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Journal of Organometallic Chemistry 604 (2000) 59–67

Novel 18-crown-6 organometallic rubidium and cesium complexes containing cyclopentadienyl, indenyl, pentamethylcyclopentadienyl, and fluorenyl as carbanions

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Received 13 January 2000; received in revised form 24 March 2000

Abstract

The synthesis of base-free cyclopentadienyl-, indenyl-, pentamethylcyclopentadienyl-, and fluorenylrubidium and -cesium is described. Reactions of these compounds with the hexadentate Lewis base 18-crown-6 yielded new complexes of the type [MR(18-crown-6)] and [{RbFl(18-crown-6)}$_2$(L)] (M = Rb, Cs; R = Cp, Ind, Cp*, Fl; L = dimethoxyethane, dioxane). All complexes were characterized by NMR spectroscopy and X-ray structure analysis. The dominating structure element in the investigated complexes is an [MR(18-crown-6)] unit in which the alkali metal ion is in close contact with the six oxygen atoms of the crown ether. In addition, a multihapto π-interaction between the cation and carbanion was found. For all isolated complexes containing the fluorenyl ligand, [MFl(18-crown-6)] and [{RbFl(18-crown-6)}$_2$(L)], only a η^2 coordination of the aromatic C–C bond between the C$_5$- and C$_6$-ring to the metal ions was observed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rubidium; Cesium; 18-Crown-6; Cyclopentadienyl; Indenyl; Pentamethylcyclopentadienyl; Fluorenyl

1. Introduction

Alkali metal organyls of the carbanions cyclopentadienyl (Cp), indenyl (Ind), fluorenyl (Fl), and pentamethylcyclopentadienyl (Cp*) have long been known [1–4]. Complexes of the lighter elements lithium and sodium are well investigated, and their application as precursors in organometallic synthesis for s-, p-, d-, and f-block metallocenes is well documented [5]. The distinct influence of the alkali metal cation in organoalkali reagents on the regio- and stereoselectivity of various reactions makes a structural determination of these compounds valuable [6,7]. Investigations of the organometallic compounds of the heavier alkali metals potassium, rubidium, and cesium were performed only rarely for a long time [8]. In the past 5 years a few contributions in the organometallic chemistry of potassium, rubidium, and cesium complexes containing the above mentioned carbanions have appeared in literature. While the solid state structures of base-free MCp (M = K–Cs) [9–11] were investigated by means of synchrotron X-ray powder diffraction methods, the anionic cesiocene-tripeldecker sandwich complex [PPh$_4$][Cs$_2$Cp$_3$] [12], the heterobimetallic complex [Cs(18-crown-6)Pb$_2$Cp$_5$] [13], and a few Lewis base containing complexes, i.e. [KCp*(py)$_2$]$_n$ [14], [KInd(TMEDA)]$_n$ [15] or [MFl(PMDTA)]$_n$ [16] (M = Rb, Cs) were investigated by X-ray single crystal structure analysis. To enhance comprehension of the role of the alkali metal cation size, the effectivity of additional ligands, and the charge distribution of the counterion that influences the aggregation number and the bonding fashion between cation and anion in alkali metal organyls, more structural data about the heavier congeners of lithium and sodium are needed.

Recently we reported on the 18-crown-6 complexes of KCp, KInd, KFl, and KCp* in which monomeric and dimeric aggregates were built [17]. In the case of KFl(18-crown-6), an unusual η^6 interaction between cation and anion was observed. Within this work we

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PII: S0022-328X(00)00202-3

report on the synthesis of new rubidium and cesium organyls MR (R = Cp, Ind, Fl, and Cp*) and their complexes with the crown ether 18-crown-6. In all cases X-ray single crystal structure determinations of the new MR(18-crown-6) complexes (M = Rb, Cs) were carried out and provide for the first time crystallographic data for MCp* and MInd compounds of rubidium and cesium.

2. Results and discussion

2.1. Synthesis

The redox reaction of rubidium or cesium metal with cyclopentadiene (HCp) or pentamethylcyclopentadiene (HCp*) in tetrahydrofuran or toluene yielded the base-free white products RbCp, CsCp, RbCp* and CsCp* (Eq. (1)). These compounds are pyrophoric or at least highly sensitive to air. The reaction of indene (HInd) or fluorene (HFl) with rubidium or cesium metal in polar solvents is problematic with regards to the yielding of uniform metallation products. This has already been reported for the reaction between rubidium or cesium and fluorene [18]. Instead of carrying out a redox reaction of the C–H acide hydrocarbons with the metals, a metallation was performed using the strong bases $RbN(SiMe_3)_2$ and $CsN(SiMe_3)_2$ as reagents in diethyl ether. This gave the required products in yields of 80–98% (Eq. (2)). The indenyl compounds RbInd and CsInd are light green and immediately decompose when in contact with air to a dark brown solid. The orange products RbFl and CsFl are also very sensitive to air and change their colors to yellow brown when in contact with air. All obtained base-free compounds can be stored under argon at room temperature (r.t.) for months without decomposition. Except for RbCp*, all compounds are soluble in tetrahydrofuran at r.t. or at 60°C. RbCp* can be dissolved in hot diglyme or in pyridine.

$$M + HR \rightarrow MR + 0.5H_2 \qquad (1)$$

where M = Rb, Cs; R = Cp, Cp*.

$$MN(SiMe_3)_2 + HR \rightarrow MR + HN(SiMe_3)_2 \qquad (2)$$

where M = Rb, Cs; R = Ind, Fl.

Reactions of the rubidium or cesium organyls with the Lewis base 18-crown-6 gave complexes of the type [MR(18-crown-6)] (**1**–**6**) in yields of 30–90% (Eq. (3)). The synthesis was carried out in tetrahydrofuran for the organic rests Cp, Cp* and Ind. Toluene was used as a solvent to obtain the fluorenyl complexes [RbFl(18-crown-6)]∗0.5toluene (**7**) and [CsFl(18-crown-6)]∗0.5toluene (**8a**). Recrystallization of **8a** from diethyl ether/dimethoxyethane delivered the solvent-free complex [CsFl(18-crown-6)] (**8**).

$$MR + 18\text{-crown-6} \rightarrow [MR(18\text{-crown-6})] \qquad (3)$$

where M = Rb, R = Cp (**1**), Cp* (**3**), Ind (**5**), Fl (**7**) and M = Cs, R = Cp (**2**), Cp* (**4**), Ind (**6**), Fl (**8**).

