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The Synthesis and Characterization of Compounds of the Type $Hg\{1\text{-}C_6H_4\text{-}2\text{-}C(H){=}NC_6H_{5-n}R_n\}_2$

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The organomercurial compounds $Hg\{1\text{-}C_6H_4\text{-}2\text{-}C(H){=}NC_6H_{5-n}R_n\}_2$ (R = 4-NMe$_2$, **6a**; 4-Me, **6b**; 4-I, **6c**; 4-NO$_2$, **6d**; 2-^{i}Pr, **6e**; 2-Me, **6f**; 2,6-^{i}Pr$_2$, **6g**; 2,6-Me$_2$, **6h**) have been prepared in good overall yield from 2-bromobenzaldehyde. All of the compounds have been characterized by elemental analysis, ^{1}H NMR, ^{13}C{^{1}H} NMR, and infrared spectroscopy. In addition, compounds **6a** [$C_{30}H_{30}HgN_4$, triclinic, $P\bar{1}$, $a = 6.20000(10)$ Å, $b = 9.2315(2)$ Å, $c = 10.9069(3)$ Å, $\alpha = 85.8510(10)°$, $\beta = 89.3570(10)°$, $\gamma = 87.206(2)°$, $Z = 1$], **6b** [$C_{28}H_{24}HgN_2$, monoclinic, $P2_1/c$, $a = 12.8260(5)$ Å, $b = 14.0675(4)$ Å, $c = 6.1032(2)$ Å, $\beta = 90.0990(10)°$, $Z = 2$], **6g** [$C_{38}H_{44}HgN_2$, triclinic, $P\bar{1}$, $a = 8.2626(2)$ Å, $b = 9.8317(2)$ Å, $c = 11.8873(3)$ Å, $\alpha = 103.6650(10)°$, $\beta = 109.3350(10)°$, $\gamma = 104.627(2)°$, $Z = 1$], and **6h** [$C_{30}H_{28}HgN_2$, monoclinic, $P2_1/c$, $a = 12.5307(2)$ Å, $b = 10.9852(2)$ Å, $c = 18.2112(2)$ Å, $\beta = 104.0190(10)°$, $\gamma = 87.206(2)°$, $Z = 4$] have been characterized by low-temperature single-crystal X-ray diffraction studies, and two different molecular geometries about the central mercury atom have been observed; intramolecular contacts suggest a van der Waals radius for Hg of 2.1–2.2 Å.

Introduction

The first reported study of an organomercurial compound was described by Frankland in 1852,[1] with the first diorganomercurial synthesized in 1858 obtained by symmetrization of MeHgI using KCN![2] Since then a wide range of methods have been developed for forming a mercury−carbon bond, and they include transmetalation using electropositive alkali metal or main group organometallic reagents, mercury−hydrogen exchange, solvomercuriation, decarboxylation, desulfination, reaction with diazonium salts, carbene insertion into a mercury halogen bond and symmetrization. All of these methodologies have been comprehensively reviewed,[3] as have the solid state structures of this class of compound.[4] We recently reported[5] the synthesis, using the methodology developed by Roper et al.,[6] of some cycloruthenated complexes of the type $[RuX(CE)(\eta^2\text{-}C,N\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2]$ (X = Cl, Br, I; E = O, S) which showed an interesting *cis*-push−pull effect that was moderated by the cycloruthenated azobenzene ligand, and we showed that it is similar in nature to the tautomeric process undergone by orthohydroxyazobenzes.[7] Since it is known that 2-phenyliminophenols are known to undergo the same tautomeric process,[8] we were keen to prepare some analogous compounds. Perusal of the literature suggested that there were no examples of the symmetric diorganomercurials $Hg\{1\text{-}C_6H_4\text{-}2\text{-}C(H){=}NC_6H_{5-n}R_n\}_2$ which would be required to

