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THE ACTUAL MERCURATING SPECIES IN THE MERCURATION OF AROMATIC AMINES AND THE AMINOMERCURATION OF OLEFINS

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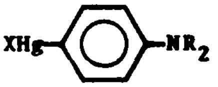
Abstract- The reactivity of π- and σ- N-mercurated and C-mercurated amines as electrophiles towards olefins and aromatic amines is studied under different reaction conditions. Depending on the ionic or covalent character of the starting mercury(II) salt, dissociated species or π-complexes **3** respectively, are found to be the most plausible mercurating species in the aminomercuration process. By contrast, complexes **3'** do not react with aromatic amines unless the former undergo prior dissociation.

The usefulness in organic synthesis of the solvomercuration of olefins is well documented.[1] While a great deal of attention has been paid to the mechanism of the oxymercuration reaction much less is known about the aminomercuration process. In this context, in a recent paper,[2] we have clarified the question of the reversibility in aminomercuration reactions. However, a question still open is the nature of the actual aminomercurating species. The following types of intermediates and mercurating species have been proposed:

a) σ-bonded N-mercurated amines[3] **1**
b) C-mercurated aromatic amines [4] **2**
c) amine-mercury(II) salt π-complexes[5] **3'**

ArNH-HgX (**1**)



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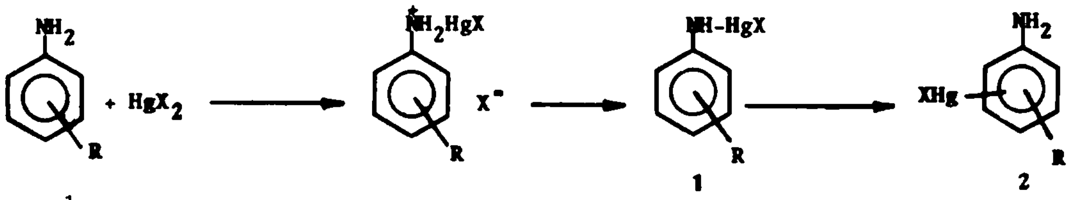
$(ArNH_2)_nHgX_2$ n=1 **3**; n=2 **3'**

To help to resolve this controversy we wish to report now our comparative study of the reactivity as electrophiles of each one of these species towards olefins and aromatic amines which can result in the aminomercuration of the olefin or the ring mercuration of the amine respectively. As we will show in the next sections species of different nature appear to operate depending on the covalent or ionic character of the mercury(II) salt.

RESULTS AND DISCUSSION

a) σ-*Bonded N-mercurated amines*

It has been suggested that mercuration of arylamines proceeds *via* rearrangement of N-mercurated products[3] **1** (Scheme 1). Since both aromatic mercuration and amino-mercuration of olefins take place through an electrophilic attack on the organic

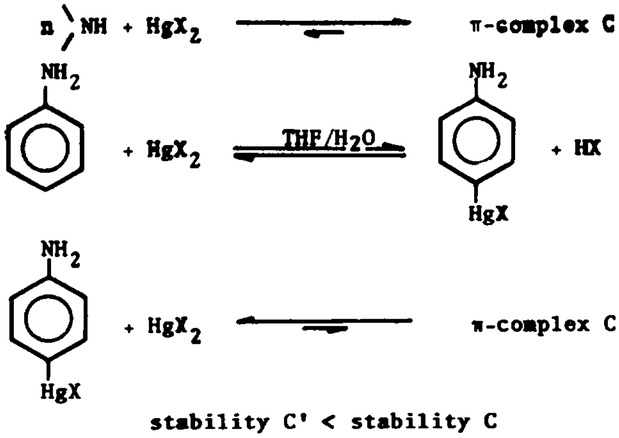


Scheme 1[1]