All compounds obtained are sensitive to air or moisture. The Cp and Cp* complexes **1**–**4** are white, the Ind complexes **5** and **6** are light green, and the Fl complexes **7** and **8** are orange.

2.2. ^{1}H-NMR spectroscopy

^{1}H-NMR spectroscopy of the complexes **1**–**8** was carried out in tetrahydrofuran-d_8. The chemical shifts of the crown ether's resonance signals vary slightly. While in the Cp and Cp* complexes (**1**–**4**) almost the same chemical shifts of the methylene protones were observed as in the free 18-crown-6 ligand (3.55 ppm), the signal is slightly shifted to upper field in the indenyl complexes **5** and **6** (3.44 and 3.41 ppm) and somewhat more so in the fluorenyl complexes **7** and **8** (3.31 and 3.21 ppm). In other fluorenyl alkali metal complexes containing polyether ligands, an upfield shift of the CH_2 protons was also observed and explained by the existence of contact ion pairs (CIP) [19]. The authors claimed that the close proximity of the ether molecule above the aromatic anion is responsible for the shielding of the ether protons. The observed proton signals of the anions Cp, Cp*, Ind, and Fl in the complexes **1**–**8** are similar to those of the related potassium compounds [17].

2.3. X-ray crystal structures

The solid state structures of the complexes **1**–**8** were investigated by single crystal structure analysis. Recrystallization was performed in dimethoxyethane (DME) (for **1**), in THF (for **2**–**6**), in toluene (for **7** and **8**), and in mixtures of diethyl ether/DME (for **7** and **8**), toluene/THF (for **7** and **8**), and toluene/dioxane (for **7**) to yield the following compositions: [RbCp(18-crown-6)]∗DME (**1a**), [CsCp(18-crown-6)]∗THF (**2a**), [RbCp*(18-crown-6)]∗0.5THF (**3a**), [CsCp*(18-crown-6)]∗0.5THF (**4a**), [RbInd(18-crown-6)] (**5**), [CsInd(18-crown-6)] (**6**), [RbFl(18-crown-6)]∗0.5toluene (**7**), [RbFl(18-crown-6)]∗0.5THF (**7a**), [{RbFl(18-crown-6)}$_2$(DME)] (**7b**), [{RbFl(18-crown-6)}$_2$(dioxane)] (**7c**), [CsFl(18-crown-6)] (**8**), [CsFl(18-crown-6)]∗ 0.5toluene (**8a**), and [CsFl(18-crown-6)]∗0.5THF (**8b**). The molecules THF and toluene appear only as crystal solvents showing no observable interaction with the metal ions, while DME and dioxane in **7b** and **7c** are coordinated to the rubidium cations (Fig. 4).

Table 1
Crystallographic data for [RbCp(18-crown-6)]∗DME (**1a**), [CsCp(18-crown-6)]∗THF (**2a**), [RbCp*(18-crown-6)]∗0.5THF (**3a**), [CsCp*(18-crown-6)]∗0.5THF (**4a**), [RbInd(18-crown-6)] (**5**), [CsInd(18-crown-6)] (**6**), [RbFl(18-crown-6)]∗0.5toluene (**7**), [{RbFl(18-crown-6)}$_2$(dioxane)] (**7c**), and [CsFl(18-crown-6)] (**8**)

	1a	**2a**	**3a**	**4a**	**5**	**6**	**7**	**7c**	**8**
Formula	$C_{21}H_{39}O_8Rb$	$C_{21}H_{37}CsO_7$	$C_{24}H_{43}O_{6.5}Rb$	$C_{24}H_{43}CsO_{6.5}$	$C_{21}H_{31}O_6Rb$	$C_{21}H_{31}CsO_6$	$C_{28.5}H_{37}O_6Rb$	$C_{54}H_{74}O_{14}Rb_2$	$C_{25}H_{33}CsO_6$
Fomula weight	504.99	534.42	521.05	568.49	464.93	512.37	561.05	1118.08	562.42
T (K)	173	173	173	173	173	173	173	173	173
Radiation (Å)	1.54178	0.71073	1.54178	0.71073	0.71073	0.71073	1.54178	1.54178	0.71073
Cryst size (mm)	2.0 × 0.1 × 0.1	0.4 × 0.3 × 0.25	0.4 × 0.3 × 0.3	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.2	1.2 × 0.25 × 0.25	0.6 × 0.5 × 0.4	0.8 × 0.3 × 0.3
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_1/n$	$P2_1/n$	$Pna2_1$	$Pna2_1$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a (Å)	8.617(3)	12.064(1)	9.647(2)	9.566(2)	19.950(4)	14.710(1)	9.628(1)	9.520(5)	8.544(6)
b (Å)	14.724(2)	11.140(1)	16.002(2)	16.378(3)	11.379(2)	18.722(1)	16.007(1)	15.424(8)	14.51(2)
c (Å)	20.021(3)	18.470(1)	17.704(2)	17.973(4)	9.911(2)	8.204(1)	17.609(1)	18.263(8)	20.52(5)
β (°)		96.05(1)	96.78(1)	96.39(3)			91.32(1)	94.22(4)	
V (Å^3)	2540.2(10)	2468.3(1)	2713.9(7)	2798.4(10)	2249.9(8)	2259.5(1)	2713.1(4)	2674(2)	2543(8)
Z	4	4	4	4	4	4	4	2	4
D_{calc} (Mg m^{-3})	1.320	1.438	1.275	1.349	1.373	1.506	1.374	1.388	1.469
μ (cm^{-1})	30.2	15.4	28.0	13.6	22.3	16.7	28.3	29.0	14.9
Index ranges	$0 \leq h \leq 10$ $0 \leq k \leq 18$ $0 \leq l \leq 25$	$-15 \leq h \leq 12$ $-14 \leq k \leq 14$ $-15 \leq l \leq 23$	$0 \leq h \leq 12$ $0 \leq k \leq 14$ $-22 \leq l \leq 22$	$-2 \leq h \leq 13$ $-2 \leq k \leq 23$ $-25 \leq l \leq 25$	$-25 \leq h \leq 25$ $-14 \leq k \leq 10$ $-12 \leq l \leq 13$	$-20 \leq h \leq 18$ $-20 \leq k \leq 25$ $-11 \leq l \leq 9$	$0 \leq h \leq 12$ $-20 \leq k \leq 2$ $-22 \leq l \leq 22$	$0 \leq h \leq 12$ $-19 \leq k \leq 0$ $-23 \leq l \leq 22$	$-1 \leq h \leq 11$ $-18 \leq k \leq 18$ $-26 \leq l \leq 1$
2Θ max (°)	152.6	55.0	152.7	60.1	57.6	58.0	152.9	152.9	55.0
Independent reflections	3022	10658	5075	8212	5256	4929	5691	5605	5846
Observational data ($I > 2\sigma_I$)	2772	10011	4319	7064	4339	4286	4770	4158	5390
No. of parameters	279	530	316	316	256	419	487	389	291
R_1 ($I > 2\sigma_I$, all data)	0.055, 0.064	0.046, 0.049	0.055, 0.064	0.040, 0.047	0.048, 0.059	0.019, 0.026	0.045, 0.056	0.054, 0.086	0.052, 0.057
wR_2 ($I > 2\sigma_I$, all data)	0.136, 0.146	0.109, 0.110	0.150, 0.159	0.098, 0.103	0.112, 0.116	0.035, 0.037	0.118, 0.134	0.125, 0.150	0.132, 0.138
GoF	1.055	1.108	1.068	1.098	1.031	1.016	1.088	1.080	1.034
Largest difference peak (e Å^{-3})	0.752, −0.744	1.241, −0.904	0.746, −2.150	2.720, −2.137	0.796, −1.131	0.361, −0.395	0.862, −1.694	0.806, −1.143	1.249, −0.779

