Syntheses, Characterizations, and Crystal Structures of β -Diketiminato Compounds of Pentafluorophenyl Group 12 Derivatives, HC{[C(Me)N(C₆H₃-2,6-i-Pr₂)]₂}MC₆F₅ (M = Zn, Cd)

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Abstract. The reactions of $H_2C[C(Me)N(C_6H_3-2,6-i-Pr_2)]_2$ ((DPP)₂NacNacH) and Zn(C₆F₅)₂ · 2 EtCN or Cd(C₆F₅)₂ · 2 MeCN in a molar ratio of approximately 1:1 selectively gave the derivatives (DPP)₂NacNacMC₆F₅ (M = Zn, Cd) in excellent yields. No reaction was observed between (DPP)₂NacNacH and Hg(C₆F₅)₂ under similar conditions. Reactions with Hg(C₆F₅)OCOMe yielded the products of dismutation, Hg(C₆F₅)₂ and Hg(OCOMe)₂.

 $(DPP)_2NacNacZnC_6F_5$ crystallises as a 1:1 adduct with THF with two independent molecules per unit cell (triclinic, $P\bar{1}$ (no. 2)). The

zinc atom is tetrahedrally surrounded by the chelating ligand, the pentafluorophenyl group and one THF molecule. A similar situation is found in the 1:1 adduct of $(DPP)_2NacNacCdC_6F_5$ and DMF (monoclinic, P2₁/n (no. 14)), while in the donor-free compound (CDCl₃ and H₂O co-crystallize) the cadmium atom is nearly ideally trigonal planar co-ordinated (orthorhombic, Pbnm (no. 62)).

Keywords: Cadmium; N-Ligands; Pentafluorophenyl; Zinc

Synthesen, Charakterisierungen und Kristallstrukturen von β -Diketiminato-Verbindungen der Pentafluorphenylverbindungen der Elemente der Gruppe 12, HC{[C(Me)N(C₆H₃-2,6-i-Pr₂)]₂}MC₆F₅ (M = Zn, Cd)

Inhaltsübersicht. Die Reaktionen von $H_2C[C(Me)N(C_6H_3-2,6-i-Pr_2)]_2$ ((DPP)₂NacNacH) und Zn(C₆F₅)₂ · 2 EtCN bzw. Cd(C₆F₅)₂ · 2 MeCN in einem molaren Verhältnis von ungefähr 1:1 führen selektiv zu den Verbindungen (DPP)₂NacNacMC₆F₅ (M = Zn, Cd) in sehr guten Ausbeuten. Zwischen (DPP)₂NacNacH und Hg(C₆F₅)₂ werden unter ähnlichen Bedingungen keine Reaktionen beobachtet. Umsetzungen mit Hg(C₆F₅)OCOMe führen zu Dismutierungen in Hg(C₆F₅)₂ und Hg(OCOMe)₂.

 $(DPP)_2NacNacZnC_6F_5$ kristallisiert als 1:1 Addukt mit THF mit zwei unabhängigen Molekülen je Elementarzelle (triklin, P1 (Nr.

Introduction

Zn(C₆F₅)₂ [1] and especially Cd(C₆F₅)₂ [2] compounds have turned out to be good nucleophilic pentafluorophenyl group transfer reagents in very different types of reactions. Especially reactions of Cd(C₆F₅)₂ and H-acidic reagents, HX, were investigated primarily yielding C₆F₅H and derivatives with a Cd(C₆F₅)X moiety [3–6]. With this knowledge, we investigated the reaction behaviour of M(C₆F₅)₂ (M = Zn, Cd, Hg) and the widely used β-diketimine, (DPP)₂NacNacH [7].

