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Ligand Influences on Homoleptic Group 12 *m*-Terphenyl Complexes†

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Abstract:

Three *m*-terphenyl ligands $2,6\text{-}Ar_2C_6H_3^-$ [Ar = $2,6\text{-}Me_2C_6H_3$ (2,6-Xyl); $3,5\text{-}Me_2C_6H_3$ (3,5-Xyl); $2,3,4,5,6\text{-}Me_5C_6$ (Pmp)] have been used to stabilise three series of two-coordinate Group 12 diaryl complexes; $(2,6\text{-}Ar_2C_6H_3)_2M$ [M = Zn, Cd, Hg; Ar = 2,6-Xyl **1**-**3**; 3,5-Xyl **4**-**6**; Pmp **7**-**9**], where differing steric demands on the metal centres are imparted. These are the first homoleptic d-block complexes featuring any of these ligands. Complexes **1**-**9** have been characterised in solution and the solid state; the analysis of structural changes produced by differences in ligand properties is reported. In particular, complexes **4**-**6** show smaller C–M–C bond angles and contain secondary ligand interactions that are not seen in the analogous complexes **1**-**3** and **7**-**9**.

† Electronic supplementary information (ESI) available: Crystallographic data for complexes **1**-**9**, molecular structures and crystallographic data for iodides $2,6\text{-}Ar_2C_6H_3I$ (Ar = 2,6-Xyl, 3,5-Xyl, Pmp) and $[2,6\text{-}(3,5\text{-}Xyl)_2C_6H_3Li]_2$. CCDC-989599-989611 contain the supplementary data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1. Introduction

Since the first report of diethylzinc by Edward Frankland in 1848,[1] the investigation of the synthesis and reactivity of organogroup 12 complexes has become an important research area, driven by the use of these compounds in catalysis and materials chemistry. Examples of this include the key role which organozinc reagents play in a range of fundamental organic transformations,[2] copolymerisation reactions between carbon dioxide and epoxides to yield polycarbonate compounds,[3] alkali-metal mediated zincation reactions,[4] cadmium complexes as molecular precursors for photoluminescent quantum dot synthesis[5] and mercury compounds as ligand transmetallation reagents.[6]

The number of two-coordinate Group 12 organometallic complexes in the literature is relatively low, as solid state structures often contain secondary interactions which result in a metal coordination number of greater than two.[7,8] Due to this, more sterically demanding ligands have been utilised to stabilise lower coordination numbers, for example in the *m*-terphenyl complex $(2,6\text{-Mes}_2C_6H_3)_2Hg$ (Mes $= 2,4,6\text{-Me}_3C_6H_2$).[9] The use of sterically demanding *m*-terphenyl ligands in Group 12 chemistry has led to the synthesis and structural characterisation of the first series to feature homologous Group 12 M–M bonds $(2,6\text{-}Dipp_2C_6H_3)_2M_2$ (M = Zn, Cd, Hg; Dipp $= 2,6\text{-}^iPr_2C_6H_3)$, the hydride compounds $[(2,6\text{-}Dipp_2C_6H_3)MH]_n$ (M = Zn, Cd, n = 2; M = Hg, n = 1)[10,11] and $(\eta^5\text{-}C_5H_5)_2Zr(ZnC_6H_3\text{-}2,6\text{-}Trip_2)_2$ (Trip $= 2,4,6\text{-}^iPr_3C_6H_2$), which contains a Zn−M−Zn (M = transition metal) moiety.[12]

Our previous investigations have shown that changes in *m*-terphenyl ligand architectures can result in significant differences in structure, bonding and small molecule reactivity.[13-15] We are interested in deducing how subtle changes in the steric pocket offered by the *m*-terphenyl ligands can affect the coordination environment around the metal centre, with the eventual aim to tailor the ligand sterics towards the investigation of bonding and small molecule reactivity. To this end we report three series of two-coordinate Group 12 *bis*-terphenyls of the form $(2,6\text{-}Ar_2C_6H_3)_2M$ (M = Zn, Cd, Hg; Ar = 2,6-Xyl, 3,5-Xyl, Pmp), which represent the first series of

structurally authenticated homoleptic Group 12 *bis*-terphenyl complexes. Comparison of the crystal structures of these compounds as a function of flanking aryl group illustrates how the manipulation of the steric pocket provided by these ligands influences the structures of the complexes. The general structures of the ligands used in this investigation are shown in Fig. 1.
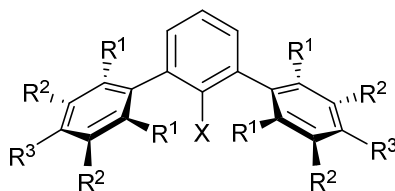

Fig. 1. The *m*-terphenyls used in this investigation: R^1 = Me, R^2 = R^3 = H (2,6-Xyl); R^1 = R^3 = H, R^2 = Me (3,5-Xyl); R^1 = R^2 = R^3 = Me (Pmp).

2. Results and Discussion

2.1 Synthesis and spectroscopic characterisation

The reaction between the three lithium complexes $[2,6-Ar_2C_6H_3Li]_2$ (Ar = 2,6-Xyl; 3,5-Xyl; Pmp)[16,17] and $ZnCl_2$, $CdCl_2$ or $HgBr_2$ in a mixture of toluene and THF at room temperature yields the diaryl complexes $[2,6-(2,6-Xyl)_2C_6H_3]_2M$ (M = Zn **1**, Cd **2**, Hg **3**), $[2,6-(3,5-Xyl)_2C_6H_3]_2M$ (M = Zn **4**, Cd **5**, Hg **6**) and $[2,6-Pmp_2C_6H_3]_2M$ (M = Zn **7**, Cd **8**, Hg **9**), respectively, in low to moderate yields according to Scheme 1, although it must be stressed that these are yields of crystalline materials and are not optimised. Crystallisation of **1-6** was achieved by slow cooling to −30 °C of hexane solutions of the complexes. Crystals of **7·0.5C₆H₁₄** and **9** were obtained by storage of saturated hexane solutions at room temperature, whereas slow cooling to 6 °C of a saturated hexane solution of **8** proved successful for crystal growth. Complexes **1-9** have been characterised by NMR spectroscopy, elemental analysis and mass spectrometry, and from the results of single crystal X-ray structure determinations.
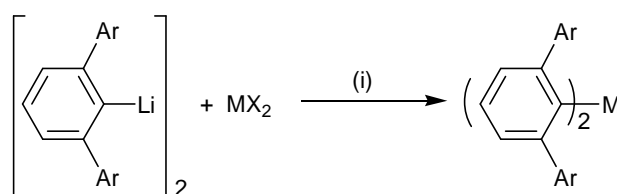
Scheme 1. Synthesis of diaryl complexes $(2,6\text{-}Ar_2C_6H_3)_2M$ (M = Zn, Cd, Hg; Ar = 2,6-Xyl **1-3**; 3,5-Xyl **4-6**; Pmp **7-9**). Reaction conditions: (i) Toluene/THF, −78 °C→RT, 16 h, −2 LiX.

