

Supporting information for

# **Pentadienyl chemistry of the heavy alkaline-earth metals revisited**

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*Table of Content:*

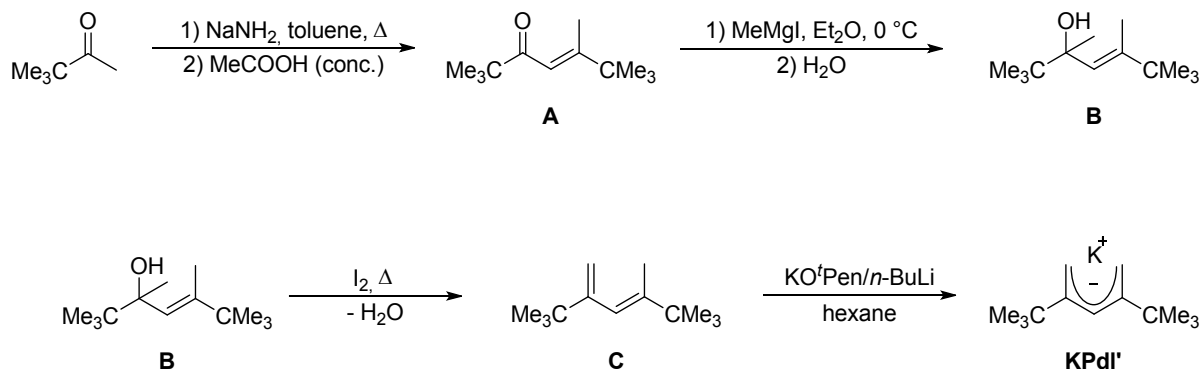
1. Experimental Details	S 2
2. Crystallographic Details	S 7
3. References	S 8

## 1. Experimental Details

**General considerations.** All synthetic and spectroscopic manipulations were carried out under an atmosphere of purified nitrogen, either in a Schlenk apparatus or in a glovebox. Solvents were dried and deoxygenated either by distillation under a nitrogen atmosphere from sodium benzophenone ketyl (THF) or by an MBraun GmbH solvent purification system (all other solvents). NMR data were recorded on a Bruker DPX 200, Bruker DRX 400, a Bruker Avance III 400 or a Bruker Avance II 300 spectrometer at ambient temperature unless stated otherwise. The residual solvent signal was used as a chemical shift reference ( $\delta_{\text{H}}$  7.16 for benzene, 7.26 for chloroform, 3.58 ppm for  $\alpha$ -H of THF) for the  $^1\text{H}$  spectra and the solvent signal ( $\delta_{\text{C}}$  128.06 for benzene, 77.17 for chloroform, 67.21 ppm for  $\alpha$ -C of THF) for the  $^{13}\text{C}$  spectra. Elemental analyses were performed by combustion and gas chromatographic analysis with an Elementar varioMICRO instrument. Despite several attempts, the carbon values for complexes **1-3** were lower than expected because of incomplete combustion and the extreme air-sensitivity of these compounds. Nevertheless, low carbon values were also observed in alkylcyclopentadienyl complexes of the heavy alkaline-earth metals, e.g. ref. 1, ref. 2 and literature cited therein, and ref. 3.

### Ligand synthesis.

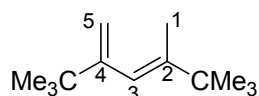
Potassium (2,4-di(*tert*-butyl)pentadienide,  $\text{K}[2,4-(\text{Me}_3\text{C})_2\text{C}_5\text{H}_5]$  (**KPdI'**)<sup>4</sup> was prepared according to a slightly modified literature procedure as detailed below.



**Preparation of 2,2,5,6,6-pentamethyl-4-hepten-3-one (A).** To a suspension of  $\text{NaNH}_2$  (256 mmol, 0.65 equiv.) in toluene (200 mL), pinacolone (39.5 g, 394 mmol, 1 equiv.) was slowly added with stirring. During the addition the suspension turned yellow and it was heated at  $90^\circ\text{C}$  for 6 h. After the reaction had cooled to ambient temperature the reaction mixture was carefully hydrolysed with glacial acetic acid (18.8 mL). During this process a colourless precipitate was formed, which was separated by filtration. The solution was extracted with  $\text{Et}_2\text{O}$  (3 x 60 mL). The organic extracts were combined, washed with

water (80 mL) and dried over MgSO<sub>4</sub>. The solvent was removed under dynamic vacuum and the ketone **A** was purified by distillation (68-74 °C/0.4 mbar) and obtained as colourless liquid. Yield: 19.4 g (108 mmol, 54%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 6.33 (q, 1H, CH, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 2.01 (d, 3H, CH<sub>3</sub>, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 1.09 (s, 9H, CMe<sub>3</sub>), 1.07 (s, 9H, CMe<sub>3</sub>) ppm.