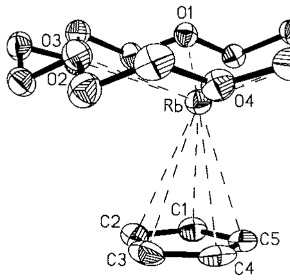

Fig. 1. Drawing of [RbCp(18-crown-6)]*DME (**1a**). The DME molecule and H atoms are not shown. Distances (Å): Rb–O: 2.881(6)–3.041(5), mean value 2.964; Rb–C: 3.116(8)–3.259(8), mean value 3.181; Rb–Cp$_{\text{centroid}}$: 2.954. The drawings of the complexes **3a**, **4a**, and **5** are similar. Distances for **3a** (Å): Rb–O: 2.934(3)–3.076(3), mean value 3.018; Rb–C: 3.154(4)–3.193(4), mean value 3.174; Rb–Cp$^*_{\text{centroid}}$: 2.937. Distances for **4a** (Å): Cs–O: 3.086(2)–3.226(2), mean value 3.154; Cs–C: 3.253(2)–3.290(2), mean value 3.270; Cs–Cp$^*_{\text{centroid}}$: 3.040. Distances for **5** (Å): Rb–O: 2.843(3)–3.033(3), mean value 2.940; Rb–C: 3.178(4)–3.210(4), mean value 3.193; Rb–C$_5$-ring $_{\text{centroid}}$: 2.956.

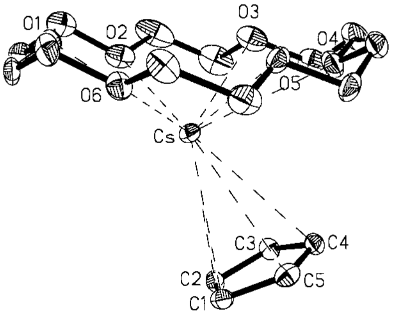

Fig. 2. Molecular structure of [CsCp(18-crown-6)]*THF (**2a**) (without THF molecule and H atoms). Distances (Å): Cs(1)–O: 3.091(4)–3.309(4), mean value 3.192; Cs(1)–C: 3.305(6)–3.447(5), mean value 3.382; Cs(1)–Cp$_{\text{centroid}}$: 3.166. The drawing of the complex **6** is similar. Distances for **6** (Å): Cs–C: 3.393(1)–3.437(2), mean value 3.417; Cs–C$_5$-ring $_{\text{centroid}}$: 3.196.

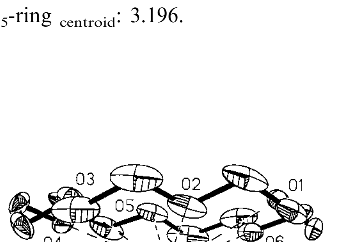

Fig. 3. Drawing of CsFl(18-crown-6) (**8**). H atoms are not shown. Distances (Å): Cs–O: 3.045(6)–3.278(8), mean value 3.124; Cs–C(13) 3.247(8), Cs–C(12) 3.355(8). The drawing of the complex **7** is similar. Distances for **7** (Å): Rb–O: 2.881(2)–3.015(2), mean value 2.945; C–O(18-crown-6): 1.415(3)–1.431(3), mean value 1.425; C–C(18-crown-6): 1.492(4)–1.507(4), mean value 1.499.

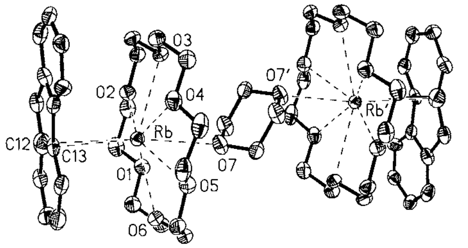

Fig. 4. Drawing of [{RbFl(18-crown-6)}$_2$(dioxane)] (**7c**). H atoms and the disorder of the fluorenyl ring is not shown. Distances (Å): Rb–O(18-crown-6): 2.857(4)–3.001(4), mean value 2.917; Rb–O(7) 3.077(4); Rb–C is not given because of disorder of the fluorenyl ring.

Table 1 and Figs. 1–4 provide the crystallographic results[1].

2.3.1. Description of the Cp, Ind, and Cp complexes (**1a**, **2a**, **3a**, **4a**, **5**, and **6**)*

The six complexes MR(18-crown-6) (M = Rb, Cs; R = Cp, Ind, Cp*) are built up by mononuclear contact ion pairs (CIP). The metal cations are surrounded by one 18-crown-6 ligand slightly above the equatorial plane and from below they are coordinated by the carbanions via the C$_5$-ring (i.e. Figs. 1 and 2).

