Homoleptic Organometallic Compounds of Zinc, Cadmium, and Mercury, Intramolecularly Stabilized by Amine Ligands

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Homoleptic intramolecularly stabilized organozinc, -cadmium, and -mercury compounds MR_2, with R bearing an amino function, have been synthesized from the corresponding metal dichlorides MCl_2 and the lithium salts $LiC_6H_4CH_2NEt_2$-2 (**1**), $LiC_6H_3(CH_2NMe_2)_2$-2,6 (**2**), $LiC_6H_3(CH_2NEt_2)_2$-2,6 (**3**), $(LiCH_2CH_2CH_2)_2NMe$ (**4**), and $LiCH_2CH_2CH_2NC_5H_{10}$ (**5**). The crystal structures of $Hg(C_6H_4CH_2NEt_2\text{-}2)_2$ (**1c**), $[M(CH_2CH_2CH_2)_2NMe]_2$ [M = Zn (**4a**), Hg (**4c**)], and of $M(CH_2CH_2CH_2NC_5H_{10})_2$ [M = Zn (**5a**), Cd (**5b**)] have been determined by X-ray diffraction. **4a** and **4c** form dimers with an unusual coordination number (three) of the central metal.

Introduction

Diorganometal compounds of the group 12 elements are of increasing interest in connection with the development of MOVPE techniques (**M**etal **O**rganic **V**apor **P**hase **E**pitaxy) for the generation of type II-VI semiconductors. In particular, the dimethyl or diethyl derivatives of zinc, cadmium, and mercury have been used as precursors[1a][1b][1c]. Unfortunately, these compounds are highly water sensitive and, with the exception of the zinc compounds, extremely toxic. It was to be expected that the use of *N*-donor functionalized ligands, which are able to coordinate intramolecularly with the metal center by formation of chelate rings, should result in a considerable increase in the stability of such organometallic derivatives. Although numerous dialkyl-metal compounds of the group 12 elements are known which are intermolecularly stabilized by mono-, bi-, and tridentate amines, e.g. by NMe_3, NEt_3, py[2], 2,2′-bipy[2][3][4][5][6][7][8][9][10], 1,10-phen[2][3][4][10], tmeda[6][7][11], *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teeda)[2][4], (−)-sparteine[12], and triazines $(RNCH_2)_3$ (R = Me, Et, *i*Pr)[13], only a few intramolecularly *N*-stabilized species are known. $Zn(CH_2CH_2CH_2NMe_2)_2$, synthesized by Boersma et al. in 1978, was the first and, to date, the best investigated compound of this type[14][15][16]. The corresponding cadmium species and the corresponding diethylamino derivative of zinc were prepared by Thiele et al.[16], the diorganozinc, -cadmium, and -mercury compounds bearing 2-$Me_2NC_6H_4CH_2$- and/or 2-$Me_2NCH_2C_6H_4$- as arylamino ligands by Atwood et al.[17], van Koten et al.[18], and O′Brien et al.[19]. Deacon et al. succeeded in synthesizing bis[2-(pyridin-2′-yl)phenyl]mercury and bis[2-(pyrazol-1′-yl)phenyl]mercury[20]. A comprehensive paper concerning the structure of organomercury compounds and their secondary interactions has been published by Kuz′mina and Struchkov[21].

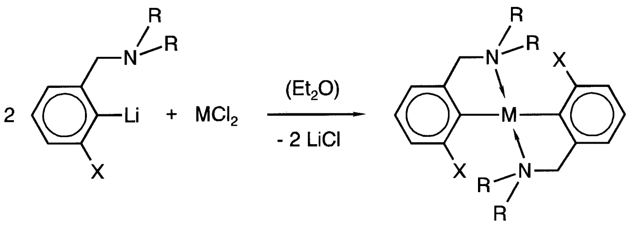
In this paper we present some interesting new homoleptic compounds of the group 12 elements with alkyl- and arylamine ligands.

Results and Discussion

1. Intramolecularly Stabilized Arylamino Compounds

The reaction of two equivalents of $LiC_6H_4CH_2NEt_2$-2 (**1**)[22][23][24][25], $LiC_6H_3(CH_2NMe_2)_2$-2,6 (**2**), or $LiC_6H_3(CH_2NEt_2)_2$-2,6 (**3**)[22][26] with one equivalent of MCl_2 (M = Zn, Cd, or Hg) gave the corresponding diorganozinc compounds **1a**, **2a**, **3a**, the diorganocadmium compounds **1b, 3b**, and the diorganomercury compounds **1c**, **2c**, **3c** in yields of 64 to 85% (Scheme 1). The lower yields obtained for **1b**, **3b**, and **2c** were caused by some decomposition accompanied by precipitation of metallic cadmium or mercury. With the exception of **3c**, which is a highly viscous liquid, all other derivatives are colorless solids at room temperature.

Scheme 1



1 - 3

1a - 3c

1 X = H, R = Et
2 X = CH_2NMe_2, R = Me
3 X = CH_2NEt_2, R = Et

M = Zn **1a**, Cd **1b**, Hg **1c**
M = Zn **2a**, Hg **2c**
M = Zn **3a**, Cd **3b**, Hg **3c**

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Table 1. ^{1}H- and ^{13}C-NMR data of the arylamino compounds **1a**−**3c**

	^{1}H-NMR δ [ppm]				^{13}C-NMR δ [ppm]			
	CH_3	CH_3CH_2	CH_2C_{aryl}	$C_{aryl}H$	CH_3	CH_3CH_2	CH_2C_{aryl}	$C_{aryl}-1$
1a	0.64	2.52	3.52	7.10···8.02	8.75	45.25	61.79	157.75
1b	0.77	2.43	3.44	7.09···7.40	10.33	45.90	62.07	160.72
1c	1.09	2.69	3.68	7.24···7.97	11.21	46.39	61.60	171.10
2a	2.16	–	3.36	6.96···7.27	45.60	–	65.00	159.10
2c	2.19	–	3.41	7.02···7.18	48.25	–	71.58	176.00
3a	0.85	2.63	3.74	7.29···7.43	10.35	46.09	63.42	158.44
3b	0.86	2.61	3.49	7.08···7.33	10.27	45.81	63.52	163.69
3c	0.92	2.58	3.70	7.16···7.36	10.13	45.41	61.17	171.74

Within each group of compounds, the ^{1}H-NMR signal of the methyl protons and the ^{13}C-NMR signal of the phenyl carbon atom bound to the metal center shift to lower fields on going from the zinc to the mercury species. In the spectra of the cadmium and mercury derivatives **1b**, **2c**, and **3c**, ^{1}H- and ^{13}C-metal coupling was observed. The coupling constants of **1b** [$^3J(^1H,^{111/113}Cd)$ = 26, 19 Hz and $^{2,3}J(^{13}C,^{113}Cd)$ = 20, 12 Hz] are in the expected range[27][28]. The coupling constants of **3c** [$^{1,2,3}J(^{13}C,^{199}Hg)$ = 714, 22, 42 Hz] demonstrate that the usual relationship $^1J > {}^3J > {}^2J$ is also valid for the spin pair ^{13}C,^{199}Hg[29], while the absolute values ^2J and ^3J of **3c** and ^3J of **2c** (40.5 Hz) are somewhat smaller than those given in the literature[26][27]. The appearance of one NMR signal for both of the amino functions of each ligand in **2a**−**2c** and **3a**−**3c** indicates a dynamic behaviour of these complexes in solution. Selected NMR data of the arylamino compounds are summarized in Table 1.

