury–carbon vibration at frequencies similar to those for ArHgCl.

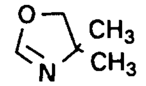


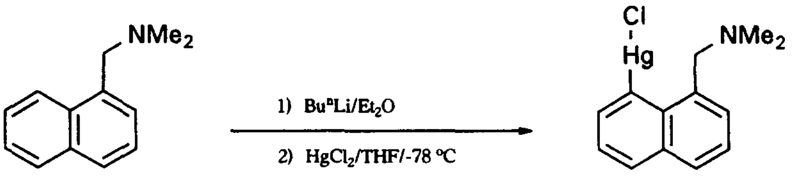
(3)

1q Y = CH$_2$NMe$_2$ 2q M = HgCl

1r Y = NMe$_2$ 2r M = HgCl

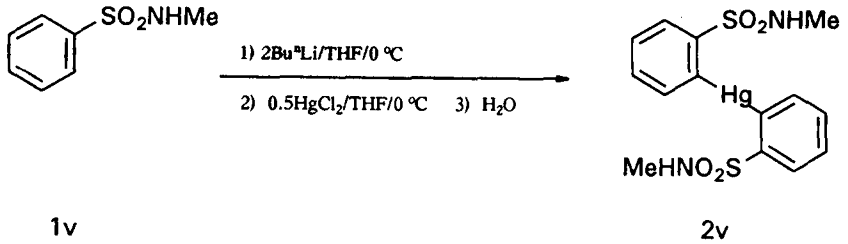
2s M = SnPh$_3$

1t Y =  2t M = HgCl

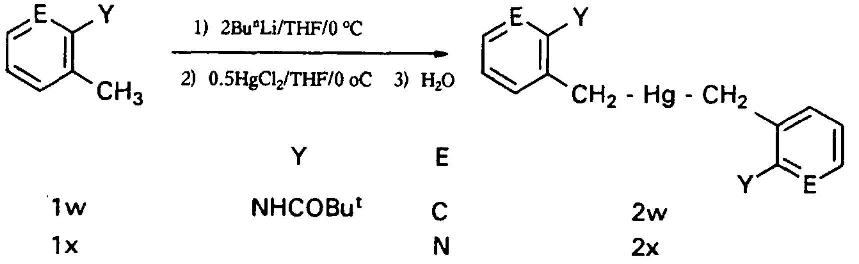


(4)

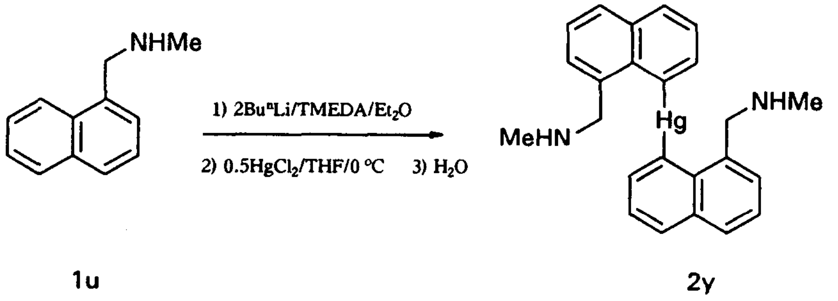
1u 2u



(5)



(6)



(7)

It has been proposed that the frequency ν(Hg–Cl) would be related to the coordination number of the mercury [27], in that a value lower than that of [Hg(C_6H_5)Cl] (331 cm^{-1}) might indicate an Hg–N interaction. This suggestion fails to take into account the electronic properties (inductive and field effects) of the various substituents on the aromatic ring, which are bound to influence the strengths of both the mercury–carbon and mercury–chlorine bonds. Correspondingly a range of ν(Hg–Cl) values is observed.