In **1a**, **3a**, **4a**, and **5** the crown ether ligands and aromatic anions are arranged parallel to each other. We found that the angles of the O$_6$-planes and the C$_5$-planes are in the range of 172.4(2)–179.7(2)° (O$_6$-plane: best plane through the six oxygen atoms of the 18-crown-6 ligand; C$_5$-plane: best plane through the C$_5$-ring of the anion). The complexes [CsCp(18-crown-6)]*THF (**2a**) and [CsInd(18-crown-6)] (**6**) are different (i.e. Fig. 2). Here we observed bent molecules with angles between the O$_6$- and C$_5$-planes of 154.7(5)° and 160.1(5)° (**2a**, there are two different molecules in the asymmetric unit) and 155.4(5)° (**6**). Compared to the recently published potassium complexes [KR(18-crown-6)] [17], which are built up in an analogous fashion, bent molecules of this type are only observed within the cesium compounds. The reason for this finding is not clear at this point.

All six oxygen atoms of the Lewis base interact with the metal cations. The crown like shape of the ligand

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[1] The structure determination of the complexes **7a**, **7b**, **8a**, and **8b** have shown that parts of the molecules were disordered. Therefore only selected crystallographic data are given here: **7a**: $C_{27}H_{37}O_{6.5}Rb$, f.w. = 551.04 g mol^{-1}, monoclinic, $P2_1/n$, $a = 9.630(3)$, $b = 15.592(2)$, $c = 17.903(8)$ Å, $\beta = 90.20(3)°$, $V = 2688.1(15)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.362$ g cm^{-3}; **7b**: $C_{54}H_{76}O_{14}Rb_2$, f.w. = 1120.08 g mol^{-1}, monoclinic, $P2_1/n$, $a = 9.687(7)$, $b = 15.666(7)$, $c = 17.889(5)$ Å, $\beta = 90.91(4)°$, $V = 2715(2)$ Å^3, $Z = 2$, $D_{\text{calc}} = 1.370$ g cm^{-3}; **8a**: $C_{28.5}H_{37}CsO_6$, f.w. = 608.49 g mol^{-1}, monoclinic, $P2_1/n$, $a = 9.607(2)$, $b = 16.846(8)$, $c = 17.271(3)$ Å, $\beta = 94.74(2)°$, $V = 2785.6(15)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.451$ g cm^{-3}; **8b**: $C_{27}H_{37}O_{6.5}Cs$, f.w. = 598.49 g mol^{-1}, monoclinic, $P2_1/n$, $a = 9.740(1)$, $b = 16.043(1)$, $c = 17.682(1)$, $\beta = 90.27(1)°$, $V = 2763.07(6)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.439$ g cm^{-3}.

causes three shorter and three longer M–O-distances, which is found before for the 18-crown-6 ligand, i.e. in the inorganic complexes [RbNCS(18-crown-6)]$_2$ [20], [Rb(18-crown-6)]$_2$[Cu$_2$Cl$_4$] [21], and [CsNCS(18-crown-6)]$_2$ [20,22], and one organometallic cesium compound ([Cs(18-crown-6)Pb$_2$Cp$_5$] [23]). The bonding type of the anions to the metal ions is always pentahapto. This bonding mode is very symmetrical for the Ind$^-$ and Cp*$^-$ anions (variation of the M–C distances 1.5–2.1%), whereas a less symmetrical M–C bonding for the Cp$^-$ anions (variation 5.8–6.1%) was observed. The metal carbon bond lengths are very similar within the rubidium compounds (mean value (Å): **3a**: 3.17, **1a**: 3.18, **5**: 3.19). This is not the case for the cesium compounds. Here we found the following order of Cs–C bond lengths: Cp* (**4a**, 3.27 Å) < Cp (**2a**, 3.38 Å) < Ind (**6**, 3.41 Å). It is remarkable that, in the complex [CsCp*(18-crown-6)]∗0.5THF, the complex with the shortest Cs–C bond lengths, the shortest Cs–O distances were also observed. Within the analogous built potassium compounds, [KR(18-crown-6], a deviated order of the anions regarding the K–C distances was observed: Cp$^-$ < Ind$^-$ < Cp*$^-$ [17]. Sterically repulsion between the 18-crown-6 and the Cp* ligand causes a longer K–C bond length in the [KCp*(18-crown-6)] complex than in the compounds [KCp(18-crown-6)] or [KInd(18-crown-6)]. A comparison of the M–C distances in **1a** and **2a** with the compounds RbCp [9], CsCp [10], and [PPh$_4$][Cs$_2$Cp$_3$] [12] showed very similar values for the same type of metal (mean value): **1a**: 3.18 Å; RbCp: 3.18 Å, 3.19 Å; **2a**: 3.38 Å; CsCp: 3.35 Å, 3.38 Å; [PPh$_4$][Cs$_2$Cp$_3$]: 3.33 Å, 3.35 Å. Significantly longer are the Cs–C bond lengths in the recently published complex [Cs(18-crown-6)Pb$_2$Cp$_5$] [23] (Cs–C 3.298(5)–3.712(5) Å; mean value 3.51 Å), where the Cp$^-$ anion bridges a Cs$^+$ and a Pb^{2+} cation.

*2.3.2. Description of the Fl complexes (**7**, **7c**, and **8**)*

The fluorenylrubidium(18-crown-6) and fluorenylcesium(18-crown-6) complexes (**7**, **7a**–**c**, **8**, **8a**,**b**) are built up by the unit MFl(18-crown-6) (M = Rb, Cs) as the fundamental group. Although the fluorenyl ring is always disordered in the crystal structures (except in **8**) and, thus, the exact metal carbon bond lengths cannot be discussed, the same bonding type of the fluorenyl anions to the cations was observed in all structures (i.e. Fig. 3).

