



## Synthesis and structural characterization of (COT)Pr(C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe)(THF) containing the chelating 9-(2-methoxyethyl)fluorenyl ligand

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### ABSTRACT

Treatment of 9-(2-methoxyethyl)fluorene, C<sub>13</sub>H<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**1**), with potassium hydride in THF/toluene in the presence of 18-crown-6 afforded orange-red crystalline K(18-crown-6)C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**2**) in 59% yield. A “constrained geometry”-type praseodymium complex containing the 9-(2-methoxyethyl)fluorenyl ligand, (COT)Pr(C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe)(THF) (**3**), was prepared by treatment of dimeric [(COT)Pr(μ-Cl)(THF)<sub>2</sub>] (COT = η<sup>8</sup>-cyclooctatetraenyl) with *in situ* prepared KC<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe. The molecular structures of **1**, **2**, and **3** were determined by single-crystal X-ray diffraction.

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## 1. Introduction

The organometallic chemistry of the group 3 and rare earth metals continues to be a highly attractive field of research, especially due to the numerous applications of organolanthanides in catalysis [1] and organic synthesis [2]. Among the catalytically active organolanthanide compounds, half-sandwich complexes containing linked cyclopentadienyl-amido ligands have attracted considerable attention as olefin polymerization catalysts. A variety of organo-rare earth complexes containing such bifunctional ligands have been reported by (among others) the groups of Bercaw [3], Hou [4], Marks [5], Okuda [6], and Piers [7]. Most of the complexes investigated so far contain bifunctional cyclopentadienyl ligands, while the corresponding constrained-geometry organolanthanide complexes based on indenyl or fluorenyl ligands are much less explored [8,9]. For example, a series of constrained-geometry group 3 metal complexes containing the fluorenyl-based ligands [(3,6-<sup>t</sup>Bu<sub>2</sub>C<sub>13</sub>H<sub>6</sub>)SiR<sub>2</sub>N<sup>t</sup>Bu]<sup>2-</sup> (R = Me, Ph) was reported by Carpentier et al. and explored as catalysts for ethylene and methylmethacrylate (MMA) polymerization [8]. Harder [9b] and Cowley [10] reported the lithium and calcium complexes comprising the

aminoethyl-functionalized fluorenyl ligand [C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sup>-</sup>. We describe here the first-time use of the readily accessible pendant-arm 9-(2-methoxyethyl)fluorenyl ligand [C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe]<sup>-</sup> in organolanthanide chemistry.

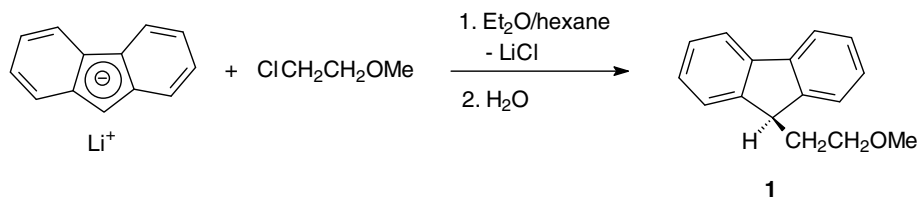
## 2. Results and discussion

The starting material 9-(2-methoxyethyl)fluorene, C<sub>13</sub>H<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**1**), was first prepared 20 years ago by Streitwieser et al. starting from *in situ* formed fluorenyllithium with 2-methoxyethyl methanesulfonate (no yields given) [11]. Later, van der Zeijden et al. reported a more straightforward synthesis of **1** starting from fluorenyllithium and 2-methoxyethyl chloride, ClCH<sub>2</sub>CH<sub>2</sub>OMe [12]. It was, however, found that this route is hampered by the formation of side products such as fluorene and the unwanted disubstituted fluorene derivative C<sub>13</sub>H<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>OMe)<sub>2</sub>-9,9. Surprisingly, while Streitwieser et al. described **1** as “large white crystals” [11], van der Zeijden et al. obtained the material in the form of a “yellow oil” (55% yield) [12]. Despite these obvious drawbacks we used a slight modification of the latter method and obtained the compound according to Scheme 1 in 48% isolated yield and high purity after chromatographic purification.