In fact, only five of the present ArHgCl compounds exhibit ν(Hg–Cl) lower than 331 cm^{-1} (**2a**, **2c**, **2k**, **2u**, **2v**; Table 5). These all contain amide or sulphonamide substituents which are the most electronegative of any of those studied. The other compounds all have higher Hg–Cl stretching frequencies. In no case, therefore, is

Table 1
References for ligand preparative methods and lithiations

	a	b	c	d	e	f	g	h	i	j	k	l	m
Synthesis	[9]	[9]	[9]	[9]	[9]	[9]	[9]	[9]	[9]	[9]	[11]	[11]	[10]
Lithiation				[16]	[16]	[16]	[16]	[16]	[17]	[16] [a]	[18]	[18]	

	n	o	p	q	r	s	t	u	v	w	x	y
Synthesis	[10]	[10]	[10]	[9]	[9]	[9]	[10]	[9]	[11]	[12]	[12]	[9]
Lithiation		[15]	[15]	[16]	[14]	[14]	[15]	[13]		[19]	[19]	[17]

[a] Efficient lithiation requires the presence of TMEDA.

strong Hg–N interaction likely. It may be significant that **2k** has the highest Hg–C stretching frequency of those recorded (468 cm^{-1}; vs. **2m**, 446; **2o**, 452; **2p**, 450; **2t**, 445 cm^{-1}).

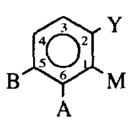
It is also worth noting that the vibrations associated with the substituent groups show shifts to low frequency relative to the uncoordinated aromatic molecules (Table 5). These shifts could be interpreted as being the result of an interaction between the nitrogen atom and the mercury centre in the solid state. However, in the case

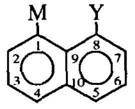
Table 2
Analytical data [a] and yields

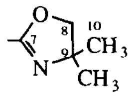
Compound	%C	%H	%N	%Cl	%Hg	*m*/*z*(M) [b]	Yield (%)
2a	22.0	1.4	3.5	10.2			17
	(21.9)	(1.6)	(3.6)	(10.0)			
2b	27.8	2.5	3.4	9.1			21
	(28.1)	(2.6)	(3.6)	(9.2)			
2c	37.4	4.4	5.4	6.9			10
	(37.6)	(4.5)	(5.5)	(6.9)			
2d	30.2	3.6	3.5	9.1	49.9	402	73
	(30.0)	(3.5)	(3.5)	(8.9)	(50.1)	(401)	
2e	31.0	4.0	3.0	8.2	46.5	430	79
	(30.7)	(3.7)	(3.2)	(8.3)	(46.6)	(431)	
2f	32.1	3.9	6.9	8.7	49.0	415	65
	(32.0)	(4.1)	(6.6)	(8.8)	(48.5)	(414)	
29	29.9	3.2	3.6	9.0	49.6	400	71
	(30.0)	(3.5)	(3.5)	(8.9)	(50.1)	(401)	
2h	32.0	4.0	6.7	8.5		415	54
	(31.9)	(4.1)	(6.6)	(8.6)		(414)	
2i	33.7	3.9	6.3	8.7		427	60
	(33.7)	(4.4)	(6.6)	(8.3)		(428)	
2j	28.4	3.3	3.6	9.2		388	25
	(28.0)	(3.1)	(3.6)	(9.2)		(387)	
2k	22.6	2.3	3.2	8.7			52
	(22.8)	(2.4)	(3.3)	(8.4)			
2l	58.5	5.0	2.7				30
	(58.4)	(4.7)	(2.6)				
2m	32.2	2.9	3.2	8.6	48.8	412	43
	(32.2)	(2.9)	(3.4)	(8.7)	(48.9)	(411)	
2n	66.2	5.1	2.5				63
	(66.4)	(5.2)	(2.7)				
20	32.3	2.7	3.3	8.9	49.0	442	57
	(32.7)	(3.2)	(3.2)	(8.1)	(48.5)	(441)	
2p	34.6	3.7	6.1	8.2		455	82
	(34.4)	(3.8)	(6.2)	(7.8)		(454)	
2q	31.2	3.6	3.6	9.7		386	55
	(31.2)	(3.6)	(3.6)	(9.2)		(385)	
2r [c]	26.8	3.2	4.2	10.4			36
	(29.2)	(3.2)	(3.8)	(9.6)			
2s	67.0	5.6	2.9			485	41
	(67.0)	(5.6)	(2.9)			(485)	
2t	32.5	3.4	3.0	8.7		424	43
	(34.0)	(3.3)	(3.3)	(8.4)		(425)	
2u	36.8	3.6	3.4	8.8	48.0	541	30
	(37.1)	(3.3)	(3.3)	(8.4)	(47.8)	(542)	
2v	29.8	2.7	4.9			543	21
	(31.1)	(3.0)	(5.2)			(542)	
2w	49.9	5.5	4.8				30
	(49.9)	(5.7)	(4.8)				
2x	45.4	4.9	9.5			585	54
	(45.3)	(5.1)	(9.6)			(584)	
2y	53.0	4.1	5.2			541	22
	(53.3)	(4.4)	(5.2)			(542)	

