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ARYLMERCURY(II) COMPOUNDS INVOLVING INTRAMOLECULAR COORDINATION VIA 2-Me_2NCH_2- AND CHIRAL (*S*)-2-Me_2NCHMe-RING SUBSTITUENTS

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Summary

Arylmercury compounds of the type Ar_2Hg and ArHgX (X = Cl, OAc) have been synthesized and characterized by ^1H and ^{13}C NMR spectroscopy; the Ar group was either 2-$Me_2NCH_2C_6H_4$ or (*S*)-2-$Me_2NCH(Me)C_6H_4$, both of which contain N-donor ligands. The observation of anisochronous NMe resonances in (*S*)-2-$Me_2NCH(Me)C_6H_4HgX$ (X = Cl, OAc) at low temperature indicates that in solution the mercury centre is three-coordinate as a result of stable intramolecular Hg—N coordination.

Introduction

Introduction of built-in ligands into the *ortho*-position of the aryl group in arylmetal compounds has been shown to be a useful method of stabilizing the metal—carbon bond. Thus, a variety of stable both homo- and hetero-nuclear arylmetal(IB) compounds have been reported, which, when soluble, have discrete polynuclear structures involving intramolecular coordination from the built-in ligands [1—3]. For the corresponding homonuclear arylgold(I) compounds no spectroscopic evidence for intramolecular coordination, which would make the Au atom three-coordinate, was obtained either for the solid or solutions [4].

In some cases arylmetal(IB) compounds have been shown to possess valuable transmetallating properties [5], and this has been used in this study for the synthesis of arylmercury compounds of the type Ar_2Hg and ArHgX; Ar = 2-$Me_2NCH_2C_6H_4$, (*S*)-2-$Me_2NCH(Me)C_6H_4$. In these compounds the built-in N-donor

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ligand is available for coordination to the mercury atom.

The coordination behaviour of organogold(I) and bis(organo)mercury(II) compounds is very similar; in both cases the metal atom prefers to be linearly two-coordinate [6—8]. Deviations from linearity have been found to occur when bulky substituents are introduced in the *ortho*-position of the aryl group, e.g. $\{2,4,6\text{-(t-Bu)}_3C_6H_2\}_2Hg$ [9] and $2,6\text{-(MeO)}_2C_6H_3AuPPh_3$ [4].

In contrast to the bis-organo-mercury compounds, the mono-organo-mercury compounds RHgX give three-coordinate 1/1 and four-coordinate 1/2 complexes, RHgXL and $RHgXL_2$, respectively, with many electron donor compounds L [10]. Furthermore, introduction of substituents in the mercury-bound organo group R in RHgX may likewise result in a change of the linear coordination geometry. The occurrence of intramolecular coordination in compounds containing alkyl groups such as $XCH_2C(CH_3)(OCH_3)CH_2HgY$ (X, Y = Cl, Br), has been deduced from changes in the chemical shifts and coupling constants [11—13].

In this paper we report the synthesis of arylmercury compounds containing built-in ligands (2-Me_2NCH_2 and (*S*)-2-Me_2NCHMe) as well as unequivocal evidence for intramolecular Hg—N coordination leading to a three-coordinated metal centre.

Experimental

All reactions are carried out under dry oxygen-free nitrogen. The solvents were dried by standard techniques prior to use. The NMR spectra were recorded using Varian T-60 and A-60 (^1H) and Bruker WP 80 (^{13}C) spectrometers. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht (The Netherlands). Molecular weight measurements were carried out with a Hewlett—Packard Vapour Pressure Osmometer, Model 320 B.

The aryllithium [14] and arylcopper [1c,15,16] reagents were prepared by published methods.

Synthesis of $(2\text{-Me}_2NCH_2C_6H_4)_2Hg$

(a) $(2\text{-Me}_2NCH_2C_6H_4)Cu$ (3.29 mmol) was slowly added to a stirred suspension of $HgCl_2$ (1.62 mmol) in benzene (25 ml) to give a green precipitate. The mixture was stirred for 18 h, and the green solid was then filtered off. The slightly green filtrate was passed through a 10 cm column of Al_2O_3. Concentration of the resulting colourless solution to 1 ml by evaporation of the solvent in vacuo, was followed by addition of 3 ml of pentane. The mixture was cooled to —30° C and set aside for 12 h, after which the liquid was decanted to leave Ar_2Hg as white needles, which were dried in vacuo. Yield 26%.