9-(2-Methoxyethyl)fluorene (**1**) made by the synthetic route outlined in Scheme 1 forms pale yellow (almost colorless) crystals

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**Scheme 1.** Synthesis of 9-(2-methoxyethyl)fluorene,  $C_{13}H_9CH_2CH_2OMe$  (**1**).

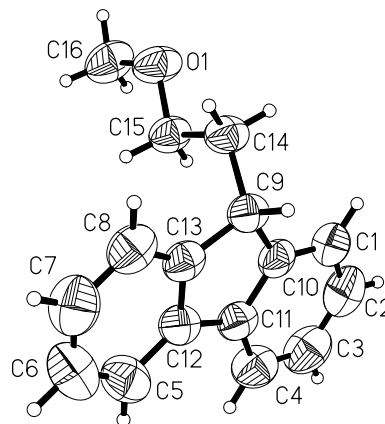
melting at 58–60 °C. The NMR data ( $^1H$ ,  $^{13}C$ ) were in good agreement with those reported in the literature [11,12]. The compound was also structurally characterized by single-crystal X-ray diffraction. Well-formed, very pale yellow single-crystals of **1** were obtained by slow cooling of a hot saturated solution of the compound in ethanol. Selected bond lengths and angles for **1** are listed in Table 1. Fig. 1 depicts the molecular structure of **1**. The X-ray study confirmed the presence of pure 9-(2-methoxyethyl)fluorene (**1**) with the molecule showing no unexceptional structural features. With 1.4011(14) and 1.4057(16) Å the C–O distances in the 2-methoxyethyl substituent are virtually identical. The angle at O1 is 112.66(11)°. The geometry as well as distances or angles within the 13-membered ring system of **1** are virtually identical with those reported for the unsubstituted hydrocarbon fluorene [13].

Among the possible alkali metal derivatives of **1**, only the lithium compound had been mentioned in previous reports [11,12]. This species was generated by deprotonation of **1** with *n*-butyllithium in THF or diethyl ether solution and used *in situ* for UV–Vis studies [11] or further reactions [12]. For example, an *in situ* prepared solution of  $LiC_{13}H_8CH_2CH_2OMe$  was employed as starting material for the synthesis of the first mono(fluorenyl) zirconium trichloride complex,  $[(C_{13}H_8CH_2CH_2OMe)ZrCl_2(\mu-Cl)]_2$  [12]. We found that rapid deprotonation of **1** can also be achieved by using potassium hydride. A nicely crystalline, orange-red potassium derivative of **1** was obtained by carrying out the deprotonation reaction in the presence of 18-crown-6 according to Scheme 2.

The product precipitated directly from the reaction mixture and was isolated in 59% yield (m. p. 128 °C). The NMR data were consistent with the formation of a 1:1 adduct of  $KC_{13}H_8CH_2CH_2OMe$  with 18-crown-6. The IR spectrum showed a strong band attributable to the C–O valence vibrations. Recrystallization of the resulting orange powder from THF/toluene (1:1) afforded orange-red, air- and moisture-sensitive single crystals suitable for X-ray diffraction. The structure determination confirmed the presence of  $K(18\text{-crown-6})C_{13}H_8CH_2CH_2OMe$  (**2**), which is characterized by a polymeric zigzag chain structure in the solid state. Table 2 gives selected bond lengths and angles for **2**. Fig. 2 shows the asymmetric unit (2a) and the polymeric zigzag chain structure (2b) of **2**. The interaction between the fluorenyl ring system and the potassium ion can be described as  $\eta^2$  with K...C distances of 3.3277(14) (C2)