moiety by the mercury in the presence of amine, according to this interpretation, compounds **1** could also be the active species in the aminomercuration of olefins. However, σ-bonded aminomercurials **1** could only be generated by treatment of a solution of the corresponding amine and mercury(II) salt with sodium bicarbonate or triethylamine, that is, are formed only in the presence of bases stronger than the aromatic amines. On the other hand, compounds **1** exhibited a very low reactivity and solubility in organic solvents. For instance, when **1a** (for compounds **1**, **2** and **3** see Table 1) was stirred with THF solutions of *ortho-*, *meta-*, and *para*-toluidine respectively at room temperature for two days, no exchange of amine could be detected. Compounds **1** only could be converted into the corresponding π-complexes **3** by stoichiometric addition of acid. When the aminomercuration of 1,5-cyclooctadiene with **1a** as the mercurating agent was attempted under standard conditions[2] the free olefin was recovered unchanged after sodium borohydride reduction of the reaction mixture. These results allow to rule out the possibility of the participation of σ-bonded aminomercurials **1** as mercurating species in the aminomercuration of olefins or the ring mercuration of aromatic amines.

b) *C-Mercurated aromatic amines* **2**

It is well documented that aminomercuration of olefins with aromatic amines takes place much faster than with their aliphatic counter parts. In the search for an explanation to this fact, Lattes et al.[4] have claimed that 'the aminomercuration of a double bond with aniline is only possible in aqueous media, i.e. in such conditions that the aromatic ring is previously mercurated' (Scheme 2). The effects of this preliminary ring mercuration, as stated by Lattes, would be: a) to destroy the preformed amine-mercuric salt π-complex (C) preventing the reaction and b) to generate *para*-mercurated amine of lowered basicity in the reaction media which would produce less strong π-complexes (C') with the mercury. The lowered basicity of this amine[4] is due to the electron-withdrawing character of the mercury ($\sigma^+=0.11$)[6] which



Scheme 2[4]

is comparable to that of an atom of chlorine. However, in these experiments[4] a two-fold excess of free primary aromatic amine is always present and, hence, it is not clear what the chance is of the *para*-mercurated amine of lowered basicity either to give the π-complex (C') or paticipate in the aminomercuration process. Furthermore, we have already shown[2] how, for instance, *para*-toluidine gives slightly better yields than aniline in the aminomercuration of *cis,cis*-1,5-cyclooctadiene and *para*-toluidine does not give any ring mercurated derivative under our experimental conditions.[2] On the other hand, it is claimed[4] that aminomercuration of 1-heptene with aniline gives after sodium borohydride reduction 74% yield of isolated 2-phenylaminoheptane. Therefore, it should be concluded that the mercury attached to the ring is still able to act as a mercurating species towards the olefin. To check this new possibility mercury(II) acetate was replaced by 4-acetoxymercuryaniline **2a** or 4-acetoxymercury-N,N-diethylaniline **2c** in the aminomercuration of *cis,cis*-1,5-cyclooctadiene. However, no reaction was observed to take place in two days either in anhydrous THF, THF/water or THF/water/acetic acid (to reproduce the reaction media in the aminomercuration with mercury(II) acetate) as the solvents (Scheme 3). Compounds **2a,c** also

$$\mathbf{2}(\mathrm{a\ or\ c}) + C_6H_5NH_2 + 1{,}5\text{-COD} \xrightarrow{\text{solvent}} \text{no reaction}$$

Scheme 3

failed to mercurate aromatic amines even in the presence of acetic acid to promote the exchange. Thus, it appears clear that the enhanced reactivity of aromatic amines in aminomercuration reactions should not be attributed to the existence of a previous ring mercuration, but only to the diminished basicity of the aromatic amine itself, which enables a stronger interaction mercury(II)-olefin.

c) *Amine-mercury(II) salt π-complexes* **3** *and* **3'**

Mercuric halides other than fluoride have structures in which covalent bonding is important and easily form π-complexes **3** and **3'** with amine ligands, specially primary amines, increasing the co-ordination number of the metal to three and / or four[7,8] (Scheme 4). The strength of the complex **3** correlates well to the steric hindrance and nucleophilicity at the nitrogen site; complexes of tertiary aromatic amines cannot be isolated since σ-bonded *para*-mercurated amines are readily formed.

