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Crystal Structures and Chemical Properties of Dimesitylcadmium and Dimesitylmercury

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Abstract. Mesityllithium was used to synthesize dimesitylcadmium and dimesitylmercury from $CdCl_2$ and $HgCl_2$, respectively. X-ray-crystallographic data show that the group 12 metal compounds M[Mes]$_2$ (M = Zn, Cd, Hg) are isomorphous (monoclinic, $P2_1/n$). The asymmetric unit of M[Mes]$_2$ (M = Zn, Cd, Hg) consists of one mesityl group bonded to the metal atom, which is related to the second substituent by an inversion center. In addition we have investigated the reaction of BBr_3 with M[Mes]$_2$ (M = Cd, Hg) for our understanding of the reactivity of donor-free group 12 mesityl compounds. The reaction of M[Mes]$_2$ (M = Cd, Hg) with an excess of BBr_3 produces $MesBBr_2$. UV-induced conversion of Hg[Mes]$_2$ in benzene yielded quantitatively mesitylene and mercury whereas irradiation of a chloroform solution of Hg[Mes]$_2$ for 1290 min (λ_{max} = 510 nm) gave mesitylene, Hg[Mes]Cl, and $HgCl_2$ in a ratio of 6:4:1. Slow concentration of the reaction solution led to the deposition of X-ray quality crystals of the addition compound of two Hg[Mes]Cl molecules and $HgCl_2$ (monoclinic space group $P2_1/n$).

Introduction

Since the first synthesis of dimesitylmercury in 1895 by *Michaelis* many applications of synthesized diarylmercury compounds have been documented.[1] Despite the long existence and common usage of dimesitylmercury, its structure has not yet been investigated well. However, detailed structural information concerning the extent of coordination and association in organometallic compounds is important in understanding their physical behavior and chemical reactivity.

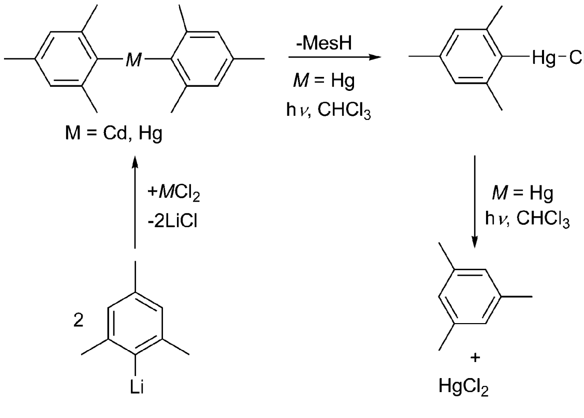
Due to its prominence, several preparation routes to Hg[Mes]$_2$ have been described in the literature: (i) dimesitylmercury was obtained from the reaction of MesBr and sodium amalgam,[1] (ii) Hg[Mes]$_2$ could also be synthesized by the reaction of $HgCl_2$ with MesMgBr in a 1:2 stoichiometry,[2,3] (iii) the reaction of the diazonium chloride $MesN_2Cl$ with copper in the presence of $HgCl_2$ yielded Hg[Mes]$_2$,[4] and at last (iv) the dimesitylmercury could be prepared by reaction of the boronic acid $MesB(OH)_2$ with Hg[OAc]$_2$.[5] In contrast to the long-standing known preparation routes of Hg[Mes]$_2$, the first synthesis of the corresponding cadmium compound Cd[Mes]$_2$ has been reported very recently.[6]

In this paper we report for the first time the structures of solvent-free, unsupported Cd[Mes]$_2$ and Hg[Mes]$_2$. In addition we present here the reactivity of M[Mes]$_2$ (M = Cd, Hg) towards BBr_3 and we describe the UV-induced decomposition reaction of Hg[Mes]$_2$.

Results and Discussion

Our group has recently reported on the chemical and structural features of group 12 compounds of the type MR_2.[7–10] On the basis of these previous investigations we are now interested in the solid-state structures of donor-free dimesitylcadmium and dimesitylmercury. As shown in Scheme 1, we could synthesize solvent-free M[Mes]$_2$ (M = Cd, Hg) when MCl_2 (M = Cd, Hg) was treated with two equivalents of Li[Mes][11] in thf at ambient temperature. The mesityllithium was completely consumed overnight, (as determined by NMR spectroscopy). Changing the solvent to benzene, filtering, and slowly concentrating the filtrate leads to the deposition of X-ray quality crystals of solvent-free M[Mes]$_2$ (M = Cd, Hg).