**Table 1**  
Selected bond lengths (Å) and angles (°) for  $C_{13}H_9CH_2CH_2OMe$  (**1**)

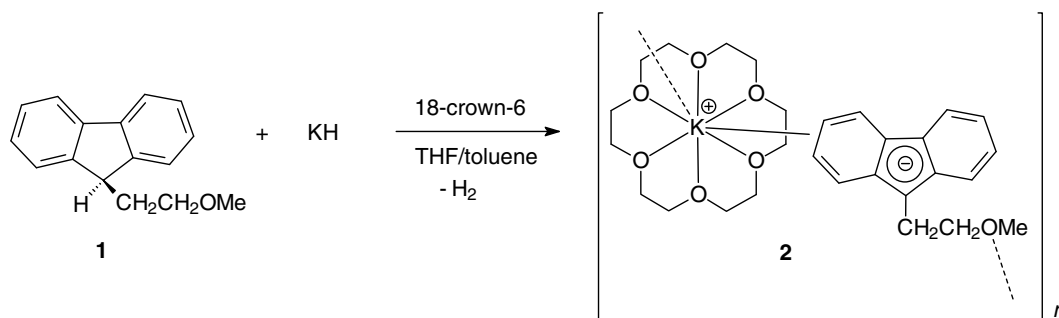
C1–C2	1.381(2)	C1–C10	1.3686(19)
C2–C3	1.374(2)	C3–C4	1.365(2)
C4–C11	1.3822(19)	C5–C6	1.367(2)
C5–C12	1.3818(19)	C6–C7	1.377(2)
C7–C8	1.370(2)	C8–C13	1.3753(18)
C9–C10	1.5084(18)	C9–C13	1.5054(18)
C9–C14	1.5306(17)	C10–C11	1.3861(18)
C11–C12	1.4609(19)	C12–C13	1.3864(18)
C14–C15	1.4948(17)	C15–O1	1.4011(14)
O1–C16	1.4057(16)		
C15–O1–C16	112.66(11)	C13–C9–C10	102.09(11)
C13–C9–C14	114.88(11)	C10–C9–C14	114.86(11)



**Fig. 1.** Molecular structure of 9-(2-methoxyethyl)fluorene,  $C_{13}H_9CH_2CH_2OMe$  (**1**) with thermal ellipsoids at the 50% probability level.

and 3.1486(14) Å (C3). The structural chemistry of alkali metal fluorenides has been intensively investigated in the past [14–16]. This chemistry is characterized by a large variety of coordination modes and hapticities ranging from  $\eta^1$  to  $\eta^6$ . The potassium-fluorenyl interaction in the closely related 18-crown-6 adducts of unsubstituted potassium fluorenyl,  $KC_{13}H_9(18\text{-crown-6})\cdot 0.5$  toluene,  $[KC_{13}H_9(18\text{-crown-6})][KC_{13}H_9(18\text{-crown-6})(THF)]$ , and  $(\mu\text{-DME})[KC_{13}H_9(18\text{-crown-6})]_2$  (DME = 1,2-dimethoxyethane) is  $\eta^6$  to one of the benzene rings in all cases. In these compounds the K...C distances are in the range of 3.234(4)–3.566(3) Å [16b]. In the early study by Streitwieser et al. [11] it was clearly shown by UV–Vis spectroscopy that the pendant-arm  $CH_2CH_2OMe$  moiety is bonded as a chelating ligand *via* oxygen to lithium, thereby accounting for the markedly increased stability of  $LiC_{13}H_8CH_2CH_2OMe$  as compared to other fluorenyllithiums lacking this possibility of internal chelate formation. In **2**, the potassium ion is bonded in the typical manner to all six oxygen atoms of the crown ether, thereby disrupting a chelating interaction with the  $CH_2CH_2OMe$  function which is most likely present in the absence of 18-crown-6. However, instead of an intramolecular K...O bonding interaction, intermolecular coordination of the  $CH_2CH_2OMe$  oxygen to a potassium ion of a neighboring molecule results in a polymeric zigzag chain structure as shown in Fig. 2b. Thus the coordination polyhedron of the  $K^+$  ion can be described as slightly distorted hexagonal bipyramidal. Polymeric solid-state structures have frequently been encountered in the chemistry of alkali metal fluorenides. A typical example is the recently reported compound  $KC_{13}H_9(pmdta)\cdot$  toluene [16f]. Like **2**, this compound crystallizes as a polymeric zigzag chain. In this case, however, the fluorenyl moieties act as  $\mu^2\text{-}\eta^1:\eta^5$  bridges between the potassium ions [16f].

