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Main-Group Chemistry of the 2,4,6-Tris(trifluoromethyl)phenyl Substituent: X-ray Crystal Structures of $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Zn$, $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Cd(MeCN)$, and $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Hg$

Sally Brooker, Norbert Bertel, Dietmar Stalke, Mathias Noltemeyer, Herbert W. Roesky,
George M. Sheldrick, and Frank T. Edelmann*

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, FRG

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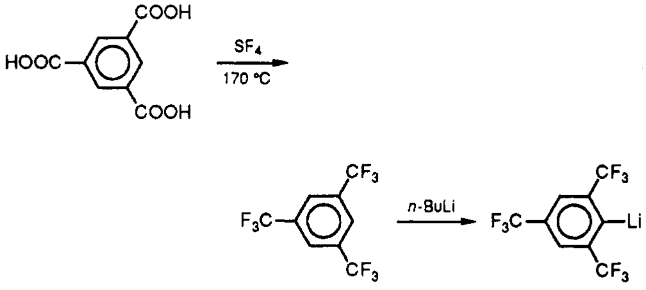
The molecular structures of $(R_F)_2Zn$ (**3**), $(R_F)_2Cd(MeCN)$ (**4a**), and $(R_F)_2Hg$ (**5**) have been determined by X-ray crystallography (R_F = 2,4,6-tris(trifluoromethyl)phenyl). For **3**: triclinic, $P\bar{1}$, $a = 8.339$ (3) Å, $b = 9.064$ (2) Å, $c = 13.499$ (4) Å, $\alpha = 88.38$ (3)°, $\beta = 87.79$ (4)°, $\gamma = 76.85$ (2)°, $V = 992.6$ (5) Å^3, $Z = 2$, and $R = 3.92\%$. For **4a**: monoclinic, $P2_1/c$, $a = 10.876$ (3) Å, $b = 16.79$ (1) Å, $c = 13.865$ (5) Å, $\beta = 112.81$ (2)°, $V = 2334$ (2) Å^3, $Z = 4$, and $R = 3.49\%$. For **5**: monoclinic, $P2_1/n$, $a = 8.842$ (2) Å, $b = 7.891$ (2) Å, $c = 15.294$ (3) Å, $\beta = 92.20$ (3)°, $V = 1066.3$ (4) Å^3, $Z = 2$, and $R = 5.73\%$. A characteristic structural feature of all three derivatives is weak metal–fluorine interactions. $(R_F)_2Zn$ and $(R_f)_2Cd(MeCN)$ represent the first examples of structurally characterized two- and three-coordinate monomeric diarylzinc and -cadmium compounds, respectively.

Introduction

A general way of stabilizing low coordination numbers around main-group elements is to use sterically demanding substituents. Bulky ligands such as mesityl, 2,4,6-tri-*tert*-butylphenyl ("super-mesityl"), or 2,6-diisopropylphenyl have been successfully employed. The 2,4,6-tris(trifluoromethyl)phenyl substituent, $2,4,6\text{-}(CF_3)_3C_6H_2$ (R_F), represents an ideal combination of sterically *and* electronically stabilizing factors. This ligand was introduced into main-group chemistry by Chambers et al. in 1987.[1] Since then, it has become an extremely versatile building block for the synthesis of low-coordinate main-group compounds. For example, the diphosphene $R_FP{=}PR_F$ is the most stable of all known diphosphene derivatives.[2] A number of sulfur and selenium compounds containing the R_F substituent have also been described.[3,4] More recently, the first monomeric diaryllead(II) compound, $(R_F)_2Pb$, has been synthesized and structurally characterized.[5] Another aspect of these recent developments is the derivative chemistry of 2,4,6-tris(trifluoromethyl)phenol (R_FOH) and the corresponding thiol R_FSH.[6-8] Herein we report the X-ray structural investigations of zinc, cadmium, and mercury compounds containing the $2,4,6\text{-}(CF_3)_3C_6H_2$ substituent.