* Dr. Wieland Tyrra Institut für Anorganische Chemie Universität zu Köln Greinstr. 6 D-50939 Köln E-mail: tyrra@uni-koeln.de 2)). Das Zinkatom in dieser Verbindung ist tetraedrisch durch den Chelatliganden, die Pentafluorphenylgruppe und ein THF-Molekül koordiniert. Eine vergleichbare Koordination wird in dem Addukt aus (DPP)₂NacNacCdC₆F₅ und DMF (monoklin, P2₁/n (Nr. 14)) gefunden, wohingegen in der Donator-freien Verbindung (CDCl₃ und H₂O kokristallisieren) das Cadmiumatom nahezu ideal trigonal planar koordiniert ist (orthorhombisch, Pbnm (Nr. 62)).

Results and Discussion

Two more or less general pathways for the synthesis of $Ar_2NacNac$ element compounds have been established in the literature: (i) halide substitutions using compounds of general formula $Ar_2NacNacM$ (M = alkali metal) and (ii) acidolysis of organoelement compounds [8].

We decided to use the second synthetic pathway to investigate the behaviour of bis(pentafluorophenyl)group 12 derivatives, $M(C_6F_5)_2$ (M = Zn, Cd, Hg) towards the wellestablished derivative, (DPP)₂NacNacH (Scheme 1).

In the case of the zinc and cadmium compounds, the reactions proceeded selectively to yield the expected derivatives (DPP)₂NacNacMC₆F₅ (M = Zn, Cd) in very good yields. The reactions were terminated when the integrative ratio of (DPP)₂NacNacMC₆F₅ (M = Zn, Cd) and C₆F₅H was 1:1 and no signals of the starting materials were detected in the ¹⁹F NMR spectra. No reaction was observed treating Hg(C₆F₅)₂ and (DPP)₂NacNacH in different solvents even at elevated temperatures (EtCN, 50 °C).



Scheme 1 Reactions of $M(C_6F_5)_2$ and $(DPP)_2NacNacH$

Again, no ¹⁹F NMR spectroscopic evidence for the formation of (DPP)₂NacNacHgC₆F₅ was found in 1:2 reactions of Hg(C₆F₅)OCOMe (¹⁹F-NMR (C₆D₆): $\delta = -117.9$, ${}^{3}J_{Hg,F} = 565 \text{ Hz}, \text{ F-2,6}; -152.0, {}^{5}J_{Hg,F} = 28 \text{ Hz}, \text{ F-4};$ -160.0, ${}^{4}J_{Hg,F} = 185$ Hz, F-3,5) and (DPP)₂NacNacH. $Hg(C_6F_5)_2$ (¹⁹F-NMR (C₆D₆): $\delta = -119.7$, ³J_{Hg,F} = 434 Hz, F-2,6; -152.1, F-4; -159.8, ${}^{4}J_{Hg,F} = 113$ Hz, F-3,5)) and $Hg(OCOMe)_2$ were identified as products of the reaction as shown in Eq. (1), while (DPP)₂NacNacH was recovered unchanged.

2 Hg(C₆F₅)OCOMe
$$(DPP)_2NacNacH$$
 Hg(C₆F₅)₂ + Hg(OCOMe)₂ (1)

 $(DPP)_2NacNacMC_6F_5$ (M = Zn, Cd) were isolated as colourless moisture sensitive compounds and characterized by EI mass spectrometry, ¹⁹F, ¹³C, ¹H and ¹¹³Cd NMR spectroscopy as well as elemental analyses.

¹³C and ¹H NMR values are consistent with those reported for a variety of related compounds ((DPP)2Nac-NacM) [e.g. 9-13], while ¹⁹F and ¹³C NMR data of the C₆F₅ group were found in the expected regions [e.g. 1, 2, 4, 5, 14]. The ¹¹³Cd NMR signal of (DPP)₂NacNacCdC₆F₅ was shifted significantly from that of the starting material (-237 ppm vs. -466 ppm [15]).