In order to test the suitability of the 9-(2-methoxyethyl)fluorenyl ligand in organolanthanide chemistry, a reaction of the potassium derivative with dimeric  $[(COT)Pr(\mu-Cl)(THF)_2]_2$  was carried out. The dimeric cyclooctatetraenyl lanthanide dichlorides are well established as precursors for the synthesis of mixed-ligand  $(COT)Ln(Cp)$ -type sandwich complexes [17]. Praseodymium was



**Scheme 2.** Synthesis of  $K(18\text{-Crown-6})C_{13}H_8CH_2CH_2OMe$  (**2**).

**Table 2**

Selected bond lengths (Å) and angles (°) for  $K(18\text{-Crown-6})C_{13}H_8CH_2CH_2OMe$  (**2**)

K–O1	2.7784(10)	K–O2	2.8263(11)
K–O3	2.7728(11)	K–O4	2.7989(10)
K–O5	2.8267(11)	K–O6	2.8161(11)
K–O7	2.8381(10)	K–C2	3.3277(14)
K–C3	3.1486(14)	C9–C10	1.4199(19)
C9–C13	1.4223(19)	C9–C14	1.4991(18)
C10–C11	1.4505(18)	C11–C12	1.433(2)
C12–C13	1.4528(19)		
C15–O7–C16	110.09(10)	C10–C9–C13	107.06(11)
C10–C9–C14	125.94(12)	C13–C9–C14	126.77(12)

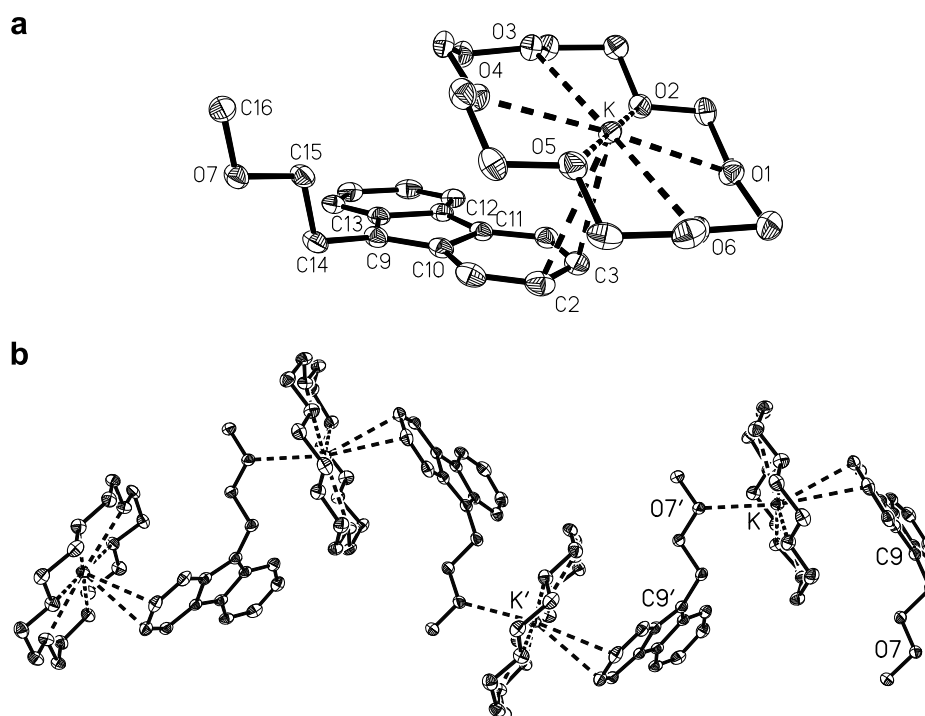
Symmetry operation: (\*) =  $x - 0.5, -y + 1, z - 0.5$ .

chosen as a typical representative of the large early lanthanide ions. Their coordination sphere is often sterically more difficult to saturate than that of the smaller late lanthanide ions. In this case it was found that *in situ* prepared  $KC_{13}H_8CH_2CH_2OMe$  could be conveniently used as starting material to introduce the 9-(2-methoxyethyl)fluorenyl ligand. Treatment of a THF solution of  $KC_{13}H_8CH_2CH_2OMe$  with  $[(COT)Pr(\mu-Cl)(THF)_2]_2$  in a molar ratio