$$ArNH_2 + HgX_2 \overset{k_3}{\rightleftharpoons} \underset{\mathbf{3}}{(ArNH_2).HgX_2}$$

$$\mathbf{3} + ArNH_2 \overset{k_4}{\rightleftharpoons} \underset{\mathbf{3'}}{(ArNH_2)_2.HgX_2}$$

Scheme 4

Following this trend, π-complexes **3** derived from secondary aromatic amines are always contaminated by substantial amounts of the corresponding *para*-mercurated compounds **2** and cannot be transformed into the corresponding σ-bonded N-mercurated compounds **1** under similar conditions to those employed with primary aromatic amines to obtain this type of products. Thermodynamic data for other mono-, di-, tri-, or tetracoordinated mercury(II) complexes[7] show that the stability constants K_1 and K_2 on the one hand and K_3 and K_4 on the other are of comparable magnitude and increase approximately with the nucleophilicity of the ligand in the order $K_1>K_2>>K_3>K_4$. This agrees well with numerous reports which have appeared on the formation of aromatic amine-mercury(II) complexes of variable stoichiometry.[4] In this context, it is noteworthy that the reactivity of *para*-anisidine in the aminomercuration of olefins resembles more that observed in the case of aliphatic amines than the corresponding to the less basic aromatic amines such as *para*-chloroaniline, aniline, or *para*-

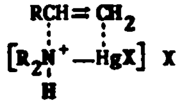
Table 1. Data for Compounds **1**, **2**, **3**, and **3'**

Compound	Ar or R	X	Yield%	M.p.	Molecular Formula	Elemental analysis Found Hg% (calc)	N% (calc)
1a	C_6H_5	Cl	88	190(d)	C_6H_6ClHgN	60.90(61.13)	4.20(4.27)
2a	H	OAc	86	148[a]	$C_8H_9HgNO_2$	56.90(57.02)	3.96(3.98)
2b	H	Cl	50	192(d)	$C_6H_6Cl_2HgN$	53.55(55.16)	3.65(3.85)
2c	C_2H_5	OAc	69	98[b]	$C_{12}H_{17}HgNO_2$	49.08(49.18)	3.28(3.43)
2d	C_2H_5	Cl	52	155(d)	$C_{10}H_{14}ClHgN$	51.90(52.20)	3.58(3.64)
3a	C_6H_5	OAc	93	92	$C_{10}H_{13}HgNO_4$	46.90(48.83)	3.30(3.41)
3b	C_6H_5	Cl	82	160(d)	$C_6H_7Cl_2HgN$	54.98(55.01)	3.80(3.84)
3'a	C_6H_5	OAc	92	84	$C_{16}H_{20}HgN_2O_4$	39.07(39.72)	2.68(2.77)
3'b	C_6H_5	Cl	80	140(d)	$C_{12}H_{14}Cl_2HgN_2$	43.74(43.82)	2.95(3.05)

[a] Recrystallized from hexane/chloroform. [b] Recrystallized from hexane.

toluidine. For instance, no mercuration of styrene[4] or 1,5-cyclooctadiene is found in 15 minutes with mercury(II) acetate and *para*-anisidine.

Griffith et al.[5] have suggested that the rate determining step in aminomercurations could be either the direct addition of the complexes to the olefin substrate *via* a four centered transition state **4** or slow dissociation of HgX^+ from the strong amine-mercury π-complexes.



$$\begin{array}{c} RCH{=}CH_2 \\ [R_2N^+{-}HgX]\ X^- \\ H \end{array}$$

4

However, the formulation of a four-centered transition state **4**, which implies the *cis*-addition, can be disregarded, at least for mercurations with ionic mercury(II) salts, since Lattes and Gasc[4] have shown by ^1H-NMR that aminomercuration with mercury(II) acetate and excess of amine in aqueous THF media takes place as a *trans*-addition. The possibility of transformation of the *cis*-adduct into the *trans*-isomer could be argued but, it is unlikely to occur since we have already proved[2] the irreversibility of the aminomercuration under these conditions.