EI mass spectra (20 eV) exhibit the molecular peaks $[(DPP)_2NacNacZnC_6F_5]^+$ (m/z) =650 [M]⁺ = [C₃₅H₄₁F₅N₂⁶⁵Zn]⁺; 100 %) and [(DPP)₂NacNacCdC₆F₅]⁺ $(m/z = 698 \text{ [M]}^+ = [C_{35}H_{41}F_5N_2^{112}\text{Cd}]^+; 40\%)$ as well as

Table 1 Crystal Data and Structure Refinement Parameters for $(DPP)_2NacNacZnC_6F_5 \cdot THF (I), (DPP)_2NacNacCdC_6F_5 \cdot DMF (II) and$ (DPP)₂NacNacCdC₆F₅ (III).

	Ι	II	III
empirical formula	C78Ha8F10N4O2Zn2	C28H48F5N2OCd	C26H41F5N2OCl2Cd
crystal system	triclinic	monoclinic	orthorhombic
space group	PĪ (no. 2)	$P2_1/n$ (no. 14)	Pbnm (no. 62)
a / pm	1272.7(1)	986.2(1)	1088.8(1)
b / pm	1597.5(2)	1665.1(1)	1743.8(2)
c / pm	1811.9(2)	2324.5(2)	1983.3(2)
α / \deg	84.54(1)	(_)	(-)
β/deg	89.36(1)	95.57(1)	
γ / deg	88.63(1)		
volume / nm ³	3.666(1)	3.726(1)	3.766(1)
Z.	2	4	4
formula mass	1444.34	770.19	831.46
$\rho_{\rm mata}/g{\rm cm}^{-3}$	1.308	1.373	1.467
μ/mm^{-1}	0.728	0.644	0.848
absorption correction	numerical	numerical	numerical
F			
transmission max / min	0.7334 / 0.9295	0.8259 / 0.9500	0.7439 / 0.9253
θ range / deg	1.60-29.64	2.51-27.33	2.05-27.38
total data collected	70290	57492	40069
index range	$-17 \le h \le 17$	$-12 \le h \le 12$	$-14 \le h \le 13$
	$-22 \le k \le 22$	$-21 \le k \le 21$	$-22 \le k \le 22$
	$-25 \le 1 \le 24$	$-30 \le 1 \le 29$	$-25 \le 1 \le 25$
unique data	20429	8320	4325
observed data	9208	5670	2389
diffractometer		STOE Image Plate Diffraction	System
radiation		Mo-K α (Graphit-Monochromator, λ	= 71.073 pm
temperature / K	170(2)	170(2)	170(2)
R	0.0751	0.0524	0.1168
R indexes $[I > 2\sigma I]$	$R_1 = 0.0415$	$R_1 = 0.0347$	$R_1 = 0.0599$
	$wR_2 = 0.0798$	$wR_2 = 0.0786$	$wR_2 = 0.1423$
R indexes (all data)	$R_1 = 0.1159$	$R_1 = 0.0572$	$R_1 = 0.1087$
it indenes (un dutu)	$wR_2 = 0.0951$	$wR_2 = 0.0849$	$wR_2 = 0.1613$
goodness of fit (S_{aba})	0.954	1.049	1.069
goodness of fit (S_{oll})	0.744	0.917	0.877
no. of variables	870	626	313
F(000)	1520	1592	1692
largest difference map	-0.996 / 0.520	-0.676 / 0.636	-1.001 / 1.213
hole / peak [e 10^{-6} pm ⁻³]			

 $\begin{array}{l} R_1 = \Sigma \left\| F_o \right| - \left| F_c \right| / \Sigma \left| F_o \right|, wR_2 = \left[\Sigma \ w \ (\left| F_o \right|^2 - \left| F_c \right|^2 \)^2 \ / \ \Sigma \ w \ (\left| F_o \right|^2 \)^2 \]^{1/2}, \\ S_2 = \left[\Sigma \ w \ (\left| F_o \right|^2 - \left| F_c \right|^2 \)^2 \ / \ (n-p) \]^{1/2}, \ \text{with} \ w = 1 \ / \ [\sigma^2 \ (F_o)^2 + \ (0.0427 \cdot P)^2] \ \text{for} \ I, \end{array}$