We found that M[Mes]$_2$ (M = Cd, Hg) organyl compounds are much less moisture-sensitive than mesityllithium. Moreover, in



Scheme 1. Synthesis of M[Mes]$_2$ (M = Cd, Hg) and UV-induced decomposition reaction of Hg[Mes]$_2$.

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the literature it was reported that no reaction has taken place between Hg[Mes]$_2$ and Brønstedt acids like HCl.[1] In our study we investigated the reaction of M[Mes]$_2$ (M = Cd, Hg) with the Lewis acid BBr$_3$. The reaction of M[Mes]$_2$ (M = Cd, Hg) with an excess of BBr$_3$ produces MesBBr$_2$.[16] However, in both cases a reddish precipitate was formed additionally. We found that M[Mes]$_2$ (M = Cd, Hg) are light-sensitive compounds. When a benzene solution of Hg[Mes]$_2$ was irradiated with a high-pressure mercury lamp ($\lambda_{\max}$ = 510 nm), a gray-metallic precipitate formed. After 690 min the ^{1}H and ^{13}C NMR spectra of the reaction solution revealed exclusively signals which could be assigned to mesitylene. However, in chloroform UV-induced conversion of Hg[Mes]$_2$ took another course than in benzene. When a chloroform solution of Hg[Mes]$_2$ was irradiated for 1290 min ($\lambda_{\max}$ = 510 nm), mesitylene, Hg[Mes]Cl, and HgCl$_2$ were formed in a 6:4:1 ratio (Scheme 1). Slow concentration of the reaction solution led to the deposition of X-ray quality crystals of the addition compound of two Hg[Mes]Cl molecules and HgCl$_2$. In this context it should be noted when a chloroform solution of Hg[Mes]$_2$ was irradiated for 130 h, mesitylene and HgCl$_2$ could be isolated.[12]

X-ray quality crystals of M[Mes]$_2$ (M = Cd, Hg) were grown from benzene. The solid-state structures of the homologues M[Mes]$_2$ (M = Zn,[13] Cd, Hg) resemble each other closely. Moreover the group 12 metal compounds M[Mes]$_2$ (M = Zn, Cd, Hg) are isomorphous and crystallize in the monoclinic space group $P2_1/n$. Since Cd[Mes]$_2$ is isomorphous to Hg[Mes]$_2$, only dimesitylmercury is depicted (Figure 1). Selected bond lengths and angles for all structurally characterized M[Mes]$_2$ (M = Cd, Hg) compounds can be found in Table 1 and in the caption of Figure 1. The asymmetric unit of M[Mes]$_2$ (M = Zn, Cd, Hg) consists of one mesityl group bonded to the metal atom, which is related to the second substituent by an inversion center. Consequently, the central C–M–C unit is strictly linear in M[Mes]$_2$ (M = Zn, Cd, Hg) and the two aryl groups are coplanar with respect to each other. In this context it should be noted that a characteristic feature of group 12 compounds of the type MR_2 with bulky ligands (e.g. R = Si*t*Bu$_3$,[7] Si(SiMe$_3$)$_3$,[15] N(SiMe$_3$)$_2$[9]) is the linearity of the E–M–E bond axis. However, the central E–M–E units in the solid-state structures of M[SiH(Si*t*Bu$_3$)$_2$]$_2$ (M = Zn, Cd, Hg)[8] and Zn[P*t*Bu$_2$]$_2$[10] deviate from linearity due to interactions between the metal atoms with H–Si bond in M[SiH(Si*t*Bu$_3$)$_2$]$_2$ and between the zinc atom with the lone pair of the phosphorus atom in Zn[P*t*Bu$_2$]$_2$, respectively. The structures of M[Mes]$_2$ (M = Zn, Cd, Hg) and Hg[Mes]Cl reveal weak contacts from the carbon atoms of the mesityl rings to the metal atoms of neighboring molecules. These M–C distances (>3.3 Å) are much longer than the shortest intermolecular Li–C contacts in Li[Mes] (Table 1). In Table 1 the metrical parameters of unsupported M[Mes]$_2$ (M = Zn, Cd, Hg) and supported Hg[Mes]Cl have been compared with those of solvate-free mesityllithium[11] and thf complexed dimesitylmagnesium [Mg(thf)$_2$][Mes]$_2$.[16]