The mass spectra of **1a**, **1b**, **1c**, **2c**, **3a**, and **3c** show the peak for the corresponding molecular ion, whereas the spectra of the zinc and cadmium species **2a** and **3b** show only ligand fragments.

Crystallization of **1c** from Et_2O/*n*-pentane afforded crystals suitable for X-ray structure determination. The molecular structure of **1c** is depicted in Figure 1a, and selected bond lengths and bond angles are listed in Table 2. The structure may be compared with that of the corresponding methylamine derivatives $M(C_6H_4CH_2NMe_2\text{-}2)_2$ (M = Cd[19] and Hg[17]). The angle C1−M−C1′ becomes larger with increasing radius of the central metal. This angle is 174° in $Cd(C_6H_4CH_2NMe_2)_2$, exactly 180° in $Hg(C_6H_4CH_2NMe_2)_2$ and nearly 180° in **1c** [176.7(1)°]. The same trend is observed for the angle N−M−N′ {$M(C_6H_4CH_2NMe_2)_2$: M = Cd (116.12°), Hg (180°); **1c** [151.2(2)°]}. Accordingly, the geometric arrangement of the ligands around the metal atom changes from a distorted trigonal bipyramid with one vacancy in the equatorial plane for $Cd(C_6H_4CH_2NMe_2)_2$, to a square planar system in **1c** and $Hg(C_6H_4CH_2NMe_2)_2$. The bond distance Hg−C1 in **1c** [206.9(4) pm] is similar to that in $Hg(C_6H_4CH_2NMe_2)_2$ (210 pm) and other mercury diaryl compounds[20][21][30][31]. The Hg−N distance [294.2(3) pm] is only slightly longer than that in the *N*-methyl derivative (289 pm), but it is still in the same range as other comparable Hg−N interactions[20][21][32]. The Hg···Hg distance [349.3(3) pm] in **1c** is remarkably short at just over twice the van der Waals radius of mercury (173 pm[32]). Figure 1b shows that two molecules of **1c** are situated very close to one another, resulting in a slight bend of the phenyl groups out of the phenylmercury plane away from the Hg···Hg axis. One of the two ethyl substituents at each nitrogen atom avoids close contact by being situated in the same direction, whereas the second ethyl group remains in the plane. A similar effect

Figure 1a. ORTEP plot of the molecular structure of **1c**

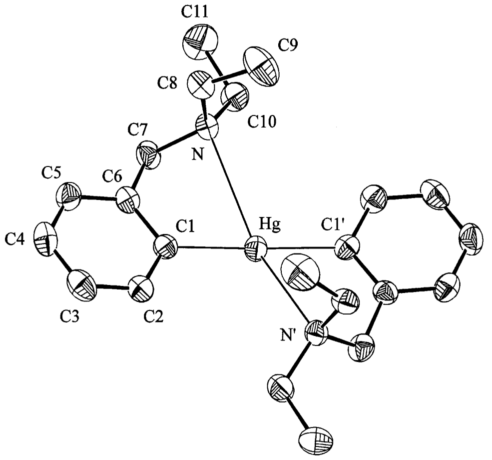


Figure 1b. PLUTON plot of two molecules of **1c** in the crystal

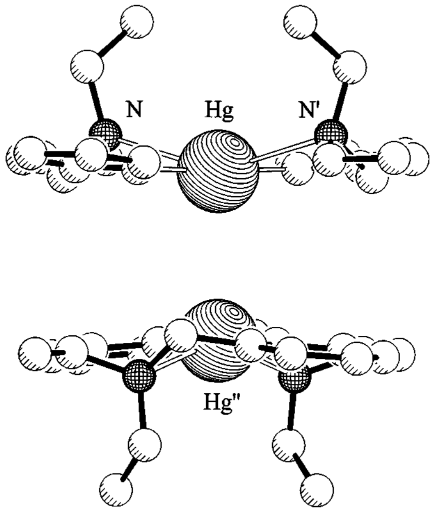


Table 2. Selected bond lengths [pm] and angles [°] of **1c**. E.s.d.s are given in parentheses

atoms	bond lenghts	atoms	bond angles
Hg···Hg''	349.3(3)	N−Hg−N'	151.2(2)
Hg−N	294.2(3)	C1−Hg−C1'	176.7(1)
Hg−C1	206.9(4)	N−Hg−C1	71.3(1)
C1−C2	139.8(5)	C2−C1−Hg	121.5(3)
C1−C6	140.4(5)	C6−C1−Hg	121.2(3)

Symmetry transformations used to generate equivalent atoms: ': − *x*, 1/2 − *y*, *z*. − '': 1/4 − *y*, 1/4 + *x*, 5/4 − *z*.

was observed in the analogous compound $Cd(C_6H_4CH_2NMe_2)_2$ with a Cd···Cd distance of 317.6 pm and this is probably caused by weak crystal packing forces[19]. The arrangement of the molecules in terms of the metal···metal axis differs: it is staggered for **1c** with an angle of 90° and eclipsed for the cadmium derivative. Surprisingly, this phenomenon of crystal packing with short metal···metal contacts was not detected in $Hg(C_6H_4CH_2NMe_2)_2$[17].

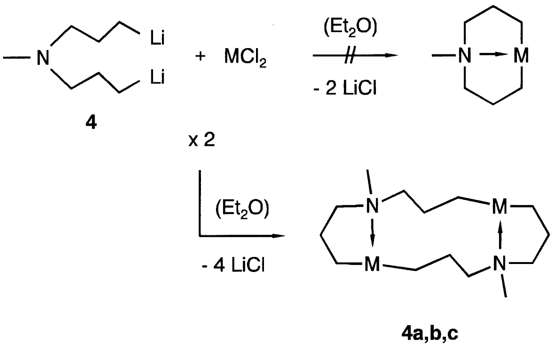
Unfortunately, it was not possible to obtain crystals suitable for X-ray investigations of **2a**, **2c**, **3a**, **3b**, and **3c** in which the appropriate metal is bonded to tridentate amino ligands. However, we also solved the crystal and molecular structure of the starting material $LiC_6H_3(CH_2NEt_2)_2$-2,6 (**3**)[33] which has recently been published by Hey-Hawkins et al.[34].

