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Bis(alkylcyclopentadienyl)cadmium Complexes and Alkylcyclopentadienyl(mesityl)cadmium: Synthesis and Structure

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Cadmium diiodide tetrahydrofuran adduct was prepared from the elements in tetrahydrofuran and converted to bis(alkylcyclopentadienyl)cadmium complexes with sodium tetraisopropylcyclopentadienide or sodium 1,2,4-tri(*tert*-butyl)cyclopentadienide. Both products are fluxional in solution, and for bis{tri(*tert*-butyl)cyclopentadienyl}cadmium η^1,η^1-bonding has been observed in the solid state. With 1 equiv each of sodium 1,2,4-tri(*tert*-butyl)cyclopentadienide and mesitylmagnesium bromide the aryl complex mesityl{tri(*tert*-butyl)cyclopentadienyl}cadmium could be obtained from cadmium diiodide in moderate yield.

Introduction

Due to its position in the periodic table cadmium is a member of the d-block elements, but is normally not regarded as a transition metal, because it always retains a d^{10} electron configuration in its compounds.[1] Therefore, several textbooks treat cadmium organyls within chapters on organometallic compounds of main group elements (e.g., refs 2, 3). While some bis(cyclopentadienyl)cadmium complexes with additional donor ligands have been structurally characterized,[4,5] there is no structural information available on base-free bis(cyclopentadienyl)cadmium compounds. The parent compound [Cd(C_5H_5)$_2$] is insoluble in unpolar solvents[6] and has an unknown, probably polymeric structure. Its permethylated derivative [Cd(C_5Me_5)$_2$] is pentane-soluble and light-sensitive and could not be obtained as single crystals.[7] The lack of experimental data as well as the perspective of using alkylated cyclopentadienylcadmium complexes as mild and easily available alkylcyclopentadienyl transfer agents stimulated our interest in bis(alkylcyclopentadienyl)cadmium compounds.

Results and Discussion

When tetraisopropylcyclopentadienylsodium was reacted with the tetrahydrofuran adduct of cadmium diiodide, light yellow, air- and moisture-sensitive bis(tetraisopropylcyclopentadienyl)cadmium (**1**) was obtained in 75% yield (see Experimental Section). **1** is decomposed by direct sunlight within 1−2 days, but shows no signs of photolysis under normal fluorescent laboratory illumination. **1** melts at 145 °C, but was repeatedly found to decompose within a few hours upon sublimation in an oil pump vacuum around 100 °C, which provided only a low yield of microcrystalline sublimate. Crystals of **1** grown from hexane solution at room temperature were twinned, and X-ray diffraction gave only unsatisfactory results (see Experimental Section; for a line drawing of **1** see Figure 1).

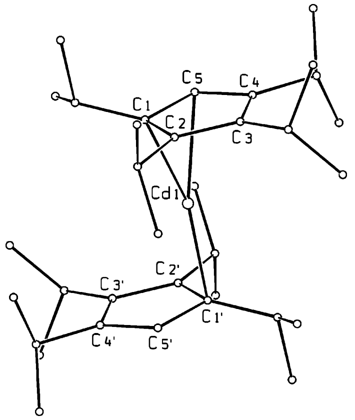

Figure 1. Line drawing of bis(tetraisopropylcyclopentadienyl)cadmium (**1**). The central atom shown corresponds to one of two Cd positions very close to each other and related by a center of symmetry. The second Cd position has been omitted for clarity.

The Cd central atom is disordered between two positions related by a center of symmetry and is coordinated to one of the two five-membered rings in an η^2-bonding mode (Cd−C 2.24(2) Å, 2.35(2) Å) and to the other in an η^1-bonding mode (Cd−C 2.27(2) Å). The other Cd···C distances are all more than 2.67 Å, in contrast to the η^1/η^5 situation found for bis(tetraisopropylcyclopentadienyl)zinc.[8]