(b) $(2\text{-Me}_2NCH_2C_6H_4)Li$ (2 mmol) was suspended in diethyl ether (20 ml) at —80° C and a solution of $HgCl_2$ (1 mmol) in THF (10 ml) added. The mixture was stirred for 2 h, then allowed to warm to room temperature and stirred for another 2 h. It was then filtered and the filtrate was concentrated. The residue was dissolved in the minimum amount of hot pentane, and the solution was slowly cooled to —30° C. Ar_2Hg was isolated by filtration and dried in vacuo. Yield 85%.

Synthesis of 2-$Me_2NCH_2C_6H_4HgCl$

(a) ArHgCl can be prepared via procedures analogous to those described above for Ar_2Hg, starting from either 1 equivalent of ArCu (yield 34%) or ArLi (yield 84%). The yield of ArHgCl, when $HgCl_2$ was added to ArCu, was only 1%.

(b) A solution of Ar_2Hg (1 mmol) and $HgCl_2$ (1 mmol) in THF (20 ml) was stirred for 1 day then filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from pentane to give pure ArHgCl. Yield 95%.

Synthesis of 2-$Me_2NCH_2C_6H_4HgOAc$

ArHgOAc was prepared from Ar_2Hg and $Hg(OAc)_2$ via procedure (b) described above for ArHgCl.

Reaction of $HgCl_2$ with ArCu · CuCl

ArCu · CuCl (1.1 mmol) was added slowly to a suspension of $HgCl_2$ (0.62 mmol) in benzene (25 ml), and the mixture was stirred for 18 h. An unstable yellow-brown precipitate was formed. Work-up via procedure (a) described above for Ar_2Hg, did not give any arylmercury compound.

Attempted synthesis of {(S)-2-$Me_2NCH(Me)C_6H_4$}$_2$Hg

Attempts to prepare {(*S*)-Ar}$_2$Hg starting from (*S*)-ArCu and $HgCl_2$ via procedure (a) described above for Ar_2Hg always gave mixtures of {(*S*)-Ar}$_2$Hg and (*S*)-ArHgCl. The synthesis via (*S*)-ArLi was unsuccessful because of extensive decomposition of the reactants.

Synthesis of (S)-2-$Me_2NCH(Me)C_6H_4HgCl$

(*S*)-ArHgCl was prepared by procedure (a) described above for Ar_2Hg, starting from $HgCl_2$ and 1 equivalent of (*S*)-ArCu. Yield 47%.

Synthesis of (S)-2-$Me_2NCH(Me)C_6H_4HgOAc$

$MeCO_2Ag$ (0.66 mmol) was added to a solution of (*S*)-ArHgCl (0.65 mmol) in benzene (15 ml) and the mixture was stirred for 18 h in the dark. It was then filtered and the filtrate was evaporated to dryness. The residue was recrystallized from pentane to give white needles of (*S*)-ArHgOAc. Yield 42%.

Results and discussion

The arylmercury compounds $(2\text{-}Me_2NCH_2C_6H_4)_2Hg$ (Ar_2Hg) and $(2\text{-}Me_2NCH_2C_6H_4)HgCl$ (ArHgCl), respectively, were isolated from 1/2 and 1/1 reactions of $HgCl_2$ with ArCu (tetramer) [1c] or ArLi, respectively. (*S*)-2-$Me_2NCH(Me)C_6H_4HgCl$ ((*S*)-ArHgCl) was obtained from the 1/1 reaction of $HgCl_2$ and (*S*)-ArCu [15], while ArHgOAc and ArHgCl were synthesized via the ligand exchange reactions between Ar_2Hg and the respective HgX_2 (X = OAc, Cl). (*S*)-ArHgOAc was isolated from the reaction of (*S*)-ArHgCl with AgOAc. These new mercury compounds were identified by elemental analyses (Table 1) and ^1H and ^{13}C NMR (Tables 2 and 3); molecular weight determinations indicate that they are monomeric in chloroform.