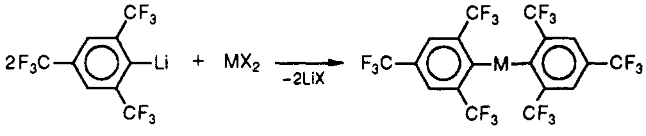
The starting material, 1,3,5-tris(trifluoromethyl)benzene (**1**), was first prepared by McBee and Sanford in 1950.[9] In 1989 we reported an improved synthesis which makes **1** readily available in large quantities and reproducible high yields (ca. 90%).[2] The preparation of **1** involves treatment of benzene-1,3,5-tricarboxylic acid with SF_4 (170 °C, 48 h). The key intermediate in the synthesis of R_F derivatives of main-group elements is R_FLi (**2**), which is obtained via direct metalation of **1** using *n*-butyllithium. The molecular structure of **2** has recently been determined by X-ray crystallography. In the solid state, **2** forms a dimeric 1:1 adduct with diethyl ether. Each lithium is bonded to two carbon atoms, an oxygen of diethyl ether, and two fluorines from ortho CF_3 groups.[10]



1 **2**

Results and Discussion

Reaction of **2** with anhydrous dihalides of zinc, cadmium, and mercury gives compounds **3–5** in moderate yields.



2

3: M = Zn, X = Cl
4: M = Cd, X = I
5: M = Hg, X = Cl

The syntheses of $(R_F)_2Zn$[11] and $(R_F)_2Hg$[1] have been mentioned previously in the literature. The hitherto unknown cadmium compound **4** was prepared analogously from cadmium diiodide. The zinc derivative **3** can be purified either by vacuum distillation or by recrystallization from hexane, whereas **5** is easily obtained in a pure form by

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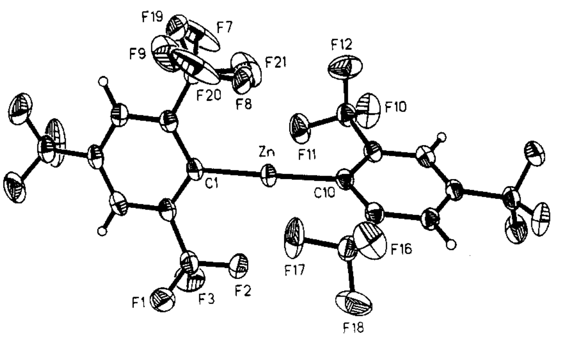


Figure 1. Molecular structure of $(R_F)_2Zn$ (**3**) (50% thermal ellipsoids). Both components of the disordered ortho CF_3 group are shown (occupancies: F7, F8, F9, 0.78; F19, F20, F21, 0.22). Selected interatomic distances (Å) and angles (deg): Zn–C1 = 1.949 (3), Zn–C10 = 1.950 (3), Zn–F2 = 2.544 (6), Zn–F8 = 2.532 (6), Zn–F21 = 2.733 (6), Zn–F11 = 2.609 (6), Zn–F17 = 2.561 (6), F2–F17 = 3.096 (8), F11–F8 = 3.384 (8), F11–F21 = 2.879 (8), F12–F8 = 3.384 (8), F12–F21 = 2.856 (8), C1–Zn–C10 = 170.0 (1).

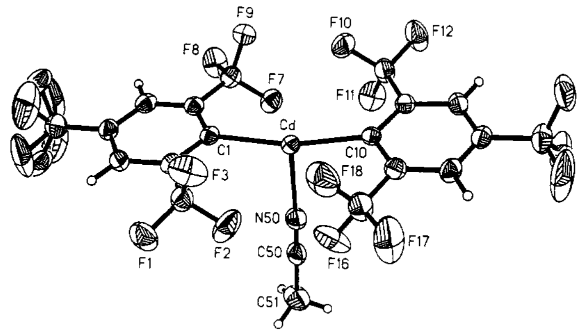
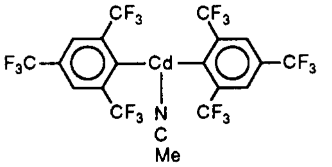