NMR spectra of **1** at room temperature are similar to the spectra of octaisopropylferrocene.[9] Upon cooling of an octadeuterotoluene solution, however, signal coalescence was observed at temperatures as low as 215 K for the two isopropyl methyne protons and 210 K for the methyl groups. Cooling to 195 and finally 185 K produced still only one ring proton signal for the two equivalent rings and was not enough for decoalescence to occur, while solvent mixtures of CD_2Cl_2 with $CDCl_3$

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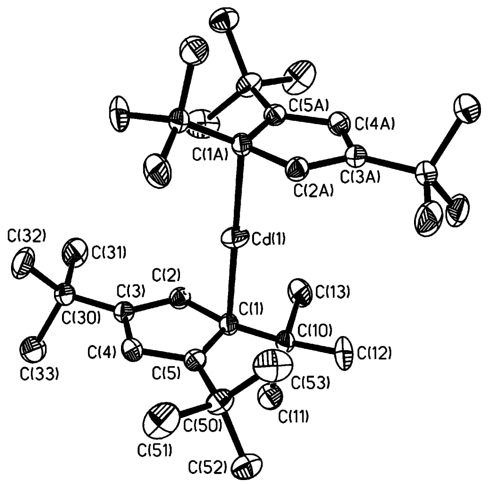
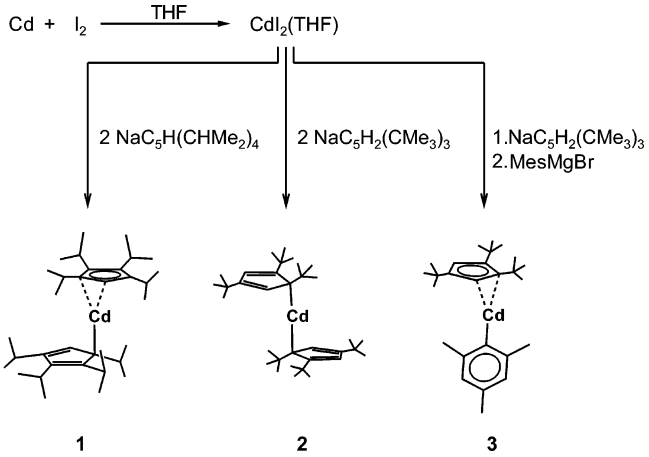


Figure 2. Crystal structure of the bis{tri(*tert*-butyl)cyclopentadienyl} complex **2**. Selected distances (Å) and angles (deg): Cd1−C1 2.201(2), Cd1−C2 2.659(2), Cd1−C5 2.740(2), C1−C2 1.477(3), C2−C3 1.367(3), C3−C4 1.426(3), C4−C5 1.380(3), C5−C1 1.499(3), Cd1−C1−C10 116.27(15), angles between Cp plane and lines C1−Cd1 92.8(2), C1−C10 30.3(3) (50% probability ellipsoids).

Scheme 1. Synthesis of Compounds 1−3



suitable for lower temperatures produced a colorless precipitate with decomposition of **1**.

A similar procedure gave light yellow bis{tri(*tert*-butyl)cyclopentadienyl}cadmium (**2**) in 79% yield as a hexane-soluble, crystalline material, whose thermal stability is higher than that of **1**. **2** melts without decomposition at 143 °C and could be obtained as single crystals suitable for X-ray diffraction by sublimation at 100 °C during 12 h in a glass tube sealed under vacuum.

The crystal structure of **2** (Figure 2) is very similar to bis{tri(*tert*-butyl)cyclopentadienyl}mercury (**3**).[10]

Both complexes exhibit an η^1 coordination of both five-membered rings to the central atom and a linear carbon−metal−carbon arrangement (the Cd atom of **2** is located on a crystallographic center of symmetry). Bonding may include a weak ring−Cd π donation, tilting the ring toward the metal as discussed and illustrated by Schrock et al.,[7] but the Cd−C distances are 21% and 24% longer for C2 and C5 than for C1 (cf. caption of Figure 2). The observed metal−ring geometry parallels that of main group cyclopentadienyl complexes such as $[(C_5HR_4)AsCl_2]$ (**4**, R = $CHMe_2$),[11] whose structure closely resembles **2** not only because of the η^1 coordination but also because the C−As bond is sticking out of the ring plane approximately at a right angle like the C−Cd bond in **2** (92.5° for **2** vs 86.9° for **4**) and because of the localized intra-ring single and double bonds (cf. caption of Figure 2). The Cd−C bonds of **2** (2.201(2) Å) are significantly shorter than those observed in donor complexes of bis(cyclopentadienyl)cadmium (>2.30 Å)[4,5] but still longer than the Hg−C bonds of **3** (2.153(3) Å), a consequence of the lanthanide contraction.