 $\vec{w} = 1 / [\sigma^2 (F_o)^2 + (0,1000 \cdot P)^2] \text{ for III and } w = 1 / [\sigma^2 (F_o)^2 + (0,0529 \cdot P)^2] \text{ for III were } P = (F_o^2 + 2F_c^2) / 3. F_c^* = k F_c [1+0,001 \cdot |F_c|^2 \lambda^3 / \sin(2\theta)]^{-1/4}.$

$\frac{(\text{DPP})_2\text{NacNacZnC}_6\text{F}_5 \cdot \text{THF (I)}}{(\text{DPP})_2\text{NacNacZnC}_6\text{F}_5 \cdot \text{THF (I)}}$				
Zn 1 – N 2	197.9(2)	N 1 – Zn 1 – C 4	128.3(1)	
Zn 1 – C 4	201.1(2)	N 2 – Zn 1 – C 4	126.5(1)	
Zn 1 – O 1	221.0(2)	C 4 – Zn 1 – O 1	100.1(1)	
N 1 – C 1	132.9(3)	O1 – Zn 1 – N 1	96.5(1)	
C 1 – C 2	140.1(4)	O 1 – Zn 1 – N 2	97.4(1)	
C 2 – C 3	140.3(3)	Zn 1 – N 1 – C 1	118.7(2)	
C 3 – N 2	133.9(3)	N 1 – C 1 – C 2	124.6(2)	
		C 1 – C 2 – C 3	130.4(2)	
		C 2 – C 3 – N 2	124.1(2)	
Zn 2 – N 3	199.3(2)	N 3 – Zn 2 – N 4	98.6(1)	
Zn 2 – N 4	197.9(2)	N 3 – Zn 2 – C 8	127.3(1)	
Zn 2 – C 8	201.3(2)	N 4 – Zn 2 – C 8	126.8(1)	
Zn 2 – O 2	220.3(2)	C 8 – Zn 2 – O 2	100.4(1)	
N 3 – C 5	133.7(3)	O 2 – Zn 2 – N 3	96.8(1)	
C 5 – C 6	140.0(4)	O 2 – Zn 2 – N 4	98.7(1)	
C 6 – C 7	140.3(3)	Zn 2 – N 3 – C 5	118.5(2)	
C 7 – N 4	133.1(3)	N 3 – C 5 – C 6	124.4(2)	
		C 5 – C 6 – C 7	130.6(2)	
		C 6 – C 7 – N 4	124.2(2)	
(DPP) ₂ NacNac	$CdC_6F_5 \cdot DMF$ (II)		
Cd – N 1	219.2(2)	N 1 – Cd – N 2	90.0(1)	
Cd - N2	221.3(2)	$N_1 - Cd - O_1$	99.1(1)	
Cd – O 1	235.5(2)	N 1 – Cd – C 4	130.3(1)	
Cd – C 4	216.9(3)	N 2 – Cd – O 1	95.4(1)	
N 1 – C 1	132.1(3)	N 2 – Cd – C 4	133.8(1)	
C 1 – C 2	141.2(4)	O 1 – Cd – C 4	98.5(1)	
C 2 – C 3	141.3(4)	Cd – N 1 – C 1	122.7(2)	
C 3 – N 2	133.1(4)	Cd – N 2 – C 3	121.3(2)	
		N 1 – C 1 – C 2	125.1(2)	
		C 1 – C 2 – C 3	131.3(2)	
		C 2 – C 3 – N 2	125.7(2)	
(DPP) ₂ NacNac	$CdC_6F_5 \cdot (H_2O \cdot$	CDCl ₃) (III)		
Cd - N3	216.8(4)	$N_{3} - Cd - N_{3}'$	90.5(2)	
Cd - C 8	214.5(7)	$N_{3} - Cd - C_{8}$	134.8(1)	
$N_3 - C_6$	131.8(6)	$N_3 - C_6 - C_7$	125.1(5)	
$C_{6} - C_{7}$	141.4(6)	C 6 - C 7 - C 6'	131.6(7)	