Both ArCu and ArLi can be used as arylating agents but better results were

TABLE 1

PHYSICAL DATA

Compound [a]	Anal. (Found (Calcd.) (%))				Mol. wt. [b]	M.p. (°C)	Appearance
	C	H	N	O			
Ar_2Hg	45.42	5.21	5.89		465	72	White needles
	(46.10)	(5.17)	(5.97)		(469)		
ArHgCl	28.89	3.40	3.70		387	73	White needles
	(29.18)	(3.24)	(3.78)		(370)		
ArHgOAc	32.44	3.49	3.48	7.32			White cubes
	(33.54)	(3.81)	(3.56)	(8.13)			
(*S*)-ArHgCl	30.11	3.43	3.51		402	70	White needles
	(31.43)	(3.64)	(3.64)		(384)		
(*S*)-ArHgOAc	34.85	4.23	3.70	7.27	408	— [c]	White needles and cubes
	(35.33)	(4.17)	(3.43)	(7.85)	(408)		

[a] Ar = $2\text{-}Me_2NCH_2C_6H_4$; (*S*)-Ar = (*S*)-$2\text{-}Me_2NCH(Me)C_6H_4$. [b] Osmometric, in chloroform. [c] Hygroscopic.

TABLE 2

^{1}H NMR DATA FOR *ortho*-SUBSTITUTED ARYLMERCURY COMPOUNDS AND THE FREE LIGANDS [a]

Compound	NCH_3	CH_x	CH_3	CH_3—CO_2	Aryl protons
ArH	2.15(s)	3.25(s)			7.20(m)
Ar_2Hg	2.25(s)	3.43(15)(s)			7.20(m)
ArHgCl	2.26(s)	3.41(10)(s)			7.0—7.4(m)
ArHgOAc	2.30(s)	3.41(s)		2.06(s)	7.20(m)
(*S*)-ArH	2.17(s)	3.20(q)	1.33(d)		7.25(s)
(*S*)-ArHgCl	2.26(s) [c]	3.47(18)(q)	1.29(d)		6.9—7.3(m)
(*S*)-ArHgOAc	2.23(s) [d]	3.41(q)	1.30(d)	2.09(s)	7.0—7.4(m)

[a] Ar = $2\text{-}Me_2NCH_2C_6H_4$; (*S*)-Ar = (*S*)-$2\text{-}Me_2NCH(Me)C_6H_4$. [b] Recorded at room temperature in $CDCl_3$; δ relative to TMS; $J(^{199}Hg—^1H)$ (Hz) in parentheses. [c] 2.51 and 2.21 ppm at 212 K; [d] 2.53 and 2.20 ppm at 209 K.

obtained with the organolithium reagents; the yields were typically 30% for the ArCu and 90% for the ArLi route. The poor results with ArCu are partly due to the difficulties of removing traces of CuCl and $HgCl_2$. The yields are further reduced, when the ArCu is present in excess relative to $HgCl_2$, possibly owing to the formation of ArCu · CuCl. This type of polynuclear species has poor arylating properties [5], and this suggestion is supported by the observation that reaction of ArCu · CuCl with $HgCl_2$ gave an intractable solid and not ArHgCl or Ar_2Hg.

However, arylation via organocopper compounds was an effective preparation for the mercury complexes, in particular when the routes through the organolithium reagents failed. For example, $HgCl_2$ gave metallic mercury when treated with (*S*)-ArLi, but pure (*S*)-ArHgCl was obtained from reaction of $HgCl_2$ with (*S*)-ArCu:

$$HgCl_2 + 2\text{-}Me_2NCH(Z)C_6H_4M \rightarrow 2\text{-}Me_2NCH(Z)C_6H_4HgCl + MCl$$

$$HgCl_2 + 2\ 2\text{-}Me_2NCH(Z)C_6H_4M \rightarrow \{2\text{-}Me_2NCH(Z)C_6H_4\}_2Hg + 2\ MCl$$

(M = Li or Cu)

TABLE 3

^{13}C NMR DATA FOR *ortho*-SUBSTITUTED ARYLMERCURY COMPOUNDS [a, b]