[a] Calculated values in parentheses. [b] Calculated molar mass for most abundant isotopes, ^{202}Hg, ^{35}Cl, ^{120}Sn. [c] Showed signs of decomposition after 48 h.

Table 3
^{1}H NMR data[a]







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Code	M	Y	Substituents	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	H^{11}	H^{12}
2a	HgCl	CONH$_2^8$			8.0d	7.55d	7.4d	7.6d		7.9s				
ccs					−0.2	−0.2	−0.05	−0.15		−0.2				
2b	HgCl	CON(H)CH$_2^8$CH$_3^9$			7.45d	7.4m	7.4m	7.6d		3.45q	1.2t	6.35s		
ccs					−0.25	0.05	0.05	0.25		0.05	−0.5	0.05		
2c	HgCl	CON(CH$_2^8$CH$_3^9$)$_2$	6-CON(CH$_2^{10}$CH$_3^{11}$)$_2$		7.4d	7.3dd	7.4d			3.4s	1.2s			
cccs					0.15	0.05	0.15			0.15	0.1			
2d	HgCl	CH$_2^7$N(CH$_3^8$)$_2$	5-OCH$_3^9$		7.05d	6.7dd		6.95	3.3s	2.25s	3.7s			
ccs					−0.1	−0.1		0.15	0.05	0.1	0.0			
2e	HgCl	CH$_2^7$N(CH$_3^8$)$_2$	6-OCH$_3^9$, 5-OCH$_3^{10}$		7.7d	7.85d			3.3s	2.25s	3.8s	3.75s		
ccs					1.0	1.05			0.0	0.1	−0.05	0.0		
2f	HgCl	CH$_2^7$N(CH$_3^8$)$_2$	5-N(CH$_3^9$)$_2$		7.0d	6.7dd		6.75d	3.1s	2.2s	2.85s			
J_{Hg}								229						
ccs					−0.1	0.1		0.15	−0.15	0.1	0.0			
2g	HgCl	CH$_2^7$N(CH$_3^8$)$_2$	6-OCH$_3^9$		6.7d	7.15d	6.75d		3.15s	2.25s	3.7s			
ccs					0.0	0.35	−0.05		−0.15	0.1	0.0			
2h	HgCl	CH$_2^7$N(CH$_3^8$)$_2$	6-N(CH$_3^9$)$_2$		6.75d	7.1dd	6.95d		3.35s	2.2s	2.75s			
ccs					0.4	0.0	0.35		0.05	0.05	0.1			
2i	HgCl	CH$_2^7$N(CH$_3^8$)$_2$	6-CH$_2^9$N(CH$_3^{10}$)$_2$		7.2m	7.1m		7.3s	3.4s	2.3s	3.3s	2.2s		
ccs					−0.1	−0.1		−0.2	0.1	0.15	0.0	0.05		
2j	HgCl	CH$_2^7$N(H^8)CH$_3^9$	6-OCH$_3^{10}$			6.65d	7.1dd	6.7d		3.6s	1.5sb	2.3s	3.65s	
ccs						0.05	−0.05	−0.1		0.0	0.2	−0.05	−0.05	
2k[b]	HgCl	SO$_2$N(CH$_3^7$)$_2$			7.8m	7.5dd	7.6dd	7.8m	2.6s					
2l[c]	SnPh$_3$	SO$_2$N(CH$_3^7$)$_2$			7.7d	7.4m	7.45m	7.75d	2.3s					
ccs					0.05	−0.05	0.0	0.3	0.25					
2m[d]	HgCl	oxaz			7.4d	7.35dd	7.5dd	7.85d		4.2s		1.35s		
J_{Hg}								207						
2n[d,e]	SnPh$_3$	oxaz			7.35m	7.35m	7.6m	7.9d		3.9s		0.65s		
J_{Sn}								75						
2o	HgCl	oxaz	5-OCH$_3^{11}$		7.7d	6.75dd		7.85d		4.15s		1.3s	3.75s	
J_{Hg}								228						
ccs					−0.1	−0.1		0.05		0.15		0.05	0.0	
2p	HgCl	oxaz	5-N(CH$_3^{11}$)$_2$		7.6d	6.5dd		7.6d		4.1s		1.3s	3.95s	
J_{Hg}								240						
ccs					−0.1	−0.05		1.05		0.1		0.0	1.0	
2q	CH$_2^9$HgCl	CH$_2^7$N(CH$_3^8$)$_2$			7.1d	6.95m	6.95m	7.1d	3.55s	2.1s	2.95s			
J_{Hg}											295			
ccs					−0.05	−0.2	−0.2	−0.05	0.25	−0.2	0.8			
2r	CH$_2^8$HgCl	N(CH$_3^7$)$_2$			7.15d	7.1dd	6.95dd	7.2d	2.65s	2.8s				
J_{Hg}										236				
ccs					0.05	0.0	−0.15	0.25	0.05	0.55				