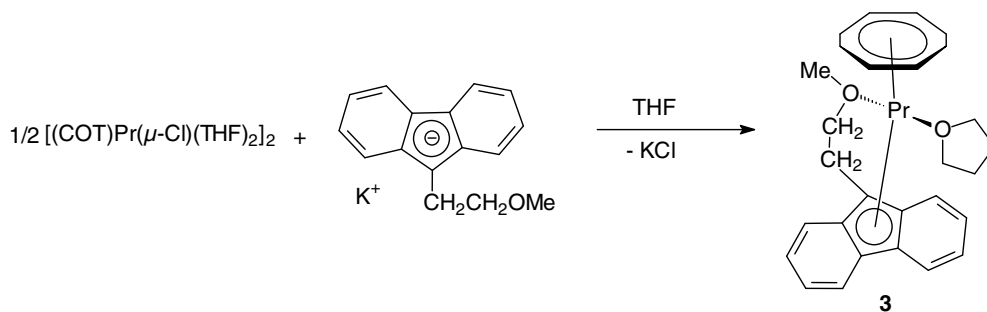
of 2:1 according to Scheme 3 afforded the new praseodymium sandwich complex **3** in moderate yield (45%).

The product  $(COT)Pr(C_{13}H_8CH_2CH_2OMe)(THF)$  (**3**) was isolated in the form of yellow, highly air-sensitive single-crystals which were suitable for X-ray diffraction (Fig. 3, Table 3). As shown in Fig. 3, the central praseodymium atom is formally 9-coordinated by an  $\eta^8$ -cyclooctatetraenyl ligand, the chelating 9-(2-methoxyethyl)fluorenyl ligand bonded  $\eta^5$  through the five-membered ring, and an additional THF ligand. As expected, the oxygen atom of the pendant-arm  $CH_2CH_2OMe$  functionality participates in the coordination to praseodymium. The corresponding Pr–O bond length is 2.5590(14) Å, while the Pr–O distance to the oxygen atom of the THF ligand is 2.6023(15) Å.

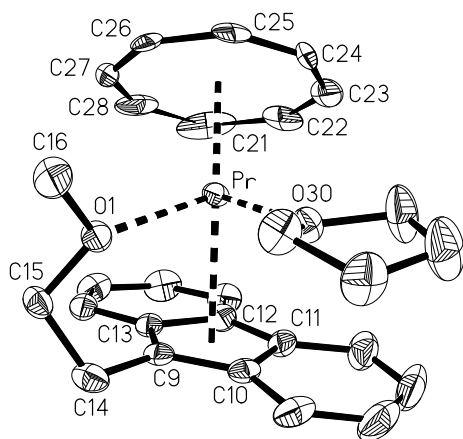
Due to the change of the hybridization mode from  $sp^3$  to  $sp^2$  at the carbon atom C9, the C9–C10 and C9–C13 bond lengths are significantly shorter in the anionic  $(C_{13}H_8CH_2CH_2OMe)^-$  ligand in **2** and **3** as compared to the neutral precursor  $C_{13}H_9CH_2CH_2OMe$  (**1**; bond lengths in **1**: C9–C10 1.5084(18) and C9–C13 1.5054(18) Å; in **2**: C9–C10 1.4199(19) Å, C9–C13 1.4223(19) Å; in **3**: C9–C10 1.419(3) Å, C9–C13 1.415(3) Å). Furthermore, the comparison of



**Fig. 2.** (a) Asymmetric unit of  $[K(18\text{-Crown-6})C_{13}H_8CH_2CH_2OMe]_n$  (**2**) with thermal ellipsoids at the 50% probability level (H atoms not shown for clarity). (b) Polymeric chain of  $[K(18\text{-Crown-6})C_{13}H_8CH_2CH_2OMe]_n$  (**2**) with thermal ellipsoids at the 50% probability level (four units shown; H atoms omitted for clarity; Symmetry operation: (\*) =  $x - 0.5, -y + 1, z - 0.5$ ).



**Scheme 3.** Synthesis of  $(\text{COT})\text{Pr}(\text{C}_{13}\text{H}_8\text{CH}_2\text{CH}_2\text{OMe})(\text{THF})$  (**3**).



**Fig. 3.** Molecular structure of  $(\text{COT})\text{Pr}(\text{C}_{13}\text{H}_8\text{CH}_2\text{CH}_2\text{OMe})(\text{THF})$  (**3**) with thermal ellipsoids at the 50% probability level (H atoms and disorder of the COT ligand not shown for clarity).