 Table 2 Selected Internuclear Distances / pm and Angles / deg for

 I, II and III

fragments known from the fragmentation of further zinc and cadmium derivatives either containing the $(DPP)_2Nac-Nac$ or the C_6F_5 moiety.

Results of Crystal Structure Analyses

Details of single crystal structure analyses of $(DPP)_2NacNacZnC_6F_5 \cdot THF$ (I), $(DPP)_2NacNacCdC_6F_5 \cdot DMF$ (II) and $(DPP)_2NacNacCdC_6F_5$ (III) are summarized in Tables 1 and 2.

Molecular structure of $(DPP)_2NacNacZnC_6F_5 \cdot THF(I)$

I (Figure 1) crystallises in the triclinic space group $P\bar{I}$ (no. 2) with two independent molecules per unit cell. The coordination around the zinc atom is distorted tetrahedral with two nitrogen atoms of the chelating (DPP)₂NacNac, the ipso-carbon atom of the C₆F₅ group and the oxygen atom



Fig. 1 Coordination around Zn 1 (compound **I**) with the atomic labeling scheme (H-atoms are omitted for clarity, the coordination around Zn 2 is almost the same (confer Table 2)). Thermal ellipsoids are shown at 50% probability.

of the THF molecule acting as ligand atoms. A six-membered heterocycle is build up exhibiting a boat conformation with the zinc atom and the opposite carbon atom forming prow and stern. Deviations from least square planes (N1-C1-C3-N2 and N3-C5-C6-N4) of the two independent units were calculated [16] to be 37.1(1) pm for Zn 1 and 35.7(1) pm for Zn2 and 10.7(3) pm for C1 and 11.6(3) pm for C5, respectively. It has to be noted that the ring containing the atom Zn2 is significantly twisted compared with that of the other independent molecule containing the atom Zn1.

The zinc-nitrogen bond length of 197.9(2) and 199.3(2) pm (identical for both ZnN_2C_3 cores) and the angle N-Zn-N 98.6(1) (98.9(1))° are in the typical range of related zinc derivatives such as (DPP)₂NacNacZnEt [10], (DPP)₂NacNacZnC=CPh [11] and (DPP)₂NacNacZnR (R = Me, Ph, t-Bu) [9]. In comparison with structural data reported for ZnC_6F_5 compounds, the Zn-C bond lengths found for I (201.1(2) (201.3(2)) pm) are in good agreement with those reported for $Zn(C_6F_5)_2 \cdot 2$ THF [3] but as expected significantly deviate from those found for the donorfree molecule $Zn(C_6F_5)_2$ (192.6(4), 193.0(4) pm) [17]. By contrast to the structure of $Zn(C_6F_5)_2 \cdot 2$ THF [3], the Zn-O contact in I is significantly elongated (220.3(2) (221.0(3)) pm vs. 209.3(2) / 211.3(3) pm [3]).

Molecular structure of $(DPP)_2NacNacCdC_6F_5 \cdot DMF(\mathbf{II})$

II (Figure 2) crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with four molecules per unit cell. Again as outlined for the zinc derivative, the coordination around the metal atom is strongly distorted tetrahedral with two nitrogen bonds, one carbon bond and one oxygen bond to the



Fig. 2 Asymmetric unit of II. Coordination around Cd with the atomic labeling scheme (H-atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability.