In all complexes the alkali metal cations are located above the bond between the carbon atoms C12 and C13, which is the bond between the center of the five-membered ring and the center of one six-membered ring. The Cs–C12 and Cs–C13 bond lengths in compound **8** (Fig. 3), in which the fluorenyl ring is not disordered, are 3.247(8) and 3.355(8) Å long. Much longer are the next Cs–C distances to the carbon atoms C5 (3.820(11) Å) or C8 (3.657(9) Å). This finding is different from the bonding type of the fluorenyl ligand in the related complexes of the lighter element potassium ([KFl(18-crown-6)]∗0.5toluene and [{KFl(18-crown-6}$_2$(DME)] [17]). In these complexes an asymmetric η^6 C$_6$-ring interaction of the Fl$^-$ anion to the K$^+$ cation was observed. The best plane through the oxygen atoms of the crown ether is parallel to the best plane through the 13 carbon atoms of the fluorenyl ring for all rubidium derivatives and the cesium compounds **8a** and **8b** (177.7–179.0°). For the cesium complex **8** an angle of 165.7° between these planes was found. In the complexes **7b** and **7c** two of the above mentioned RbFl(18-crown-6) units are bridged by the bidentate ligands DME (**7b**) or dioxane (**7c**, Fig. 4). The same tendency to build up binuclear complexes was observed for the related potassium derivatives [17]. Within the fundamental unit MFl(18-crown-6) (M = Rb, Cs) the bonding mode of the crown ether to the metal cations are comparable to the situation described for the Cp, Ind, and Cp* compounds in Section 2.3.1. The M–O bond lengths are in the same range.

Single crystal structures of the compounds [RbFl(PMDTA)]$_n$, [CsFl(THF)]$_n$, and [CsFl(PMDTA)]$_n$ were mentioned in previous literature [16]. The observed coordination modes of the cations in these three complexes were above the C$_5$- or the C$_6$-ring of the fluorenyl anion (Cs–C distances were not given in [16] because parts of the molecules were disordered). This shows that the previously discussed location of the cations between the C$_5$- and the C$_6$-ring in the MFl(18-crown-6) complexes descries a new fashion of how a fluorenyl anion can be connected to Rb$^+$ and Cs$^+$ cations. It is worth mentioning that all known single crystal structures of alkli metal fluorenyl complexes with Lewis bases of the lighter elements lithium and sodium show the Li$^+$ or Na$^+$ cations above the C$_5$-ring of the anion (i.e. [LiFl(Et$_2$O)$_2$] [24] or [NaFl(PMDTA)] [25]).

3. Experimental

3.1. General procedures

All reactions were carried out under an atmosphere of dry argon using conventional Schlenk techniques. Solvents were freshly distilled from sodium (toluene, dimethoxyethane and dioxane), potassium (THF) or a sodium/potassium alloy (cyclopentane, *n*-hexane, and diethyl ether). 18-crown-6 was dried over P$_2$O$_5$ under reduced pressure for 4 weeks. Cyclopentadiene, pentamethylcyclopentadiene and indene were freshly distilled, while fluorene was used without further purification. RbN(SiMe$_3$)$_2$ and CsN(SiMe$_3$)$_2$ were prepared as described in previous literature [26,27]. IR spectra: Perkin–Elmer FT-IR 1720 spectrometer, nujol suspension. NMR spectra: Varian Gemini 200 BB spectrometer, 200 MHz (^{1}H), 50.3 MHz (^{13}C), THF-d_8, TMS.

3.2. Synthesis of RbCp

Cyclopentadiene (1.5 ml, 1.38 g, 20.9 mmol) was added to rubidium metal (1.35 g, 15.8 mmol) in tetrahydrofuran (200 ml) at −40°C. The mixture was allowed to warm to r.t. and heated for 1 h at 50°C. The nearly clear solution was filtered while still warm, parts of the tetrahydrofuran (90%) were distilled under reduced pressure, and cyclopentane (100 ml) was added. The obtained precipitate was separated, washed twice with cyclopentane (2 × 50 ml) and dried at 10^{-2} torr. Yield: 1.89 g (84%) white, pyrophoric, and very air-sensitive powder. Dec. > 220°C. The compound is not soluble in cyclopentane or diethyl ether, but is soluble in hot THF. Anal. Calc. for C_5H_5Rb: C, 39.9; H, 3.4. Found: C, 39.9; H, 3.7%. IR: ν 3059 (s), 3037 (m), 1013 (s), 1004 (s), 735 (m), 720 (vs), 698 (vs), and 669 (s) cm^{-1}.

3.3. Synthesis of CsCp [12]

CsCp was prepared as described for RbCp: Cesium metal (0.95g, 7.1 mmol), tetrahydrofuran (45 ml), cyclopentadiene (0.9 ml, 0.89 g, 13.4 mmol), cyclopentane (50 ml). Yield: 1.30 g (93%) product was obtained as a white, very air-sensitive powder. Dec. > 210°C. The solubility is the same as found for RbCp. Anal. Calc. for C_5H_5Cs: C, 30.3; H, 2.6. Found: C, 30.4; H, 2.7%. IR: ν 3082 (w), 3056 (s), 1023 (s), 1010 (s), 712 (s), and 670 (vs) cm^{-1}.

3.4. Synthesis of RbCp*

Pentamethylcyclopentadiene (3.5 ml, 3.05 g, 22.4 mmol) was added at r.t. to rubidium metal (1.53 g, 17.9 mmol) in toluene (50 ml). The reaction mixture was heated for 2 h at 80°C until the metal disappeared and a white suspension formed. The precipitate was filtered, washed with cyclopentane and dried at 10^{-2} torr. Yield: 2.48 g (63%) product was obtained as a white, pyrophor, very air-sensitive powder. M.p.: not melted or decomposed < 300°C. The compound is soluble in pyridine or hot diglyme, less soluble in hot DME, but not soluble in THF. Anal. Calc. for $C_{10}H_{15}Rb$: C, 54.4; H, 6.8. Found: C, 53.3; H, 6.9%. IR: ν 2719 (s), 1350 (m), 1264 (m), 1157 (m), 1082 (vs), 1064 (s), 1001 (w), and 643 (m) cm^{-1}.

3.5. Synthesis of CsCp*

Cesium metal (0.44 g, 3.31 mmol), pentamethylcyclopentadiene (0.52 g, 0.6 ml, 3.83 mmol) and THF (25 ml) were refluxed for 1 h and filtered while still hot. The hot solution was allowed to cool to r.t. and diethyl ether (20 ml) was added. The suspension was filtered, the white precipitate was washed twice with diethyl ether (2 × 10 ml) and dried at 10^{-2} torr. Yield: 0.72 g (81%) product was obtained as a white, pyrophor, very air-sensitive powder. M.p.: not melted or decomposed > 350°C. Solubility: soluble in hot THF, but not soluble in diethyl ether or *n*-hexane. Anal. Calc. for $C_{10}H_{15}Cs$: C, 44.8; H, 5.6. Found: C, 44.2; H, 5.6%. IR: ν 2750 (s), 2717 (vs), 1568 (w), 1264 (w), 1157 (w), 1082 (m), and 1064 (m) cm^{-1}.