Because of sigmatropic shifts of the metal in solution, ^{1}H NMR spectra of **2** show a 4:18:36 signal pattern with the three singlets corresponding to two symmetry-equivalent rings, each one featuring two ring protons and two sets of *tert*-butyl groups in a 1:2 ratio. In the ^{13}C NMR spectra three signals are observed for ring carbon atoms and four signals for two sets of *tert*-butyl groups. The coupling constants $^1J_{\mathrm{Cd,C}}$ are similar for C2/C4 (the two ring−CH units) and C3 (the C^{t}Bu unit between the two ring−CH moieties) with 12.6 and 14.9 Hz, whereas C1/C5 (the two vicinal C^{t}Bu groups of the five-membered ring) exhibit a 95.2 Hz coupling constant. This observation identifies C1 and C5 (the latter is magnetically equivalent in solution as a consequence of cadmium migration) as the most favorable bonding partners for the metal atom, which is due to release of steric strain because it allows one of the bulky *tert*-butyl neighbors in the 1- and 2-position to bend out of the ring plane.[12] This could be a reason why **2** does not adopt the η^3 coordination predicted for the bis(cyclopentadienyl)cadmium parent compound.[13] The cadmium satellites observed in the ^{1}H NMR spectra of **1** and **2** according to their intensity and to the shape of some of the satellite signals appear to be superpositions of satellites due to proton coupling with ^{111}Cd and ^{113}Cd nuclei (I = 1/2), which are of almost equal abundance (12.75% vs 12.26%).

When cadmium diiodide was reacted with 1 equiv each of tri(*tert*-butyl)cylopentadienylsodium and mesitylmagnesium bromide, colorless, extremely air- and moisture-sensitive tri(*tert*-butyl)cyclopentadienylmesitylcadmium (**3**) was obtained in 43% yield. **3** melts at 105 °C, is very light-sensitive, and shows the first signs of photolysis under fluorescent laboratory illumination after 3 h. A few single crystals could be obtained by sublimation for 6 h at 90 °C in a glass tube sealed under vacuum. X-ray diffraction revealed a Cd central atom coordinated to the five-membered ring in an η^2-bonding mode and to the mesityl fragment in a σ-bonding mode, but the quality of the data set is unsatisfactory and a detailed discussion of structural parameters of **3** is not warranted. NMR spectra of **3** show three singlets corresponding to the five-membered ring, similar to **2**, and three signals for the mesityl fragment. ^{13}C{^{1}H} NMR spectra show the typical resonances for the tri(*tert*-butyl)cyclopentadienyl ligand except for one substituted ring carbon atom, whose signal is hidden under the solvent peak. The $^1J_{\mathrm{Cd,C}}$ and $^3J_{\mathrm{Cd,C}}$ coupling

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(12) The direct migration of Cd from C1 to C5 would require the *tert*-butyl group bound to C1 to come back into the ring plane, while the alkyl group attached to C5 is tilted out of the ring plane. The activation barrier for such a passage of vicinal ^{t}Bu groups past each other should be rather high and may likely result in an oscillation with reversal of the migration direction at C1 and C5, which divides this activation energy in two separate parts. A similar example has been observed for $[(C_5HR_4)AsCl_2]$ (R = $CHMe_2$),[11] where NMR spectra indicate an oscillation of the $AsCl_2$ substituent between C1 and C4 via C5 and not via C2/C3.

(13) Budzelaar, P. H. M.; Engelberts, J. J.; van Lenthe, J. H. *Organometallics* **2003**, *22*, 1562.