DMF molecule. A six-membered cadmium containing ring is build up exhibiting a boat conformation with the cadmium atom and the opposite carbon atom forming prow and stern. Deviations of the cadmium atom and the opposite carbon atom from a least square plane [16] are of comparable size as determined for the zinc compound **I**, 35.4(1) pm for cadmium and 12.7(3) pm for carbon.

While numerous zinc compounds with NacNac ligands have been crystallographically characterised [8], only one NacNacCd derivative has been mentioned so far [13].

Nevertheless, structural differences between $(DPP)_2Nac-NacCdC_6F_5 \cdot DMF$ and $(DPP)_2NacNacCd(\mu-I)_2Li(OEt_2)_2$ [13] concerning the CdN₂C₃ core are of minor significance.

Cd-N bond lengths are found to be 219.2(2) and 221.3(2) pm, respectively. The Cd-C bond to the pentafluorophenyl group (216.9(3) pm) is elongated by up to 6 pm compared with donor-free Cd(C₆F₅)₂ (210.9(3) / 211.1(3) pm) [14] but absolutely in the range of Cd-C bond lengths of further structurally characterised Cd(C₆F₅) compounds varying from 216 to 221 pm [3–6].

Molecular structure of $(DPP)_2NacNacCdC_6F_5$ (III) (CDCl₃ and H₂O co-crystallize)

III (Figure 3) crystallises in the orthorhombic space group Pbnm (no. 62) with 4 molecules per unit cell. Each molecule is characterised by a mirror plane through C3, Cd, C4 as well as the co-crystallising solvent molecules. The CdN_2C_3 core as well as the C_6F_5 group are co-planar additionally supporting the high symmetry of this molecule. By contrast to the structures of I and II described above, no significant deviation of the positions of the cadmium atom and the opposite carbon atom from the idealised plane are observed



Fig. 3 Asymmetric unit of **III**. Coordination around Cd with the atomic labeling scheme (H-atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability.

(0.0(1) pm for Cd; 0.4(8) pm for C) revealing nearly ideal planarity for the CdN₂C₃ core.

The Cd-C bond length is estimated to be 214.5(7) pm, shorter than those found for the DMF-adduct II (216.9(3) pm) and also the Cd-N bonds are significantly shorter (216.8(4) vs. 220.3 pm (mean value)).

Experimental Part

General methods

Schlenk techniques were used throughout all manipulations. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H , ^{19}F , ^{13}C) and a Bruker AMX 300 spectrometer ($^{13}C{^{19}F}$, ^{13}Cd). External standards were used in all cases (^{1}H , ^{13}C : Me₄Si; ^{19}F : CCl₃F; ^{113}Cd : Me₂Cd). Acetone-D₆ was used as an external lock (5 mm tube) in reaction control measurements while an original sample of the reaction mixture was measured in a 4 mm insert. Mass spectra were run on a Finnigan MAT 95 spectrometer using the electron impact method (20 eV). Intensities are referenced to the most intensive peak of a group. Visible decomposition points were determined using the apparatus HWS Mainz 2000. CHN analyses were carried out with a HEKAtech Euro EA 3000 apparatus.

The following compounds were prepared according to literature procedures: $Zn(C_6F_5)_2 \cdot 2$ EtCN [18], $Cd(C_6F_5)_2 \cdot 2$ MeCN [2], $Hg(C_6F_5)_2$ [18] and (DPP)₂NacNacH [19]. $Hg(C_6F_5)OCOMe$ was received from Dipl.-Chem. F. Schulz as a gift.