2. Intramolecularly Stabilized Alkylamino Compounds

We used tridentate bis(3-lithiopropyl)methylamine, $(LiCH_2CH_2CH_2)_2NMe$[35] (**4**), and bidentate 3-(*N*-piperidino)propyllithium, $LiCH_2CH_2CH_2NC_5H_{10}$[36] (**5**), for the synthesis of compounds **4a** to **4c**, and **5a** to **5c**.

The 5,13-diaza-5,13-dimethyl-1,9-dimetallacyclohexadecanes **4a−c** were prepared by treating equimolar amounts of MCl_2 (M = Zn, Cd, Hg) with $(LiCH_2CH_2CH_2)_2NMe$ in Et_2O at ambient temperatures (Scheme 2). The colorless and moisture sensitive compounds were isolated with yields of 75% for the Zn compound **4a** and 72% for the Hg derivative **4c**. The yield of the Cd species **4b** was only 49% due to decomposition during the reaction and precipitation of metallic cadmium. As indicated by the mass spectra of **4b** and **4c**, and as proved by X-ray structural analysis of **4a** and **4c**, the compounds **4a** to **4c** form dimers consisting of sixteen-membered rings.

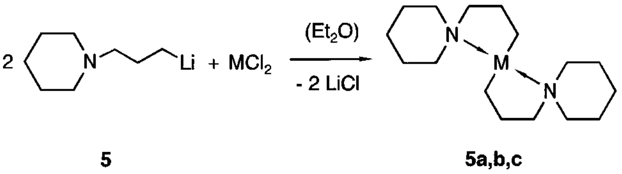
Scheme 2



M = Zn **4a**, Cd **4b**, Hg **4c**

Treating MCl_2 (M = Zn, Cd, Hg) with a twofold amount of $Li(CH_2)_3NC_5H_{10}$ in Et_2O produced the bis(3-*N*-piperidino)propylmetal compounds **5a** to **5c** (Scheme 3) with yields of 76%, 65%, and 58%, respectively. The reaction with $HgCl_2$ was accompanied by the elimination of some metallic mercury. **5a** and **5b** are colorless crystalline solids which melt at 80°C or decompose above 90°C, respectively. **5b** changes color to yellow on exposure to light. **5c** forms colorless prisms at −20°C, but is a liquid at room temperature. The mass spectra of the three compounds show the molecular ion peak, but only with very low intensity. The first step in the fragmentation of **5b** and **5c** is the separation of the ligand as a whole, a process which could not be observed for **5a**.

Scheme 3



M = Zn **5a**, Cd **5b**, Hg **5c**

Table 3. ^1H- and ^{13}C-NMR data of the alkylamino compounds **4a−5c**

no.	^1H NMR δ [ppm] MC*H*$_2$	C*H*$_2$	C*H*$_2$N	NC*H*$_3$	^{13}C NMR δ [ppm] M*C*H$_2$	*C*H$_2$	*C*H$_2$N	N*C*H$_3$
4a	0.32[a]	1.85[a]	2.23[a]	1.86[a]	8.46	25.87	61.17	41.87
4b	0.67	2.01	2.25	1.89	12.14	32.56	61.89	41.93
4c	0.99	2.06	2.25	1.91	27.58	37.56	62.20	41.95
5a	0.48	1.29	2.19	–	8.22	24.82	64.06	–
5b	0.59	1.31	2.14...19	–	13.29	26.31	64.30	–
5c	1.08	1.34	2.21	–	25.08	36.72	63.36	–

[a] *T* = 65°C.

Table 4. Selected bond lengths [pm] and angles [°] of **4a** and **4c**. E.s.d.s are given in parentheses

atoms	bond lengths		atoms	bond angles	
	4a (M = Zn) [a]	**4c** (M = Hg) [b]		**4a** (M = Zn) [a]	**4c** (M = Hg) [b]
M−C1	197.9(3)	209(2)	C1−M−C7	156.38(13)	176.7(5)
M−C7	198.3(3)	209(2)	C1−M−N	87.38(11)	76.3(6)
M−N	221.6(2)	277.4(11)	C7−M−N	112.51(11)	102.7(5)
C1−C2	152.9(4)	156(2)	C4−N−M	103.8(2)	102.4(7)
C2−C3	152.1(4)	148(2)	C5−N−M	118.7(2)	120.6(8)
C5−C6′	152.2(4)	149(2)	C3−N−M	102.9(2)	97.6(7)
C6′−C7′	152.7(4)	156(2)	C2−C1−M	105.4(2)	110.1(11)

Symmetry transformations used to generate equivalent atoms: [a] ′: $-x + 1, -y + 2, -z + 2$. – [b] ′: $-x + 1, -y + 1, -z$.

Figure 2. ORTEP plot of the molecular structure of **4a**

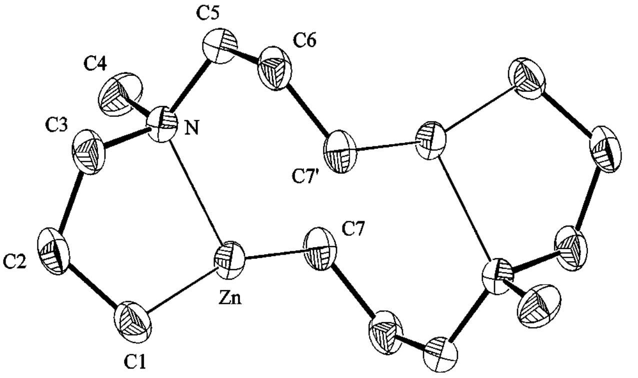
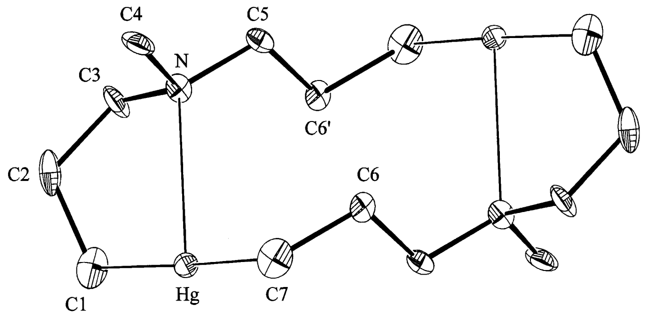


Figure 3. ORTEP plot of the molecular structure of **4c**



In a similar way to other homoleptic dialkyl complexes of the group 12 elements[13][37], comparison of the ^{1}H- and ^{13}C-NMR spectra of the alkylamino compounds shows a shift in the signals due to the metal-bonded CH_2 groups to lower fields on going from the zinc to the appropriate mercury derivative (Table 3).The NMR spectra of **4a, 4b** and **4c** show only one signal for the two different methylene groups bonded to the metal centers indicating a dynamic behaviour in solution. X-ray structure determinations performed on the metallacyclohexadecanes **4a** and **4c** (suitable crystals were obtained from *n*-pentane) prove the dimeric nature of the molecules in the solid state (Figures 2 and 3, Table 4). Each of the two metal atoms is coordinated to two carbon atoms belonging to different ligand molecules and one nitrogen atom. The sum of the angles C1−M−C7, C1−M−N, and C7−M−N is 356° for **4a** and **4c**, and this indicates that the four atoms essentially lie in a plane with a