The NMR spectroscopic measurements on **1-9** all indicate one ligand environment in solution. This is in contrast to the NMR spectra recorded for $(2,6\text{-}Naph_2C_6H_3)_2Zn$ and $(2,6\text{-}Naph_2C_6H_3)_2M(OEt_2)$ (M = Cd, Hg; Naph = $1\text{-}C_{10}H_7$), where *syn* and *anti* ligand conformations lead to multiple isomers of the complexes in solution.[14] The cadmium and mercury NMR spectra for **2**, **3**, **5**, **6**, **8** and **9** each shows a single peak ($^{113}Cd\{^1H\}$ range = 393.47 to 466.08 ppm and $^{199}Hg\{^1H\}$ range = −546.31 to −702.88 ppm) and are in the ranges observed for similar diaryl compounds.[14,18] In both the $^{113}Cd\{^1H\}$ and $^{199}Hg\{^1H\}$ NMR spectra of these complexes the chemical shifts follow a broad upfield trend with increasing the steric demands on the metals: $[2,6\text{-}(3,5\text{-}Xyl)_2C_6H_3]_2M > [2,6\text{-}(2,6\text{-}Xyl)_2C_6H_3]_2M > [2,6\text{-}Pmp_2C_6H_3]_2M$.

2.2 Crystallographic characterisation

Apart from the solid state structure of **7·0.5C_6H_14**, which crystallised with half a molecule of hexane in the asymmetric unit, there are no solvent molecules present within the crystal structures of these complexes. As a consequence of the steric demands of the *m*-terphenyl ligands, complexes **1-9** are monomeric in the solid state. The nearest M···M separations are $d(Zn···Zn)$ = 9.7 Å (for **4**), $d(Cd···Cd)$ = 10.5 Å (for **2**) and $d(Hg···Hg)$ = 9.9 Å (for **3**). The solid state structures of these compounds feature the metal centres bound to two terphenyl ligands and the metal centres are two-coordinate in all cases. This is in contrast to the Group 12 complexes of the $2,6\text{-}Naph_2C_6H_3^-$ ligand where the cadmium and mercury diaryls are three-coordinate $[(2,6\text{-}Naph_2C_6H_3)_2M(OEt_2)$ (M = Cd, Hg)],[14] and is presumably due to the overall lower steric demands of the 1-naphthyl moiety

compared to the 2,6-Xyl, 3,5-Xyl or Pmp substituents. Relevant bond lengths and angles for **1-3** can be found in Table 1, for **4-6** in Table 2 and for **7-9** in Table 3.

Table 1. Selected bond lengths (Å) and angles (°) for **1-3**.

	1 (M = Zn)	**2** (M = Cd)	**3** (M = Hg)
C(1)–M(1)	1.949(4)	2.115(5)	2.087(6)
C(23)–M(1)	1.944(4)	2.228(5)	2.101(5)
C(1)–M(1)–C(23)	178.7(2)	179.9(3)	177.1(2)
C(1)plane···C(23)plane	83.6(2)	84.2(3)	86.62(18)
C(1)plane···flanking aryl plane	88.4(2)	82.2(3)	83.34(16)
	80.73(19)	87.0(3)	83.65(16)
	83.0(2)	84.3(3)	83.8(2)
	84.1(2)	84.8(3)	87.4(2)

The Zn−C distances for **1** [Zn(1)−C(1) = 1.949(4) Å, Zn(1)−C(23) = 1.944(4) Å], **4** [Zn(1)−C(1) = 1.9362(13) Å, Zn(1)−C(23) = 1.9402(13) Å] and **7** [Zn(1)−C(1) and Zn(1)−C(29) = 1.939(3) Å], are similar and to each other and to the values for two-coordinate $(2,6-Naph_2C_6H_3)_2Zn$ [Zn−C = 1.946(2) and 1.955(2) Å].[14] Cd−C bond lengths for **2**, **5** and **8** and Hg−C bond lengths for **3**, **6** and **9** also occur in relatively narrow ranges [Cd−C = 2.112(2)-2.130(2) Å and Hg−C = 2.087(5)-2.102(6) Å] and are similar to those found for other two-coordinate cadmium[8,19] and mercury diaryls.[9,20] The shorter M–C distance in the mercury diaryls compared to their cadmium analogues is attributed to the smaller covalent radius of mercury compared to cadmium, and is presumably due to a combination of relativistic effects and the lanthanide contraction.[10,21]

Table 2. Selected bond lengths (Å) and angles (°) for **4-6**.

	4 (M = Zn)	**5** (M = Cd)	**6** (M = Hg)
C(1)–M(1)	1.9362(13)	2.119(2)	2.093(6)
C(23)–M(1)	1.9402(13)	2.130(2)	2.102(6)
C(1)–M(1)–C(23)	171.18(5)	174.10(9)	176.4(2)
C(1)plane···C(23)plane	86.67(4)	86.63(7)	86.03(19)
C(1)plane···flanking aryl plane	56.11(5)	52.71(9)	55.6(2)
	51.26(5)	56.33(9)	57.8(2)
	50.04(5)	45.00(10)	49.6(2)

40.36(5)   48.69(10)   47.1(2)