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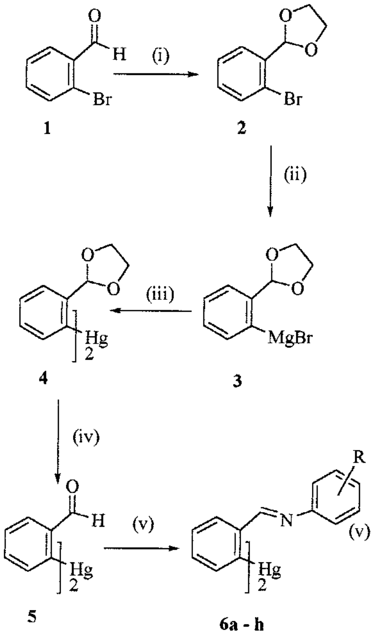
10.1021/ic010881q CCC: $22.00

Table 1. Physical, Analytical,[a] and Infrared Data[b] for **2**, **4**, **5**, and **6a**−**h**

compd	color	yield (%)	anal. data C	H	N	IR (cm^{-1})
2 1-BrC_6H_4-2-$CHOCH_2OCH_2$	colorless liquid	95	47.4 (47.2)	3.9 (4.0)		
4 Hg(1-C_6H_4-2-$CHOCH_2OCH_2$)	white	74	43.5 (43.3)	3.6 (3.6)		
5 Hg(C_6H_4-2-CHO)	white	88	41.1 (40.9)	2.5 (2.5)		1680, ν(CO)
6a Hg{1-C_6H_4-2-C(H)═NC_6H_4-4-NMe_2}	yellow	69	55.9 (55.7)	4.7 (4.7)	8.5 (8.7)	1618, ν(CN)
6b Hg{1-C_6H_4-2-C(H)═NC_6H_4-4-Me}	white	76	57.1 (57.1)	4.1 (4.1)	4.6 (4.8)	1624, ν(CN)
6c Hg{1-C_6H_{4-}2-C(H)═NC_6H_4-4-I}	off-white	73	38.3 (38.4)	1.9 (2.2)	3.2 (3.4)	1620, ν(CN)
6d Hg{1-C_6H_4-2-C(H)═NC_6H_4-4-NO_2}	yellow	75	48.1 (48.0)	2.6 (2.8)	8.5 (8.6)	1624, ν(CN) 1585, 1335 (NO_2)
6e Hg{1-C_6H_4-2-C(H)═NC_6H_4-2-^{i}Pr}	white	81	59.5 (59.6)	5.2 (5.0)	4.3 (4.3)	1618, ν(CN)
6f Hg{1-C_6H_4-2-C(H)═NC_6H_4-2-Me}	white	67	56.9 (57.1)	4.0 (4.1)	4.7 (4.8)	1628, ν(CN)
6g Hg{1-C_6H_4-2-C(H)═NC_6H_3-2,6-^{i}Pr_2}	white	84	62.5 (62.6)	6.1 (6.1)	3.8 (3.8)	1637, ν(CN)
6h Hg{1-C_6H_4-2-C(H)═NC_6H_3-2,6-Me_2}	white	82	58.5 (58.4)	4.7 (4.6)	4.6 (4.6)	1633, ν(CN)

[a] Calculated values in parentheses. [b] Spectra recorded as Nujol mulls between KBr plates; all bands strong.

Scheme 1 [a]



[a] (i) $HOCH_2CH_2OH$, $PhCH_3$, 4-$MeC_6H_4SO_3H$, 24 h; (ii) Mg, THF, 3 h; (iii) $HgBr_2$, 18 h; (iv) 4-$MeC_6H_4SO_3H$, $CH_3C(O)CH_3$ 12 h; (v) $R_nC_6H_{5-n}NH_2$, EtOH, 3 h.

prepare these compounds, so we set about determining a strategy to synthesize them.