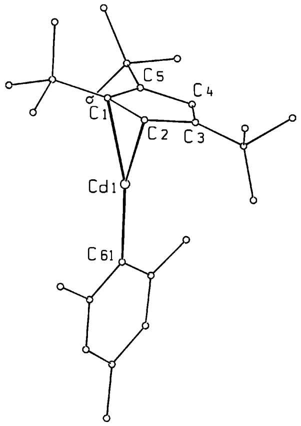

Figure 3. Line drawing of mesityl(tetraisopropylcyclopentadienyl)cadmium (**3**).

constants are comparable with those observed for **2**. The mesityl fragment produces six resonances as expected.

Conclusions

It has been demonstrated that cyclopentadienylcadmium compounds with bulky alkyl substituents are suitable for normal handling, storage, and even purification and crystal growth by sublimation.

The different thermal stability of the $CdC_{34}H_{58}$ isomers $[\{C_5H(CHMe_2)_4\}_2Cd]$ (**1**) and $[\{C_5H_2(CMe_3)_3\}_2Cd]$ (**2**) may be attributable to differences in the steric peoperties of the two $C_{17}H_{29}$ ligands employed in this work. The η^1,η^1-bonded structure of **2** illustrates the close relationship between cadmium and mercury and contrasts with expectations based on theoretical calculations, which predict an η^3,η^3-bonded structure for the parent compound.

The formation of mesityl{tri(*tert*-butyl)cyclopentadienyl}-cadmium by sequential reaction of cadmium diiodide with sodium 1,2,4-tri(*tert*-butyl)cyclopentadienide and mesitylmagnesium bromide is likely to proceed via a mono(ring)cadmium iodide intermediate.

Experimental Section

Cadmium Diiodide Tetrahydrofuran Adduct. Iodine (8.00 g, 31.5 mmol) and freshly cut pieces of cadmium metal (4.00 g, 35.6 mmol) were stirred with refluxing tetrahydrofuran overnight. The warm solution was filtered and allowed to cool to room temperature. The product crystallized as colorless needles, which were isolated from the mother liquor and dried in an oil pump vacuum to yield 12.3 g (28 mmol, 89%) of white powder. Anal. (%) Calcd for $C_4H_8CdI_2O$ (438.33 g/mol): C 10.96, H 1.84. Found: C 11.1, H 2.0.

Bis(tetraisopropylcyclopentadienyl)cadmium (1). To a solution of cadmium diiodide tetrahydrofuran adduct (438 mg, 1 mmol) in 20 mL of tetrahydrofuran was added 2 equiv (512 mg, 2 mmol) of sodium tri(*tert*-butyl)cyclopentadienide. The solution turned yellow immediately and the solvent was evaporated to dryness. Extraction with hexane (25 mL), filtration, and evaporation gave a light yellow, microcrystalline powder (432 mg, 0.75 mmol, 75%), which melted at 145 °C under argon and sublimed slowly with concomitant and predominant decomposition above 100 °C in an evacuated and sealed capillary. Anal. Calcd for $C_{34}H_{58}Cd$ (579.24): C, 70.50; H, 10.09. Found: C, 69.9; H, 10.0. ^1H NMR (400 MHz, 298 K, C_6D_6): δ 4.67 (s with satellites, 2H, ring H, $^2J_{Cd,H} = 86.9$ Hz), 3.18 (m, 4H, C*H*Me$_2$), 3.05 (m, 4H, C*H*Me$_2$), 1.39 (d, ^3J(HH) = 7.34 Hz, 12 H, C*H*$_3$), 1.37 (d, ^3J(HH) = 7.33 Hz, 12 H, C*H*$_3$), 1.16 (d, ^3J(HH) = 6.75 Hz, 12 H, C*H*$_3$), 1.04 (d, ^3J(HH) = 6.75 Hz, 12 H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 134.4 (s with satellites, 4C, ring-*C*CHMe$_2$, $^1J_{Cd,C} = 16.6$ Hz), 132.7 (s, 4C, ring-*C*CHMe$_2$), 74,7 (s with satellites, 2C, ring-*C*H, $^1J_{Cd,C} = 150.0$ Hz), 29.0 (s, 4C, *C*HMe$_2$), 27.5 (s, 4C, *C*HMe$_2$), 27.4 (s with satellites, 4C, *C*H$_3$, $^3J_{Cd,C} = 9.3$ Hz), 24.4 (s with satellites, 4C, *C*H$_3$, $^3J_{Cd,C} = 13.9$ Hz), 24.2 (s with satellites, 4C, *C*H$_3$, $^3J_{Cd,C} = 11.1$ Hz), 23.9 (s with satellites, 4C, *C*H$_3$, $^3J_{Cd,C} = 14.8$ Hz).