Figure 2. Molecular structure of $(R_F)_2Cd(MeCN)$ (**4a**) (50% thermal ellipsoids). Both components of the disordered para CF_3 group are shown (occupancies: F4, F5, F6, 0.80; F19, F20, F21, 0.20). Selected interatomic distances (Å) and angles (deg): Cd–C1 = 2.184 (3), Cd–C10 = 2.181 (3), Cd–N50 = 2.421 (3), Cd–F2 = 2.892 (6), Cd–F7 = 2.797 (6), Cd–F10 = 2.931 (8), F7–F11 = 2.819 (8), F9–F10 = 2.785 (8), C1–Cd–C10 = 165.7 (1), C1–Cd–N50 = 94.1 (1), C10–Cd–N50 = 100.2 (1).

sublimation. In contrast, the cadmium derivative **4** is thermally more labile. During an attempted distillation, **4** decomposed completely, with formation of metallic cadmium. All three compounds are readily soluble in nonpolar organic solvents such as toluene or hexane. In the case of **4**, the solubility in hexane is so high that it becomes difficult to recrystallize the material from this solvent. Subsequently acetonitrile was found more suitable for the purification of $(R_F)_2Cd$. Therefore, **4** was isolated and characterized as its MeCN adduct $(R_F)_2Cd(MeCN)$ (**4a**).



4a

The single-crystal X-ray structural analyses reveal that $(R_F)_2Zn$, $(R_F)_2Cd(MeCN)$, and $(R_F)_2Hg$ are monomeric in the solid state (Figures 1–3). In all three compounds, the central metal atom binds two R_F moieties. This results in two-coordinate zinc and mercury, but in the cadmium compound three-coordination is observed due to the additional binding of a solvent acetonitrile molecule.

Both the zinc and the cadmium structures described here are unique. In the case of zinc, only three diaryl compounds have been previously structurally characterized, to our knowledge. Two of these are the four-coordinate compounds $(C_6F_5)_2Zn{\cdot}2X$ (X = THF[12] or tetramethyltetrazene[13]), and the third is $(Ph_2Zn)_2$ which was reported by Markies et al. in 1990.[14] The two-coordinate monomeric structure of $(R_F)_2Zn$ therefore represents a new structural type for diarylzinc compounds. The formation of this novel monomer, in contrast to the dimeric structure observed for $(Ph_2Zn)_2$, is due to the steric and electronic properties of the ortho CF_3 substituents of R_F. To minimize steric congestion and electrostatic repulsion, the two aromatic rings are twisted at 67.1° with respect to one another. A list of the shorter intramolecular F–F and Zn–F contacts is given in the caption of Figure 1.

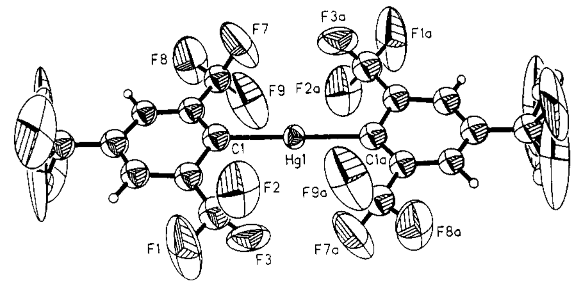


Figure 3. Molecular structure of $(R_F)_2Hg$ (**5**) (50% thermal ellipsoids). Both components of the disordered para CF_3 group are shown (occupancies: F4, F5, F6, 0.51; F19, F20, F21, 0.49). Selected interatomic distances (Å) and angles (deg): Hg1–C1 = 2.15 (2), Hg1–F2 = 3.23 (3), Hg1–F3 = 3.12 (3), Hg1–F7 = 3.28 (3), Hg1–F9 = 3.12 (3), F2–F9a = 2.83 (4), F3–F7a = 2.80 (4), C1–Hg1–C1a = 180.

$(R_F)_2Cd(MeCN)$ is, to our knowledge, the first structurally characterized three-coordinate diarylcadmium.[15] The cadmium atom has a planar "T-shaped" coordination geometry. The bound acetonitrile group does not distort the C1–Cd–C10 angle (165.7 (1)°) much from linearity. As seen in the zinc compound, the two R_F moieties are twisted somewhat from coplanarity. However, the twist angle is only 4.7° in this case as the larger central metal atom has increased the separation between opposing ortho CF_3 groups sufficiently to alleviate severe F–F steric congestion and electrostatic repulsion.