Results and Discussion

Starting from 2-bromobenzaldehyde the orthomercuriated phenylimines **6a**−**h** were prepared in good overall yield as illustrated in Scheme 1. The new compounds have all been characterized by elemental analysis and infrared spectroscopy (Table 1) and ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy (Tables 2 and 3); additionally compounds **6a**, **6b**, **6g**, and **6h** have been further characterized by single-crystal X-ray diffraction studies; see Table 4 for selected bond lengths (Å) and angles (deg). It should be noted here that during the course of this work an alternative route to **5** has been described.[9]

The ^{1}H NMR spectra are all consistent with the formulation of compounds **2**, **4**, **5**, and **6a**−**h**; in particular, incorporation of mercury was readily confirmed by the observation of ^{199}Hg satellites (Table 2). Assignment of the ^{13}C{^{1}H} NMR data was carried out with the aid of Dept 135 spectra, the presence of ^{199}Hg satellites, and published substituent effects;[10] see Figure 1 for numbering scheme.

Compounds **6a**, **6b**, **6g**, and **6h** have also been characterized by a low-temperature single-crystal X-ray diffraction study; except for **6g**, where there was disorder in one of the ^{i}Pr groups, the hydrogen atoms were located in the difference map; see Figures 2−5 for ORTEP[11] representations showing the atomic numbering schemes (because of the disorder in the ^{i}Pr group C(14)−C(16) in compound **6g**, for clarity only one orientation is shown in Figure 4) and Table 4 for selected bond lengths (Å) and angles (deg). Further, compounds **6a**, **6b**, and **6g** all display a center of inversion, whereas **6h** does not. In all cases the Hg(II) coordination geometry is linear. The distance between the imine nitrogen and mercury center (approximately 2.8 Å) is slightly less than the sum of the van der Waals radii (3.05 Å),[12] see later discussion, and substantially longer than the sum of the covalent radii (2.18 Å),[12] so at best there is a weak interaction.

In all of the structures the imine phenyl group rotates out of the plane to minimize steric interactions with the hydrogen

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Table 2. ^{1}H NMR Data for Compounds^a **2**, **4**, **5**, and **6a**−**h**

compd	δ
2	7.6−7.3 (m, 4H, aryl-H); 6.13 (s, 1H, CH); 4.3−3.9 (m, 4H, CH_2)
4	7.6−7.3 (m, 4H, aryl-H); 5.87 (s, J_{HHg} 9.4, 1H CH); 4.3−3.9 (m, 4H, CH_2)
5	10.24 (s, J_{HHg} 10.4, 1H, CHO); 7.9−7.4 (m, 4H, aryl-H)
6a	8.76 (s, J_{HHg} 11.8, 1H CH); 7.7−7.3 (m, 4H, aryl-H); 7.09 (d, J_{HH} 9.0, 2H, aryl-H); 6.6 (d, J_{HH} 9.0, 2H, aryl-H); 2.91 (s, 6H, NCH_3)
6b	8.73 (s, J_{HHg} 11.8, 1H CH); 7.7−7.3 (m, 4H, aryl-H); 7.03 (m, 4H, aryl-H); 2.31 (s, 3H, CH_3)
6c	8.65 (s, J_{HHg} 11.8, 1H CH); 7.7−7.3 (m, 4H, aryl-H); 7.53 (d, J_{HH} 8.8, 2H, aryl-H); 6.75 (d, J_{HH} 8.8, 2H, aryl-H)
6d^b	8.68 (s 1H, CH); 8.14 (d, J_{HH} 9.0, 2H, aryl-H); 7.7−7.4 (m, 4H, aryl-H); 7.08 (d, J_{HH} 9.0, 2H, aryl-H)
6e	8.51 (s 1H, J_{HHg} 9.8, CH); 7.6−7.1 (m, 7H, aryl-H); 6.68 (m, 1H, aryl-H); 3.47 (sep, J_{HH} 7.2, 1H, CH); 0.85 (d, J_{HH} 7.2, 6H, CH_3)
6f	8.50 (s 1H, J_{HHg} 10.4, CH); 7.6−7.0 (m, 7H, aryl-H); 6.73 (m, 1H, aryl-H); 2.15 (s, 3H, CH_3)
6g	8.44 (s 1H, J_{HHg} 11.9, CH); 7.6−7.0 (m, 7H, aryl-H); 3.07 (sep, J_{HH} 6.8, 2H, CH); 1.14 (d, J_{HH} 6.8, 12H, CH_3)
6h	8.42 (s 1H, J_{HHg} 11.6, CH); 7.6−7.3 (m, 4H, aryl-H); 7.0−6.9 (m, 3H, aryl-H); 2.09 (s, 6H, CH_3)

^{a} Spectra recorded in $CDCl_3$ at 298 K; coupling constants in hertz. ^{b} Sample poorly soluble.