Bis{tri(*tert*-butyl)cyclopentadienyl}cadmium (2). To a solution of cadmium diiodide tetrahydrofuran adduct (438 mg, 1 mmol) in 20 mL of tetrahydrofuran was added 2 equiv (512 mg, 2 mmol) of sodium tri(*tert*-butyl)cyclopentadienide. The solution turned yellow immediately and the solvent was evaporated to dryness. Extraction with hexane (25 mL), filtration, and evaporation gave a light yellow, microcrystalline powder (456 mg, 0.79 mmol, 79%), which melted at 143 °C under argon and sublimed slowly above 100 °C in an evacuated and sealed capillary. Anal. Calcd for $C_{34}H_{58}Cd$ (579.24): C, 70.50; H, 10.09. Found: C, 70.2; H, 10.1. ^1H NMR (400 MHz, 298 K, C_6D_6): δ 6.39 (s with satellites, 4H, ring-CH, $^2J_{Cd,H} = 9.2$ Hz), 1.344 (s, 36H, CH$_3$), 1.341 (s, 18H, CH$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, C_6D_6): δ 139.0 (s with satellites, 2C, *C*CMe$_3$, $^1J_{Cd,H} = 14.9$ Hz), 125.2 (s with satellites, 4C, *C*CMe$_3$, $^1J_{Cd,C} = 95.2$ Hz), 113.3 (s with satellites, 4C, ring-*C*H, $^1J_{Cd,C} = 12.6$ Hz), 34.3 (s with satellites, 12C, CH$_3$, $^3J_{Cd,C} = 13.8$ Hz),34.2 (s, *C*Me$_3$), 32.2 (s, *C*Me$_3$), 32.1 (s with satellites, 6C, *C*H$_3$, $^3J_{Cd,C} = 9.2$ Hz).

(Mesityl){tri(*tert*-butyl)cyclopentadienyl}cadmium (3). To a suspension of cadmium diiodide tetrahydrofuran adduct (438 mg, 1 mmol) in 20 mL of diethyl ether were successively added 1 equiv (256 mg, 1 mmol) of sodium tri(*tert*-butyl)cyclopentadienide and 1 equiv of mesitylmagnesium bromide diethyl ether adduct. The mixture was stirred for 3 min at room temperature and the solvent was evaporated to dryness. Extraction with hexane (25 mL), filtration, and evaporation gave a colorless, microcrystalline powder (199 mg, 0.43 mmol, 43%), which melted at 105 °C under argon and sublimed with considerable decomposition above 90 °C in an evacuated and sealed capillary. Anal. Calcd for $C_{26}H_{40}Cd$ (465.01): H, 8.67. Found: H, 8.37. Due to the extreme air and moisture sensitivity of **3**, we have been unable to obtain satisfactory carbon values in this case. ^1H NMR (400,13 MHz, 298 K, C_6D_6): δ 6.82 (s, 2H, ring-CH), 6.50 (s with satellites, 2H, ring-CH, $^2J_{Cd,H} = 14.3$ Hz), 2.39 (s, 6H, ring-Me), 2.17 (s, 3H, ring-Me),1.49 (s, 18H, CMe$_3$), 1.32 (s, 9H, CMe$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, C_6D_6): δ 160.1 (s, 1C, *ipso*-C, mesityl, intensity too low for observation of Cd satellites), 153.8 (s, 2C, mesityl-ring *ortho*-CMe), 144.5 (s with satellites, 2C, C-CMe$_3$, $^1J_{Cd,C} = 14.6$ Hz), 132,7 (s, 1C, mesityl-ring-*para*-CMe), (1C, C-CMe$_3$ and mesityl-ring-CH, both hidden under the solvent signal), 120.0 (s with satellites, 2C, Cp-ring-CH, $^1J_{Cd,C} = 13.2$ Hz), 35.1 (s with satellites, 6C, CH$_3$, $^1J_{Cd,C} = 15.9$ Hz), 34.5 (s, 2C, CMe$_3$), 33.2 (s, 2C, mesityl-ring-*ortho*-CH$_3$), 30.6 (s, 1C, mesityl-ring-para-CH$_3$), 30.4 (s with satellites, 3C, CH$_3$, $^1J_{Cd,C} = 9.7$ Hz), 29.7 (s, 1C, CMe$_3$).