**Preparation of 2,2,3,6,6,-heptamethylhept-4-en-3-ol (B).** Magnesium (3.29 g, 135 mmol, 1.20 equiv.) and Et<sub>2</sub>O (150 mL) was added to a 500 mL flask equipped with an additional funnel, nitrogen inlet, reflux condenser and a magnetic stirring bar. Methyl iodide (19.2 g, 135 mmol, 1.20 equiv) was diluted in Et<sub>2</sub>O (60 mL), transferred into the dropping funnel and the Grignard reaction was started by the addition of 5 mL of the MeI/Et<sub>2</sub>O mixture. The remaining MeI/Et<sub>2</sub>O solution was then slowly added to keep the reaction mixture at reflux. After complete addition the reaction mixture was heated at reflux for additional 2 h and then stirred for 5 h at ambient temperature. Remaining Mg metal was removed by filtration, ketone **A** (19.4 g, 107 mmol, 1.00 equiv) was slowly added at 0 °C and the resulting suspension was stirred for 12 h at ambient temperature. The colourless suspension was carefully hydrolysed with water (5 mL), neutralized with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution (30 mL) and then washed with saturated aqueous NaCl-solution (30 mL). The aqueous phase was extracted with Et<sub>2</sub>O (3 x 30 mL) and the organic extracts were combined and dried over MgSO<sub>4</sub>. The solvent was removed at a rotary evaporator to give the crude product in 95% yield (20.0 g, 101 mmol). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 5.41 (q, 1H, CH, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 1.87 (d, 3H, CH<sub>3</sub>, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 1.27 (s, 3H, CH<sub>3</sub>), 0.97 (s, 9H, CMe<sub>3</sub>), 1.02 (s, 9H, CMe<sub>3</sub>) (the OH proton was not observed) ppm.