**Table 3**  
Selected bond lengths (Å) and angles ( $^\circ$ ) for  $(\text{COT})\text{Pr}(\text{C}_{13}\text{H}_8\text{CH}_2\text{CH}_2\text{OMe})(\text{THF})$  (**3**)

Pr–O30	2.5590(14)	Pr–C <sub>5c</sub> <sup>a</sup>	2.644(2)
Pr–O1	2.6023(15)	Pr–C <sub>8c</sub> <sup>b</sup>	1.968(9)
Pr–C9	2.767(2)	Pr–C10	2.905(2)
Pr–C11	2.993(2)	Pr–C12	2.999(2)
Pr–C13	2.873(2)	Pr–C21	2.632(12)
Pr–C22	2.628(8)	Pr–C23	2.644(17)
Pr–C24	2.689(18)	Pr–C25	2.745(16)
Pr–C26	2.731(9)	Pr–C27	2.699(10)
Pr–C28	2.673(16)	C9–C13	1.415(3)
C9–C10	1.419(3)	C9–C14	1.484(3)
C10–C11	1.434(3)	C11–C12	1.430(3)
C12–C13	1.431(3)		
O30–Pr–O1	77.31(5)	C <sub>5c</sub> –Pr–C <sub>8c</sub>	141.1(2)
C13–C9–C10	106.59(18)	C13–C9–C14	126.7(2)
C10–C9–C14	126.0(2)		

<sup>a</sup> C<sub>5c</sub> = centre of the five-membered ring.

<sup>b</sup> C<sub>8c</sub> = centre of the eight-membered ring.

the aromatic C–C distances within the five-membered rings of the anionic ligands in **2** and **3** show an identical range, no matter whether the C<sub>5</sub>-system is coordinated to a metal centre as in **3**, or not, as observed in **2** (aromatic C–C bond lengths within the C<sub>5</sub>-ring system in **2**: 1.4199(19)–1.4528(19) Å; in **3**: 1.415(3)–1.434(3) Å). Both effects were previously observed for organometallic complexes with unsubstituted fluorenyl anions [13–16].

In summarizing the results reported here, we succeeded in the synthesis and structural characterization of two new metal complexes containing the chelating 9-(2-methoxyethyl)fluorenyl ligand. In both cases the pendant-arm CH<sub>2</sub>CH<sub>2</sub>OMe functionality participates in the coordination to the metal atom, though in different ways. In the potassium derivative **2** the C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe

moiety acts as bridging ligand resulting in a polymeric zigzag chain structure. Chelating coordination of a lanthanide metal was found in the praseodymium complex **3**. These results clearly establish the 9-(2-methoxyethyl)fluorenyl anion as a useful ligand in alkali metal and organolanthanide chemistry.

### 3. Experimental

#### 3.1. General procedures

The reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. All solvents were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under vacuum prior to use. The starting material [(COT)Pr(μ-Cl)(THF)<sub>2</sub>]<sub>2</sub> was prepared according to the literature procedure [18]. Fluorene, *n*-butyllithium, potassium hydride, 18-crown-6, and 2-methoxyethyl chloride were obtained from commercial suppliers and used as received. <sup>1</sup>H (400 MHz) and <sup>13</sup>C (101 MHz) NMR spectra were recorded in THF-*d*<sub>8</sub> solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. The IR spectra were recorded using KBr pellets on a Perkin Elmer FT-IR spectrometer system 2000 between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. Microanalyses of the compounds were performed using a Leco CHNS 923 apparatus. The X-ray crystallographic studies were carried out on a Bruker AXS SMART CCD with Mo K<sub>α</sub>-radiation (λ = 0.71073 Å) and graphite monochromator (Table 4). Absorption correction of the datasets was performed with the program SADABS [19]. The structures were solved by direct methods using SHELXS-97 [20] and refined by full-matrix least-squares on F<sup>2</sup> using SHELXL-97 [21]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Compound **2** crystallizes as a racemic twin (refinement with TWIN and BASF option). The COT ligand in **3** is disordered and was refined with two positions for each atom and with restrained bond lengths for the C–C distances (SADI option; first ring 1.393(3) Å, second ring 1.375(3) Å). For more information see Supplementary material.