2s [f]	CH$_2^8$HgCl	N(CH$_3^7$)$_2$		7.2m	7.0dd	6.9dd	7.9d	2.15s	2.8s					
J_{Sn}									71					
ccs				0.1	−0.1	0.05	0.95	0.35	0.55					
2t	CH$_2^{11}$HgCl	oxaz		7.2d	7.15dd	7.25dd	7.75d		3.95s		1.35s	3.0s		
J_{Hg}												273		
ccs				−0.4	0.0	0.25	0.60		0.05		0.1	0.6		
2u	HgCl	CH$_2^{11}$N(CH$_3^{12}$)$_2$	7.45d	7.75dd	7.4d	7.35d	7.75dd	7.3d				3.75s	2.2s	
J_{Hg}			235											
ccs			0.05	0.35	0.1	0.05	0.05	−0.45				0.05	0.0	
2v	HgAr [g]	SO$_2$N(H^8)C^{7}H$_3$		7.95d	7.55m	7.35m	6.0td	2.55s	1.6s					
J_{Hg}							210							
ccs				0.15	0.05	0.15	−1.5	0.0	−3.0					
2w	CH$_2^{10}$HgAr [g]	NH^{10}COC(CH$_3^9$)$_3$		7.15d	7.0m	7.0m	6.9d	7.6sb			1.1s	2.15s		
J_{Hg}												135		
ccs				−0.15	−0.15	0.05	−0.2	0.4			−0.15	0.0		
2x	CH$_2^{10}$HgAr [g]	NH^{10}COC(CH$_3^9$)$_3$		7.95d	6.95m	7.4d	8.75s			1.1s	2.1s			
J_{Hg}											143			
ccs				0.5	−0.5	0.75	0.35			−0.05	−0.05			
2y	HgAr [g]	CH$_2^{11}$N(H^{13})CH$_3^{13}$	8.0d	7.4dd	7.7d	7.6d	7.3dd	7.75d				4.4s	2.45s	1.5sb
ccs			0.6	0.0	0.3	−0.1	−0.1	−0.4				0.2	−0.05	0.1