Figure 4. ORTEP plot of the molecular structure of **5a**

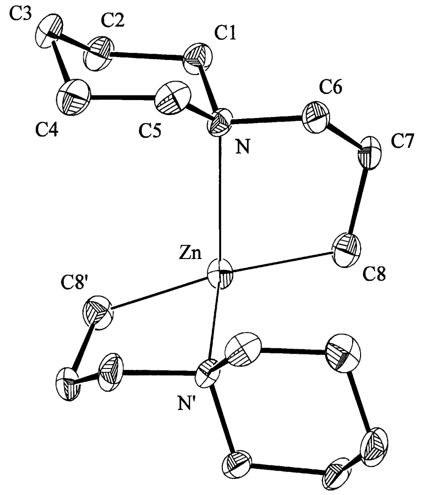
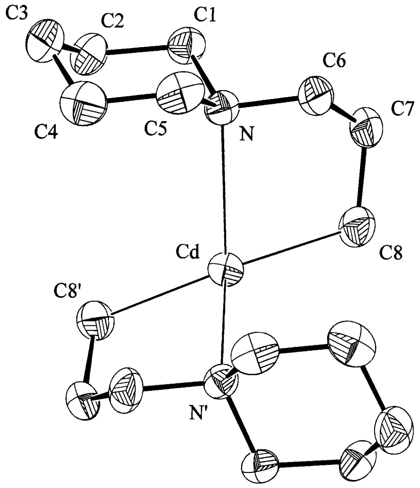


Table 5. Selected bond lengths [pm] and angles [°] of **5a** and **5b**. E.s.d.s are given in parentheses

atoms	bond lengths		atoms	bond angles	
	5a (M = Zn)	**5b** (M = Cd)		**5a** (M = Zn)	**5b** (M = Cd)
M−C8	199.2(3)	216.4(2)	C8−M−C8′	155.5(2)	166.2(2)
M−N	240.4(2)	264.2(2)	C8−M−N′	110.04(11)	109.62(8)
N−C5	146.9(4)	146.7(3)	C8−M−N	84.75(11)	78.84(8)
N−C1	147.2(4)	146.6(2)	N−M−N′	107.47(12)	107.42(7)
C3−C4	151.5(5)	151.1(4)	C1−N−M	110.0(2)	110.03(12)
C4−C5	151.9(5)	151.0(4)	C5−N−M	121.8(2)	119.29(14)
C6−C7	151.1(5)	151.7(4)	C6−N−M	96.1(2)	96.90(12)
			C7−C8−M	110.2(2)	110.7(2)

Symmetry transformation used to generate equivalent atoms: ′: $-x, y, -z + 1/2$.

Figure 5. PLUTON plot of the molecular structure of **5b**



more or less T-shaped ligand arrangement around the metal atoms. Thus, the linear arrangement of the ligands usually found in dialkylzinc and -mercury compounds is not changed to a significant extent by the additional coordination of the nitrogen atom, indicating only a weak interaction [C1−Zn−C7 156.38(13)°; C1−Hg−C7 176.7(5)°]. This agrees with the relatively long M−N distances [Zn−N 221.6(2) pm; Hg−N 277.4(11) pm]. The M−C1 distances [Zn−C1 197.9(3) pm; Hg−C1 209(2) pm] are in the normal range for comparable complexes[9][11][12][15][31][38][39]. The triple coordination of the metal atoms is extremely unusual for group-12 elements.

The molecular structures of **5a** and **5b** (crystals suitable for X-ray structural analysis were obtained by crystallization from *n*-pentane) show the metal atom to be tetracoordinated by the binding methylene carbon and the nitrogen atom of each of the two ligands (Figures 4 and 5, Table 5). The intramolecular stabilization of the metal center by the nitrogen atom seems to be as weak in **5a** and **5b** as it was in the case of the metallacyclohexadecanes **4a** and **4c** because the distances Zn−N [240.4(2) pm] and Cd−N [264.2(2) pm] are also quite long. Furthermore, as in **4a** and **4c** and also in the comparable tetracoordinated $Zn(CH_2CH_2CH_2NMe_2)_2$[15], the C8−M−C8′ angle is closer to 180° [**5a** Zn: 155.5(2)°; **5b** Cd: 166.2(2)°] than to a tetrahedral angle. Similar long M−N distances and large C8−M−C8′angles are known in some intermolecular amine-stabilized dialkylmetal species, e.g. $[M(CH_2CMe_3)_2\cdot tmeda]$ (M = Zn: 241.1 pm, 148°; M = Cd: 264.2 pm, 157°)[11]. In a similar way to $Cd(C_6H_4CH_2NMe_2)_2$[19], comparable donor stabilized cadmium[11][40] and zinc complexes $Zn(CH_2CH_2CH_2X)_2$ (X = NMe_2, PPh_2, OMe, SMe)[15][38][41], the coordination sphere around the metal center is more accurately described as a distorted trigonal bipyramid with one vacancy in the equatorial plane than as a tetrahedron. The piperidyl rings in **5a** and **5b** have a chair conformation turning away from the metal center.

Conclusion

Aryl- and alkylamino metal compounds of the group-12 elements have been synthesized and the molecular structure of some representative examples investigated. In comparison to the linear structure of pure diaryl or dialkyl compounds of group-12 elements, the intramolecular metal−nitrogen coordination through chelate ring formation has only a weak influence on the geometry of the molecules, a situation which is similar to that in intermolecularly *N*-stabilized diorgano metal derivatives of these elements.

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Experimental Section

1. General: The starting anhydrous metal chlorides (Merck) were dried under vacuum and stored under an argon atmosphere. The aryl- and alkylamine ligand systems and their lithium compounds (**1** to **5**) were prepared using known procedures. All reactions yielding organometallic species were performed using standard Schlenk techniques under dry argon and in dry solvents distilled from sodium/benzophenone. − Melting points and thermal decomposition temperatures were determined in sealed capillaries under argon with an HWG-SG 2000, HWS Mainz, and are uncorrected. − NMR (Bruker ARX 200): ^1H NMR (200 MHz): ext. TMS; $^{13}C\{^1H\}$ NMR (50.26 MHz): ext. TMS; ^{113}Cd NMR (400 MHz): ext. $Cd(CH_3)_2$. − MS (Varian MAT 311 A) analyses were carried out using electron impact ionisation with 70 eV. − Elemental analyses: Perkin-Elmer Series II CHNS/O analyser 2400.