X-ray quality crystals of Hg[Mes]Cl·0.5HgCl$_2$ were grown from the reaction solution at ambient temperature. Selected bond lengths and angles for Hg[Mes]Cl·0.5HgCl$_2$ are found in the caption of Figure 2 and Table 1. The addition compound Hg[Mes]Cl·0.5 HgCl$_2$ crystallizes in the monoclinic space group $P2_1/n$ with one half molecule in the asymmetric unit, which is related to its second half via a crystallographic inversion center (Hg(2) atom in Figure 2). The Hg–C bond

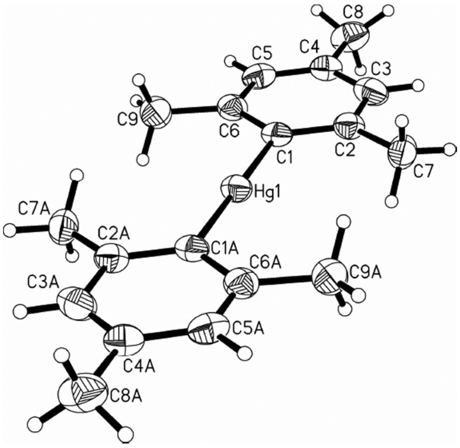

Figure 1. Molecular structure of Hg[Mes]$_2$ in the solid state. Selected bond lengths /Å and bond angles /°: Hg(1)–C(1) 2.080(6), C(1)–C(2) 1.409(9), C(1)–C(6) 1.413(8), C(2)–C(3) 1.407(10), C(2)–C(7) 1.492(9), C(3)–C(4) 1.392(9), C(4)–C(5) 1.391(10), C(4)–C(8) 1.514(9), C(5)–C(6) 1.384(9), C(6)–C(9) 1.510(9); C(1)#1–Hg(1)–C(1) 179.999(1). Selected bond lengths /Å and bond angles /° of Cd[Mes]$_2$: Cd(1)–C(1) 2.114(7), C(1)–C(6) 1.395(9), C(1)–C(2) 1.396(10), C(2)–C(3) 1.421(12), C(2)–C(7) 1.499(11), C(3)–C(4) 1.374(11), C(4)–C(5) 1.385(11), C(4)–C(8) 1.512(10), C(5)–C(6) 1.412(10), C(6)–C(9) 1.510(11); C(1)–Cd(1)–C(1)#1 179.999(1). Symmetry transformation used to generate equivalent atoms: #1 –x, –y + 1, –z + 1.

Table 1. Selected bond lengths /Å of unsupported Li[Mes] and M[Mes]$_2$ (M = Zn, Cd, Hg) as well as of supported Hg[Mes]Cl and Mg[Mes]$_2$.

	M–C[a)]	M–C[b)]	C=C[c)]	C–CH$_3$[c)]
Li[Mes][11]	2.16	2.40	1.40	1.53
Zn[Mes]$_2$[13]	1.94	3.73	1.39	1.52
Cd[Mes]$_2$	2.11	3.66	1.40	1.51
Hg[Mes]$_2$	2.08	3.75	1.40	1.51
Hg[Mes]Cl[d)]	2.05	3.32	1.40	1.51
[Mg(thf)$_2$][Mes]$_2$[16]	2.17	5.72	1.40	1.52

a) Intramolecular, b) intermolecular, c) average, d) supported with 0.5 equivalent of HgCl$_2$.

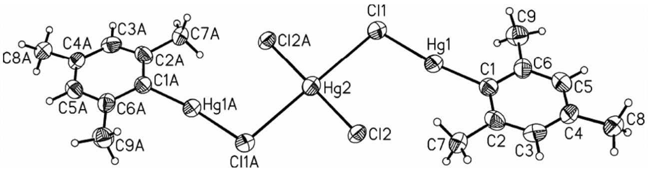

Figure 2. Molecular structure of Hg[Mes]Cl·0.5HgCl$_2$ in the solid state. Selected bond lengths /Å and bond angles /°: Hg(1)–C(1) 2.045(12), Hg(1)–Cl(1) 2.348(3), Cl(1)–Hg(2) 2.969(3), C(1)–C(2) 1.407(16), C(1)–C(6) 1.436(16), C(2)–C(3) 1.373(18), C(2)–C(7) 1.519(16), C(3)–C(4) 1.382(17), C(4)–C(5) 1.382(17), C(4)–C(8) 1.484(18), C(5)–C(6) 1.400(16), C(1)–Hg(1)–Cl(1) 172.6(3).