In $(R_F)_2Hg$ the two-coordinate mercury atom lies on an inversion center resulting in a linear C1–Hg–C1a linkage. A 0° twist angle between the planes of the two aromatic rings is observed. These two features have been seen before in Ph_2Hg, $(p\text{-}MeC_6H_4)_2Hg$, and *transoid*-$(o\text{-}HC_6F_4)_2Hg$ (Table I). However, for *cisoid*-$(o\text{-}MeC_6H_4)_2Hg$, $(C_6F_5)_2Hg$, $[2,4,6\text{-}(MeO)_3C_6H_2]_2Hg$, and $(2,4,6\text{-}Bu^t{}_3C_6H_2)_2Hg$, the angle at Hg deviates from 180° and the two aromatic rings are

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Table I. Structural Data for Some Diarylmercurials

	Hg–C (Å)	C–Hg–C (deg)	twist angle (deg)	ref
Ph_2Hg	2.085 (7)	180^a	0	16
$(p\text{-}MeC_6H_4)_2Hg$	2.08 (2)	180^a	0	17
transoid-$(o\text{-}HC_6F_4)_2Hg$	2.096 (16)	180^a	0	18
cisoid-$(o\text{-}MeC_6H_4)_2Hg$	2.09 (1)	178.0 (4)	58.9	19
$(C_6F_5)_2Hg$	2.09, 2.10	176.2 (12)	59.4 (12)	20
$[2,4,6\text{-}(MeO)_3C_6H_2]_2Hg$	2.07 (1)	176.7 (4)	63.5 (4)	22
$(2,4,6\text{-}Bu^t{}_3C_6H_2)_2Hg$	2.077 (6), 2.083 (6)	173.4 (2)	70.8	22
$[2,4,6\text{-}(CF_3)_3C_6H_2]_2Hg$	2.15 (2)	180^a	0	present work

[a] Hg on center of symmetry.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 3, 4a, and 5