2. Crystal Structure Determinations: Crystals of **1c**, **4a**, **4c**, **5a**, and **5b** were mounted on glass fibers and transferred to an Enraf-Nonius CAD4 four circle diffractometer (Mo-K_α radiation) equipped with a low temperature device. Data for all compounds were collected with ω-2θ scans. Intensity data were monitored after every 200 reflections through the measurement of three standard reflections. Raw data were corrected for Lorentz, polarization, and for absorption effects (DIFABS)[42]. The structures were solved using Direct Methods (SHELXS-86)[43] and the refinement of the molecules was performed using difference-Fourier methods (SHELXL-93)[44]. The older program, SHELX-76[45], was also used to prepare the data for DIFABS. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions with d_{CH} = 98 pm and U_{iso} = 8 pm^2. Molecular plots were obtained using the programs ZORTEP[46] and PLUTON[47]. Further details on crystals, data collection, and refinement are listed in Table 6.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary communication no. CCDC-100487. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int code +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk).

3. Synthesis of the Complexes

Bis(2-diethylaminomethylphenyl)zinc (**1a**): 2-Diethylaminomethylphenyllithium (**1**) (4.06 g, 24.0 mmol) was dissolved in Et_2O (100 ml) and a solution of $ZnCl_2$ (1.64 g, 12.0 mmol) in Et_2O (40 ml) was added dropwise. The mixture became pale orange, was warmed up slightly, and a white precipitate formed. After stirring for 14 h at room temperature the Et_2O was removed in vacuo. The remain-

Table 6. Crystal data and details of the structure analysis for compounds **1c**, **4a**, **4c**, **5a**, and **5b**

	1c	**4a**	**4c**	**5a**	**5b**
Formula	$C_{22}H_{32}HgN_2$	$C_{14}H_{30}N_2Zn_2$	$C_{14}H_{30}Hg_2N_2$	$C_{16}H_{32}N_2Zn$	$C_{16}H_{32}CdN_2$
Mol. mass [g mol^{-1}]	525.10	357.14	627.58	317.81	364.84
Temperature [K]	160(2)	199(2)	178(2)	165(2)	199(2)
Wavelength [Å]	0.71069	0.71069	0.71069	0.71069	0.71069
Crystal system	tetragonal	triclinic	triclinic	monoclinic	monoclinic
Space group	$I\,4_1/a$ (No. 88)	$P\,-1$ (No.2)	$P\,-1$ (No.2)	$C\,2/c$ (No.15)	$C\,2/c$ (No.15)
a [Å]	19.956(3)	7.0440(9)	7.164(2)	17.368(3)	18.089(5)
b [Å]	19.956(3)	7.1367(14)	7.879(5)	6.074(2)	6.1133(10)
c [Å]	10.566(3)	8.511(2)	8.052(2)	15.388(3)	15.399(4)
α [°]	90	99.08(2)	89.38(4)	90	90
β [°]	90	91.975(14)	75.90(2)	92.27(2)	90.87(2)
γ [°]	90	106.760(14)	73.24(4)	90	90
V [Å^3]	4208(2)	403.11(12)	421.2(3)	1622.1(8)	1702.7(7)
Z	8	1	1	4	4
$D_{calcd.}$ [g cm^{-3}]	1.66	1.471	2.474	1.301	1.423
μ(Mo-$K_α$) [mm^{-1}]	14.066	2.962	18.191	1.505	1.274
F(000)	2624	188	288	688	760
Crystal size [mm^3]	0.48×0.36×0.24	0.27×0.15×0.12	1.00×0.65×0.40	0.50×0.25×0.20	0.70×0.45×0.25
θ range for data collection [°]	1, 24	2.43, 25.02	2.61, 25.90	2.35, 24.93	2.25, 24.97
Index ranges	$0 \le h \le 22$ $0 \le k \le 22$ $0 \le l \le 12$	$0 \le h \le 8$ $-8 \le k \le 8$ $-10 \le l \le 10$	$-8 \le h \le 8$ $-9 \le k \le 9$ $0 \le l \le 9$	$0 \le h \le 20$ $-18 \le l \le 18$ $0 \le k \le 7$	$-21 \le h \le 21$ $0 \le l \le 18$ $0 \le k \le 7$
Refl. collected	2078	1547	1748	1462	1569
Independent refl.	1533 (R_{int} = 0.02)	1420 (R_{int} = 0.0120)	1587 (R_{int} = 0.2613)	1411 (R_{int} = 0.1057)	1503 (R_{int} = 0.0289)
Absorption corr.	DIFABS	None	DIFABS	None	ψ-scan 1.00 and 0.91
Refinement method	Full-Matrix-Least-Squares on F	Full-Matrix-Least-Squares on F^2	Full-Matrix-Least-Squares on F^2	Full-Matrix-Least-Squares on F^2	Full-Matrix-Least-Squares on F^2
Data / restraints / parameters	1533 / 0 /122	1420 / 0 / 83	1484 / 0 / 83	1408 / 0 / 87	1499 / 0 / 87
Goodness-of-fit on F^2	−	1.120	1.089	1.073	1.053
Final R indices [I>2σ(I)]	$R1$ = 0.0204 $wR1$ = 0.0142	$R1$ = 0.0278 $wR2$ = 0.0724	$R1$ = 0.0570 $wR2$ = 0.1485	$R1$ = 0.0469 $wR2$ = 0.1212	$R1$ = 0.0192 $wR2$ = 0.0545
R indices (all data)	−	$R1$ = 0.0301 $wR2$ = 0.0740	$R1$ = 0.0725 $wR2$ = 0.2115	$R1$ = 0.0514 $wR2$ = 0.1293	$R1$ = 0.0205 $wR2$ = 0.0650
Largest diff. peak and hole; min./max. [eÅ^{-3}]	0.39 / −0.38	0.560 / −0.834	30.227 / −40.557	10.504 / −10.212	0.496 / −0.345

ing pale yellow solid was suspended in *n*-hexane. The reaction mixture was filtered through a fine glass frit and the filtrate volume was reduced to about 50 ml. Storing at −20°C yielded 3.98 g (85%) of colorless crystalline **1a**, m.p. 40°C. − ^{1}H NMR (C_6D_6): δ = 0.64 (t, ^3J = 7.2 Hz, CH_3), 2.52 (q, ^3J = 7.2 Hz, CH_3CH_2), 3.52 (s, CH_2C_{aryl}), 7.10-8.02 (m, $C_{aryl}H$). − ^{13}C NMR (C_6D_6): δ = 8.75 (CH_3), 45.25 (CH_3CH_2), 61.79 (CH_2C_{aryl}), 125.1 (*C*-3), 126.16 (*C*-5), 126.22 (*C*-4), 139.38 (*C*-6), 146.73 (*C*-2), 157.75 (*C*-1). − MS; *m*/*z* (%): 388 (5) [M(^{64}Zn)$^+$], 316 (8) [M$^+$ − NEt_2], 226 (8) [$ZnC_6H_4CH_2NEt_2{}^+$], 162 (89) [$C_6H_4CH_2NEt_2{}^+$], 148 (58) [$C_6H_4CH_2NEtMe^+$], 91 (100) [$C_7H_7{}^+$], and others. − $C_{22}H_{32}N_2Zn$ (389.90): calcd. C 67.77, H 8.27, N 7.18; found C 67.60, H 8.06, N 7.41.