Table 3. ^{13}C{^{1}H} NMR Data for Compounds^{a,b} **2**, **4**, **5**, **6a**−**c**, and **6e**−**h**

compd	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9) C(9′)	C(10) C(10′)	C(11)	other resonances
2	122.8	132.8	130.4	127.3	127.7	136.5						CH, 102.4
												CH_2, 65.3
4	167.3	138.0	129.4	127.4	128.9	143.9						CH, 105.4, *J* 56
	J 1316	*J* 82	*J* 110		*J* 84	*J* 36						CH_2, 65.0
5	168.5	139.2	134.4	128.1	135.2	144.0						CO, 195.6, *J* 48.
	J 1251	*J* 80	112		87	*J* 44						
6a	167.1	139.3	130.5	126.9	132.3	144.6	159.2	139.9	122.9	112.81	149.3	NCH_3, 41.2
		J 114	*J* 121		*J* 82	19	*J* 56					
6b	167.4	139.3	131.2	127.1	133.0	144.0	162.9	148.2	120.9	129.6	135.7	CH_3, 21.0
	J 1488	*J* 100	*J* 122		*J* 84	*J* 22	*J* 48					
6c^c	167.4	139.3	131.8	127.4	133.5	143.5	164.2	150.2	123.0	138.1	90.4	
6e	167.3	139.1	131.3	127.3	133.4	143.5	164.6	149.9	142.4	126.3	125.7	CH, 27.7
	J 1449	*J* 88	*J* 119		*J* 82	*J* 20	*J* 50		118.7	125.0		CH_3, 23.2
6f	167.4	139.2	131.3	127.3	133.4	143.5	164.6	151.2	131.9	130.0	126.6	CH_3, 18.3
	J 1460	*J* 98	*J* 119		*J* 83	*J* 28	*J* 46		118.4	125.4		
6g	166.9	138.1	131.6	127.5	133.1	142.7	166.6	149.5	139.1	123.0	124.1	CH, 28.1
	J 1487	*J* 89	*J* 117		*J* 85	*J* 19	*J* 48					CH_3, 23.6
6h	166.8	139.0	131.6	127.3	133.0	142.9	167.2	151.2	127.7	127.9	123.6	CH_3, 18.6
	J 1468	*J* 90	*J* 117		*J* 87	*J* 23	*J* 51					

^{a} All spectra recorded in $CDCl_3$ at 298 K. ^{b} All coupling constants are J_{CHg} in hertz. ^{c} Poorly soluble, unable to observe coupling constants.

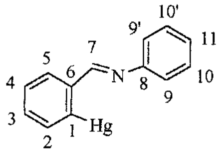

Figure 1. Numbering scheme for ^{13}C{^{1}H} NMR data.

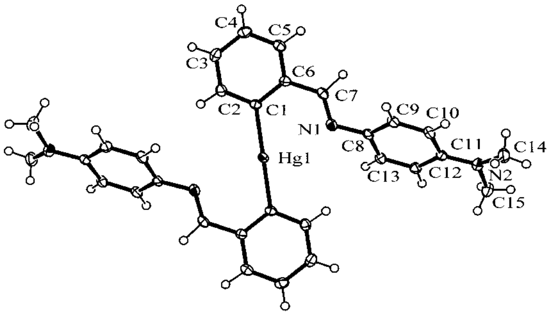

Figure 2. ORTEP representation of **6a** showing the atomic numbering scheme, ellipsoids at 50%.