[2.045(12) Å] in Hg[Mes]Cl·0.5 $HgCl_2$ is somewhat shorter than the corresponding bond lengths in Hg[Mes]$_2$, as shown in Table 1.

Experimental Section

All experiments were carried out under dry argon or nitrogen using standard Schlenk and glove box techniques. Chloroform was dried with CaH_2 and freshly distilled prior to use. Benzene and thf were distilled from sodium/benzophenone. Li[Mes] was prepared according to a published procedure.[11] All other starting materials were purchased from commercial sources and used without further purification. NMR spectra were recorded with a Bruker DPX 250, a Bruker Avance 300, and a Bruker Avance 400 spectrometer. Elemental analyses were performed at the microanalytical laboratories of the Universität Frankfurt. Mass spectra were recorded with a Fisons VG Platform II instrument. GC was performed with a Finnigan Trace GC with Trace MS 2000 series. An UV lamp of the type TQ 150 Z2 has been used for the photochemical experiments.

***M*[Mes]$_2$:** *M*Cl_2 [0.015 g 0.08 mmol (Cd), 0.022 g, 0.08 mmol (Hg)] was suspended in thf (10 mL). After adding of mesityllithium (0.020 g, 0.16 mmol) at room temperature, the reaction mixture was stirred for 10 h. All volatiles were removed from the yellow solution in vacuo and the residue was extracted with benzene (10 mL). The extract was filtered through a frit. Slow concentration of the filtrate led to the deposition of X-ray quality crystals of *M*[Mes]$_2$ at ambient temperature.

Cd[Mes]$_2$: Yield: 0.017 g (68 %). M.p.: >250 °C. **^{1}H NMR** (300.0 MHz, $CDCl_3$): δ = 6.92 (s, 4 H, *meta*-Ph), 2.51 (s, 6 H, *ortho*-Me), 2.29 (s, 3 H, *para*-Me). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ = 155.7 (*ipso*-Mes), 145.0 (*ortho*-Mes), 138.1 (*para*-Mes), 126.4 (*meta*-Mes), 27.7 (*ortho*-Me), 21.1 (*para*-Me). **ESI$^+$** *m/z* (%): 355.9 (4.5) 354.9 (72.9) 354.0 (21.9) 352.9 (100) 351.8 (40.0) 351.0 (85.7) 350.0 (32.0) 349.1 (57.4) $[M + 1]^+$, calcd. for $[M + 1]^+$ 356.1 (4.7) 355.1 (25.3) 354.1 (18.7) 353.1 (100) 352.1 (54.5) 351.1 (85.1) 350.1 (48.3) 349.1 (39.6).

Hg[Mes]$_2$: Yield: 0.026 g (75 %). $C_{18}H_{22}Hg$ (438.96): C, 49.25, H, 5.05, Found C, 49.13, H, 5.16 %. **^{1}H NMR** (400.1 MHz, $CDCl_3$): δ = 7.02 (s, 4 H, *meta*-Ph), 2.52 (s, 12 H, *ortho*-Me), 2.31 (s, 6 H, *para*-Me). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ = 169.8 (*ipso*-Mes), 144.4 (*ortho*-Mes), 137.9 (*para*-Mes), 128.1 (*meta*-Mes), 24.4 (*ortho*-Me), 21.9 (*para*-Me). **^{199}Hg NMR:** see ref.[18]

Reaction of *M*[Mes]$_2$ (*M* = Cd, Hg) with BBr_3: A NMR tube was charged with *M*[Mes]$_2$ [2 mg, 0.008 mmol (Cd); 6 mg, 0.014 mmol (Hg)] in 1 mL C_6D_6 to which BBr_3 [0.006 mL, 16 mg, 0.064 mmol (Cd); 0.008 mL, 21 mg, 0.084 mmol (Hg)] was added. In both cases the NMR spectra of the reaction solution revealed exclusively signals that could be assigned to literature-known $MesBBr_2$[17] and BBr_3. Additionally, a reddish precipitate formed in both cases.

Irradiation of Hg[Mes]$_2$ in Benzene: Hg[Mes]$_2$ (2 mg, 4.556 µmol) and benzene (0.5 mL) were combined. The colorless solution was irradiated with a high-pressure mercury lamp (λ_{max} = 510 nm) for 780 min. An accompanying formation of mercury was observed. The ^{1}H and ^{13}C NMR spectra of the reaction solution revealed exclusively signals that could be assigned to mesitylene.