The C−M−C angles in 2,6-Xyl and Pmp-substituted complexes **1-3** and **7-9** [175.78(12)°-180°] (Fig. 2) are similar to the essentially linear coordination displayed by the zinc diaryl Mes$_2$Zn,[7,22] and (p-CF$_3$C$_6$H$_4$)$_2$Zn[23] as well as two-coordinate Mes$_2$Cd and the mercury diaryls Mes$_2$Hg[8] and [2,6-Mes$_2$C$_6$H$_3$]$_2$Hg.[9] All of the solid state structures of these complexes contain one molecule in the asymmetric unit apart from **8** and **9** (Fig. 2) which contain one quarter of a molecule in the asymmetric unit with the rest being generated by symmetry (symmetry operation = $-x + \frac{1}{4}$, $-y + \frac{1}{4}$, z), leading to C–M–C angles of 180°.
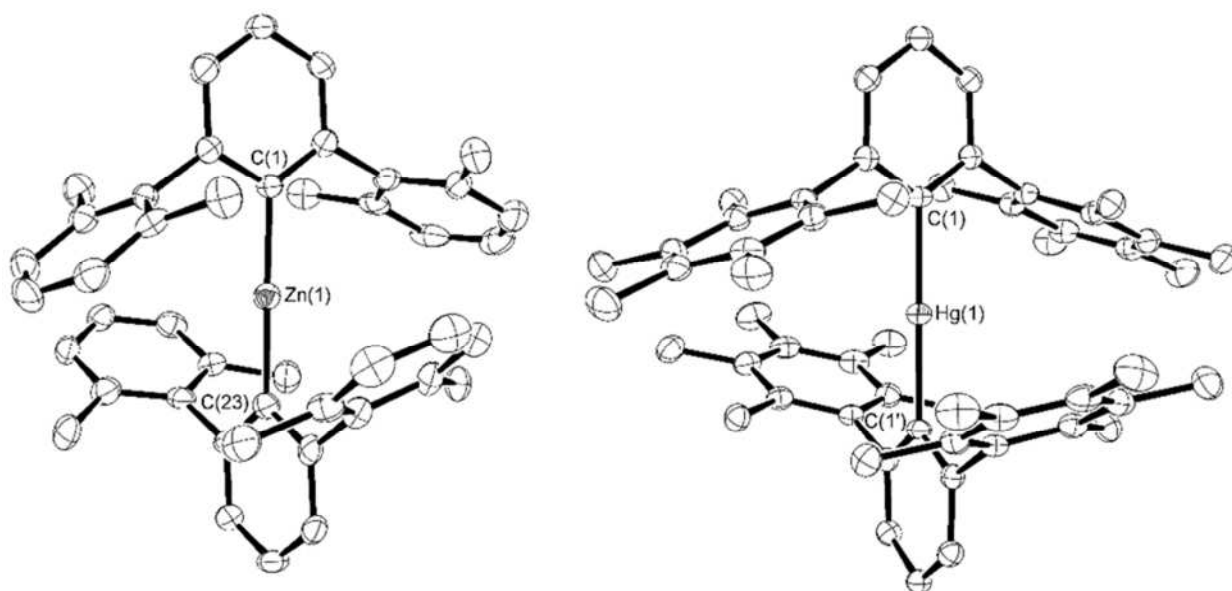
Fig. 2. Crystal structures of [2,6-(2,6-Xyl)$_2$C$_6$H$_3$]$_2$Zn (**1**; left) and (2,6-Pmp$_2$C$_6$H$_3$)$_2$Hg (**9**; right) highlighting the linearity in the C–M–C angles for these complexes. Displacement ellipsoids are set at the 50% probability level and hydrogen atoms omitted for clarity. Symmetry operation: ' = $-x + \frac{1}{4}$, $-y + \frac{1}{4}$, z.

The C−Zn−C angle in the 3,5-Xyl substituted **4** [171.18(15)°] deviates more from linearity than in the 2,6-Xyl and Pmp-substituted diaryls (Fig. 3). Such a deviation has also been observed in the analogous two-coordinate terphenyl (2,6-Naph$_2$C$_6$H$_3$)$_2$Zn [168.27(9)°],[14] and in the case of **4**

this brings *ortho*-hydrogen atoms on the flanking 3,5-xylyl rings into proximity with the Zn(II) centre [distances H(8)···Zn(1) = 2.564 Å, H(16)···Zn(1) = 2.874 Å, H(34)···Zn(1) = 2.594 Å, H(42)···Zn(1) = 2.499 Å; C(8)···Zn(1) = 2.8159(13) Å, C(16)···Zn(1) = 3.1385(14) Å, C(34)···Zn(1) = 2.9250(13) Å, C(42)···Zn(1) = 2.9245(13) Å are within the sum of van der Waals radii for these elements].[24,25] This has been attributed to the placement of the methyl groups on the flanking aryl ring being positioned away from the central metal in the complex allowing rotation of the flanking aryl groups. The angles between the best mean planes of the flanking 3,5-xylyl groups and the central aryl ring in **4** lie in the range 40.36(5)-56.11(5)° and are significantly more acute than the analogous values for **1** [80.73(19)-88.4(2)°] and **7** [78.21(10)-88.88(10)°], presumably for steric reasons. The two metal-substituted aryl rings in these zinc complexes are oriented almost perpendicular to each other in order to reduce steric strain, with the torsion angle between the planes of the two metal-substituted aryl rings varying between 83.6(2)° (for **1**) and 89.07(10)° (for **7**).
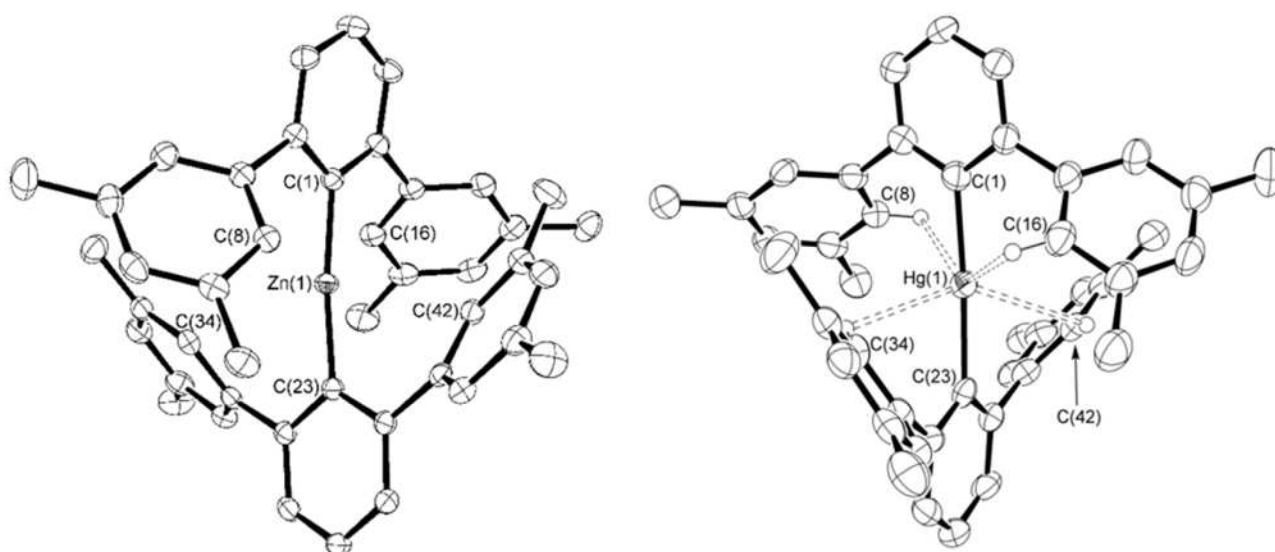
Fig. 3. Molecular structures of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$]$_2$Zn (**4**; left) and [2,6-(3,5-Xyl)$_2$C$_6$H$_3$]$_2$Hg (**6**; right; showing possible secondary ligand interactions as dashed lines). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The 3,5-xylyl-substituted **5** and **6** (Fig. 3) show smaller deviations from linearity as opposed to **4** [174.10(9)° for **5** and 176.4(2)° for **6**] which is similar to $(C_6F_5)_2Cd$ [173.9(1)°].[19b] **5** and **6** show a comparable orientation of the flanking aryls to **4** which again results in the *ortho*-hydrogen atoms on the flanking aryl groups being closer to the central cadmium(II) [H(8)···Cd(1) = 2.9259 Å, H(16)···Cd(1) = 2.8028 Å, H(34)···Cd(1) = 2.7151 Å, H(42)···Cd(1) = 2.5981 Å; C(8)···Cd(1) = 3.233(3) Å, C(42)···Cd(1) = 3.099(3) Å, C(34)···Cd(1) = 3.064(3) Å, C(16)···Cd(1) = 3.067(3) Å] and mercury(II) [H(8)···Hg(1) = 2.9668 Å, H(16)···Hg(1) = 2.9023 Å, H(34)···Hg(1) = 2.6504 Å, H(42)···Hg(1) = 2.7901 Å; C(8)···Hg(1) = 3.241(7) Å, C(16)···Hg(1) = 3.140(7) Å, C(34)···Hg(1) = 3.064(7) Å, C(42)···Hg(1) = 3.114(6) Å]. As for **4** these distances are all within the sum of the relevant van der Waals radii (C–Cd = 3.95 Å; C–Hg = 3.92 Å).[24] The angles formed between the flanking 3,5-Xyl groups and the central aryl ring in **5** [range 45.00(10)-56.33(9)°] and **6** [range 47.1(2)-57.8(2)°] are broadly similar to those for **4**. The torsion angle between the two planes of the central metal substituted aryl rings on each ligand are similar to each other [84.2(3)° (**2**), 86.62(19)° (**3**), 86.63(7)° (**5**), 86.03(19)° (**6**), 78.33(10)° (**8**) and 78.46(18)° (**9**)], being approximately perpendicular to reduce the steric interactions between the two ligands.