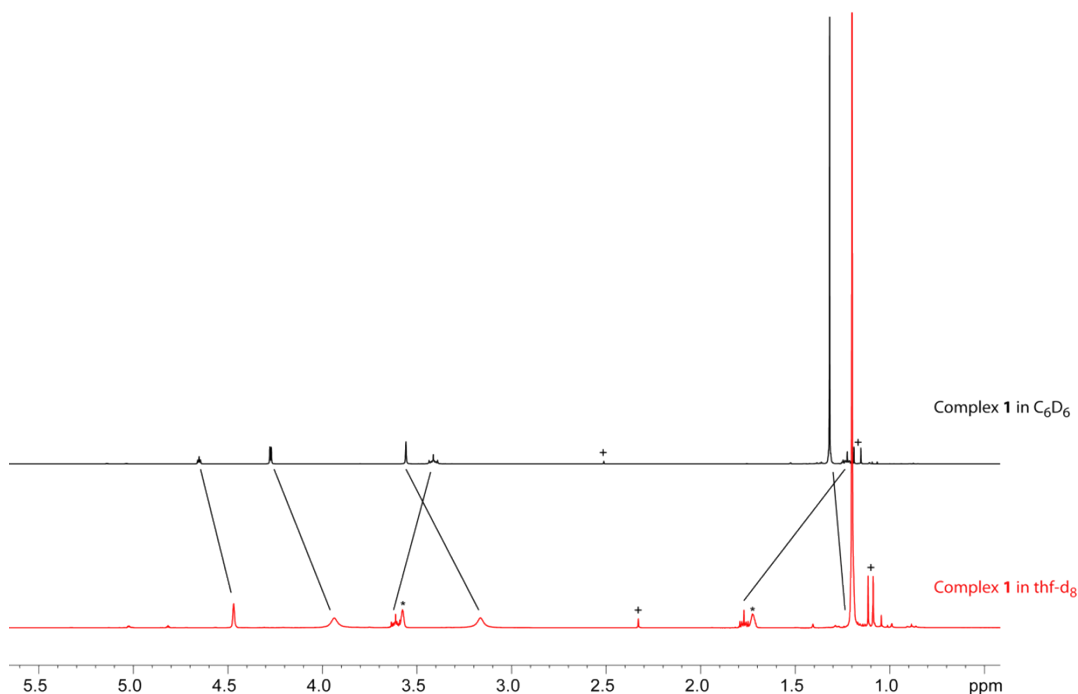


**Preparation of 2,2,3,6,6,-heptamethylhept-5-methylene-hept-3-ene (C).** Iodine (50 mg) was added to **B** (20.0 g, 101 mmol) and the mixture was heated under reflux for 1 h. The reaction mixture was allowed to cool to room temperature and then fractionally distilled over a Vigreux column (15 cm) (94 °C/1 mbar). In contrast to the original work-up procedure,<sup>4</sup> the final purification was accomplished by column chromatography (silica flash gel, pentane, R<sub>f</sub> = 0.96) to give product **C** in 78% yield (15.2 g, 84.3 mmol). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 5.87 (br, 1H, CH), 5.01 (d, 1H, CH<sub>2</sub>, J = 2.0 Hz), 4.59 (t, 1H, CH<sub>2</sub>, J = 2.0 Hz), 1.69 (d, 3H, CH<sub>3</sub>, <sup>4</sup>J = 1.3 Hz), 1.08 (s, 9H, CMe<sub>3</sub>), 1.04 (s, 9H, CMe<sub>3</sub>) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 298 K): δ 156.0 (C4), 145.8 (C2), 121.8 (C3), 109.4 (C5), 36.5 (CMe<sub>3</sub>), 36.4 (CMe<sub>3</sub>), 29.4 (C(CH<sub>3</sub>)<sub>3</sub>), 29.3 (C(CH<sub>3</sub>)<sub>3</sub>), 14.2 (C1) ppm.

**Preparation of K[2,4-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>] (KPdl').** To potassium amylate (KO'Pen) (4.20 g, 33.3 mmol) dissolved in hexane (200 mL), 1,3-pentadiene **C** (6.00 g, 33.3 mmol) was added at -78 °C. *n*-BuLi (22 mL, 35.0 mmol, 1.6 M in hexane) was added slowly at -78 °C and the reaction mixture was allowed to warm to ambient temperature and stirred for 12 h at 40 °C. During this time the colour changed from light yellow to dark red-brown. After filtration the dark brown precipitate was washed extensively with hexanes (5 x 20 mL) and THF (3 x 20 mL) to remove the red-brown colour. The product was dried under dynamic vacuum and isolated as a beige, highly pyrophoric powder. Yield: 4.10 g (18.8 mmol, 56%). **KPdl'** acted as a strong base, and deprotonation of toluene was observed when solid **KPdl'** was washed with toluene. Furthermore, it was essential to wash **KPdl'** extensively until a nearly colourless powder was obtained, since otherwise dramatically reduced yields were obtained in subsequent reactions. <sup>1</sup>H NMR (300 MHz, thf-*d*<sub>8</sub>, 298 K): δ 3.73 (t, 2H, CH, <sup>4</sup>*J* = 2.0 Hz), 3.56 (t, 1H, CH<sub>2</sub>, <sup>4</sup>*J* = 2.0 Hz), 3.22 (d, 2H, CH<sub>2</sub>, <sup>4</sup>*J* = 1.8 Hz), 1.16 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, THF-*d*<sub>8</sub>, 298 K): δ 157.3 (CCMe<sub>3</sub>), 78.7 (CH), 72.6 (CH<sub>2</sub>), 38.0 (CMe<sub>3</sub>), 32.6 (CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, THF-*d*<sub>8</sub>, 298 K): δ 32.6 (CH<sub>3</sub>), 38.0 (CMe<sub>3</sub>), 72.6 (CH<sub>2</sub>), 78.7 (CH), 157.3 (CCMe<sub>3</sub>) ppm. Anal. calcd. for C<sub>13</sub>H<sub>23</sub>K (218.42): C, 71.49; H, 10.61. Found: C, 70.90; H, 10.62.