On the other hand, we have examined the existence of the hypothetical HgX^+ species or free HgX_2 as the actual mercurating agents by comparison between the reactivity of complexes **3** and **3'** towards primary and tertiary aromatic amines and olefins, and found that the course of the mercuration depends on three interrelated factors, namely, i) the amine/mercury(II) ratio, ii) the nature of the anion associated to mercury(II), and iii) the nature of the solvent. The ability of the aromatic amines and olefins to undergo C-mercuration grows in the order primary aromatic amine < tertiary aromatic amine < olefin as shown by competitive mercurations.

Compounds **3'a** and **3'b** do not react in dry THF $\{E_T(30)=37.4\}$[9] with N,N-dithylaniline which, on the other hand, readily reacts in absence of primary amine with mercury(II) acetate or chloride to give **2c** or **2d** respectively. By contrast, **3'a** does react under similar conditions with 1,5-cyclooctadiene to afford **5**[2] in 50% yield after sodium borohydride reduction. The same reaction also takes place in dry dioxane $\{E_T(30)=36.0)\}$[9] (see runs 1-4, Table 2). Then, free HgX_2 or HgX^+ species should not be necessarily invoked to account for the mercuration of olefins. When the proticity of the solvent is increased the aromatic C-mercuration takes place more easily. For instance, π-complex **3'a** leads to the corresponding **2a** by stirring in THF/water (3:1) or MeOH/water (1:1) at room temperature. In the same way, **3'a** reacts with N,N-diethylaniline to afford **2c**. When the π-complex **3'** derives from mercury(II) chloride the conversion of **3'b** into the corresponding C-mercurated product **2b** cannot be detected

Table 2. Mercuration of Olefins and Amines with π-Complexes **3** and **3'** as Mercurating Agents

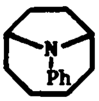
Run	Mercurating Agent	Amine or Olefin	Solvent	Reaction Time (h)	Product	Yield %^{a}
1	**3'a**	$C_6H_5N(C_2H_5)_2$	THF (anh)	24	n.r.	—
2	**3'b**	$C_6H_5N(C_2H_5)_2$	THF (anh)	48	n.r.	—
3	**3'a**	1,5-COD	THF (anh)	15	**5**	50
4	**3'a**	1,5-COD	Dioxane (anh)	48	**5**	72
5	**3'a**	—	THF/water (3:1)	14	**2a**	80
6	**3'a**	—	Methanol/water(1:1)	2	**2a**	83
7	**3'a**	$C_6H_5N(C_2H_5)_2$	THF/water (10:1)	48	**2c**	73
8	**3'b**	$C_6H_5NH_2$	THF/water (3:1)	24	n.r.	—
9	**3'b**	$C_6H_5N(C_2H_5)_2$	THF/water(5:1)	48	n.r.	—
10	**3'a**	1,5-COD	THF/water (10:1)	2	**5**	73
11	**3'b**	1,5-COD	THF/water (10:1)	48	**6**	33
12	**3'b**	1,5-COD	THF/methanol (10:1)	48	**6**	20
13	**3'b**	1,5-COD	Acetonitrile (anh)	48	**6**	60
14	**3'b**	1,5-COD	Nitromethane (anh)	48	**6**	60
15	**3'b**	1,5-COD	Dichloromethane	48	**6**	60
16	**3b**	1,5-COD	THF/water (10:1)	48	**6**	64
17	**3'b**	1,5-COD	THF/water (10:1)	20	**6**	33
18	**3b**	1,5-COD	THF (anh)	24	**6**	20
19	**3'b**	1,5-COD	THF (anh)	24	n.r.	—
20	**3b**	$C_6H_5N(C_2H_5)_2$	Acetonitrile	14	n.r.	—
21	**3b**	$C_6H_5N(C_2H_5)_2$	THF/water (3:1)	14	n.r.	—
22	**3a**	$C_6H_5N(C_2H_5)_2$	THF (anh)	14	**2c**	50
23	**3a**	1-Hexene	THF/water (3:1)	48	**7**	85
24	**3a**	1-Hexene	Acetonitrile	48	**7**	91
25	**3b**	1-Hexene	THF	48	n.r.	—
26	**3b**	1-Hexene	Acetonitrile	48	**7**	68
27	**3b**	*Trans*-4-octene	Acetonitrile	48	n.r.	—
28	**3a**	Cyclohexene	THF (anh)	48	**8**	54
29	**3a**	Cyclohexene	Nitromethane	48	**8**	99
30	**3b**	Cyclohexene	THF	48	n.r.	—
31	**3b**	Cyclohexene	Acetonitrile	48	n.r.	—
32	**3b**	Cyclohexene	Acetonitrile	48	n.r.	—
33	**3b**	1,4-Cyclohexadiene	Acetonitrile	48	n.r.	—
34	**3b**	1-Hexene	THF ($NaHCO_3$)	48	**7**	58
35	**3b**	1,5-COD	THF ($NaHCO_3$)	48	**5**	68