Table 3. Selected bond lengths (Å) and angles (°) for **7-9**. Symmetry operation: ' = $-x + \frac{1}{4}$, $-y + \frac{1}{4}$, z.

	7 (M = Zn)	**8** (M = Cd)	**9** (M = Hg)
	C(n) = C(29)	C(n) = C(1')	C(n) = C(1')
C(1)–M(1)	1.939(3)	2.112(2)	2.099(4)
C(n)–M(1)	1.939(3)	2.112(2)	2.099(4)
C(1)–M(1)–C(n)	175.78(12)	180	180
C(1)plane···C(n)plane	89.07(10)	78.33(10)	78.46(18)
C(1)plane···flanking aryl plane	85.37(10)	85.79(5)	85.99(7)
	78.21(10)		
	87.21(9)		
	88.88(10)		

3. Conclusions

Three series of crystallographically characterised two-coordinate Group 12 *bis*-terphenyl complexes (2,6-Ar$_2$C$_6$H$_3$)$_2$M (M = Zn, Cd, Hg; Ar = 2,6-Xyl **1**-**3**; 3,5-Xyl **4**-**6**; Pmp **7**-**9**), have been reported. These are the first homoleptic d-block complexes featuring any of these ligands. Their isolation and characterisation allows the analysis of structural changes produced by relatively subtle differences in ligand properties, particularly sterics, and in this case to a smaller extent, electronics. Complexes **4**-**6** show smaller C–M–C bond angles and contain secondary ligand interactions that are not seen in the analogous complexes **1**-**3** and **7**-**9**.

4. Experimental

4.1 General

All manipulations were carried out under an argon or nitrogen atmosphere using standard Schlenk line or glove box techniques. Hexane, THF and toluene were pre-dried over Na wire prior to passing through a column of activated alumina (hexane) or distilled over Na/benzophenone (THF) or potassium (toluene), followed by storage over a potassium mirror (hexane, toluene) or 4 Å molecular sieves (THF). Lithium complexes [2,6-Ar$_2$C$_6$H$_3$Li]$_2$ (Ar = 2,6-Xyl, 3,5-Xyl, Pmp)[16,17] and anhydrous ZnCl$_2$ and CdCl$_2$ were prepared by minor modifications of literature methods.[26] HgBr$_2$ was dried *in vacuo* at room temperature for 24 hours prior to use. Benzene-d$_6$ (Goss) was dried over potassium and degassed with three freeze-pump-thaw cycles prior to use. ^{1}H, ^{13}C{^{1}H}, ^{113}Cd{^{1}H} and ^{199}Hg{^{1}H} NMR spectra for these complexes were collected on Bruker DPX 400, AV 400 or AV(III) 400 spectrometers. Residual signals of solvent were used for reference for ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and chemical shifts are quoted in ppm relative to TMS (^{1}H and ^{13}C{^{1}H}), 0.1 M Cd(ClO$_4$)$_2$/D$_2$O solution (^{113}Cd{^{1}H}) and HgMe$_2$ (^{199}Hg{^{1}H}). Elemental analyses were performed by Mr Stephen Boyer, Microanalysis Service, London Metropolitan University. Mass Spectrometry was performed by Dr Mick Cooper at the University of Nottingham and by the EPSRC National Mass

Spectrometry Facility, Swansea University. (**Caution**: Cadmium and mercury compounds are known for their toxicity, and great care must be taken in their manipulation.)