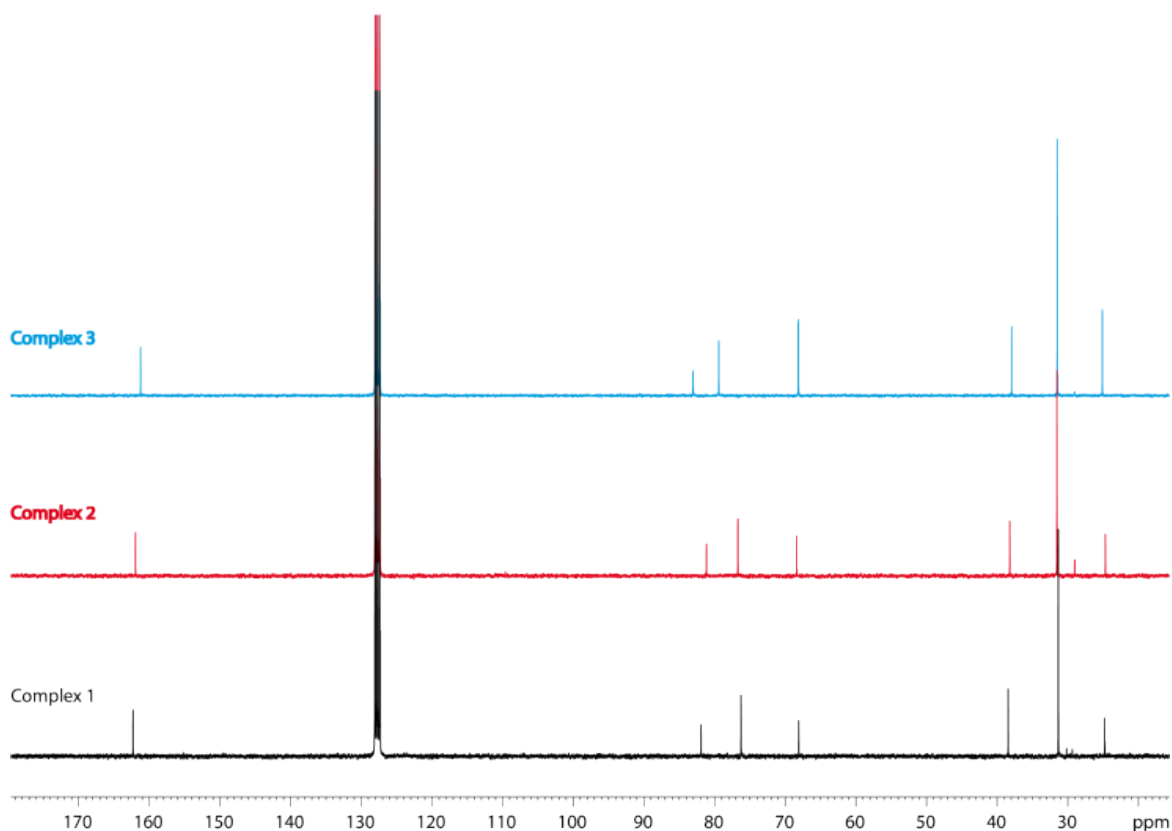
**KPdl'** was very poorly soluble in diethyl ether and only slightly soluble in tetrahydrofuran. Single crystals of **1** as its THF-adduct [(thf)K(μ-η<sup>5</sup>:η<sup>5</sup>-PdI')]<sub>∞</sub> were grown from concentrated THF solutions at -30 °C.

**Preparation of [(η<sup>5</sup>-2,4-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ca(thf)] (**1**).** To a solution of CaI<sub>2</sub> (135 mg, 0.46 mmol) in THF (15 mL) was added a slurry of K[2,4-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>] (200 mg, 0.92 mmol) in THF (10 mL) at room temperature. The resulting yellow solution was stirred for 2 h and a colourless solid was formed. After evaporation of the solvent, the yellow solid residue was extracted with pentane (3 x 5 mL). The filtered extract was concentrated and cooled to -30°C to give pale yellow crystals. Yield: 63 mg (0.13 mmol, 29%). Anal. calcd. for C<sub>30</sub>H<sub>54</sub>O<sub>2</sub>Ca (470.84): C, 76.53; H, 11.56. Found: C, 74.11; H, 11.26. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 4.65 (t, 1H, CH, <sup>4</sup>*J* = 2.3 Hz), 4.27 (d, 2H, CH<sub>2</sub>, <sup>4</sup>*J* = 2.3 Hz), 3.56 (s, 2H, CH<sub>2</sub>), 3.42 (m, 2H, α-*H* thf), 1.32 (s, 18H, CCH<sub>3</sub>), 1.23 (m, 2H, β-*H* thf) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 162.7 (CCMe<sub>3</sub>), 82.3 (CH), 76.6 (CH<sub>2</sub>), 68.4 (thf α-C), 38.8 (CMe<sub>3</sub>), 31.7 (CH<sub>3</sub>), 25.1 (thf β-C) ppm. When complex **1** was dissolved in thf-*d*<sub>8</sub> the PdI' resonances broadened and moved up-field, whereas the coordinated thf-resonances experienced a down-field shift. Nevertheless, we were unable to reproduce the previously reported <sup>1</sup>H NMR spectrum of **1**.<sup>5</sup>



**Figure S1.**  $^1\text{H}$  NMR spectrum of  $[(\eta^5\text{-}2,4\text{-}(\text{Me}_3\text{C})_2\text{C}_5\text{H}_5)_2\text{Ca}(\text{thf})]$  (**1**) recorded in  $\text{C}_6\text{D}_6$  and  $\text{thf-}d_8$  solvent at ambient temperatures. Resonances marked with \* and + correspond to  $\text{C}_4\text{D}_7\text{O}$  and trace amounts of HPdl' in the sample, respectively.