Compound	Temperature (K)	NCH_3	CH_x	CH_3	Acetate		Aryl group					
					CH_3	CO_2	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Ar_2Hg	310	45.0	67.1				n.o.	147.1	128.4	126.6	126.2	138.0
								(37)	(70)	n.o.	(113)	(94)
ArHgCl	310	44.6	64.7				n.o.	144.5	129.1	128.7	127.5	137.3
		(11)	(101)						(178)	n.o.	(212)	n.o.
ArHgOAc	310	44.6	64.8		22.9	177.0	n.o.	144.2	129.0	128.5	127.2	137.5
		(10)	(110)						(170)	(32)	(213)	(133)
(S)-ArHgCl	300	42.4	66.0	21.5			150.6	147.3	128.5	128.8	127.3	137.4
			(94)						(168)	(32)	(213)	(139)
	210	40.5	65.3	22.1			150.4	146.1	128.4	128.5	127.1	136.8
		44.4	(92)						(170)	n.o.	(220)	(145)
(S)-ArHgOAc [c]	270	42.3	65.7	21.8 [d]	22.6 [d]	176.2	150.7	141.0	128.1	128.1	126.6	137.1
			(95)						(172)	(31)	(218)	(146)
	210	40.4	64.7	22.4 [d]	22.7 [d]	175.8	150.7	139.9	127.5	127.5	126.1	136.2
		43.5	(93)									
								C(1)	C(2,6)	C(3,5)	C(4)	
ArH	310	44.7	63.9					138.5	128.4	127.6	126.4	
(S)-ArH	310	43.0	65.6	20.4				143.2	127.9	127.1	126.7	

[a] Ar = $2\text{-}Me_2NCH_2C_6H_4$; (*S*)-Ar = (*S*)-$2\text{-}Me_2NCH(Me)C_6H_4$. [b] Recorded in $CDCl_3$; δ relative to TMS; $J(^{199}Hg-^{13}C)$ (Hz) in parentheses. [c] Recorded in CD_2Cl_2. [d] Tentative assignment, n.o. = not observed.

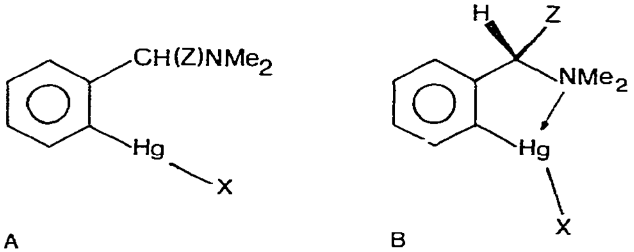

Fig. 1. Possible coordination geometries of Hg in 2-$Me_2NCH(Z)C_6H_4HgX$ (Z = H, Me).

The mercury atom in the monomeric compounds Ar_2Hg, ArHgX and (*S*)-ArHgX (X = Cl, OAc) is at least two-coordinate, since it is bonded to the substituent X and to the aryl group (Fig. 1a). The latter bonding is shown by the $J(^{199}Hg—^{1}H)$ and $J(^{199}Hg—^{13}C)$ couplings (Tables 2 and 3). In principle, the mercury atom can become three-coordinate by additional interaction of the internal *ortho* ligands Me_2NCH_2 and (*S*)-$Me_2NCH(Me)$ (Fig. 1b). Moreover, the acetato group in the compounds ArHgOAc and (*S*)-ArHgOAc may be bond to give a chelate.

With regard to the question of whether intramolecular Hg—N coordination occurs in these Ar_2Hg and ArHgX complexes the ^{1}H and ^{13}C NMR data are not very informative. The ^{1}H and ^{13}C chemical shifts for the Me_2NCH_2 nuclei in Ar_2Hg, ArHgX and free $Me_2NCH_2C_6H_5$ (ArH) are almost equal (see Tables 2 and 3). Although the ^{13}C chemical shifts and coupling constants are slightly temperature dependent, no conclusion concerning possible Hg—N interaction could be drawn.

By contrast, the ^{1}H and ^{13}C NMR spectra of the monomeric compounds (*S*)-ArHgX (X = Cl, OAc), which contain a stable chiral benzylic carbon centre, provide unambiguous evidence for Hg—N coordination. At low temperature anisochronous resonances are observed for the C and H atoms of the NMe_2 group. This points to coordination of the N atom resulting in a blocked inversion at nitrogen on the NMR time scale, because only in this situation is the N atom in a stable tetrahedral array, so producing diastereotopic Me groups. Upon raising the temperature the two signals start to coalesce, resulting in one isochronous resonance at ambient temperature (See Fig. 2), suggesting occurrence of a fast NMR process involving pyramidal inversion at nitrogen which would render the methyl groups homotopic.