3.6. Synthesis of RbInd

A solution of $RbN(SiMe_3)_2$ (2.40 g, 9.8 mmol) in diethyl ether (20 ml) was added at r.t. to a solution of indene (2.0 ml, 1.99 g, 17.1 mmol) in diethyl ether (20 ml). A green precipitate appeared. The reaction mixture was stirred for 2 h. The product was separated, washed with cyclopentane (60 ml) and dried at 10^{-2} torr. Yield: 1.63 g (83%) product was obtained as a light green, very air-sensitive powder. Dec. > 110°C. Solubility: good in THF but not in cyclopentane or diethyl ether. Anal. Calc. for C_9H_7Rb: C, 53.9; H, 3.5. Found: C, 53.6; H, 3.9%. IR: ν 3061 (m), 3025 (m), 1578 (w), 1321 (vs), 1258 (s), 1218 (m), 1040 (m), 748 (vs), 717 (s), and 433(m) cm^{-1}.

3.7. Synthesis of CsInd

CsInd was prepared in the same manner as described for RbInd. $CsN(SiMe_3)_2$ (3.42 g, 11.7 mmol) in diethyl ether (20 ml), indene (2.3 ml, 2.29 g, 19.7 mmol) in diethyl ether (20 ml). Yield: 2.31 g (79%) product was obtained as a light green, very air-sensitive powder. Dec. > 103°C. Solubility: The same as found for RbInd. Anal. Calc. for C_9H_7Cs: C, 43.6; H, 2.8. Found: C, 42.7; H, 2.9%. IR: ν 3053 (m), 3025 (m), 1333 (m), 1322 (vs), 1259 (s), 1218 (m), 1040 (m), 995 (m), 764 (s), 752 (vs), and 719 (s) cm^{-1}.

3.8. Synthesis of RbFl

The compound was prepared in the same manner as described for RbInd. $RbN(SiMe_3)_2$ (1.23 g (5.0 mmol) in diethyl ether (20 ml) was added to a solution of fluorene (2.00 g, 12.0 mmol) in diethyl ether (20 ml). Yield: 1.23 g (4.9 mmol, 98%) product was obtained as an orange, very air-sensitive powder. Dec. > 133°C. Solubility: the same as found for RbInd. Anal. Calc. for $C_{13}H_9Rb$: C, 62.3; H, 3.6. Found: C, 61.1; H, 3.7%. IR: ν 3038 (s), 3016 (s), 1566 (vs), 1442 (vs), 1323 (vs), 1223 (vs), 1108 (s), 985 (vs), 779 (s), 771 (vs), 765 (vs), 759 (vs), 750 (vs), 739 (s), 731 (vs), and 433 (s) cm^{-1}.

3.9. Synthesis of CsFl

The compound was prepared in the same manner as described for RbInd. $CsN(SiMe_3)_2$ (1.21 g, 4.1 mmol) in diethyl ether (20 ml) was added to a solution of fluorene (0.66 g, 4.0 mmol) in diethyl ether (20 ml). Yield: 1.06 g (89%) product was obtained as an orange, very air-sensitive powder. Dec. > 127°C. The solubility is the same as found for RbInd. Anal. Calc. for $C_{13}H_9Cs$: C, 52.4; H, 3.0. Found: C, 50.1; H, 3.3%. IR: ν 3049 (w), 3028 (w), 1565 (m), 1439 (m), 1324 (vs), 1226 (m), 983 (w), 755 (vs), and 723 (vs) cm^{-1}.

3.10. Synthesis of [RbCp(18-crown-6)] (**1**)

18-crown-6 (1.35 g, 5.1 mmol) was added to a solution of RbCp (0.74 g, 4.9 mmol) in THF (50 ml). After heating the mixture at 50°C for 2 h, an almost clear solution formed. The solution was filtrated while still warm and stored at 5°C. The product started to precipitate as a white solid. To complete precipitation, diethyl ether (30 ml) was added. The product was separated, washed twice with diethyl ether (2 × 20 ml) and dried at 10^{-2} torr. Yield: 0.90 g (44%) of a white, air-sensitive product was obtained. Dec. > 125°C. The compound is soluble in warm THF or DME, but not soluble in diethyl ether or cyclopentane. Anal. Calc. for $C_{17}H_{29}O_6Rb$: C, 49.2; H, 7.1; O, 23.1. Found: C, 49.0; H, 7.1; O, 22.6%. ^{1}H-NMR: δ 5.62 (s, 5H, Cp), 3.54 (s, 24 H, OCH$_2$) ppm. ^{13}C{^{1}H}-NMR: δ 104.7 (Cp), 71.0 (OCH$_2$) ppm. IR: ν 3052 (m), 1557 (w), 1109 (vs), 1005 (m), 835 (m), and 692 (s) cm^{-1}. Recrystallization of **1** from warm DME (70°C and storage at 5°C for a day yielded X-ray quality crystals of the formula [RbCp(18-crown-6)]∗DME (**1a**).

3.11. Synthesis of [CsCp(18-crown-6)] (**2**)

Compound **2** was prepared in the same manner as described for **1**. 18-crown-6 (1.32 g, 5.0 mmol) was added to a solution of CsCp (0.89 g, 4.5 mmol) in THF (30 ml). Yield: the product (1.61 g, 78%) was obtained as a white, air-sensitive powder. Dec. > 114°C. Compound **2** is soluble in warm THF, less soluble in warm diethyl ether and not soluble in cyclopentane. Anal. Calc. for $C_{17}H_{29}CsO_6$: C, 44.2; H, 6.3; O, 20.8. Found: C, 43.9; H, 6.4; O, 20.7%. ^{1}H-NMR: δ 5.58 (s, 5H, Cp), 3.52 (s, 24 H, OCH$_2$) ppm. ^{13}C{^{1}H}-NMR: δ 105.9 (Cp), 71.0 (OCH$_2$) ppm. IR: ν 3050 (m), 1350 (s), 1251 (m), 1137 (m), 1109 (vs), 1057 (w), 1005 (w), 959 (m), and 696 (m) cm^{-1}. To grow single crystals, the compound (0.15 g) was dissolved in THF (10 ml) at 50°C, filtrated while still warm and stored at 5°C. After 1 day colorless crystals of the formula [CsCp(18-crown-6)]∗THF (**2a**) were formed, suitable for an X-ray structure analysis.