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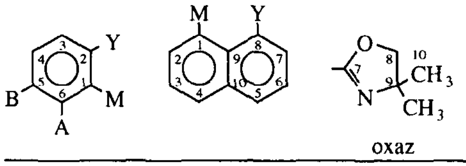
[a] Abbreviations: b, broad; d, doublet; dd, doublet of doublets; m, multiplet; s, singlet. [b] In DMSO. [c] SnPh$_3$: *o*, 7.55m; *m*, 7.3m; *p*, 7.3m. [d] Ligand **1k** is the 2-Br of 2-I derivative; ccs values not comparable with the others given here. [e] SnPh$_3$: *o*, 7.5m; *m*, 7.25m; *p*, 7.25m. [f] SnPh: *o*, 7.25m; *m*, 7.2m; *p*, 7.2m. [g] Bis-organomercury compound.

Table 4
^{13}C NMR data



Code	M	Y	Substituents	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}
2a	HgCl	C^7ONH_2		155.1	141.5	141.3	131.5	135.4	131.4	174.6					
J_{Hg}				2566	115	271		180	73						
ccs				22.8	3.2	9.0	−0.3	0.0	−0.6	2.4					
2b	HgCl	$C^7ON(H)C^8H_2C^9H_3$		150.6	141.4	130.6	128.0	127.0	136.9	173.7	30.9	13.5			
J_{Hg}						207	34	151	113						
ccs				22.1	6.6	2.1	1.1	−4.3	10.0	6.2	−4.0	−1.4			
2c	HgCl	$C^7ON(C^8H_2C^9H_3)_2$	$6\text{-}CON(C^{10}H_2C^{11}H_3)_2$	155.6	146.5	130.8	131.0	130.8	146.4	176.5	43.6	17.2			
J_{Hg}				94	94		58								
ccs				27.2	9.1	4.1	6.9	4.1	9.1	6.3	2.5	3.9			
2d	HgCl	$C^8H_2N(C^8H_3)_2$	$5\text{-}CO^9H_3$	150.1	135.8	129.3	113.8	158.3	122.7	64.0	44.5	55.4			
J_{Hg}				2472	46	199	33	267	158	188		25			
ccs				20.0	5.1	−0.5	0.1	−0.2	9.0	0.5	−0.5	0.4			
2e	HgCl	$C^8H_2N(C^8H_3)_2$	$6\text{-}OCH^9H_3$, $5\text{-}OC^{10}H_3$	142.2	136.1	124.1	112.6	151.6	151.7	63.0	44.4	60.8	55.7		
J_{Hg}				1924		202	22			101					
ccs				21.2	4.8	13.6	0.8	3.2	3.0	−1.0	−0.7	5.1	0.0		
2f	HgCl	$C^7H_2N(C^8H_3)_2$	$5\text{-}N(C^9H_3)_2$	149.7	131.5	129.3	112.6	149.8	120.8	64.1	44.6	40.8			
J_{Hg}				2449	47	194	32	242	175	100					
ccs				19.4	5.9	−1.0	−0.4	−0.1	8.6	0.3	0.0	−0.6			
2g	HgCl	$C^7H_2N(C^8H_3)_2$	$6\text{-}OC^9H_3$	145.3	136.9	109.1	130.1	121.2	161.9	64.0	44.5	55.2			
J_{Hg}						110		172		112					
ccs				32.8	−6.5	−12.1	1.2	7.1	2.5	−0.2	−0.8	−0.3			
2h	HgCl	$C^7H_2N(C^8H_3)_2$	$6\text{-}N(C^9H_3)_2$	146.7	144.7	118.1	123.3	129.5	159.0	64.9	44.6	45.8			
ccs				18.0	5.1	4.9	12.0	12.0	8.4	0.0	−0.8	5.2			
2i	HgCl	$C^7H_2N(C^8H_3)_2$	$6\text{-}C^9H_2N(C^{10}H_3)_2$	148.8	137.8	129.4	128.7	143.0	137.7	64.5	45.2	63.9	44.4		
J_{Hg}				2467	203	174	32	27	144	37					
ccs				20.0	0.4	0.6	−0.1	5.6	8.9	0.6	0.1	0.0	0.7		
2j	HgCl	$C^7H_2N(H)C^8H_3$	$6\text{-}OC^9H_3$	146.1	136.2	121.2	130.1	109.0	161.9	55.1	35.2	55.2			
J_{Hg}						111		174		110					
ccs				23.1	−5.6	0.2	0.9	−0.4	2.3	−9.2	−10.1	0.0			
2k[a]	HgCl	$SO_2N(C^7H_3)_2$		155.9	144.3	136.5	142.5	132.9	133.0	44.6					
J_{Hg}				1667		182	44	170	53	12					
2l[b]	$SnPh_3$	$SO_2N(C^7H_3)_2$		144.3	143.2	139.4	139.9	132.3	128.4	37.5					
J_{Sn}				566		37.8	9.4	37.8							
ccs				15.5	7.9	10.6	1.8	−0.6	0.3	3.5					
2m[c]	HgCl	oxaz		151.3	132.6	136.9	128.4	136.0	128.0	166.6	80.9	62.4	28.3		
J_{Hg}				2584		133	44	211	144	104		12.7			
2n[c,d]	$SnPh_3$	oxaz		141.3	133.7	138.8	130.3	131.1	127.6	163.2	80.1	67.5	27.7		
J_{Sn}				543	20.8	42.5		55.4							
2o	HgCl	oxaz	$5\text{-}OC^{11}H_3$	153.0	124.6	130.0	113.0	162.3	122.7	166.5	80.8	67.2	28.3	55.4	
J_{Hg}				2603	32	172	303	265	151						
ccs				23.2	3.8	0.2	−0.2	0.5	9.5	4.5	1.0	−0.1	0.1	−0.7	