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Single crystal structure determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted in glass capillaries. Single-crystal X-ray data were collected on a STOE image-plate diffractometer (IPDS II) by using graphite-monochromatised MoK α radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Intensity data for I and II were collected at 170 K in 180 frames with ω -scans ($0 \le \omega \le 180^\circ$; $\psi = 0^\circ$, $0 \le \omega \le 180^\circ$; $\psi = 90^\circ$, $\Delta \omega = 2^{\circ}$, exposure time of 2 min for I and 4 min for II) in the 2 θ range of 2.3 to 59.5° for I and 1.9 to 54.8° for II. The intensity data for III were collected at 170 K in 130 frames with ω-scans (0 $\leq \omega \leq 180^{\circ}; \psi = 0^{\circ}, 0 \leq \omega \leq 80^{\circ}; \psi = 90^{\circ}, \Delta \omega = 2^{\circ},$ exposure time of 5 min) in the 2 θ range of 1.9 to 54.8°. The structures were solved by direct methods SHELXS-97 [20] and difference Fourier syntheses. Full matrix least squares structure refinements against [F²] were carried out using SHELXL-93 [21]. Compound I crystallized in the triclinic space group P1 with two independent molecules per unit cell. The hydrogen atoms in I were placed geometrically and held in the riding mode. The H atom positions for II and III were taken from the difference Fourier card at the end of the refinement (except the solvent molecules CDCl₃ and H₂O in III). Numerical absorption corrections were applied after optimisation of the crystal shapes (X-RED [22] and X-SHAPE [23]). The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Details of the refinements are given in Table 1 [24]. Selected internuclear distances and angles are presented in Table 2. Deviations from least square planes to confirm the conformations of the MN₂C₃ cores in all derivatives were carried out with the program PARST97 [16].

Synthesis of $(DPP)_2NacNacZnC_6F_5$

A solution of 0.46 g (1.10 mmol) (DPP)₂NacNacH in 5 ml CH₂Cl₂ was slowly dropped to a well stirred solution of 0.58 g (1.13 mmol) Zn(C₆F₅)₂ · 2 EtCN in 5 ml CH₂Cl₂ at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 days. All volatile components were distilled off in vacuo. The remaining colourless solid was washed with four portions (5 ml each) of cold n-pentane (-30 °C) to remove traces of the starting materials. The washing liquor was disposed. The remaining residue was dissolved in 20 ml n-pentane at room temperature, the solution directly concentrated in *vacuo* to one third and stored for several days at -30 °C. After approximately 3 days, a micro-crystalline solid began to precipitate which was collected after disposal of n-pentane. Careful drying in vacuo gave 0.65 g (91 %) (DPP)₂NacNacZnC₆F₅ with a visible melting point of 96 - 97 °C.

Analytical Data $C_{35}H_{41}F_5N_2Zn$ (650.09): C 63.14 (calcd. 64.66), H 6.38 (6.35), N 4.52 (4.30) %.

Single crystals of $(DPP)_2NacNacZnC_6F_5 \cdot THF$ were grown on storing an n-pentane / THF (10 :1 = v/v) solution of $(DPP)_2NacNacZnC_6F_5$ for several days at -30 °C.

NMR data (*C*₆*D*₆): ¹⁹**F**: δ = -115.11 (m, 2F, F-2,6), -154.63 (t, 1F, F-4), -161.25 (m, 2F, F-3,5). ¹**H**: δ = 7.02 (m, 6H, ArH), 5.06 (s, 1H, H_β), 3.23 (sept., 4H, CH(CH₃)₂), 1.67 (s, 6H, α-CH₃), 1.24 (d, 12H, CH(CH₃)₂), 1.11 (d, 12H, CH(CH₃)₂). ¹³C{¹**H**}: δ = 169.6 (*C*_α), 148.4 (*C*-2,6 ¹J_{C,F} ≈ 228 Hz), 143.6 (*C*_{ipso}), 142.0 (*C*_o), 140.5 (C-4, ¹J_{C,F} ≈ 249 Hz), 136.7 (C-3,5, ¹J_{C,F} ≈ 251 Hz), 126.7 (*C*_p), 124.0 (*C*_m), 114.2 (C-1,²J_{C,F} ≈ 61 Hz), 96.6 (*C*_β), 28.6 (CHMe₂), 23.9 (CHMe₂), 23.9 (CHMe₂).