Bis(2-diethylaminomethylphenyl)cadmium (**1b**): In a similar way to **1a**, $CdCl_2$ (2.93 g, 16 mmol) and **1** (5.41 g, 32 mmol) yielded 4.12 g (59%) of colorless crystalline **1b**, m.p. 62°C. Although the mixture was protected from light during the reaction, the formation of cadmium metal was observed. − ^{1}H NMR (C_6D_6): δ = 0.77 (t, ^3J = 7.2 Hz, CH_3), 2.43 (q, ^3J = 7.2 Hz, CH_3CH_2), 3.44 (s, CH_2C_{aryl}), 7.09-7.40 (m, $C_{aryl}H$), 7.94 [dd, sat.,^3J = 6.6 Hz, ^4J = 1.3 Hz, ^3J(^{1}H,$^{111/113}$Cd) = 26/19 Hz, C-6*H*]. − ^{13}C NMR (C_6D_6): δ = 10.33 (CH_3), 45.90 (CH_3CH_2), 62.07 [sat., ^3J(^{13}C,^{113}Cd) = 12 Hz, CH_2C_{aryl}], 126.31 (*C*-3), 126.40 (*C*-5), 126.91 (*C*-4), 140.30 [sat.,^2J(^{13}C,^{113}Cd) = 20 Hz, *C*-6], 147.21 (*C*-2), 160.72 (*C*-1). − ^{113}Cd NMR (C_6D_6): δ = −163.10. − MS; *m*/*z* (%): 439 (3) [M(^{114}Cd)$^+$], 365 (7) [M$^+$ − NEt_2], 274 (8) [$CdC_6H_4NEt_2{}^+$], 114 (5) [Cd$^+$], and others, as for **1a**. − $C_{22}H_{32}CdN_2$ (436.91): calcd. C 60.48, H 7.38, N 6.41; found C 60.89, H 7.59, N 7.12.

Bis(2-diethylaminomethylphenyl)mercury (**1c**): In a similar way to **1a**, $HgCl_2$ (2.71 g, 10 mmol) and **1** (3.38 g, 20 mmol) yielded 4.37 g (83%) of colorless crystalline **1c**, m.p. 74°C. − ^{1}H NMR (C_6D_6): δ = 1.09 (t, CH_3), 2.69 (q, CH_3CH_2), 3.68 (s, CH_2C_{aryl}), 7.24−7.97 (m, $C_{aryl}H$). − ^{13}C NMR (C_6D_6): δ = 11.21 (CH_3), 46.39 (CH_3CH_2), 61.60 (sat., CH_2C_{aryl}), 126.79 (*C*-3), 127.09 (*C*-5), 129.19 (*C*-4), 138.86 (sat., *C*-6), 148.03 (sat., *C*-2), 171.10 (*C*-1). − MS; *m*/*z* (%): 526 (6) [M(^{202}Hg)$^+$], 497 (5) [M$^+$ − Et], 453 (2) [M$^+$ − NEt_2], 202 (<1) [Hg$^+$], and others as for **1a**. − $C_{22}H_{32}HgN_2$ (525.10): calcd. C 50.32, H 6.14, N 5.33; found C 50.80, H 6.38, N 5.35.

Bis[2,6-bis(dimethylaminomethyl)phenyl]zinc (**2a**): A solution of 2,6-bis(dimethylaminomethyl)phenyllithium (**2**) (0.23 g, 1.16 mmol) in Et_2O (30 ml) was mixed in portions with $ZnCl_2$ (0.079 g, 0.58 mmol). The mixture was stirred for 12 h and during this time a white precipitate formed. The suspension was chilled and filtered through a fine glass frit. The pale yellow filtrate was stored at −20°C and gave 0.19 g (73%) of colorless crystalline **2a**, m.p. 94°C. − ^{1}H NMR ([D_8]THF): δ = 2.16 (s, CH_3), 3.36 (s, CH_2), 6.96−7.27 (m, $C_{aryl}H$). − ^{13}C NMR ([D_8]THF): δ = 45.60 (CH_3), 65.00 (CH_2), 128.10 (*C*-3,5), 130.00 (*C*-4), 140.30 (*C*-2,6), 159.10 (*C*-1). − MS; *m*/*z* (%): 192 (33) [$C_6H_4(CH_2NMe_2)_2{}^+$], 149 (100) [$C_6H_4(CH_3)CH_2NMe_2{}^+$], and others. − $C_{24}H_{38}N_4Zn$ (447.99): calcd. C 64.35, H 8.55, N 12.51; found C 64.19, H 8.44, N 12.62.

Bis[2,6-bis(dimethylaminomethyl)phenyl]mercury (**2c**): In a similar way to **2a**, $HgCl_2$ (0.25 g, 0.93 mmol) and **2** (0.37 g, 1.87 mmol) yielded 0.31 g (57%) of colorless fine crystalline **2c**, m.p. 139°C. The mixture was protected from light; although during the reaction, the formation of mercury metal was observed. − ^{1}H NMR ([D$_8$]THF): δ = 2.19 (s, CH_3), 3.41 (CH_2), 7.02-7.18 (m, C$_{aryl}H$). − ^{13}C NMR ([D$_8$]THF): δ = 48.25 (CH$_3$), 71.58 [sat., $^{3}J(^{13}C,^{199}Hg)$ = 40.5 Hz, CH$_2$], 129.20 (C-3,5), 130.60 (C-4), 150.80 (sat., C-2,6), 176.00 (sat., C-1). − MS; m/z (%): 584 (<1) [M(^{202}Hg)$^+$], 202 (1) [Hg$^+$], and others as for **2a**. − $C_{24}H_{38}HgN_4$ (583.19): calcd. C 49.43, H 6.57, N 9.61; found C 49.21, H 6.33, N 9.48.

Bis[2,6-bis(diethylaminomethyl)phenyl]zinc (**3a**): A solution of **3** (1.07 g, 4.2 mmol) in Et_2O (40 ml) was mixed in portions with $ZnCl_2$ (0.29 g, 2.1 mmol). The reaction mixture warmed up slightly. After stirring for 16 h at room temperature the solvent was removed in vacuo. The remaining solid was suspended in *n*-pentane. The mixture was filtered through a fine glass frit, and the filtrate volume was reduced to about 20 ml. Storing at −20°C yielded 0.82 g (70%) of colorless fine crystalline **3a**, m.p. 102°C. − ^{1}H NMR (C_6D_6): δ = 0.85 (t, ^{3}J = 7.1 Hz, CH_3), 2.63 (q, ^{3}J = 7.1 Hz, CH$_3$CH_2), 3.74 (s, CH_2C$_{aryl}$), 7.29-7.43 (m, CH_{aryl}). − ^{13}C NMR (C_6D_6): δ = 10.35 (CH$_3$), 46.09 (CH$_3$$CH_2$), 63.42 ($CH_2C_{aryl}$), 124.85 ($C$-3,5), 126.68 ($C$-4), 147.54 ($C$-2,6), 158.44 ($C$-1). − MS; m/z (%): 558 (15) [M(^{64}Zn)$^+$], 529 (3) [M$^+$ − C_2H_5], 310 (17) [$ZnC_6H_3(CH_2NEt_2)_2^+$], 247 (100) [$C_6H_3(CH_2NEt_2)_2^+$], and others. − $C_{32}H_{54}N_4Zn$ (560.20): calcd. C 68.61, H 9.72, N 10.00; found C 68.40, H 9.69, N 10.11.