2p	HgCl	oxaz	5-$N(C^{11}H_3)_2$	157.0	122.3	123.6	114.4	155.9	132.3	170.2	83.6	70.3	32.0	43.6	
J_{Hg}				1735		164	29	42	173						
ccs				27.3	5.4	−6.1	3.4	3.7	21.3	7.6	4.8	3.5	3.7	3.6	
2q	C^9H_2HgCl	$C^7H_2N(C^8H_3)_2$		140.7	133.7	131.5	123.5	125.4	129.2	63.2	44.6	30.3			
J_{Hg}				37		56	46	61	122	13		1569			
ccs				3.5	−3.6	1.2	−1.4	−0.2	0.6	1.0	−1.1	11.1			
2r	C^8H_2HgCl	$N(C^7H_3)_2$		135.0	150.5	136.8	124.1	119.7	130.3	44.6	30.1				
J_{Hg}						37		37	182		1564				
ccs				2.8	−2.4	5.5	−2.4	−3.0	11.8	0.2	11.6				
2s [e]	$C^8H_2SnPh_3$	$N(C^7H_3)_2$		143.8	151.3	119.4	123.7	125.4	129.5	44.4	18.7				
J_{Sn}				75.4	25.6	13.0	9.6	14.7	35.7						
ccs				11.6	−1.6	−11.9	−2.8	2.7	3.0	0.0	0.2				
2t	$C^{11}H_2HgCl$	oxaz		142.8	123.8	131.0	130.6	130.1	125.3	163.2	77.8	68.7	28.6	37.5	
J_{Hg}				175	85	21		46	59					1626	
ccs				16.3	−13.9	0.0	1.0	5.6	−3.1	1.4	−0.4	1.4	−0.1	16.3	
2u	HgCl	$C^{11}H_2N(C^{12}H_3)_2$		146.9	138.3	125.1	125.4	130.8	131.0	131.1	136.8	135.3	133.7	66.0	45.3
J_{Hg}				1924	92	138	36						64		
ccs				18.6	10.8	−0.6	0.4	6.3	5.1	3.2	0.1	2.8	−0.1	3.5	−0.3
2v	HgAr [f]	$SO_2N(H)C^7H_3$		163.9	145.3	132.0	127.7	139.2	129.4	29.1					
J_{Hg}				830		109		78	70						
ccs				35.0	6.6	3.1	0.2	0.8	1.9	−0.2					
2w	$C^{10}H_2HgAr$ [f]	$NHC^7OC^8(C^9H_3)_3$		140.6	133.2	126.3	123.9	126.2	128.6	176.8	38.9	27.3	41.1		
J_{Hg}													660		
ccs				4.7	4.3	−4.0	−2.8	1.3	5.6	0.3	−0.8	−0.4	23.5		
2x	$C^{10}H_2HgAr$ [f]	$NHC^7OC^8(C^9H_3)_3$		147.6	138.3	143.1	122.2	137.9	176.7	39.4	27.7	39.8			
J_{Hg}												717			
ccs				11.7	9.4	20.1	−2.7	11.2	0.2	−0.3	0.0	22.2			
2y	HgAr [f]	$C^{11}H_2N(H)C^{12}H_3$		167.4	128.8	135.4	125.1	126.6	123.4	126.5	143.4	133.3	132.7	55.2	36.9
J_{Hg}				943		95							55		
ccs				39.7	2.8	10.0	1.5	1.0	−2.7	−1.7	7.7	1.5	−1.2	1.4	0.3
A [g]	HgCl	$C^7H_2N(C^8H_3)_2$		149.2	144.0	127.5	128.8	129.1	137.3	64.7	44.6				
J_{Hg}				2471	52	212	31	168	142	102	11				
ccs				20.5	5.5	−0.9	1.3	2.7	9.8	0.7	−0.4				
B [h]	HgCl	$C^7H(C^8H_3)N(C^9H_3)_2$		150.6	147.3	128.5	128.8	127.3	137.4	66.0	21.5	42.4			
J_{Hg}						178		212		94					
ccs				22.7	4.1	0.6	1.7	0.6	10.3	0.4	1.1	−0.8			
C [h,j]	HgCl	$C^7H(C^8H_3)N(C^9H_3)_2$		150.4	146.1	128.4	127.1	128.5	136.8	65.3	22.1	40.5, 44.4			
J_{Hg}						170		220	145	92					
ccs [k]				22.5	2.9	0.5	1.4	0.4	9.7	−0.3	1.7	−2.5, +1.4			