[a] Based on mercurating agent

in similar reaction times (runs 5-9, Table 2). On these grounds *it is likely that dissociated HgX^+ or HgX_2 act as mercurating agents only when mercury(II) acetate and polar solvents are used.* The enhanced reactivity of olefins if compared to that of aromatic amines towards π-complexes **3'** and its dependence on the solvent proticity is again found in reactions with *cis,cis*-1,5-cyclooctadiene (runs 10-15, Table 2). It is noteworthy that similar results are obtained (reaction times and yields) when aminomercurations are carried out with mercury(II) salts in the presence of an excess of free amine (see experimental) or by using only complexes **3'** as aminomercurating reagents. However, *a great increase in yield is observed when a 1:1 amine/mercury(II) salt ratio is employed,* that is, when π-complexes **3b**[10] are used as the aminomercurating reagents in the absence of free amine in the reaction medium (runs 16-19, Table 2). Moreover, it should be noted that while **3'b** fails in the aminomercuration of *cis,*

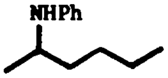
cis-1,5-cyclooctadiene in anhydrous THF, complex **3b** does react under similar conditions (runs 18,19, Table 2). By contrast, π-complex **3b** fails in the ring mercuration of N,N-diethylaniline even in polar solvents (runs 20,21, Table 2). This shows again that *free mercury(II) chloride is not involved in the aminomercuration of olefins.* This conclusion cannot be extended to the mercuration with mercury(II) acetate since π-complex **3a** does react with N,N-diethylaniline even in anhydrous THF to give **2c**. Since **3'a** does not react with N,N-diethylaniline under similar conditions, the possibility of an attack of the undissociated species **3a** on the aromatic ring cannot be ruled out (runs 1,22, Table 2).

The reactivity of the complexes **3** and **3'** derived from mercury(II) chloride towards olefins is much lowered when compared to that of those derived from mercury (II) acetate. Brown et al.[10] studied the relative rates of oxymercurations of representative olefins in an aqueous tetrahydrofuran system, and reported the structure-reactivity trends. We have found that only the olefins showing the highest reactivity can be aminomercurated with covalent mercuric salts (runs 23-33, Table 2). Olefins with high chelating ability (i.e. 1,5-COD) are the most suitable ones to undergo aminomercuration with **3b** and give the best yields in addition products. The addition of solid sodium bicarbonate to fix the hydrogen chloride evolved in the course of the aminomercuration, allowed an important increase in the observed yield (runs 34,35, Table 2).