4.2 Syntheses

Synthesis of [2,6-(2,6-Xyl)$_2$C$_6$H$_3$]$_2$M (M = Zn 1, Cd 2, Hg 3). A mixture of [2,6-(2,6-Xyl)$_2$C$_6$H$_3$Li]$_2$ (200 mg, 0.34 mmol) and MX$_2$ (0.34 mmol, MX$_2$ = ZnCl$_2$, CdCl$_2$, HgBr$_2$) in toluene (50 mL) and THF (5 mL) at –78 °C was allowed to warm slowly to room temperature and stirred for 12 hours. Removal of solvent *in vacuo* and extraction of the resulting white solid with hexane (20 mL) followed by storage for 24 hours at –30 °C resulted in clear, colourless crystals of **1**-**3** in isolated yields of 54 mg (25%), 43 mg (19%) and 78 mg (30%), respectively, suitable for X-ray diffraction studies. **Data for 1.** ^{1}H NMR (C$_6$D$_6$, 400.07 MHz, 298 K): δ (ppm) = 1.79 (s, 24H, *o*-CH$_3$ of Xyl), 6.76 (d, 4H, *J* = 7.5 Hz, *m*-H of C$_6$H$_3$), 7.02 (m, 12H, *m- and p*-H of Xyl), 7.11 (t, 2H, *J* = 7.5 Hz, *p*-H of C$_6$H$_3$). ^{13}C{^{1}H}NMR (C$_6$D$_6$, 100.63 MHz, 298 K) δ (ppm) = 22.2 (*o*-CH$_3$ of Xyl), 125.9 (*m*-CH of C$_6$H$_3$), 127.6 (*m*-CH of Xyl), 128.5 (*p*-CH of Xyl), 129.3 (*p*-CH of C$_6$H$_3$), 136.6 (*o*-C of Xyl), 146.3 (*o*-C of C$_6$H$_3$), 150.3 (*i*-C of Xyl), 152.3 (*i*-C of C$_6$H$_3$). IR (nujol mull) *v*/cm^{-1} = 1614 (w), 1558 (w), 1261 (m), 1075 (m, br), 1030 (m, br), 804 (m), 768 (m), 741 (m). Elemental analysis C$_{44}$H$_{42}$Zn: calcd. C 83.07, H 6.65; found C 82.86, H 6.50. EI-MS: *m/z* (%) = 634.2 (6%) [M]$^+$, 619.2 (2%) [M – Me]$^+$, 350.1 (2%) [(2,6-Xyl)$_2$C$_6$H$_3$Zn]$^+$, 284.2 (100%) [(2,6-Xyl)$_2$C$_6$H$_3$]$^+$, 270.1 (11%) [(2,6-Xyl)$_2$C$_6$H$_3$ – Me]$^+$, 255.1 (14%) [(2,6-Xyl)$_2$C$_6$H$_3$ – 2Me]$^+$, 240.1 (4%) [(2,6-Xyl)$_2$C$_6$H$_3$ – 3Me]$^+$. **Data for 2.** ^{1}H NMR (C$_6$D$_6$, 400.07 MHz, 298 K): δ (ppm) = 1.80 (s, 24H, *o*-CH$_3$), 6.87 (d, 4H, *J* = 7.6 Hz, *m*-H of C$_6$H$_3$), 7.01 (m, 12H, *m- and p*-H of Xyl), 7.14 (t, 2H, *J* = 7.5 Hz, *p*-H of C$_6$H$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.63 MHz, 298 K) δ (ppm) = 21.2 (*o*-CH$_3$ of Xyl), 124.9 (*m*-CH of C$_6$H$_3$), 126.9 (*m*-CH of Xyl), 127.8 (*p*-CH of Xyl), 128.1 (*p*-CH of C$_6$H$_3$), 135.7 (*o*-C of Xyl), 146.6 (*o*-C of C$_6$H$_3$), 149.4 (*i*-C of Xyl), 161.6 (*i*-C of C$_6$H$_3$). ^{113}Cd{^{1}H} NMR (C$_6$D$_6$, 88.77 MHz, 298 K): δ (ppm) = 403.52. IR (nujol mull) *v*/cm^{-1} = 1614 (w), 1261 (m), 1096 (w, br), 1029 (m, br), 802

(m, br), 768 (w), 739 (w). Elemental analysis $C_{44}H_{42}Cd$: calcd. C 77.35, H 6.20; found C 77.26, H 6.29. EI-MS: m/z (%) = 684.3 (20%) $[M]^+$, 669.3 (4%) $[M - Me]^+$, 399.1 (5%) $[(2,6-Xyl)_2C_6H_3Cd]^+$, 284.0 (100%) $[(2,6-Xyl)_2C_6H_3]^+$ 270.0 (25%) $[(2,6-Xyl)_2C_6H_3 - Me]^+$, 255.0 (15%) $[(2,6-Xyl)_2C_6H_3 - 2Me]^+$. **Data for 3.** ^{1}H NMR (C_6D_6, 400.07 MHz, 298 K): δ (ppm) = 1.78 (s, 24H, o-CH$_3$), 6.92 (d, 4H, J = 7.5 Hz, m-H of C_6H_3), 7.04 (m, 14H, p-H of C_6H_3 and m- and p-H of Xyl). ^{13}C{^{1}H} NMR (C_6D_6, 100.63 MHz, 298 K) δ (ppm) = 21.8 (o-CH$_3$ of Xyl), 127.2 (m-CH of C_6H_3), 127.6 (m-CH of Xyl), 128.1 (p-CH of Xyl), 128.7 (p-CH of C_6H_3), 136.7 (*quaternary*-C$_{Ar}$), 145.2 (o-C of C_6H_3), 149.0 (i-C of Xyl), 172.4 (i-C of C_6H_3). ^{199}Hg{^{1}H} NMR (C_6D_6, 71.67 MHz, 298 K) δ (ppm) = −679.77. IR (nujol mull) v/cm^{-1} = 2732 (w), 1924 (w), 1852 (w), 1614 (w), 1579 (w), 1562 (w), 1260 (m), 1161 (m), 1077 (m, br), 1030 (m, br), 803 (m), 767 (s), 743 (m). Elemental analysis $C_{44}H_{42}Hg$: calcd. C 68.51, H 5.49; found C 68.39, H 5.54. EI-MS: m/z (%) = 772.3 (3%) $[M]^+$, 284.2 (100%) $[(2,6-Xyl)_2C_6H_3]^+$, 270.1 (16%) $[(2,6-Xyl)_2C_6H_3 - Me]^+$, 255.1 (15%) $[(2,6-Xyl)_2C_6H_3 - 2Me]^+$, 240.1 (4%) $[(2,6-Xyl)_2C_6H_3 - 3Me]^+$.

Synthesis of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$]$_2$M (M = Zn 4, Cd 5, Hg 6). A mixture of [2,6-(3,5-Xyl)$_2$C$_6$H$_3$Li]$_2$ (200 mg, 0.34 mmol) and MX$_2$ (0.34 mmol, MX$_2$ = ZnCl$_2$, CdCl$_2$, HgBr$_2$) in toluene (50 mL) and THF (5 mL) at –78 °C were allowed to warm slowly to room temperature and stirred for 12 hours. Removal of solvent *in vacuo* and extraction of the resulting white solid with hexane (20 mL) followed by storage for 24 hours at –30 °C resulted in clear colourless crystals of **4-6** in isolated yields of 90 mg (41%), 154 mg (67%) and 30 mg (11%) respectively suitable for study by X-ray diffraction. **Data for 4.** ^{1}H NMR (C_6D_6, 400.07 MHz, 298 K): δ (ppm) = 2.04 (s, 24H, m-CH$_3$), 6.62 (s, 4H, p-H of Xyl), 6.97 (s, 8H, o-H of Xyl), 7.11 (t, 2H, J = 7.5 Hz, p-H of C_6H_3), 7.50 (d, 4H, J = 7.5 Hz, m-H of C_6H_3). ^{13}C{^{1}H} NMR (C_6D_6, 100.63 MHz, 298 K) δ (ppm) = 21.1 (m-CH$_3$ of Xyl), 125.0 (m-CH of C_6H_3), 125.5 (o-CH of Xyl), 128.3 (p-CH of C_6H_3), 128.7 (p-CH of Xyl), 138.8 (m-C of Xyl), 148.1 (o-C of C_6H_3), 150.9 (i-