X-ray Crystallography. Bis(tetraisopropylcyclopentadienyl)cadmium (1). Attempted crystal structure determination on a twinned crystal of the cadmium complex $C_{34}H_{58}Cd$ (**1**): IPDS diffractometer with imaging system (Stoe), Mo Kα radiation, $\lambda = 71.073$ pm, $2\theta_{max} = 51.34°$, $T = 193(2)$ K, crystal dimensions 0.21 × 0.12 × 0.07 mm^3, triclinic, space group $P\bar{1}$ (No. 2), lattice parameters (193 K): $a = 8.461(2)$ Å, $b = 9.543(2)$ Å, $c = 11.470(2)$ Å, $\alpha = 109.24(2)°$, $\beta = 109.48(3)°$, $\gamma = 97.19(3)°$, $V = 795.2(3)$ Å^3, $Z = 1$, $\rho_{calc} = 1.210$ g cm^{-1}, μ(Mo Kα) = 7.05 cm^{-1}, no absorption corrections, transmission factors 0.79654 to 0.94494, structure solution: direct methods (SHELXS-97), full-matrix least-squares refinement based on F_o^2 (SHELXL-97), 5121 reflections, 2044 unique reflections, 172 parameters, R1(2821 $F_o > 2\sigma(F_o)$) = 0.0647, overlapping reflections due to twinning were omitted for refinement, wR2(all) = 0.1737, disorder of the Cd atom.

Bis{tri(*tert*-butyl)cyclopentadienyl}cadmium (2). Crystal structure determination of the cadmium complex $C_{34}H_{58}Cd$ (**2**): IPDS diffractometer with imaging system (Stoe), Mo Kα radiation, $\lambda = 71.073$ pm, $2\theta_{max} = 53.56°$, 276 images with $0° \leq \phi \leq 250.2°$ and $\Delta\phi = 0.9°$, $T = 193(2)$ K, crystal dimensions $0.25 \times 0.25 \times 0.16$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), lattice parameters (193 K): $a = 8.9989(5)$ Å, $b = 11.6066(9)$ Å, $c = 15.7313(10)$ Å, $\beta = 98.804(7)°$, $V = 1673.72(19)$ Å^3, $Z = 2$, $\rho_{calc} = 1.185$ gcm^{-1}, μ(Mo Kα) = 6.91 cm^{-1}, no absorption corrections, transmission factors 0.8463 to 0.8975, structure solution: direct methods (SIR97), full-matrix least-squares refinement based on F_o^2 (SHELXL-97), 17 136 reflections, 3450 unique reflections, 169 parameters, R1-(2821 $F_o > 2\sigma(F_o)$) = 0.0284, wR2(all) = 0.0678, residual electron density +0.345 to −0.500 e/Å^3, no disorder, CH and CH$_3$ groups have been refined as rigid groups with variable torsion angles (C−H = 0.96 Å, C−C−H and H−C−H = 109.5°).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre; copy of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK; fax +44 1223 336033 (CCDC xxxxxxxxxxx).

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Supporting Information Available: Crystallographic data, labeling diagrams, tables giving atomic positions and anisotropic thermal parameters, bond distances, and angles are available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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