5[2]

6[2]



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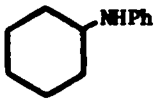

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CONCLUSIONS

The differences observed in the course of the aminomercuration of primary and secondary aromatic amines suggest that aminomercuration of olefins could take place through alternative routes as a function of the mercury(II) salt employed and the basicity, degree of alkylation and steric hindrance at the amine nitrogen. In any case, it seems to be demonstrated that complete dissociation of complexes **3** or formation of a four centered transition state **4**, should not be invoked, at least as a general rule to explain the aminomercuration of olefins and also, that preliminary ring mercuration or formation of intermediate σ-bonded N-mercurated amines can be doubtless disregarded. Conversely, we suggest that the actual mercurating entity when mercuric salts of great co-ordinating ability are used (i.e. mercury(II) chloride), is a three coordinated mercury species which can coordinate to the olefin to give a new complex **9**; this step is then followed by formation of the aminomercurial (Scheme 5). In the systems under discussion here this means that **3'b** must first dissociate to form a tricoordinate species before reaction can take place. In the case of **3'b** this means dissociation into the amine and **3b** which is the reactive species. This interpretation is strongly supported by the fact that much superior

$$\mathbf{3'} \rightleftharpoons \mathbf{3} + \mathrm{ArNH_2}$$

$$\mathbf{3} + \text{olefin} \rightleftharpoons \underset{\mathbf{9}}{[(\mathrm{ArNH_2})(\text{olefin})]\cdot\mathrm{HgX_2}}$$

$$\mathbf{9} \longrightarrow \text{aminomercurial} + \mathrm{HX}$$

Scheme 5

yields are obtained from olefins with high coordinating ability (i.e. 1,5-COD) and also when mercurations are carried out in polar solvents using pure **3b** as the aminomercurating agent rather than in the presence of an excess of amine. This trend is observed when one compares run 16 with run 17 and run 18 with run 19 (Table 2). According to this interpretation, aromatic amines will react faster than their aliphatic counterparts, since the stability constant K_4 corresponding to the complex **3'** will be smaller in the first case, an also because the gap between the π-basicity of the alkene and the n-basicity of the amine will be small enough to allow the olefin to compete with the amine for the mercury. Care should be taken in extending these conclusions to reactions with ionic mercury(II) salts,[11] since in this case, the dissociation of the salt renders electrophilic species responsible for the mercuration.

Table 3. Spectral Data for Compounds in Tables 1 and 2

Compound[a]	^{1}H-NMR	^{13}C-NMR
1a[b]	4.9(s,1H), 6.4-7.1(m,5H)	
2a[b]	1,9(s,6H), 4.9(s,2H), 6.4-7.0(m,4H)	175.32(s), 148.70(s), 137.21(d), 130.37(s), 114.68(d), 23.66(q)
2b[b]	5.0(s,2H), 6.4-7.1(m,4H)	148.49(s), 136.96(d), 136.70(s), 114.35(d)
2c[c]	1.15(t,6H), 2.1(s,3H), 3.3(q,4H), 6.5-7.2(m,4H)	176.32(s), 147.26(s), 136.21(d), 135.77(s), 111.39(d), 43.47(t), 23.06 (q), 12.84(q)
2d[b]	1.0(t,6H), 3.3(q,4H), 6.5-7.5(m,4H)	147.22(s), 137.12(d), 129.09(s), 111.79(d), 43.50(t), 12.46(q)
3a[b]	1.9(s,3H), 6.5-7.2(m,5H)	173.78(s), 148.72(s), 137.13(d), 128.84(d), 114.88(d), 22.12(q)
3b[b]	5.1(s,2H), 6.5-7.2(m,5H)	145.51(s), 132.97(d), 118.38(d), 116.01(d)
3'a[b]	1.9(s,6H), 6.4-7.1(m,10H)	174.99(s), 148.86(s), 137.66(d), 129.48(d), 115.53(d), 22.73(q)
3'b[b]	6.4(s,2H), 6.6-7.3(m,5H)	146.53(s), 129.77(d), 118.53(d), 116.24(d)
7[c]	0.5-1.5(m,9H), 1.6(q,1H), 2.0(q,1H) 3.1(m,1H), 3.4(m,1H), 6.2-7.1(m,5H)	145.84(s), 128.75(d), 117.01(d), 113.03(d), 51.84(d), 38.41(t), 38.04 (t), 27.65(t), 21.63(t), 13.09(q)
8[c]	1.0-2.1(m,11H), 3.4(m,1H), 6.5-7.5(m,5H)	147.50(s), 129.20(d), 116.70(d), 113.20(d), 51.50(d), 33.40(t), 25.10 (t), 26.00(t)

[a] IR Spectra were in good agreement with the proposed structures; for spectral data for compounds **5** and **6** see ref. 2.
[b] In DMSO solution
[c] In DCCl$_3$ solution

EXPERIMENTAL

Materials. Olefins, aromatic amines and mercury(II) salts were commercially available and were used as received. Tetrahydrofuran was destilled from sodium-benzophenone or potassium under argon for runs under anhydrous conditions.