3.12. Synthesis of [RbCp(18-crown-6)]* (**3**)

Compound **3** was prepared in the same manner as described for **1**. 18-crown-6 (0.74 g, 2.8 mmol) was added to a suspension of RbCp* (0.52 g, 2.4 mmol) in THF (10 ml). Cyclopentane was used for precipitation and washing of the product. Yield: 0.82 g (71%) of the product was obtained as a white, highly air-sensitive powder. Dec. > 84°C. The compound is soluble in warm THF, slightly soluble in warm diethyl ether but not soluble in cyclopentane. Anal. Calc. for $C_{22}H_{39}O_6Rb$: C, 54.5; H, 8.1; O, 19.8. Found: C, 54.5; H, 8.2; O, 19.3%. ^{1}H-NMR: δ 3.51 (s, 24 H, OCH$_2$), 2.00 (s, 15H, CH$_3$) ppm. ^{13}C{^{1}H}-NMR: δ 105.5 ($\underline{C}$–CH$_3$), 70.9 (OCH$_2$), 12.7 (C–$\underline{C}$H$_3$) ppm. IR: ν 2701 (w), 1580 (w), 1112 (vs), 1366 (m), 1350 (vs), 1248 (s), 1059 (m), 961 (vs), and 837 (s) cm^{-1}. The compound was recrystallized from warm THF and stored for 2 days at r.t., providing good crystals for X-ray structure analysis of the formula [RbCp*(18-crown-6)]∗0.5THF (**3a**).

3.13. Synthesis of [CsCp(18-crown-6)]* (**4**)

Compound **4** was prepared as described for **1**. 18-crown-6 (0.48 g, 1.8 mmol) was added to a suspension of CsCp* (0.37 g, 1.4 mmol) in THF (10 ml). Yield: 0.2 g (27%) product was obtained as a white, air-sensitive powder. Dec. > 87°C. Solubility: good in warm THF, slight in warm diethyl ether and not possible in cyclopentane. Anal. Calc. for $C_{22}H_{39}O_6Cs$: C, 49.6; H, 7.4; O, 18.0. Found: C, 49.5; H, 7.5; O, 17.3%. ^{1}H-NMR: δ 3.54 (s, 24 H, OCH$_2$), 1.95 (s, 15 H, CH$_3$) ppm. ^{13}C{^{1}H}-NMR: δ 106.5 ($\underline{C}$–CH$_3$), 71.2 (OCH$_2$), 12.4 (C–$\underline{C}$H$_3$) ppm. IR: ν 2702 (w), 1575 (w), 1106 vs), 1365 (m), 1349 (vs), 1246 (s), 1134 (s), 1057 (m), 959 (vs), and 837 (s) cm^{-1}. The compound was recrystallized from warm THF and stored for 2 days at r.t., providing good crystals for X-ray structure analysis of the formula [CsCp*(18-crown-6)]∗0.5THF (**4a**).

3.14. Synthesis of RbInd(18-crown-6) (**5**)

The compound was prepared in the same manner as described for **1**. 18-crown-6 (1.32 g, 5.0 mmol) was added to a solution of RbInd (1.00 g, 5.0 mmol) in THF (10 ml). Yield: 1.57 g (68%) product was obtained as a grey–green, very air-sensitive powder. Dec. > 95°C. Compound **5** is soluble in warm THF, less soluble in warm diethyl ether and not soluble in cyclopentane. Anal. Calc. for $C_{21}H_{31}O_6Rb$: C, 54.3; H, 6.7; O, 20.6%. Found: C, 53.7; H, 6.7; O, 20.2%. ^{1}H-NMR: δ 7.25 (m, 2 H, 4-, 7-H), 6.54 (t, 1 H, 2-H), 6.34 (m, 2 H, 5-, 6-H), 5.93 (d, 2 H, 1-, 3-H), 3.44 (s, 24 H, OCH$_2$) ppm. ^{13}C{^{1}H}-NMR: δ 130.8 (C8, C9), 118.9 (C4, C7), 118.6 (C2), 112.0 (C5, C6), 93.8 (C1, C3), 70.7 (OCH$_2$) ppm. IR: ν 3067 (m), 3027 (m), 1583 (w), 1323 (m), 1317 (m), 1252 (m), 1247 (m), 1107 (vs), 962 (s), 836 (m), 733 (s), and 690 (m) cm^{-1}. Dissolving of **5** in THF at 55°C and keeping the solution at r.t. yielded green crystals suitable for X-ray structure analysis.

3.15. Synthesis of [CsInd(18-crown-6)] (**6**)

Compound **6** was prepared in the same manner as described for **1**. 18-crown-6 (1.30 g, 4.8 mmol) was added to a solution of CsInd (1.10 g, 4.4 mmol) in THF (10 ml). Yield: 2.10 g (93%) product was obtained as a gray–green, air-sensitive powder. Dec. > 85°C. Solubility: good in warm THF, slight in warm diethyl ether and not possible in cyclopentane. Anal. Calc. for $C_{21}H_{31}CsO_6$: C, 49.2; H, 6.1; O, 18.7. Found: C, 49.0; H, 6.1; O, 18.4%. ^{1}H-NMR: δ 7.22 (m, 2 H, 4-, 7-H), 6.52 (t, 1 H, 2-H), 6.33 (m, 2 H, 5-, 6-H), 5.92 (d, 2 H, 1-, 3-H), 3.41 (s, 24 H, OCH_2) ppm. $^{13}C\{^1H\}$-NMR: δ 130.8 (C8, C9), 118.9 (C4, C7), 118.6 (C2), 112.1 (C5, C6), 94.5 (C1, C3), 71.0 (OCH_2) ppm. IR: ν 3059 (m), 3029 (w), 1581 (w), 1323 (s), 1282 (m), 1252 (s), 1135 (m), 1104 (vs), 959 (s), 835 (m), 747 (s), 733 (m), and 701 (m) cm^{-1}. Dissolving of **6** in THF at 55°C and keeping the solution at r.t. yielded green crystals suitable for X-ray structure analysis.