	x	*y*	*z*	*U*(eq)^a		*x*	*y*	*z*	*U*(eq)^a
					$(R_F)_2Zn$ (**3**)				
Zn	1494 (1)	1944 (1)	2695 (1)	27 (1)	F20	4057 (33)	3983 (15)	3856 (16)	105 (2)^b
C1	2297 (3)	1235 (3)	4000 (2)	26 (1)	F21	1502 (23)	4450 (20)	3773 (19)	85 (2)^b
C2	2348 (3)	−236 (3)	4355 (2)	27 (1)	C10	308 (4)	2707 (3)	1501 (2)	25 (1)
C3	2731 (4)	−692 (4)	5329 (2)	31 (1)	C11	−1230 (4)	3729 (3)	1552 (2)	27 (1)
C4	3075 (4)	325 (4)	5976 (2)	28 (1)	C12	−2165 (4)	4205 (3)	731 (2)	29 (1)
C5	3093 (4)	1789 (4)	5649 (2)	29 (1)	C13	−1575 (4)	3656 (3)	−190 (2)	27 (1)
C6	2707 (4)	2216 (3)	4677 (2)	27 (1)	C14	−54 (4)	2668 (3)	−286 (2)	28 (1)
C7	2022 (4)	−1415 (4)	3691 (3)	32 (1)	C15	862 (4)	2212 (3)	556 (2)	26 (1)
F1	3340 (3)	−2552 (2)	3554 (2)	46 (1)	C16	−1897 (4)	4401 (4)	2524 (3)	36 (1)
F2	1579 (3)	−880 (2)	2778 (2)	54 (1)	F10	−3531 (3)	4760 (3)	2599 (2)	60 (1)
F3	826 (3)	−2059 (3)	4045 (2)	53 (1)	F11	−1413 (3)	3454 (3)	3296 (1)	52 (1)
C8	3366 (4)	−102 (4)	7043 (2)	38 (1)	F12	−1405 (3)	5661 (3)	2697 (2)	61 (1)
F4	4222 (3)	−1514 (3)	7172 (2)	59 (1)	C17	−2631 (4)	4078 (4)	−1075 (2)	33 (1)
F5	4219 (4)	749 (3)	7479 (2)	68 (1)	F13	−3775 (3)	3279 (2)	−1111 (2)	48 (1)
F6	1974 (3)	4 (4)	7558 (2)	85 (1)	F14	−3452 (3)	5538 (2)	−1060 (2)	49 (1)
C9	2761 (4)	3800 (4)	4375 (2)	35 (1)	F15	−1766 (3)	3887 (3)	−1924 (1)	48 (1)
F7	1828 (11)	4802 (5)	4921 (5)	105 (2)^b	C18	2488 (4)	1131 (4)	397 (2)	34 (1)
F8	2392 (9)	4140 (4)	3449 (3)	68 (2)^b	F16	3472 (3)	1677 (3)	−249 (2)	57 (1)
F9	4283 (5)	4005 (4)	4425 (5)	85 (2)^b	F17	3341 (3)	821 (3)	1217 (2)	65 (1)
F19	2700 (29)	4755 (21)	5025 (12)	68 (2)^b	F18	2355 (3)	−166 (2)	28 (2)	65 (1)
					$(R_F)_2Cd(MeCN)$ (**4a**)				
Cd	7031 (1)	8555 (1)	8227 (1)	26 (1)	F9	6217 (2)	9665 (1)	5877 (2)	43 (1)
C1	4972 (3)	8624 (2)	7093 (2)	26 (1)	C10	9046 (3)	8810 (2)	9346 (3)	25 (1)
C2	3866 (3)	8484 (2)	7352 (3)	30 (1)	C11	10099 (3)	9033 (2)	9063 (3)	28 (1)
C3	2561 (3)	8454 (2)	6602 (3)	33 (1)	C12	11415 (3)	9084 (2)	9779 (3)	33 (1)
C4	2341 (3)	8564 (2)	5555 (3)	34 (1)	C13	11717 (4)	8917 (2)	10818 (3)	33 (1)
C5	3395 (4)	8702 (2)	5262 (3)	33 (1)	C14	10716 (4)	8722 (2)	11149 (3)	35 (1)
C6	4679 (3)	8735 (2)	6026 (3)	29 (1)	C15	9406 (4)	8681 (2)	10418 (3)	32 (1)
C7	4049 (4)	8378 (2)	8466 (3)	38 (1)	C16	9838 (4)	9187 (3)	7934 (3)	40 (1)
F1	3017 (3)	8035 (2)	8590 (2)	57 (1)	F10	8752 (2)	9642 (1)	7468 (2)	45 (1)
F2	5113 (3)	7983 (2)	9011 (2)	70 (1)	F11	9632 (3)	8519 (2)	7377 (2)	53 (1)
F3	4229 (3)	9073 (2)	8968 (2)	65 (1)	F12	10844 (2)	9564 (2)	7802 (2)	66 (1)
C8	943 (4)	8541 (3)	4735 (3)	48 (2)	C17	13147 (4)	8939 (3)	11569 (3)	45 (2)
F4	22 (4)	8375 (5)	5110 (3)	96 (3)^b	F13	13900 (3)	8433 (2)	11318 (2)	74 (1)
F5	593 (4)	9192 (3)	4209 (6)	102 (2)^b	F14	13699 (3)	9632 (2)	11620 (3)	110 (2)
F6	796 (5)	7975 (4)	4022 (5)	99 (2)^b	F15	13309 (3)	8743 (3)	12528 (2)	116 (2)
F19	373 (23)	7961 (15)	4718 (28)	102 (2)^b	C18	8342 (4)	8473 (3)	10814 (3)	46 (2)
F20	900 (17)	8659 (26)	3812 (15)	96 (3)^b	F16	7682 (3)	7820 (2)	10364 (2)	74 (1)
F21	284 (21)	9134 (18)	4918 (20)	99 (2)^b	F17	8798 (3)	8348 (3)	11826 (2)	110 (2)
C9	5792 (4)	8900 (2)	5679 (3)	34 (1)	F18	7412 (3)	9036 92)	10589 (3)	73 (1)
F7	6869 (2)	8449 (1)	6169 (2)	41 (1)	N50	7132 (3)	7117 (2)	8146 (3)	38 (1)
F8	5462 (3)	8797 (2)	4651 (2)	54 (1)	C50	7112 (3)	6449 (2)	8156 (3)	36 (1)
					C51	7081 (4)	5579 (2)	8158 (4)	55 (2)
					$(R_F)_2Hg$ (**5**)				
Hg1	5000	5000	0	43 (1)	C8	6776 (12)	−1880 (17)	−1940 (8)	67 (5)
C1	5644 (18)	2725 (20)	−669 (10)	59 (4)	F4	5844 (22)	−3112 (18)	−1847 (15)	99 (8)^b
C2	4506 (13)	1793 (17)	−1179 (9)	59 (4)	F5	8086 (20)	−2475 (30)	−1722 (17)	326 (25)^b
C3	5003 (22)	348 (21)	−1648 (12)	60 (5)	F6	6795 (35)	−1639 (21)	−2769 (9)	283 (26)^b
C4	6382 (19)	−323 (17)	−1455 (11)	62 (5)	F10	8105 (19)	−1891 (27)	−2246 (18)	99 (8)^b
C5	7332 (19)	505 (22)	−880 (10)	51 (4)	F11	5857 (29)	−2187 (38)	−2589 (17)	326 (25)^b
C6	7004 (13)	1925 (17)	−476 (8)	55 (4)	F12	6715 (43)	−3217 (17)	−1454 (17)	283 (26)^b
C7	2970 (19)	2549 (16)	−1360 (8)	76 (6)	C9	8118 (15)	2650 (15)	186 (9)	64 (5)
F1	2108 (14)	1609 (19)	−1847 (12)	244 (12)	F7	8612 (16)	4101 (14	−48 (10)	164 (9)
F2	3049 (15)	3984 (16)	−1747 (8)	144 (8)	F8	9286 (14)	1705 (17)	313 (10)	171 (8)
F3	2263 (12)	2803 (17)	−666 (9)	128 (7)	F9	7564 (19)	2878 (19)	934 (7)	174 (10)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Rotationally disordered para CF_3 groups, occupancies: (**3**) F7, F8, F9, 0.78; F19, F20, F21, 0.22; (**4a**) F4, F5, F6, 0.80; F19, F20, F21, 0.20; (**5**) F4, F5, F6, 0.51; F19, F20, F21, 0.49.