General methods

Solvent extracts of reaction were appropriately washed and dried (Na$_2$SO$_4$) before removal of the solvent. The following spectrometers were used: IR, Pye Unicam SP 1000 and Perkin Elmer 577 (ν_{max} given in reciprocal centimeters); ^{1}H NMR, Varian EM-390 and Varian FT-80A (chemical shifts are reported in parts per millon (δ) downfield from Me$_4$Si); ^{13}C NMR, Varian FT-80A (chemical shifts are reported in parts per millon (δ) downfield from Me$_4$Si). GC analysis were performed with a Varian 6000 Vista Series equipped with a column Chromosorb G-1.5% OV-101. For TLC and column separations silica gel (Merck) was used with toluene-hexane (4:5) as eluant.

N-Chloromercurylaniline **1a**. A stirred solution of aniline (2.9 g, 20 mmol) in methanol (50 mL) was treated with potassium bicarbonate (10 g, 100 mmol) in water (50 mL) and then, a solution of mercury (II) chloride (5.4 g, 20 mmol) in hot water (50 mL) was added. A yellow precipitate separated out of solution inmediately while carbon dioxide was evolved. The precipitate was filtered, washed with water and methanol, and dried under vacuum (5.8 g, 88%).

para-Acetoxymercurydiethylaniline **2a**. To a stirred solution of aniline (3.8 g, 40 mmol) in methanol (20 mL) a solution of mercury(II) acetate (6.4 g, 20 mmol) in water (20 mL) was added. The mixture was stirred for 3 hours and a precipitate separated out of solution. The precipitate was filtered, washed with hexane and dried under vacuum (6.0 g, 86%).

para-Chloromercuryaniline **2b**. To a stirred solution of **2a** (3.6 g, 10 mmol) in DMSO (20 mL) a solution of potassium chloride (1.6 g, 20 mmol) in water (10 mL) was added. The mixture was stirred for 8 hours and the precipitate filtered, washed with hexane and dried under vacuum (1.8 g, 50%).

(1:1) Mercury(II) acetate-aniline π-complex **3a**. Mercury (II) acetate (3.2 g, 10 mmol) was added to a stirred solution of aniline (0.9 g, 10 mmol) in THF (10 mL). A white precipitate separated out inmediately. The precipitate was filtered, washed with water and hexane and dried under vacuum (3.8 g, 93%).

(1:1) Mercury(II) chloride-aniline π-complex **3b**. To a stirred solution of aniline (0.9 g, 10 mmol) in methanol (15 mL) a solution of mercury(II) chloride (2.7 g, 10 mmol) in hot water (15 mL) was added. A white precipitate separated out of solution inmediately. The solid was filtered, washed with hexane and dried under vacuum (3.0 g, 82%).

(1:2) Mercury(II) acetate - aniline π-complex **3'a**. Mercury(II) acetate (1.6 g, 5 mmol) was added to a stirred solution of aniline (0.9 g, 10 mmol) in THF (10 mL). A white precipitate separated out of solution inmediately. The precipitate was filtered, washed with hexane and dried under vacuum (2.3 g, 92%).

(1:2) Mercury(II) chloride-aniline π-complex **3'b**. To a stirred solution of aniline (3.7 g, 40 mmol) in methanol (30 mL) a solution of mercury(II) chloride (5.4 g, 20 mmol) in hot water (30 mL) was added. A white precipitate separated out of solution inmediately. The precipitate was filtered, washed with hexane and dried under vacuum (7.5 g, 80%).