#### 3.2. Modified synthesis of 9-(2-methoxyethyl)fluorene, C<sub>13</sub>H<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**1**)

Fluorene (15.5 g, 80 mmol) was dissolved in 200 ml of diethyl ether. A 1.6 M solution of *n*-butyllithium in *n*-hexane (50 ml, 80 mmol) was added with stirring at –30 °C. The mixture was allowed to warm to room temperature and stirred overnight. Slow addition of 2-methoxyethyl chloride, ClCH<sub>2</sub>CH<sub>2</sub>OMe (7.6 g, 80 mmol), caused the precipitation of LiCl. After stirring for 1 h, water was added until the LiCl had completely dissolved. The organic layer was separated and dried over MgSO<sub>4</sub>. Filtration and evaporation of the solvent afforded a thick yellow oil which was

**Table 4**Crystal data and structure refinement for C<sub>13</sub>H<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**1**), K(18-Crown-6)C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**2**) and (COT)Pr(C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe)(THF) (**3**)

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>16</sub> H <sub>16</sub> O	C <sub>28</sub> H <sub>39</sub> KO <sub>7</sub>	C <sub>28</sub> H <sub>31</sub> O <sub>2</sub> Pr
Formula weight	224.29	526.69	540.44
Temperature	20 °C	−140 °C	−120 °C
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /n, no. 14	Monoclinic, Pn, no. 7	Monoclinic, P2 <sub>1</sub> /c, no. 14
Unit cell dimensions			
<i>a</i> (Å)	11.382(1)	9.6045(3)	16.608(1)
<i>b</i> (Å)	8.6997(8)	10.3949(3)	8.6755(5)
<i>c</i> (Å)	25.725(2)	13.5795(4)	15.912(1)
$\beta$ (°)	92.056(2)	90.201(1)	102.823(1)
Volume	2545.6(4) Å <sup>3</sup>	1355.74(7) Å <sup>3</sup>	2235.5(2) Å <sup>3</sup>
Z, calculated density	8, 1.170 Mg/m <sup>3</sup>	2, 1.290 Mg/m <sup>3</sup>	4, 1.606 Mg/m <sup>3</sup>
Absorption coefficient	0.071 mm <sup>−1</sup>	0.240 mm <sup>−1</sup>	2.202 mm <sup>−1</sup>
<i>F</i> (000)	960	564	1096
Crystal size	0.30 × 0.20 × 0.20 mm	0.40 × 0.30 × 0.25 mm	0.50 × 0.40 × 0.40 mm
Theta range for data collection	1.93–27.50°	1.96–30.51°	2.63–27.49°
Limiting indices	−14 ≤ <i>h</i> ≤ 8, −11 ≤ <i>k</i> ≤ 10, −33 ≤ <i>l</i> ≤ 32	−13 ≤ <i>h</i> ≤ 13, −14 ≤ <i>k</i> ≤ 14, −19 ≤ <i>l</i> ≤ 19	−21 ≤ <i>h</i> ≤ 21, −11 ≤ <i>k</i> ≤ 10, −20 ≤ <i>l</i> ≤ 18
Reflections collected/unique	15138/5626 [ <i>R</i> <sub>(int)</sub> = 0.0289]	24815/8120 [ <i>R</i> <sub>(int)</sub> = 0.0311]	14580/5022 [ <i>R</i> <sub>(int)</sub> = 0.0271]
Completeness to theta max.	96.1%	99.8%	97.7%
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
Max. and min. transmission	0.9859 and 0.9790	1.00 and 0.82	0.4729 and 0.4056
Refinement method	Full-matrix Least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	5626/0/316	8120/2/331	5022/56/359
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.014	1.000	1.004
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0455, <i>wR</i> <sub>2</sub> = 0.0895	<i>R</i> <sub>1</sub> = 0.0342, <i>wR</i> <sub>2</sub> = 0.0900	<i>R</i> <sub>1</sub> = 0.0234, <i>wR</i> <sub>2</sub> = 0.0585
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0810, <i>wR</i> <sub>2</sub> = 0.0979	<i>R</i> <sub>1</sub> = 0.0387, <i>wR</i> <sub>2</sub> = 0.0930	<i>R</i> <sub>1</sub> = 0.0259, <i>wR</i> <sub>2</sub> = 0.0594
Largest differences in peak and hole	0.117 and −0.134 e Å <sup>−3</sup>	0.523 and −0.183 e Å <sup>−3</sup>	0.883 and −0.783 e Å <sup>−3</sup>