*3.16. Synthesis of [RbFl(18-crown-6)]*0.5toluene* (**7**)

18-crown-6 (0.24 g, 0.9 mmol) was added to a suspension of RbFl (0.20 g, 0.8 mmol) in toluene (50 ml). The mixture was heated to 100°C until a clear orange solution was obtained. The warm solution was filtrated and kept at r.t. Cyclopentane (30 ml) was added to precipitate an orange solid. The product was filtrated, washed with cyclopentane (30 ml) and dried at 10^{-2} torr. Yield: 0.31 g (75%). Dec. > 153°C. The compound is soluble in THF, less soluble in toluene and not soluble in cyclopentane. Anal. Calc. for $C_{28.5}H_{37}O_6Rb$: C, 61.0; H, 6.6; O, 17.1. Found: C, 61.0; H, 6.6; O, 16.9%. ^{1}H-NMR: δ 7.97 (d, 2 H, 4-, 5-H), 7.37 (d, 2 H, 1-, 8-H), 7.05–7.31 (m, 2.5 H, CH–toluene), 6.84 (t, 2 H, 2-, 7-H), 6.49 (t, 2 H, 3-, 6-H), 6.10 (s, 1 H, 9-H), 3.31 (s, 24 H, OCH_2), 2.30 (s, 1.5H, CH_3–toluene) ppm. $^{13}C\{^1H\}$-NMR: δ 138.5 (C1–toluene), 137.5 (C10, C13), 129.7 (C2,2′–toluene), 128.9 (C3,3′–toluene), 126.0 (C4–toluene), 122.5 (C11, C12), 120.1 (C2, C7), 119.7 (C4, C5), 117.4 (C1, C8), 109.2 (C3, C6), 83.9 (C9), 71.8 (OCH_2), 21.5 (CH_3–toluene) ppm. IR: ν 3044 (w), 3023 (w), 1599 (w), 1569 (w), 1348 (m), 1221 (m), 1133 (w), 1109 (vs), 983 (m), 967 (m), 960 (m), 747 (m), and 721 (s) cm^{-1}. Red crystals, suitable for X-ray structure analysis, were obtained by storing a saturated solution of **7** in toluene (100°C) at r.t.

3.17. Synthesis of CsFl(18-crown-6) (**8**)

A solution of 18-crown-6 (0.29 g, 1.1 mmol) in DME (22 ml) was added to a suspension of CsFl (0.33 g, 0.7 mmol) in diethyl ether (23 ml). The mixture was stirred at 80°C for 1 h and filtrated while it was still warm. Half of the solvent (25 ml) was removed by distillation. Cyclopentane (30 ml) was added to precipitate an orange solid. The product was separated, washed with cyclopentane (30 ml) and dried at 10^{-2} torr. Yield: 0.52 g (82%) product was obtained as an orange, air-sensitive crystalline material. Dec. > 154°C. The compound is soluble in warm DME or THF, slightly soluble in warm diethyl ether or toluene, but not soluble in cyclopentane. Anal. Calc. for $C_{25}H_{33}O_6Cs$: C, 53.4; H, 5.9; O, 17.1. Found: C, 53.1; H, 5.9; O, 16.2%. ^{1}H-NMR: δ 7.95 (d, 2 H, 4-, 5-H), 7.35 (d, 2 H, 1-, 8 H), 6.85 (t, 2 H, 2-, 7-H), 6.49 (t, 2 H, 3-, 6-H), 6.10 (s, 1 H, 9-H), 3.21 (s, 24 H, OCH_2) ppm. $^{13}C\{^1H\}$-NMR: δ 137.9 (C10, C13), 123.1 (C11, C12), 119.9 (C2, C7), 119.6 (C4, C5), 117.2 (C1, C8), 109.1 (C3, C6), 84.1 (C9), 70.5 (OCH_2), ppm. IR: ν 3047 (vw), 3023 (vw), 1571 (w), 1347 (s), 1221 (m), 1133 (m), 1111 (vs), 983 (w), 963 (m), 747 (m), and 721 (s) cm^{-1}. Recrystallization of **8** from DME/diethyl ether (1:1) at 50°C yielded red crystals suitable for X-ray structure analysis.

3.18. X-ray data collection, structure determination, and refinement

Crystallographic details are provided in Table 1. The crystals of the compounds **1a**, **3a** and **7** were measured on an Enraf-Nonius CAD4 four-circle diffractometer (Cu–K_α radiation, graphite monochromator, $\omega/2\theta$-scans). An empirical absorption correction was carried out with the program DIFABS ([28], part of the program system PLATON-95 [29]) for **1a** ($T_{min} = 0.064$, $T_{max} = 0.503$). The data sets for the complexes **2a**, **5**, and **6** were collected on a Siemens axs SMART CCD system (Mo–K_α radiation, graphite monochromator, ω-scans). A full hemisphere of the reciprocal space was scanned with 1271 frames in three sets; each frame covered 0.3° in ω. An empirical absorption correction was carried out with the program SADABS [30] (**2a**: $T_{min} = 0.805$, $T_{max} = 1.000$; **5**: $T_{min} = 0.663$, $T_{max} = 1.000$; **6**: $T_{min} = 0.630$, $T_{max} = 1.000$. The data sets for the compounds **4a** and **8** were collected on a Hilger & Watts four-circle diffractometer (Mo–K_α radiation, graphite monochromator, $\omega/2\Theta$-scans). All structures were solved with direct methods (SHELXS-97) [31] and refined with full-matrix least-squares against F_o^2, using the program SHELXL-97 [32]. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were calculated in idealized positions using a riding model with isotropic temperature factors combined in different logical groups. For molecular graphics and publication materials, the program package SHELXTL (PC v.5.03) [33] was used. Special refinement procedures are given in the supplementary material.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 115199 for **1a**, 115206 for **2a**, 115201 for **3a**, 115208 for **4a**, 115200 for **5**, 115207 for **6**, 115203 for **7**, 115204 for **7a**, 115205 for **7c**, 115209 for **8**, 115210 for **8a**, and 135949 for **8b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft, which we gratefully acknowledge (grant Be 760/10-1). F. Olbrich wishes to thank Sachsen-Anhalt for a Habilitation fellowship.

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