Bis[2,6-bis(diethylaminomethyl)phenyl]cadmium (**3b**): In a similar way to **3a**, $CdCl_2$ (0.21 g, 1.14 mmol) was mixed with **3** (0.58 g, 2.28 mmol) and yielded 0.43 g (62%) of colorless crystals of **3b**, m.p. 137°C. Although the mixture was protected from light during the reaction, the formation of cadmium metal was observed. − ^{1}H NMR (C_6D_6): δ = 0.86 (t, ^{3}J = 7.2 Hz, CH_3), 2.61 (q, ^{3}J = 7.1 Hz, CH$_3$CH_2), 3.49 (s, CH_2C$_{aryl}$), 7.08-7.33 (m, C$_{aryl}H$). − ^{13}C NMR (C_6D_6): δ = 10.27 (CH$_3$), 45.81 (CH$_3$$CH_2$), 63.52 (sat., CH$_2C_{aryl}$), 124.51 (C-3,5), 126.01 (C-4), 147.54 (sat., C-2,6), 163.69 (C-1). − ^{113}Cd NMR (C_6D_6): δ = −182.58. − MS; m/z (%): 246 (2) [$C_6H_3(CH_2NEt_2)_2^+$ − H], and others as for **3a**. − $C_{32}H_{54}CdN_4$ (607.21): calcd. C 63.30, H 8.96, N 9.23; found C 63.08, H 8.94, N 9.51.

Bis[2,6-bis(diethylaminomethyl)phenyl]mercury (**3c**): In a similar way to **3a**, $HgCl_2$ (0.86 g, 3.17 mmol) and **3** (1.61 g, 6.33 mmol) yielded 1.41 g (64%) of colorless crystals of **3c** which melt below room temperature. − ^{1}H NMR (C_6D_6): δ = 0.92 (t, ^{3}J = 7.1 Hz, CH_3), 2.58 (q, ^{3}J = 7.1 Hz, CH$_3$CH_2), 3.70 (s, CH_2C$_{aryl}$), 7.16 (t, ^{3}J = 7.4 Hz, C-3,5H), 7.36 (d, ^{3}J = 7.2 Hz, C-4H). − ^{13}C NMR (C_6D_6): δ = 10.13 (CH$_3$), 45.41 (CH$_3$$CH_2$), 61.17 [sat., $^{3}J(^{13}C,^{199}Hg)$ = 42 Hz, CH$_2$C$_{aryl}$], 125.57 (C-3,5), 126.56 (C-4), 146.60 [sat., $^{2}J(^{13}C,^{199}Hg)$ = 22 Hz, C-2,6], 171.74 [sat., $^{1}J(^{13}C,^{199}Hg)$ = 714 Hz, C-1]. − MS; m/z (%): 696 (<1) [M(^{202}Hg)$^+$], 623 (2) [M$^+$ − NEt$_2$], 247 (100) [$C_6H_3(CH_2NEt_2)_2^+$], 202 (1) [Hg$^+$], and others as for **3a**. − $C_{32}H_{54}HgN_4$ (695.40): calcd. C 55.27, H 7.83, N 8.06; found C 54.84, H 8.00, N 8.07.

(5,13-Diaza)-5,13-dimethyl-1,9-dizincacyclohexadecane (**4a**): **4** (2.04 g, 16.05 mmol) was dissolved in Et_2O (150 ml) and mixed in portions with $ZnCl_2$ (2.19 g, 16.05 mmol). The reaction mixture warmed up slightly and a white precipitate formed. After stirring at room temperature for 12 h the solvent was removed in vacuo. The remaining solid was suspended in *n*-pentane and filtered through a fine glass frit. The filtrate volume was reduced to about 50 ml. Storing at −20°C yielded 2.15 g (75%) of large colorless crystals of **4a**, m.p. 71°C. − ^{1}H NMR (C_6D_6, T = 338 K): δ = 0.32 (t, ^{3}J = 7.1 Hz, ZnCH_2), 1.85 (quint, ^{3}J = 6.9/6.6 Hz, CH_2), 1.86 (s, CH_3), 2.23 (t, ^{3}J = 6.4 Hz, CH_2N). − ^{13}C NMR (C_6D_6): δ = 8.46 (ZnCH$_2$), 25.87 (CH$_2$), 41.87 (CH$_3$), 61.17 (CH$_2$N). − MS; m/z (%): 177 (6) [1/2 M(^{64}Zn)$^+$], 149 (13) [1/2 M$^+$ − CH$_2$CH$_2$], 84 (100) [$C_5H_{10}N^+$], and others. − $C_{14}H_{30}N_2Zn_2$ (357.19): calcd. C 47.08, H 8.47, N 7.84; found C 46.93, H 8.42, N 7.89.

(5,13-Diaza)-5,13-dimethyl-1,9-dicadmacyclohexadecane (**4b**): In a similar way to **4a**, $CdCl_2$ (1.20 g, 6.53 mmol) and **4** (0.83 g, 6.53 mmol) yielded 0.72 g (49%) of colorless fine crystalline **4b**, m.p. 89°C. Although the mixture was protected from light during the reaction, the formation of cadmium metal was observed. − ^{1}H NMR (C_6D_6): δ = 0.67 (t, ^{3}J = 7.0 Hz, CdCH_2), 1.89 (s, CH_3), 2.01 (quint, ^{3}J = 6.9/6.6 Hz, CH_2), 2.25 (t, ^{3}J = 6.5 Hz, CH_2N). − ^{13}C NMR (C_6D_6): δ = 12.14 (CdCH$_2$), 32.56 (CH$_2$), 41.93 (CH$_3$), 61.89 (CH$_2$N). − MS; m/z (%): 454 (<1) [M(^{114}Cd)$^+$], 227 (3) [1/2 M(^{114}Cd)$^+$], 114 (3) [Cd$^+$], and others as for **4a**. − $C_{14}H_{30}Cd_2N_2$ (451.21): calcd. C 37.27, H 6.70, N 6.21; found C 37.01, H 6.58, N 6.34.