purified by column chromatography on silica gel (eluents: 1. pentane, 2. pentane/diethyl ether (20:1), 3. diethyl ether). Evaporation of the combined pentane/diethyl ether fractions left a colorless oil, which crystallized upon standing at room temperature. Yield: 8.6 g (48%). M. p. 58–60 °C. Anal. (C<sub>16</sub>H<sub>16</sub>O, *M*<sub>w</sub> = 224.29 g/mol): C 84.8 (calc. 85.7), H 7.1 (7.2)%. IR (KBr):  $\nu$  3436 w br, 3065 w, 2996 w, 2874 s, 2834 s, 2810 m, 2360 vw br, 2061 vw, 1957 vw, 1928 vw, 1810 vw, 1607 vw, 1580 vw, 1477 m, 1450 vw, 1393 w, 1317 w, 1222 w, 1198 w, 1179 m, 1110 cs, 1027 w, 960 m, 880 w, 822 w, 784 m, 769 vs, 741 vs, 661 m, 619 w, 580 w, 459 w, 419 w cm<sup>−1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR data were in good agreement with those reported in the literature [12].

### 3.3. Preparation of K(18-crown-6)C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe (**2**)

25 ml of toluene/THF (1:1) were added to a solid mixture of potassium hydride (0.1 g, 2.5 mmol) and **1** (0.56 g, 2.5 mmol), causing rapid evolution of hydrogen and formation of a red solution. After the gas evolution had ceased, 18-crown-6 (0.66 g, 2.5 mmol) was added as a solid and stirring was continued for 12 h. The precipitated product was isolated by filtration and recrystallized from THF/toluene (1:1) to yield 0.77 g (59%) of **2** as orange-red crystals. M. p. 128 °C. Anal. (C<sub>28</sub>H<sub>39</sub>KO<sub>7</sub>, *M*<sub>w</sub> = 526.69 g/mol): C 64.8 (calc. 63.9), H 7.2 (7.5)%. IR (KBr):  $\nu$  3438 w br, 3037 vw, 2894 m br, 1973 vw, 1749 vw, 1601 vw, 1565 w, 1463 m, 1350 m, 1325 m, 1284 w, 1248 w, 1225 w, 1106 vs, 981 m, 961 m, 837 w, 748 w, 721 w cm<sup>−1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.1 MHz):  $\delta$  = 7.61 (d, 2H, H-4,5), 7.35 (d, 2H, H-1,8), 7.23 (t, 2H, H-2,7), 7.17 (t, 2H, H-3,5), 3.53 (s, 24H, CH<sub>2</sub> of 18-crown-6), 3.18 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.99 (s, 3H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.11 (t, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz):  $\delta$  = 127.9, 127.3, 127.2, 120.1 (fluorene), 71.1 (18-crown-6), 69.0 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 57.8 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 33.4 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>).

### 3.4. Preparation of (COT)Pr(C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>OMe)(THF) (**3**)

Potassium hydride (0.06 g, 1.5 mmol) and **1** (0.363 g, 1.5 mmol) were placed in a small Schlenk flask and THF (15 ml) was added. The mixture was stirred for ca. 3 h until the evolution of hydrogen

had ceased. The mixture was filtered and the clear red filtrate was combined with a solution of [(COT)Pr(μ-Cl)(THF)<sub>2</sub>]<sub>2</sub> (0.63 g, 0.75 mmol) in THF (15 ml). The mixture was stirred at reflux temperature for 24 h, cooled to room temperature and filtered through a thin layer of Celite filter aid. Concentration of the filtrate to a total volume of 20 ml and cooling to 0 °C for 4 weeks afforded yellow single-crystals of **3** (0.36 g, 45%). M. p. >300 °C (dec.). Anal. (C<sub>28</sub>H<sub>31</sub>O<sub>2</sub>Pr, *M*<sub>w</sub> = 540.44 g/mol): C 61.2 (calc. 62.2), H 5.5 (5.8)%. IR (KBr):  $\nu$  3436 w br, 2926 s, 2360 vw, 1810 vw, 1605 w, 1477 w, 1448 s, 1261 s, 1095 vs br, 1024 vs br, 948 m, 895 s, 801 vs, 739 vs, 683 s, 660 w, 620 w, 580 w cm<sup>−1</sup>. Meaningful <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** could not be obtained due to the paramagnetism of the Pr<sup>3+</sup> ion.

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### Appendix A. Supplementary data

CCDC numbers 232000, 699641 and 235549 contain the supplementary crystallographic data for compounds **1–3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.026.

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