C of Xyl), 153.6 (i-C of C_6H_3). IR (nujol mull) v/cm^{-1} = 1959 (w), 1630 (m), 1599 (w), 1261 (s), 1096 (s, br), 1020 (s, br), 799 (s, br), 671 (m). Elemental analysis $C_{44}H_{42}Zn$: calcd. C 83.07, H 6.65; found C 82.86, H 6.44. EI-MS: m/z (%) = 634.3 (35%) [M]$^+$, 349.1 (9%) [(3,5-Xyl)$_2$C$_6$H$_3$Zn]$^+$, 284.2 (22%) [(3,5-Xyl)$_2$C$_6$H$_3$]$^+$, 270.1 (18%) [(3,5-Xyl)$_2$C$_6$H$_3$ – Me]$^+$, 255.1 (17%) [(3,5-Xyl)$_2$C$_6$H$_3$ – 2Me]$^+$, 240.1 (11%) [(3,5-Xyl)$_2$C$_6$H$_3$ – 3Me]$^+$. **Data for 5.** ^{1}H NMR (C_6D_6, 400.07 MHz, 298 K): δ (ppm) = 2.07 (s, 24H, m-CH$_3$), 6.65 (s, 4H, p-H of Xyl), 7.03 (s, 8H, o-H of Xyl), 7.28 (t, 2H, J = 7.4 Hz, p-H of C_6H_3), 7.51 (d, 4H, J = 7.4 Hz, m-H of C_6H_3). ^{13}C\{^{1}H\} NMR (C_6D_6, 100.63 MHz, 298 K) δ (ppm) = 21.7 (m-CH$_3$ of Xyl), 126.1 (p-CH of C_6H_3), 126.3 (o-CH of Xyl), 128.3 (m-CH of C_6H_3), 129.2 (p-CH of Xyl), 139.1 (m-C of Xyl), 149.8 (o-C of C_6H_3), 151.4 (i-C of Xyl), 161.0 (i-C of C_6H_3). ^{113}Cd\{^{1}H\} NMR (C_6D_6, 88.77 MHz, 298 K): δ (ppm) = 466.08. IR (nujol mull) v/cm^{-1} = 2362 (w), 2342 (w), 1703 (w), 1599 (s), 1558 (m), 1260 (s), 796 (s). Elemental analysis $C_{44}H_{42}Cd$: calcd. C 77.35, H 6.20; found C 77.23, H 6.13. EI-MS: m/z (%) = 684.3 (27%) [M]$^+$, 399.1 (16%) [(3,5-Xyl)$_2$C$_6$H$_3$Cd]$^+$, 285.2 (49 %) [(3,5-Xyl)$_2$C$_6$H$_3$]$^+$, 270.1 (45%) [(3,5-Xyl)$_2$C$_6$H$_3$ – Me]$^+$, 255.1 (37%) [(3,5-Xyl)$_2$C$_6$H$_3$ – 2Me]$^+$, 239.1 (31%) [(3,5-Xyl)$_2$C$_6$H$_3$ – 3Me]$^+$. **Data for 6.** ^{1}H NMR (C_6D_6, 400.07 MHz, 298 K): δ (ppm) = 2.12 (s, 24H, CH$_3$), 6.68 (s, 4H, p-H of Xyl), 7.07 (s, 8H, o-H of Xyl), 7.19 (t, 2H, J = 7.6 Hz, p-H of C_6H_3), 7.49 (d, 4H, J = 7.5 Hz, m-H of C_6H_3). ^{13}C\{^{1}H\} NMR (C_6D_6, 100.63 MHz, 298 K) δ (ppm) = 21.8 (m-CH$_3$ of Xyl), 126.8 (o-CH of Xyl), 127.7 (p-CH of C_6H_3), 127.8 (m-CH of C_6H_3), 129.2 (p-CH of Xyl), 138.0 (m-C of Xyl), 147.0 (o-C of C_6H_3), 150.4 (i-C of Xyl), 167.8 (i-C of C_6H_3). ^{199}Hg\{^{1}H\} NMR (C_6D_6, 71.67 MHz, 298 K) δ (ppm) = –564.31. IR (nujol mull) v/cm^{-1} = 2361 (w), 2341 (w), 1560 (w), 1261 (m), 1095 (m, br), 1022 (m, br), 853 (w), 797 (m). Elemental analysis $C_{44}H_{42}Hg$: calcd. C 68.51, H 5.49; found C 68.60, H 5.52. EI-MS: m/z (%) = 772.3 (15%) [M]$^+$, 487.1 (5%) [(3,5-Xyl)$_2$C$_6$H$_3$Hg]$^+$, 285.2 (65%) [(3,5-Xyl)$_2$C$_6$H$_3$]$^+$, 270.1 (43%) [(3,5-Xyl)$_2$C$_6$H$_3$ – Me]$^+$, 255.1 (37%) [(3,5-Xyl)$_2$C$_6$H$_3$ – 2Me]$^+$, 239.1 (35%) [(3,5-Xyl)$_2$C$_6$H$_3$ – 3Me]$^+$.