Reaction of N-chloromercuryaniline **1a** *with ortho-toluidine*. To a suspension of **1a** (2.6 g, 5 mmol) in THF (20 mL), ortho-toluidine (1.6 g, 15 mmol) was added and the mixture stirred for 48 hours at room temperature. The resulting precipitate was filtered from the reaction mixture and characterized as **1a**. Solvents were removed from the liquid phase and the residue was identified as ortho-toluidine by G.C. analysis.

Conversion of N-chloromercuryaniline **1a** *into* **3b**. To a stirred solution of **1a** (1.6 g, 5 mmol) in methanol (20mL) an aqueous solution of 1.1N HCl (4.8 mL, 5 mmol) was added. After 30 min methanol was evaporated and the precipitate filtered, washed with hexane and dried under vacuum. It was identified as **3b** by its IR, ^1H NMR and ^{13}C NMR spectra.

An attempt of aminomercuration of cis,cis-1,5-cyclooctadiene with **1a**. To a suspension of **1a** (3.3 g, 10 mmol) in THF (15 mL), 1,5-COD (1,1 g, 10 mmol) and aniline (0.5 g, 5 mmol) were added. The mixture was stirred at room temperature for 48 hours. The solution was then succesively treated with aniline (2.1 mL), 0.5 M NaOH (29 mL) and $NaBH_4$ (0.3 g, 8 mmol) dissolved in 2.5M NaOH (3 mL). The mercury (0) precipitated (2.0 g, 100%), was filtered and the reaction mixture was extracted with ether. 1,5-COD was recovered unchanged from the organic layer and compounds **5** and **6** could not be detected by T.L.C. analysis.

An attempt of aminomercuration of cis,cis-1,5-cyclooctadiene with **2c**. To a solution of **2c** (4.1 g, 10 mmol) in THF (15 mL),1,5-COD (1.1 g, 10 mmol), aniline (1.4 g, 15 mmol) and acetic acid (0.6 g, 10 mmol) were added. The mixture was stirred for 48 hours at room temperature. Reduction was carried out as described above. Mercury(0) was obtained (2.0 g, 100%) and after the usual work up, 1,5-COD was recovered unchanged. Compounds **5** and **6** could not be detected by T.L.C. analysis. Other runs were performed in absence of acetic acid and anhydrous THF or THF/water mixture as solvents, giving similar results. Analogous results were obtained when *para*-acetoxymercuryaniline was used instead of *para*-acetoxymercurydiethylaniline as mercurating agent.

An attempt of C-mercuration of diethylaniline with **2a**. To a stirred solution of **2a** (0.4 g, 1 mmol) in THF (10 mL), diethylaniline (0.3 g, 2 mmol) was added. The mixture was treated with water (2 mL) and acetic acid (0.1 mL). After 48 hours of continuous stirring reduction was carried out as described above. Nearly quantitative mercury(0) precipitated and was filtered. After the usual work up **2a** and diethylaniline were recovered unchanged.

Runs listed in Table 2. General experimental procedure. The corresponding amine or olefin (5 mmol) was added to a solution of the mercurating agent (2.5 mmol) in the solvent indicated in the Table. The mixture was stirred at room temperature for the time indicated in each case. Mercurated amines were recovered upon elimination of solvents under reduced pressure, and removal of the unreacted amine by washing with hexane. Mercurated olefins were *in situ* reduced by the methods described elsewhere.[2] In runs 34 and 35, sodium bicarbonate (0.25 g, 3 mmol) was added with the olefin to the solution containingthe mercurating agent.

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[11] Our referee has suggested that in the case of using mercury(II) acetate since it is more ionic than mercury(II) chloride, the complex **3'a** can dissociate much more easily than **3'b** into $(ArNH_2)_2HgX^+$ and X^- hence there is a higher concentration of threecoordinate mercury species resulting in faster reaction. E.g. run 10 vs run 11 and run 7 vs run 9. We wish to acknowledge the referee for this and other helpful comments.