twisted relative to one another (Table I). The reasons given for these twists were steric crowding and/or electrostatic repulsion. On the basis of these arguments one might expect a twisted structure to be observed for

$[2,4,6\text{-}(CF_3)_3C_6H_2]_2Hg$ (**5**). However, no twist is observed, which suggests that the potential energy surface must actually be quite flat with respect to changes in the angle between the planes of the two rings. No intramolecular contacts of less than the sum of the van der Waals radii of mercury and fluorine (3.08 Å) are observed in either **5** or $(C_6F_5)_2Hg$. No intramolecular F–F contacts were given for the latter compound, but they are unlikely to be shorter than in **5** in which there are none less than the sum of the fluorine atoms' van der Waals radii (2.70 Å) (Figure 3 caption). The Hg–C1 distance (2.15 (2) Å) observed in **5** is the longest reported to date for a diarylmercury compound (even longer than in the severely crowded $(2,4,6\text{-}Bu^t{}_3C_6H_2)_2Hg$), and this will help to maintain the 0° twist angle.

Experimental Section

General Data. All reactions were carried out with use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled from sodium/benzophenone prior to use. 1,3,5-Tris(trifluoromethyl)benzene (**1**)[2], R_FLi (**2**),[1,2] and $(R_F)_2Hg$ (**5**)[1] were prepared according to literature methods. ^1H NMR spectra were recorded on a Bruker WP 80 SY spectrometer at 80 MHz. All other spectra were recorded on a Bruker AM 250 instrument at 62.91 MHz (^{13}C) and 75.39 MHz (^{19}F). Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer (Nujol mulls between KBr windows). Mass spectra were obtained on a Varian MAT CH 5 mass spectrometer. Melting points (uncorrected) were obtained by using a Büchi 510 apparatus. Elemental analyses were performed by the analytical laboratory of the Department of Inorganic Chemistry at Göttingen.