bound to C(2). The torsion angles (Table 4) for **6a** and **6b** (46°, 41°) are significantly less than for **6g** and **6h** (−110°, −63°), and this must be a result of the steric bulk of the hydrogen versus methyl versus ^{i}Pr (largest torsion angle) groups. A search of the CCDC[13] using a very general template that considered any compound with at least one Hg−C bond and either an inter- or intramolecular Hg−N contact within the sum of the van der Waals radii was carried out.[14] This search afforded 72 hits, of which five contained

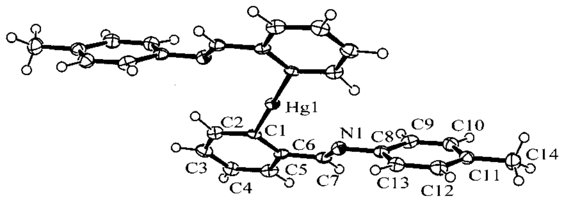

Figure 3. ORTEP representation of **6b** showing the atomic numbering scheme, ellipsoids at 50%.

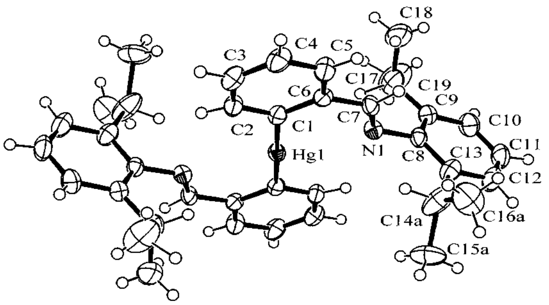

Figure 4. ORTEP representation of **6g** showing the atomic numbering scheme, ellipsoids at 50%.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6a**, **6b**, **6g**, and **6h**

compd	Hg(1)−C(1) Hg(1)−C(21)	C(6)−C(7)	C(7)−N(1)	N(1)−C(8)	Hg(1)−N(1) Hg(1)−N(2)	C(1)−Hg−C(*n*)	C(6)−C(7)−N(1)	C(7)−N(1)−C(8)	N(1)−Hg(1)−N(*n*) N(1)−Hg(1)−C(1) N(1)−Hg(1)−C(21)	C(7)−N(1)−C(8)−C(9)
6a	2.085(3)	1.483(5)	1.262(5)	1.413(4)	2.850(3)	180.0	124.3(3)	119.9(3)	180.0	46.4(5)
6b	2.082(3)	1.468(5)	1.278(4)	1.412(4)	2.854(2)	180.0	123.5(3)	120.1(3)	180.0	40.7(4)
6g	2.078(5)	1.472(6)	1.269(6)	1.418(5)	2.806(4)	180.0	123.4(4)	120.0(4)	180.0	70.2(5)
6h	2.092(2)	1.474(3)	1.271(3)	1.415(3)	2.721(2)	175.07(9)	122.8(2)	119.9(2)	72.66(8)	63.0(3)
	2.083(2)	1.477(4)	1.268(3)	1.414(3)	2.712(2)		123.1(2)	121.5(2)	110.60(8)	
									85.98(6)	

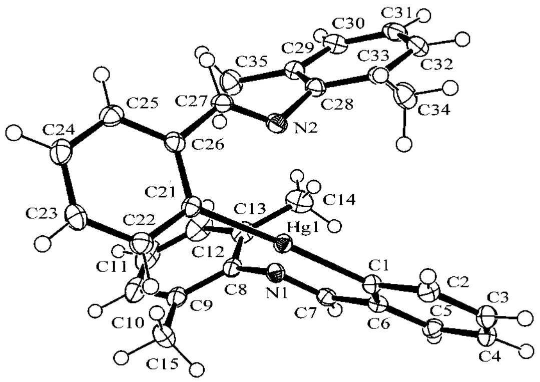
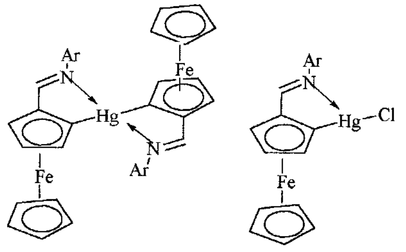


Figure 5. ORTEP representation of **6h** showing the atomic numbering scheme, ellipsoids at 50%.