Irradiation of Hg[Mes]$_2$ in Chloroform: Hg[Mes]$_2$ (2 mg, 4.556 µmol) and chloroform (1 mL) were combined. The colorless solution was irradiated with a high-pressure mercury lamp (λ_{max} = 510 nm) for 1290 min. An accompanying change of the color of the solution from colorless to yellow was observed. The ^{1}H and ^{13}C NMR spectrum of the reaction solution revealed signals that could be assigned to mesitylene and Hg[Mes]Cl in a ratio of 6:4. In order to prove this result we analyzed the reaction solution additionally by gas chromatography. Slow concentration of the solution led to the deposition of X-ray quality crystals of Hg[Mes]Cl·0.5$HgCl_2$ at ambient temperature [Yield: 1 mg (61 %)].

Hg[Mes]Cl: M.p.: 157 °C. $C_9H_{11}ClHg$ (355.23): C, 30.43, H, 3.12, Found C, 32.00, H, 3.44%. **^{1}H NMR** (300.0 MHz, $CDCl_3$): δ = 6.97 (m, 2 H, *meta*-Ph), 2.45 (br., 6 H, *ortho*-Me), 2.31 (br., 3 H, *para*-Me). **^{13}C{^{1}H} NMR** (75.5 MHz, $CDCl_3$): δ = 149.8 (*ipso*-Mes), 141.8 (*ortho*-Mes), 139.6 (*para*-Mes), 128.0 (*meta*-Mes), 26.2 (*ortho*-Me), 21.0 (*para*-Me). **ESI$^+$** *m/z* (%): 360.2 (6.8) 359.2 (5.1) 358.2 (45.9) 357.2 (21.0) 356.3 (100.0) 355.2 (58.5) 354.2 (77.5) 353.2 (52.5) 352.2 (30.9) $[M]^+$, calcd. for $[M]^+$ 360.0 (5.8) 359.0 (4.2) 358.0 (43.4) 357.0 (20.3) 356.0 (100.0) 355.0 (54.2) 354.2 (77.5) 353.0 (45.6) 352.0 (25.6).

X-ray Crystallographic Study: Data Collection: Stoe-IPDS-II diffractometer, empirical absorption correction using MULABS,[19] structure solution by direct methods,[20] structure refinement: full-matrix least-squares on F^2 with SHELXL-97.[21] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. CCDC-806453 (Cd[Mes]$_2$), CCDC-806452 (Hg[Mes]$_2$), and CCDC-808674 (Hg[Mes]Cl·0.5$HgCl_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement for Cd[Mes]$_2$: T = 173(2) K, Mo-K_α, λ = 0.71073 Å, 4691 no. of reflections collected, 1377 no. of independent reflections. R_1 = 0.0542, wR_2 = 0.1355 [$I > 2\sigma(I)$]. R_1 = 0.0803, wR_2 = 0.1482 (all data). Monoclinic crystal system, space group $P2_1/n$, Z = 2, a = 4.7083(9) Å, b = 10.9914(12) Å, c = 15.160(3) Å, β = 98.236(14)°, V = 776.5(2) Å^3.

Crystal data and structure refinement for Hg[Mes]$_2$: T = 173(2) K, Mo-K_α, λ = 0.71073 Å, 12721 no. of reflections collected, 1442 no. of independent reflections. R_1 = 0.0307, wR_2 = 0.0726 [$I > 2\sigma(I)$]. R_1 = 0.0451, wR_2 = 0.0801 (all data). Monoclinic crystal system, space group $P2_1/n$, Z = 2, a = 4.8394(4) Å, b = 10.6515(7) Å, c = 15.1239(14) Å, β = 97.501(7)°, V = 772.92(11) Å^3.

Crystal data and structure refinement for Hg[Mes]Cl·0.5$HgCl_2$: T = 173(2) K, Mo-K_α, λ = 0.71073 Å, 9981 no. of reflections collected, 2080 no. of independent reflections. R_1 = 0.0472, wR_2 = 0.1102 [$I > 2\sigma(I)$]. R_1 = 0.0560, wR_2 = 0.1148 (all data). Monoclinic crystal system, space group $P2_1/n$, Z = 2, a = 4.1064(4) Å, b = 17.1907(14) Å, c = 15.969(2) Å, β = 95.799(9)°, V = 1121.5(2) Å^3.

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