(5,13-Diaza)-5,13-dimethyl-1,9-dimercuracyclohexadecane (**4c**): In a similar way to **4a**, $HgCl_2$ (0.14 g, 0.51 mmol) and **4** (0.065 g, 0.51 mmol) yielded 0.23 g (72%) of colorless crystalline **4c**, m.p. 97°C. − ^{1}H NMR (C_6D_6): δ = 0.99 (t, ^{3}J = 6.9 Hz, HgCH_2), 1.91 (s, CH_3), 2.06 (quint, ^{3}J = 6.9/6.5 Hz, CH_2), 2.25 (t, ^{3}J = 6.5 Hz, CH_2N). − ^{13}C NMR (C_6D_6): δ = 27.58 (HgCH$_2$), 37.56 (CH$_2$), 41.95 (CH$_3$), 62.20 (CH$_2$N). − MS; m/z (%): 627 (<1) [M$^+$], 315 (<1) [1/2 M(^{202}Hg)$^+$], 202 (4) [Hg$^+$], and others as for **4a**. − $C_{14}H_{30}Hg_2N_2$ (627.59): calcd. C 26.79, H 4.82 N, 4.46; found C 26.68, H 4.80, N 4.73.

Bis[3-(N-piperidino)propyl]zinc (**5a**): $ZnCl_2$ (0.43g, 3.19 mmol) was added portionwise to a suspension of **5** (0.85g, 6.38 mmol) in Et_2O (50 ml). The cloudy reaction mixture was stirred at room temperature for 18 h. After removing the solvent and addition of *n*-pentane, the mixture was filtered through a fine glass frit. The pale yellow filtrate was concentrated to a volume of about 30 ml and yielded, after storing at −20°C, 0.77 g (76%) of colorless crystalline **5a**, m.p. 80°C. − ^{1}H NMR (C_6D_6): δ = 0.48 (t. ^{3}J = 7.1 Hz, ZnCH_2), 1.29 (m, ^{3}J = 5.5 Hz, ZnCH$_2$CH_2), 1.52 [quint, ^{3}J = 5.6 Hz, N(CH$_2$CH_2)$_2$CH$_2$], 2.01 [m, ^{3}J = 6.2 Hz, N(CH$_2$CH$_2$)$_2$CH_2], 2.19 (t, ^{3}J = 5.6 Hz, CH_2N), 2.27 [t, ^{3}J = 5.4 Hz, N(CH_2CH$_2$)$_2$CH$_2$]. − ^{13}C NMR (C_6D_6): δ = 8.22 (ZnCH$_2$), 24.82 [CH$_2$CH$_2$N(CH$_2$CH$_2$)$_2$CH$_2$], 25.37 [N(CH$_2$CH$_2$)$_2$$CH_2$], 55.05 [N($CH_2CH_2$)$_2CH_2$], 64.06 ($CH_2$N). − MS; m/z (%): 316 (<1) [M(^{64}Zn)$^+$], 127 (8) [$C_5H_{10}N(CH_2)_2CH_3^+$], 98 (100) [$C_5H_{10}NCH_2^+$], and others. − $C_{16}H_{32}N_2Zn$ (317.84): calcd. C 60.46, H 10.15, N 8.81; found C 60.37, H 9.97, N 9.24.

Bis[3-(N-piperidino)propyl]cadmium (**5b**): In a similar way to **5a**, $CdCl_2$ (0.805 g, 4.39 mmol) and **5** (1.17 g, 8.79 mmol) yielded 1.04 g (65%) of large colorless crystals of **5b**, m.p. > 90°C (dec.). − ^{1}H NMR (C_6D_6): δ = 0.59 (t, ^{3}J = 6.9 Hz, CdCH_2), 1.31 (m, ^{3}J = 5.1 Hz, CdCH$_2$CH_2), 1.56 [quint, ^{3}J = 5.6 Hz, N(CH$_2$CH_2)$_2$CH$_2$], 2.04 [m, N(CH$_2$CH$_2$)$_2$CH_2], 2.14-2.19 [m, CH_2N(CH_2CH$_2$)$_2$CH$_2$]. − ^{13}C NMR (C_6D_6): δ = 13.29 [sat., $^{1}J(^{13}C,^{111/113}Cd)$ = 307/294 Hz, CdCH$_2$], 24.94 [N(CH$_2$CH$_2$)$_2$$CH_2$], 25.88 [N(CH$_2$$CH_2$)$_2CH_2$], 26.31 [sat., $^{2}J(^{13}C,^{113}Cd)$ = 15.4 Hz, CdCH$_2$$CH_2$), 55.38 [N($CH_2CH_2$)$_2CH_2$], 64.30 [sat., $^{3}J(^{13}C,^{113}Cd)$ = 14.7 Hz, CH$_2$N]. − MS; m/z (%): 366 (<1) [M(^{114}Cd)$^+$], 240 (5) [$C_5H_{10}N(CH_2)_3Cd^+$], and others as for **5a**. − $C_{16}H_{32}CdN_2$ (364.85): calcd. C 52.67, H 8.84, N 7.68; found C 53.28, H 8.51, N 8.36.

Bis[3-(N-piperidino)propyl]mercury (**5c**): In a similar way to **5a**, $HgCl_2$ (1.09 g, 4.01 mmol) and **5** (1.07 g, 8.03 mmol) yielded 1.06

g (58%) of colorless crystalline **5c**, which melts below room temperature. Because of the formation of fine mercury metal in the mixture, the reaction time was shortened to 4 h. − ^{1}H NMR (C_6D_6): δ = 1.08 (t, ^3J = 6.7 Hz, $\mathrm{HgC}H_2$), 1.34 (m, br., $\mathrm{HgCH_2C}H_2$), 1.55 [quint, ^3J = 5.7 Hz, $\mathrm{N(CH_2C}H_2\mathrm{)_2CH_2}$], 2.12 [m, ^3J = 6.3 Hz, $\mathrm{N(CH_2CH_2)_2C}H_2$], 2.21 (t, ^3J = 6.0 Hz, $\mathrm{C}H_2\mathrm{N}$), 2.25 [m, br., $\mathrm{N(C}H_2\mathrm{CH_2)_2CH_2}$]. − ^{13}C NMR ($C_6D_6$): δ = 25.08 ($\mathrm{Hg}C\mathrm{H_2}$), 26.36 [$\mathrm{N(CH_2}C\mathrm{H_2)_2CH_2}$], 27.03 [$\mathrm{N(CH_2CH_2)_2}C\mathrm{H_2}$], 36.72 ($\mathrm{HgCH_2}C\mathrm{H_2}$), 55.16 [$\mathrm{N(}C\mathrm{H_2CH_2)_2CH_2}$], 63.36 ($\mathrm{N}C\mathrm{H_2}$). − MS; *m/z* (%): 454 (2) [M(^{202}Hg)$^+$], 327 (2) [$\mathrm{C_5H_{10}N(CH_2)_3Hg^+}$], 202 (20) [$\mathrm{Hg^+}$], and others as for **5a**. − $C_{16}H_{32}HgN_2$ (453.04): calcd. C 42.42, H 7.12, N 6.18; found C 42.17, H 7.05, N 6.38.

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