Chart 1



I II

an orthomercuriated phenylimine.[15] The closest structural analogue of the compounds **6a**, **6b**, **6g**, and **6h** is **I**, Chart 1, and has a ferrocene backbone.[15a] Interestingly, the geometry of compound **I**, about the mercury atom, most closely resembles that observed for **6a**, **6b**, and **6g**. The other four compounds are of type **II**.[15b−e] For **I** the Hg−N contacts are 3.040(6) and 2.981(6) Å, respectively, with C−Hg−C = 174.7(3)° and N−Hg−N 157.1(2)°, respectively, and for the compounds of type **II**, which contain only one Hg−N contact, the average Hg−N distance is 2.85 Å (range: 2.76−2.87 Å) and is comparable to the Hg−N distances in **6a**, **6b**, and **6g** and noticeably longer than in **6h**. One question that arises is, why does **6h** have a different coordination geometry about the mercury atom?

There is currently[16] a lot of interest in weak secondary interactions and their affect on solid state structures. To investigate whether there were any secondary interactions in any of the diorganomercurials **6a**, **6b**, **6g** and **6h**, a full Platon[17] analysis was carried out. When the normally quoted value of 1.55 Å is used for the van der Waals radius,[14] it is apparent that there are no close interactions. There is, however, some controversy[4a] concerning the van der Waals radius of mercury, with Canty and Deacon suggesting[18] a value of 1.73 Å, which is comparable to that recently

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calculated by Pyykko and Straka [1.75(7) Å],[19] but it is accepted that a value up to 2.0 Å may be possible. Further, Batsanov even proposed[20] values between 2.1 and 2.2 Å.

The closest hydrogen distance to mercury is Hg$\cdots$H(34c)C(34) 3.184(2) Å, Hg−H−C 131.3(5)°, which could only be considered a contact if the van der Waals radius of Hg was 2.0 Å, and even then it would be weak; further, this would be an agostic interaction,[21] not a hydrogen bond.[22] Calculations that have been carried out on $[Hg(CF{=}CF_2)_2]$[23] and $[Hg(CH{=}CH_2)_2]$[24] show that there is free rotation about the Hg−C bond and that there are minima when the groups are coplanar and perpendicular, with the perpendicular orientation being the lowest energy conformation. For the compound $Hg(CF{=}CF_2)_2$ the theoretical geometry optimization (MP2/DZP level) showed that there was also a shallow potential-energy minimum when the perfluorovinyl groups were nearly perpendicular [$\Phi(C{=}C\cdots C{=}C) = 98.2°$];[23] remarkably the dihedral angle in the solid state structure of **6h** [$\Phi(C(6){=}C(1)\cdots C(21){=}C(22)) = 99.7°$] is similar. However the solid state structure of $Hg(CF{=}CF_2)_2$ had coplanar vinyl groups with three intermolecular Hg$\cdots$F contacts: 2.964(5), 3.503(5), 3.129(5) Å in the solid state leading to essentially octahedral coordination about the mercury atom. For the Hg$\cdots$F contact of 3.503(5) Å to be considered within the sum of the van der Waals radii, the van der Waals radius of mercury needs to be at least 2.0 Å, a value that is similar to that required for Hg$\cdots$H(34c)C(34) and considered by others to be reasonable.[4a,18] Considering the solid state structure of **6g**, where there is some disorder in one of the isopropyl groups, in the ordered group the Hg$\cdots$H(17) distance is 3.348(3) Å with the Hg−H−C angle155.4(6)°. This almost linear orientation of Hg−H−C is not consistent with an agostic interaction,[21,22] so it should be assumed to be outside or on the limit of the sum of the van der Waals radii, hence a possible reason for the disorder seen in the other ^{i}Pr group. If this is the case, the changing nature of the agostic interaction in **6h** and **6g** makes the suggestion[20] of Batsanov of 2.1−2.2 Å for the van der Waals radius of mercury not unreasonable. It may also help to explain why the perpendicular orientation of the aryl rings in **6h** is observed: the Hg$\cdots$H distance would be within the sum of the van der Waals radii and hence strong enough to aid in stabilizing this orientation. Similarly the Hg$\cdots$F distance 3.503(5) Å in $Hg(CF{=}CF_2)_2$ would be within the sum of the van der Waals radii. Finally, these data would suggest that the secondary Hg$\cdots$N interaction is noticeably stronger than previously thought.[15]