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[a] In DMSO. [b] $SnPh_3$: 1, 140.5 (596); 2, 137.6 (18.9); 3, 128.5 (73.8); 4, 128.9 (n.o.). [c] Ligand **1k** is the 2-Br or 2-I derivative; ccs values not comparable with the others given here. [d] $SnPh_3$: 1, 143.2 (570); 2, 128.4 (n.o.); 3, 136.9 (45.7); 4, 128.6 (n.o.). [e] $SnPh_3$: 1, 135.9 (n.o.); 2, 128.7 (n.o.); 3, 136.7 (34.8); 4, 128.4 (n.o.). [f] Bis-organomercury compound. [g] Data for HgCl(damp) (damp = o-$C_6H_4CH_2NMe_2$), from Ref. [23]. [h] Data for HgCl(damp′) (damp′ = o-$C_6H_4C(H)MeNMe_2$) from Ref. [26]. [i] Data for HgCl(damp′) at 210 K [26]. [j] Relative to ligands at 310 K [26].

Table 5
IR frequencies for Hg–Cl and ligand vibrations

Compound code	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**2j**	**2k**	**2m**	**2o**	**2p**	**2q**	**2r**	**2t**	**2u**	**2v**
ν(Hg–Cl) (cm^{-1})	328	332	325	335	337	333	333	331	330	335	323	344	341	338	348	344	350	328	325
Ligand vibrations (cm^{-1}) [a]	1682(−3) [b] 1655(−5) 1599	1610(−28) [b] 1579(−22)	1618(−12) [b] 1577								1327(−5) [c] 1155(−8)	1645(−4) [d] 1582(−18) 1560(−25) 1037(−5)	1645(−4) [d] 1582(−28) 1562(−23) 1039(−7)	1631(−10) [d] 1591(−21)			1640(−8) [d] 1585(−25) 1565(−15) 1043(−1)		1300(−25) [c] 1155(−31)

[a] Figures in brackets are ccs. [b] ν(CO). [c] ν(SO_2). [d] Oxaz vibrations.

of the oxazoline derivatives, the shifts are considerably less than those for the corresponding gold(III) compounds, which are known to be strongly chelated [8].