Bis[2,4,6-tris(trifluoromethyl)phenyl]zinc (3). A 3.4-g (25-mmol) portion of anhydrous $ZnCl_2$ is added in small portions to a freshly prepared solution of R_FLi (**2**) (50 mmol) in diethyl ether/hexane, and the mixture is refluxed for 6 h. After removal of the solvent under reduced pressure, the residue is extracted with 50 mL of toluene. LiCl is removed by filtration through a thin layer of Celite, and the solvent is stripped off from the filtrate. Vacuum distillation of the crude product yields 6.5 g (41%) of a colorless oil (bp 110 °C/0.1 Torr). Colorless crystals (mp 42 °C) can be obtained by recrystallization from hexane at −25 °C. IR (ν, cm^{-1}): 1322 (vs), 1300 (vs), 1200 (vs), 1158 (vs), 928 (s). EI-MS: m/z 626 (M, 6%), 262 ($C_6H_2(CF_3)_2CF_2$, 100). ^1H NMR (C_6D_6): δ 8.10 (s, C_6H_2). ^{13}C NMR (C_6D_6): δ 144.1 (m, C1), 139.7 (q, ^2J(C,F) = 30 Hz, C2), 132.9 (q, ^2J(C,F) = 34 Hz, C4), 124.9 (m, C3), 124.4 (q, ^1J(C,F) = 273 Hz, o-CF_3), 122.8 (q, ^1J(C,F) = 273 Hz, p-CF_3). ^{19}F NMR (C_6D_6, $CFCl_3$ external): δ −62.5 (s, 6F, p-CF_3), −60.6 (s, 12F, o-CF_3). Anal. Calcd for $C_{18}H_4F_{18}Zn$ (627.6): C, 34.5; H, 0.6. Found: C, 36.3; H, 1.1.

(Acetonitrile)bis[2,4,6-tris(trifluoromethyl)phenyl]cadmium (4a). Following the procedure given for **3**, 0.25 mmol of anhydrous CdI_2 is used instead of $ZnCl_2$ and the oily crude product is recrystallized from 50 mL of acetonitrile. A yield of 6.3 g (35%) of pale yellow crystals is obtained (mp 78 °C). IR (ν, cm^{-1}): 1625 (m), 1306 (s), 1278 (vs), 1203 (s), 1174 (vs), 1123 (vs), 915 (s), 851 (m), 686 (s). EI-MS: m/z 676 ($(R_F)_2Cd$, 28%), 657 ($(R_F)_2Cd$ − F, 25), 395 (R_FCd, 100), 281 ($C_6H_2(CF_3)_3$, 11), 262 ($C_6H_2(CF_3)_2CF_2$, 46), 243 ($C_6H_2(CF_3)(CF_2)_2$, 74). ^1H NMR (C_6D_6): δ 7.90 (s, ^4J(Cd,H) = 7 Hz, C_6H_2), 0.66 (s, CH_3CN). ^{13}C NMR (C_6D_6): δ 155.8 (m, C1), 140.4 (q, ^2J(C,F) = 29 Hz, C2), 131.7 (q, ^2J(C,F) = 34 Hz, C4), 125.0 (q, ^1J(C,F) = 272 Hz, o-CF_3), 124.8 (m, C3), 123.8 (q, ^1J(C,F) = 272 Hz, p-CF_3), 118.2 (CH_3CN), 0.1 (CH_3CN). ^{19}F NMR (C_6D_6, $CFCl_3$ external): δ −63.4 (s, 6F, ^6J(Cd,F) = 2 Hz, p-CF_3), −60.6 (s, 12F, $^4J(^{111}Cd,F)$ = 23 Hz, $^4J(^{113}Cd,F)$ = 24 Hz, o-CF_3). Anal. Calcd for $C_{20}H_7CdF_{18}N$ (715.7): C, 33.6; H, 1.0. Found: C, 34.4; H, 1.1.