EI-MS (20 eV): $m/z = 650 (M^+, 100 \%), 635 ([M-Me]^+, 28 \%), 418 ([(DPP)_2NacNacH]^+, 46 \%), 403 ([(DPP)_2NacNac-Me]^+, 72 \%), 375 ([(DPP)_2NacNacH-CHMe_2]^+, 16 \%), 202 ([(DPP)NacNac-2Me]^+ 60 \%),$

168 ([C_6F_5H]^+, 5 %). Zinc containing fragments are referenced to the isotope ${}^{\delta 5}\text{Zn}.$

Synthesis of $(DPP)_2NacNacCdC_6F_5$

A solution of 0.21 g (0.50 mmol) (DPP)₂NacNacH in 5 ml toluene was slowly dropped to a well stirred solution of 0.30 g (0.56 mmol) $Cd(C_6F_5)_2 \cdot 2$ MeCN in 5 ml toluene at ambient temperature. After stirring for approximately 3 hours, the mixture became turbid and an ochre solid began to precipitate. The reaction mixture was stirred overnight and finally all volatile compounds were removed in vacuo. After washing with several small portions of n-pentane and drying in vacuo, a pale ochre solid was obtained which was identified as $(DPP)_2NacNacCdC_6F_5$. 0.30 g (86%) $(DPP)_2NacNacCdC_6F_5$ were collected. No visible melting or decomposition point was observed on heating up to 400 °C in a melting point apparatus.

Analytical Data $C_{35}H_{41}F_5N_2Cd$ (697.11): C 58.94 (calc. 60.30), H 6.02 (5.92), N 4.12 (4.01) %.

Single crystals of (DPP)₂NacNacCdC₆F₅ (CDCl₃ and H₂O co-crystallise) were grown on storing unsealed NMR samples of (DPP)₂NacNacCdC₆F₅ in CDCl₃ for several days at -30 °C. Crystals of the complex with DMF were obtained on cooling a highly diluted DMF / n-pentane solution of the donor-free derivative for one week to -30 °C.

NMR data (*CDCl₃*): ¹⁹F: δ = -111.41 (m, 2F, F-2,6, ³J_{Cd,F} = 116 Hz), -154.78 (t, 1F, F-4, ⁵J_{Cd,F} = 72 Hz), -160.81 (m, 2F, F-3,5, ⁴J_{Cd,F} = 100 Hz) ppm. ¹H: δ = 7.13 (m, 6H, ArH),4.93 (s, 1H, H_β), 3.16 (sept., 4H, CH(CH₃)₂), 1.79 (s, 6H, α-CH₃), 1.24 (d, 12H, CH(CH₃)₂), 1.07 (d, 12H, CH(CH₃)₂). ¹³C{¹H}: δ = 169.3 (C_α), 147.8 (C-2,6 ¹J_{C,F} ≈ 228 Hz), 145.2 (C_{ipso}), 140.8 (C_o), 140.3 (C-4, ¹J_{C,F} ≈ 249 Hz), 136.4 (C-3,5, ¹J_{C,F} ≈ 251 Hz), 125.5 (C_µ), 123.5 (C_µ), 116.5 (C-1,²J_{C,F} ≈ 61 Hz), 94.2 (C_β), 28.0 (CHMe₂), 24.1 (CHMe₂), 23.4 (α-CH₃).

EI-MS (20 eV): m/z = 698 (M⁺, 40 %), 683 ([M-Me]⁺, 8 %), 418 ([(DPP)₂NacNacH]⁺ 32 %), 403 ([(DPP)₂NacNac-Me]⁺, 34 %), 375 ([(DPP)₂NacNacH-CH(Me)₂]⁺, 8 %), 202 ([(DPP)NacNac-2 Me]⁺ 100 %), 168 ([C₆F₅H]⁺, 5 %). Cadmium containing fragments are referenced to the isotope ¹¹²Cd.

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