Synthesis of [2,6-(2,6-Pmp)$_2$C$_6$H$_3$]$_2$M (M = Zn 7, Cd 8, Hg, 9). A solution of [2,6-Pmp$_2$C$_6$H$_3$Li]$_2$ (200 mg, 0.27 mmol) in toluene (30 mL) was added dropwise to a solution of MX$_2$ (0.27 mmol, MX$_2$ = ZnCl$_2$, CdCl$_2$, HgBr$_2$) in a mixture of toluene (30 mL) and THF (3 mL) at –78 °C. The mixture was allowed to warm slowly to room temperature overnight with stirring. The solvent was removed *in vacuo* and the resulting solid was extracted into hexane (10 mL). **Data for 7.** The volume of the solution of **7** in hexane was reduced by half in *vacuo*, followed by storage at room temperature overnight, resulting in colourless crystals of **7·0.5C$_6$H$_{14}$** (100 mg, 24%). The crystals were dried *in vacuo* and analysed as **7**. ^{1}H NMR (C$_6$D$_6$, 400.07 MHz, 298 K): δ (ppm) = 1.94 (s, 24H, *o*-CH$_3$ of Pmp), 2.29 (s, 12H, *p*-CH$_3$ of Pmp), 2.40 (s, 24H, *m*-CH$_3$ of Pmp), 6.95 (d, 4H, *J* = 7.6Hz, *m*-H of C$_6$H$_3$), 7.29 (m, 2H, *p*-H of C$_6$H$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.63 MHz, 298 K) δ (ppm) = 17.2 (*p*-CH$_3$ of Pmp), 17.7 (*m*-CH$_3$ of Pmp), 18.4 (*o*-CH$_3$ of Pmp), 126.6 (*m*-CH of C$_6$H$_3$), 129.0 (*p*-CH of C$_6$H$_3$), 132.0 (*quaternary*-C of Pmp), 132.1 (*quaternary*-C of Pmp), 134.2 (*quaternary*-C of Pmp), 144.6 (*o*-C of C$_6$H$_3$), 152.6 (*i*-C of Pmp), 153.2 (*i*-C of C$_6$H$_3$). IR (nujol mull) v/cm^{-1} = 1614 (w), 1558 (w), 1261 (m), 1096 (m, br), 1025 (m, br), 803 (m, br), 736(w). Elemental analysis C$_{56}$H$_{66}$Zn: calcd. C 83.60, H 8.27; found C 83.42, H 8.17. EI-MS: *m/z* (%) = 802.6 (15 %) [M]$^+$, 787.6 (5 %) [M – Me]$^+$, 433.2 (0.5 %) [Pmp$_2$C$_6$H$_3$Zn]$^+$, 368.2 (100 %) [Pmp$_2$C$_6$H$_3$]$^+$, 353.2 (20 %) [Pmp$_2$C$_6$H$_3$ – Me]$^+$, 339.2 (12 %) [Pmp$_2$C$_6$H$_3$ – 2Me]$^+$, 323.1 (8 %) [Pmp$_2$C$_6$H$_3$ – 3Me]$^+$, 309.1 (5 %) [Pmp$_2$C$_6$H$_3$ – 4Me]$^+$, 294.1 (1 %) [Pmp$_2$C$_6$H$_3$ – 5Me]$^+$. **Data for 8.** Storage of **8** in hexane at 6 °C overnight resulted in colourless crystals of pure product (38 mg, 16%). ^{1}H NMR (C$_6$D$_6$, 400.07 MHz, 298 K): δ (ppm) = 1.82 (s, 24H, *o*-CH$_3$ of Pmp), 2.17 (s, 12H, *p*-CH$_3$ of Pmp), 2.26 (s, 24H, *m*-CH$_3$ of Pmp), 6.94 (d, 4H, *J* = 7.2 Hz, *m*-H of C$_6$H$_3$), 7.18 (m, 2H, *p*-H of C$_6$H$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.63 MHz, 298 K): δ (ppm) = 16.5 (*p*-CH$_3$), 17.1 (*m*-CH$_3$), 17.8 (*o*-CH$_3$), 125.7 (*m*-CH of C$_6$H$_3$), 127.9 (*p*-CH of C$_6$H$_3$), 131.1 (*quaternary*-C of Pmp), 131.7 (*quaternary*-C of Pmp), 133.5 (*quaternary*-C of Pmp), 144.5 (*o*-C of C$_6$H$_3$), 151.6 (*i*-C of Pmp), 162.5 (*i*-C of C$_6$H$_3$). ^{113}Cd{^{1}H} NMR (C$_6$D$_6$, 88.77 MHz, 298 K): δ (ppm) = 393.47. IR (nujol mull) v/cm^{-1} = 2728

(w), 1614 (w), 1563 (w), 1261 (w), 1246 (w), 1155 (w) 1100(m, br), 1061 (m, br), 1030 (m, br) 966 (w), 838 (w, br), 803 (w, br), 788 (m), 740 (m), 658 (w). Elemental analysis $C_{56}H_{66}Cd$: calcd. C 78.99, H 7.81; found C 78.71, H 7.62. EI-MS: 837.4 (2.5 %) [M – Me]$^+$, 483.2 (7.2 %) [Pmp$_2$(C$_6$H$_3$)Cd]$^+$, 368.2 (100%) [Pmp$_2$(C$_6$H$_2$)]$^+$. **Data for 9.** The solution of **9** in hexane was reduced *in vacuo* by half, followed by storage at room temperature overnight, resulting in colourless crystals of pure product (88 mg, 36%). ^{1}H NMR (C$_6$D$_6$, 400.07 MHz, 298 K): δ (ppm) = 1.61 (s, 24H, *o*-CH$_3$ of Pmp), 2.26 (s, 12H, *p*-CH$_3$ of Pmp), 2.32 (s, 24H, *m*-CH$_3$ of Pmp), 6.88 (d, 4H, *J* = 7.5 Hz, *m*-H of C$_6$H$_3$), 7.13 (t, 2H, *J* = 7.4 Hz, *p*-H of C$_6$H$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.63 MHz, 298 K): δ (ppm) = 16.6 (*p*-CH$_3$ of Pmp), 17.1 (*m*-CH$_3$ of Pmp), 17.7 (*o*-CH$_3$ of Pmp), 127.4 (*m*-CH of C$_6$H$_3$), 127.7 (*p*-CH of C$_6$H$_3$), 128.1 (*quaternary*-C of Pmp), 131.4 (*quaternary*-C of Pmp), 133.5 (*quaternary*-C of Pmp), 142.7 (*o*-C of C$_6$H$_3$), 150.7 (*i*-C of Pmp), 173.0 (*i*-C of C$_6$H$_3$). ^{199}Hg{^{1}H} NMR (C$_6$D$_6$, 71.67 MHz, 298 K) δ (ppm) −702.88. IR (nujol mull) v/cm^{-1} = 2727 (w), 1614 (w), 1569 (w), 1305 (w, br), 1261 (w), 1155 (w, br), 1104 (m, br), 1061 (m, br), 1032 (m, br), 966 (w), 838 (w), 804 (w), 788 (m), 743 (m), 657 (w). Elemental analysis $C_{56}H_{66}Hg$: calcd. C 71.57, H 7.08; found C 71.86, H 7.13. EI-MS: *m/z* (%) = 940.6 (0.3 %) [M]$^+$, 369.3 [2,6-Pmp$_2$C$_6$H$_3$]$^+$ (31.9 %), 368.3 (100 %) [2,6-Pmp$_2$C$_6$H$_2$]$^+$.