Conclusion

We have synthesized a series of bis-orthomercuriated (2-phenylimino)phenyls starting from 2-bromobenzaldehyde in good overall yield. Four of the compounds have been structurally characterized, three of which have coplanar mercuriated aryl groups and one where the mercuriated aryl rings are perpendicular. On the basis of close Hg$\cdots$H contacts we concur with others that the van der Waals radius for mercury of 1.55 Å is too short and that the suggestion of Batsanov of between 2.1 and 2.2 Å is not unreasonable.

Experimental Section

General. All chemicals were purchased from commercial sources, and solvents were dried by refluxing under N_2 over an appropriate drying agent and distilled prior to use, THF (K), $C_6H_5CH_3$ (Na), Et_2O (NaK); CH_2Cl_2 (P_4O_{10}). Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 5PC spectrometer. ^1H NMR spectra (200.2 MHz) were recorded on a Bruker DPX200 spectrometer, and $^{13}C\{^1H\}$ NMR spectra (100.55 MHz) were recorded on a Brucker DPX400 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to $C\mathit{H}Cl_3$ ($\delta = 7.26$) and $\mathit{C}HCl_3$ ($\delta = 77.0$), respectively. Elemental analyses were performed by the Microanalytical service, Department of Chemistry, UMIST.

CAUTION. Most of the experiments described involve the use of mercurial salts for the generation of diorganomercurials: These classes of compound are known to be extremely hazardous, and appropriate handling conditions should be used for their generation and disposal.

1-Br-2-(CHOCH$_2$CH$_2$)C$_6$H$_4$. To a 250 mL round-bottomed flask, fitted with a condenser and Dean and Stark trap, containing a stirrer bar, were added toluene (100 mL), ethylene glycol (10 mL), 2-bromobenzaldehyde (25 g, 0.l35 mol), and *p*-toluenesulfonic acid monohydrate (0.5 g, 2.63 mmol), and the mixture was refluxed overnight (approximately 18 h). After cooling, the solution was washed with $NaHCO_3$ (50 mL, saturated) and brine (50 mL), and the organic fraction was separated and dried over K_2CO_3. Filtration of the dried solution followed by reduced-pressure distillation afforded **2** (29.4 g, 0.128 mol, 95%); bp$_{0.1}$ 85−90 °C: see Table 1 for physical and analytical data.

Hg{1-C$_6$H$_4$-2-(CHOCH$_2$CH$_2$)}$_2$. *Caution!* To a three-necked 250 mL round-bottomed flask, fitted with a pressure-equalizing dropping funnel and a reflux condenser, under a N_2 atmosphere was added Mg (2.10 g, 0.86 mol), a stirrer bar THF (30 mL), and a few crystals of I_2. To this solution was added 1-Br-2-(CHOCH$_2$CH$_2$)C$_6$H$_4$ (20 g, 0.087 mol, THF 20 mL) from the pressure-equalizing funnel at such a rate as to create a gentle reflux. After addition was complete, the mixture was refluxed for an additional 1 h before cooling to 0 °C. The pressure-equalizing funnel was then recharged with $HgBr_2$ (27.0 g, 0.075 mol) and THF (75 mL). This solution was added dropwise over a period of 1 h and the reaction allowed to warm to room temperature. After stirring for 18 h, NH_4Cl (30 mL, saturated) was added and the organic fraction separated. The aqueous layer was extracted with toluene (75 mL), and the organic fragments were combined and dried over $MgSO_4$. Filtration and removal of the solvent under reduced pressure afforded **4** as an off-white solid (27.65 g, 0.055 mol, 74%) which was pure enough for subsequent use. The analytically pure sample (white) was obtained on recrystallization from hot EtOH: see Table 1 for physical and analytical data.