Structure Solution and Refinement. Diffraction data were collected on a Siemens-Stoe AED at −120 °C for **3** and **4a** and on an AED2 at room temperature for **5**. 2θ–ω scans, with on-line profile fitting[23] and variable scan speeds, were employed. Each structure was solved by Patterson methods (SHELXS-86) and refined by full-matrix least-squares techniques (SHELX-76, modified by the author). Rotational disorder of one CF_3 group was apparent in each structure. This was modeled by the insertion of a second component, and the fluorine atoms "opposite" each other were constrained to have equal U_{ij} values. For **5**, interatomic constraints were also applied to the disordered group. As can be seen from the thermal ellipsoid plots, the low-temperature data collections give clearly superior results. Atomic coordinates for **3**, **4a**, and **5** are listed in Table II.

Crystal data for **3**: $C_{18}H_4F_{18}Zn$, M_r = 627.6, triclinic, space group $P\bar{1}$, a = 8.339 (3) Å, b = 9.064 (2) Å, c = 13.499 (4) Å, α = 88.38 (3)°, β = 87.79 (4)°, γ = 76.85 (2)°, V = 992.6 (5) Å^3, Z = 2, d_{calcd} = 2.100 g/cm^3, μ(Mo Kα) (graphite monochromotor) = 1.43 mm^{-1}, 4463 measured reflections, 3494 unique reflections, 2987 observed reflections with $F \geq 3\sigma(F)$, $2\theta_{max}$ = 50°. Semiempirical absorption corrections were applied, all non-hydrogen atoms refined anisotropically, and hydrogen atoms inserted at calculated positions. Refinement of 344 parameters converged with R = 0.0392, R_w = 0.0443, $w^{-1} = \sigma^2(F) + 0.0003F^2$, and maximum/minimum rest electron density +0.6/−0.5 e Å^{-3}.

Crystal data for **4a**: $C_{20}H_7CdF_{18}N$, M_r = 715.7, monoclinic, space group $P2_1/c$, a = 10.876 (3) Å, b = 16.79 (1) Å, c = 13.865 (5) Å, β = 112.81 (2)°, V = 2334 (2) Å^3, Z = 4, d_{calcd} = 2.037 g/cm^3, μ(Mo Kα) (graphite monochromator) = 1.08 mm^{-1}, 6203 measured reflections, 5318 unique reflections, 4059 observed reflections with $F \geq 4\sigma(F)$, $2\theta_{max}$ = 55 °. Semiempirical absorption corrections were applied, all non-hydrogen atoms refined anisotropically, and hydrogen atoms inserted at calculated positions. Refinement of 371 parameters converged with R = 0.0349, R_w = 0.0386, $w^{-1} = \sigma^2(F) + 0.0002F^2$, and maximum/minimum rest electron density +0.6/−0.6 e Å^{-3}.

Crystal data for **5**: $C_{18}H_4F_{18}Hg$, M_r = 762.8, monoclinic, space group $P2_1/n$, a = 8.842 (2) Å, b = 7.891 (2) Å, c = 15.294 (3) Å, β = 92.20 (3)°, V = 1066.3 (4) Å^3, Z = 2, d_{calcd} = 2.376 g/cm^3, μ(Mo Kα) (graphite monochromator) = 7.38 mm^{-1}, 2277 measured reflections, 1394 unique reflections, 1156 observed reflections with $F \geq 3\sigma(F)$, $2\theta_{max}$ = 45°. Semiempirical absorption and extinction corrections were applied, mercury and fluorine atoms refined anisotropically, and hydrogen atoms inserted at calculated positions. Refinement of 138 parameters converged with R = 0.0573, R_w = 0.0955, $w^{-1} = \sigma^2(F) + 0.0004F^2$, and maximum/minimum rest electron density +1.3/−1.2 e Å^{-3}.

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Registry No. **2**, 444-40-6; **3**, 137364-24-0; **4a**, 137364-25-1; **5**, 114071-31-7; $ZnCl_2$, 7646-85-7; CdI_2, 7790-80-9.

Supplementary Material Available: Tables of crystal data, data collection, solution, and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (20 pages); tables of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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