4.3 Crystallography

Crystals of **1-9** were mounted on MicroMounts (Mitegen) using YR-1800 perfluoropolyether oil (Lancaster) and cooled rapidly in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device.[27] Diffraction data for **1-3** and **5-9** (90 K) were acquired on a Bruker SMART APEX or a Bruker SMART1000 diffractometer, equipped with graphite-monochromated Mo-K_α radiation sources (λ = 0.71073 Å), and for **4** (120 K) on an Agilent SuperNova CCD area detector diffractometer equipped with a mirror-monochromated Cu-K_α radiation source (λ = 1.54184 Å). Intensities were integrated from data recorded on 0.3° (APEX and SMART1000) or 1° (SuperNova) frames by ω rotation. Semi-empirical absorption corrections based on symmetry-equivalent and

repeat reflections (APEX and SMART1000) or Gaussian grid face-indexed absorption corrections with a beam profile correction (SuperNova) were applied. All non-H atoms were located using direct methods and difference Fourier syntheses. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Programs used were CrysAlisPro[28] and Bruker AXS SMART[29] (control), CrysAlisPro[28] and Bruker AXS SAINT[29] (integration), and SHELXS,[30] SHELXL[30] and OLEX2[31] (structure solution, structure refinement and molecular graphics). In the crystal structure of **1** a second twin component was detected: the twin law was (–1 0 0, 0 1 0, 0 0 –1) and the twin fraction refined to 0.336(14). Merohedral crystal twinning [twin law (0 1 0, 1 0 0, 0 0 –1)] was detected for **2** and the twin fraction refined to 0.3834(13). The hexane solvent molecule in **7·0.5C$_6$H$_{14}$** was extensively disordered: because this could not be modelled sensibly using alternative atomic sites PLATON SQUEEZE[32] was used to remove the contribution of the disordered solvent to the diffraction data and allow refinement against the "solvent-free" dataset.

Table 4 Crystallographic data for compounds **1**-**9**.

	1	2	3	4	5
Formula	$C_{44}H_{42}Zn$	$C_{44}H_{42}Cd$	$C_{44}H_{42}Hg$	$C_{44}H_{42}Zn$	$C_{44}H_{42}Cd$
M_w	636.15	683.18	771.37	636.15	683.18
Crystal system	Tetragonal	Tetragonal	Tetragonal	Triclinic	Triclinic
Space Group	$P4_1$	$P4_1$	$I4_1/a$	P-1	P-1
Crystal size/mm	$0.24 \times 0.20 \times 0.09$	$0.14 \times 0.12 \times 0.11$	$0.17 \times 0.14 \times 0.11$	$0.15 \times 0.10 \times 0.07$	$0.85 \times 0.47 \times 0.46$
a (Å)	10.4016(7)	10.5072(3)	20.903(9)	10.6431(7)	10.748(3)
b (Å)	10.4016(7)	10.5072(3)	20.903(9)	11.2772(6)	12.914(4)
c (Å)	31.197(4)	31.0528(17)	31.72(3)	15.6417(7)	13.331(4)
α (°)	90	90	90	81.846(4)	76.688(4)
β (°)	90	90	90	87.869(4)	83.692(4)
γ (°)	90	90	90	65.639(6)	78.257(4)
V (Å^3)	3375.3(6)	3428.3(2)	13861(14)	1692.47(16)	1759.1(9)
Z	4	4	16	2	2
T (K)	90(2)	90(2)	90(2)	120(2)	90(2)
D_{calc} (g cm^{-3})	1.252	1.324	1.479	1.248	1.29
F_{000}	1344	1416	6176	672	708
μ (mm^{-1})	0.758	0.666	4.471	1.214	0.649
θ range for data collection (°)	1.96-27.49	2.05-27.51	1.88-27.53	4.35-74.65	1.94-25.03
Max. and min. transmission	0.822 and 0.721	0.746 and 0.647	0.430 and 0.320	1.007 and 0.938	0.746 and 0.598
reflns measd	21418	42410	60540	24405	11908
independent reflns	7624	7863	7895	6784	6047
R_{int}	0.0544	0.0891	0.107	0.0206	0.0230
Final $GooF$	1.18	1.15	1.06	1.03	1.06
R_1, wR_2 [$I > 2\sigma(I)$]	0.0551, 0.105	0.0486, 0.0884	0.0427, 0.0775	0.0275, 0.0716	0.0280, 0.0678
R_1, wR_2 (all data)	0.0612, 0.109	0.0547, 0.0906	0.0734, 0.0856	0.0302, 0.0736	0.0350, 0.0702
min. and max. electron densities (e Å^{-3})	–0.37, 0.60	–0.50, 0.81	–0.47, 1.41	–0.26, 0.30	–0.55, 0.50

	6	7·0.5C_6H_{14}	8	9
Formula	$C_{44}H_{42}Hg$	$C_{59}H_{73}Zn$	$C_{56}H_{66}Cd$	$C_{56}H_{66}Hg$
M_w	771.37	847.54	851.49	939.68
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space Group	P-1	$P2_1/n$	$Fddd$	$Fddd$
Crystal size/mm	$0.25 \times 0.25 \times 0.07$	$0.16 \times 0.05 \times 0.04$	$0.16 \times 0.13 \times 0.10$	$0.11 \times 0.10 \times 0.05$
a (Å)	10.688(2)	12.178(3)	13.978(5)	13.998(3)
b (Å)	12.974(3)	22.671(5)	18.737(7)	18.670(4)
c (Å)	13.401(3)	18.854(4)	34.854(12)	34.919(8)
α (°)	76.323(3)	90	90	90
β (°)	83.448(3)	94.559(4)	90	90
γ (°)	78.253(3)	90	90	90
V (Å^3)	1763.5(6)	5189(2)	9129(5)	9126(3)
Z	2	4	8	8
T (K)	120(2)	90(2)	90(2)	90(2)
D_{calc} (g cm^{-3})	1.453	1.085	1.239	1.368
F_{000}	772	1828	3600	3856
μ (mm^{-1})	4.393	0.508	0.514	3.409
θ range for data collection (°)	2.01-27.55	2.10-25.50	2.34-27.50	1.91-27.57
Max. and min. transmission	0.43 and 0.311	0.746 and 0.572	0.746 and 0.676	0.430 and 0.324
reflns measd	15701	27280	13736	13405
independent reflns	7950	9593	2628	2653
R_{int}	0.538	0.0521	0.0305	0.0471
Final $GooF$	0.98	1.08	1.09	1.05
R_1, wR_2 [$I > 2\sigma(I)$]	0.0528, 0.0969	0.0566, 0.1335	0.0275, 0.0713	0.0254, 0.0619
R_1, wR_2 (all data)	0.0821, 0.1062	0.0744, 0.1402	0.0295, 0.0733	0.0313, 0.0648
min. and max. electron densities (e Å^{-3})	–0.87, 1.75	–0.41, 0.67	–0.31, 0.94	–0.81, 1.38

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