Hg{1-C$_6$H$_4$-2-(CHO)}$_2$. *Caution!* To **4** (10 g, mmol) dissolved in acetone (100 mL) in a 250 mL round-bottomed flask fitted with

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Table 5. Crystallographic Data for **6a**, **6b**, **6g**, and **6h**

	6a	**6b**	**6g**	**6h**
chem formula	$C_{30}H_{30}HgN_4$	$C_{28}H_{24}HgN_2$	$C_{38}H_{44}HgN_2$	$C_{30}H_{28}HgN_2$
fw	647.17	589.08	729.34	617.13
T (K)	120(2)	120(2)	150(2)	120(2)
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	6.20000(10)	12.8260(5)	8.2626(2)	12.5307(2)
b, Å	9.2315(2)	14.0675(4)	9.8317(2)	10.9852(2)
c, Å	10.9069(3)	6.1032(2)	11.8873(3)	18.2112(2)
α, deg	85.8510(10)		103.6650(10)	
β, deg	89.3570(10)	90.0990(10)	109.3350(10)	104.0190(10)
γ, deg	87.206(2)		104.627(2)	
vol, Å^3	621.86(2)	1101.20(6)	825.80(3)	2432.15(6)
Z	1	2	1	4
d(calcd), Mg/m^3	1.728	1.777	1.467	1.685
R1^a [$I > 2\sigma(I)$]	0.0248	0.0285	0.0477	0.0272
wR2^b	0.0601	0.0680	0.1123	0.0657
R1 (all data)	0.0250	0.0425	0.0488	0.0313
wR2	0.0602	0.0745	0.1128	0.0681

^{a} $R1 = \sum||F_o| - |F_c||/ \sum|F_o|$. ^{b} $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

a condenser was added *p*-toluenesulfonic acid monohydrate (0.5 g, 2.63 mmol), and the solution was refluxed for 5 h. On cooling, the solvent volume was reduced to 10 mL and the solution poured into rapidly stirred H_2O (200 mL) containing Na_2HCO_3 (1 g, 0.02 mmol). The off-white precipitate of crude **5** was collected by filtration, washed with water (50 mL), and dried. This product (7.25 g, 0.018 mol, 88%) was pure enough to use without further recrystallization. The analytically pure sample was obtained by recrystallization from hot EtOH: see Table 1 for physical and analytical data.

$Hg\{1\text{-}C_6H_4\text{-}2\text{-}(CH{=}NC_6H_4\text{-}4\text{-}NMe_2)\}_2$. *Caution!* To **5** (1 g, 2.4 mmol) dissolved in EtOH (10 mL) containing *p*-toluenesulfonic acid monohydrate (10 mg, 0.05 mmol) was added *N*,*N*-dimethylaniline (0.65 mL, 5.12 mmol), and the solution was refluxed for 1 h, during which time yellow crystals of **6a** precipitated. The solution was cooled and **6a** collected by filtration and washed with a little ice-cold EtOH to give an analytically pure solid (1.1 g, 1.68 mmol, 69%). See Table 1 for physical and analytical data.

Compounds **6b**−**h** were all prepared in an analogous fashion. See Table 1 for physical and analytical data.

Crystallography. All crystals were grown by dissolving approximately 15 mg of compound in approximately 0.3 mL of CH_2Cl_2 in a glass vial (15 × 40 mm), layering approximately 5 mL of EtOH on top, and leaving to stand for 2 days at room temperature.

All the X-ray diffraction measurements were carried out on the National Crystallographic Service Nonius Kappa CCD diffractometer, Southampton, England. Monochromatic X-rays generated by a Nonius FR591 rotating anode source were used to record ϕ scans and ω scans to fill the Ewald sphere. An Oxford cryostream cooler was used to maintain the crystals at 150 K. The structures were solved using direct methods and refined using full-matrix least-squares (SHELX-97).[25] Crystallographic details for compounds **6a**, **6b**, **6g**, and **6h** are presented in Table 5.

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Supporting Information Available: Four X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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