3. Conclusion

The mercury(II) compounds described here are all two-coordinate, both in solution and in the solid state. For ArHgCl and $ArCH_2HgCl$ there is at best a very weak interaction between the substituent nitrogen-containing groups and the mercury atom. The tetra-organotin(IV) compounds display normal four-coordination.

4. Experimental section

Reactions were carried out under nitrogen and solvents were distilled under an inert atmosphere prior to use from the appropriate drying agent [9]. IR spectra (4000–300 cm^{-1}) were recorded on a Nicolet 5PC Fourier transform infrared spectrometer in Nujol mulls between KBr plates. ^1H and ^{13}C NMR spectra were recorded on a Brucker AC-200 spectrometer at 200 and 50.3 MHz respectively, in $CDCl_3$ or $(CD_3)_2SO$ using the solvent signal as internal standard. Microanalyses were performed by the UMIST Chemistry Department Microanalytical Service and the positive ion fast atom bombardment mass spectrometry spectra by the UMIST Centre for Mass Spectrometry.

The aromatic precursors were prepared by literature methods and lithiation reactions were carried out as previously described (see Table 1 for references).

The direct mercuration reactions of the aryl-amides **1a–1c** were performed according to the method described by Ogata and Tsuchida [28].

The appropriate aryl–amide (25 mmol) was dissolved in glacial acetic acid (30 cm^3) and mercury(II) acetate (16 mmol) was added to the solution. The mixture was refluxed for 6 h, cooled, filtered and added to an aqueous solution (100 cm^3) of lithium chloride (40 mmol). The flocculent white solid formed was filtered off, washed with water and dried in vacuo.

Literature methods were used to prepare the other chloro-organomercury(II) and triphenyl-organotin(IV) compounds, and the bis(organo)mercury(II) complexes (see Table 1 for references).

The general method is as follows. The appropriate precursor (15 mmol) was dissolved in dry Et_2O or THF (depending on the solubility) (65 cm^3) and the solution was brought to the requisite temperature (−78 °C for **1m**; 0 °C for **1k**, **1o**, **1p**, **1t**, **1v–1x**; 25 °C for **1d–1j**, **1q**, **1r**, **1u** and **1y**). *n*-Butyllithium (15 mmol) in hexane was added carefully by syringe and the reaction mixture was stirred at the same temperature for 30 min (**1k**, **1m**, **1r–1u**), 4 h (**1o** and **1p**) or 24 h (**1d–1j**, **1s**, **1u**). After cooling to −78 °C, a solution of mercury(II) chloride (15 mmol) or chlorotriphenyltin(IV) (15 mmol) in dry THF was added dropwise. The solution was warmed to room temperature and stirred for another 5 h. The dark grey precipitate was filtered off, the remaining solution was evaporated to dryness and the residue was recrystallised from either diethyl ether or a mixture of diethyl ether and dichloromethane (2:1).

The bis(organo)mercury(II) compounds **2v–2y** were prepared in a very similar manner, as described below.

The appropriate precursor **1v–1y** (15 mmol) was dissolved in dry Et_2O (or THF) at 0 °C (**1w–1x**) or room temperature (**1y**), and two molar equivalents of *n*-butyllithium (30 mmol) in hexane were carefully added. The mixture was stirred for 30 min (**1w–1x**) or 24 h (**1y**) at the same temperature and was then cooled to −78 °C. Mercury(II) chloride (7.5 mmol) in solution in dry THF (75 cm^3) was added dropwise and the solution was warmed to 0 °C. Cold water (20 cm^3) was added and stirring was maintained for a further 3 h. The organic layer was separated, dried over magnesium sulphate and evaporated to dryness. The residue obtained was recrystallised from dichloromethane.

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