The fact that even as low as −90° C the H atoms of the NMe_2 group in both (*S*)-$ArAuPPh_3$ [5] and (*S*)-ArH appear as one singlet in the respective ^{1}H NMR spectra excludes the possibility that the blocked inversion at nitrogen can be explained in terms of steric hindrance by the metal substituent or of an innate slow rate of N group inversion in such ligand systems. Thus, the phenomena observed for the present complexes (*S*)-ArHgX can be related to a Hg—N interaction, which is stable on the NMR time scale at low temperature but becomes labile at ambient temperature.

A similar approach has been used to study M—N coordination in other organometallic derivatives with built-in ligands. For example, the presence of a stable Sn—N bond in ArMePhSnX [17] and a stable Cu—N bond in {(*S*)-Ar}$_4$-

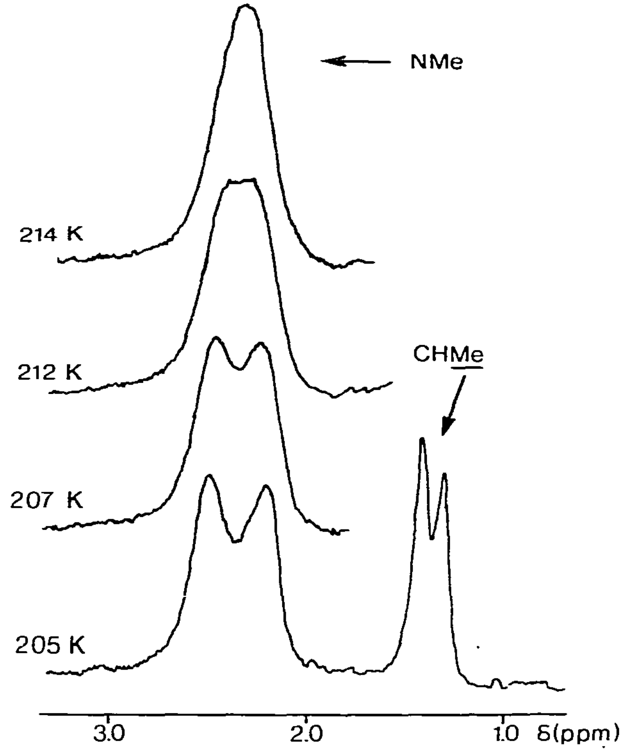

Fig. 2. Dynamic ^{1}H NMR spectra (60 MHz; δ(ppm)) of (*S*)-2-$Me_2NCH(Me)C_6H_4HgCl$ in $CDCl_3$.

Cu_4 at low temperature [15] and the absence of Au—N coordination in (*S*)-Ar-$AuPPh_3$ [4] have been unambiguously established.

The coalescence temperatures and the chemical shift differences for the (N)Me_2 nuclei in (*S*)-ArHgCl and (*S*)-ArHgOAc, as determined by ^{1}H NMR, are almost equal: 212 K, $\Delta\nu$ 18 Hz and 209 K, $\Delta\nu$ 20 Hz, respectively. This might be an indication that a possible chelation of the acetate group does not interfere significantly with the dynamic Hg—N interaction.

The conclusion that intramolecular Hg—N association occurs at low temperature is consistent with the fact that the chemical shifts for C and H atoms in the NMe_2 group and the $J(^{199}Hg—^{13}C)$ coupling constants for the carbon atoms change upon lowering the temperature from 25°C to below the coalescence temperature, e.g. $J(^{199}Hg—^{13}C)$ decreases for N*C*HR and increases for the aryl C atoms. Similar changes have been observed for other organomercury compounds upon coordination of donor atoms [10—13]. A good explanation for the sign and the amplitude of the changes is not available [18].

Although internal interactions have been reported for organo mercury compounds [11—13] the present work demonstrates that in solution such interactions can be inert on the NMR timescale, and thus determine the coordination geometry at the central mercury atom.

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