**Preparation of  $[(\eta^5\text{-}2,4\text{-}(\text{Me}_3\text{C})_2\text{C}_5\text{H}_5)_2\text{Sr}(\text{thf})]$  (**2**).** A slurry of  $\text{K}[2,4\text{-}(\text{Me}_3\text{C})_2\text{C}_5\text{H}_5]$  (200 mg, 0.92 mmol) in THF (10 mL) was added to a solution of  $\text{SrI}_2$  (157 mg, 0.46 mmol) in THF (15 mL). The resulting yellow solution was stirred for 2 h and a colourless solid precipitated. After solvent evaporation the yellow solid residue was extracted with pentane (3 x 5 mL). The filtered extract was concentrated and cooled to  $-30^\circ\text{C}$  to give pale yellow crystals. Yield: 102 mg (0.20 mmol, 43%). Anal. calcd. for  $\text{C}_{30}\text{H}_{54}\text{OSr}$  (518.38): C, 69.51; H, 10.56. Found: C, 66.24; H, 10.21.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  4.63 (t, 1H, CH,  $^4J = 2.3$  Hz), 4.26 (d, 2H,  $\text{CH}_2$ ,  $^4J = 2.3$  Hz), 3.66 (s, 2H,  $\text{CH}_2$ ), 3.32 (m, 2H,  $\alpha\text{-H}$  thf), 1.35 (s, 18H,  $\text{CCH}_3$ ), 1.17 (m, 2H,  $\beta\text{-H}$  thf) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  162.3 ( $\text{CCMe}_3$ ), 81.5 (CH), 77.0 ( $\text{CH}_2$ ), 68.7 (thf  $\alpha\text{-C}$ ), 38.5 ( $\text{CMe}_3$ ), 31.9 ( $\text{CH}_3$ ), 25.0 (thf  $\beta\text{-C}$ ) ppm.



**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of complexes **1**, **2** and **3** recorded in  $\text{C}_6\text{D}_6$  solution at ambient temperature.

**Preparation of  $[(\eta^5\text{-}2,4\text{-}(\text{Me}_3\text{C})_2\text{C}_5\text{H}_5)_2\text{Ba}(\text{thf})_2]$  (**3**).** To a solution of  $\text{BaI}_2$  (179 mg, 0.46 mmol) in THF (15 mL) was added a slurry of  $\text{K}[2,4\text{-}(\text{Me}_3\text{C})_2\text{C}_5\text{H}_5]$  (200 mg, 0.92 mmol) in THF (10 mL) at room temperature. The resulting yellow solution was stirred for 2 h and a colourless solid precipitated. After evaporating the solvent, the yellow solid residue was extracted with pentane (3 x 5 mL). The filtered extract was concentrated and cooled to  $-30^\circ\text{C}$  to give yellow crystals. Yield: 186 mg (0.29 mmol, 64%). Anal. calcd. for  $\text{C}_{34}\text{H}_{62}\text{BaO}_2$  (640.20): C, 63.79; H, 9.76. Found: C, 62.73; H, 9.71.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  4.59 (t, 1H, CH,  $^4J = 2.3$  Hz), 4.26 (d, 2H,  $\text{CH}_2$ ,  $^4J = 2.3$  Hz), 3.75 (s, 2H,  $\text{CH}_2$ ), 3.35 (m, 2H,  $\alpha\text{-H}$  thf), 1.34 (s, 18H,  $\text{CCH}_3$ ), 1.31 (m, 4H,  $\beta\text{-H}$  thf) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  161.6 ( $\text{CCMe}_3$ ), 83.4 (CH), 79.7 ( $\text{CH}_2$ ), 68.5 (thf  $\alpha\text{-C}$ ), 38.3 ( $\text{CMe}_3$ ), 31.8 ( $\text{CH}_3$ ), 25.4 (thf  $\beta\text{-C}$ ) ppm.

## 2. Crystallographic Details

Single crystals of each compound were examined under inert oil. Data were recorded at 100(2) K on Oxford Diffraction diffractometers using monochromated MoK $\alpha$  or mirror-focused CuK $\alpha$  radiation (Table S1). Absorption corrections were performed on the basis of multi-scans. The structures were refined anisotropically using the SHELXL-97 program.<sup>6</sup> Hydrogen atoms of the PdI' ligands were refined freely; methyl groups were refined as idealised rigid groups allowed to rotate but not tip. Other hydrogen atoms were refined using a riding model starting from calculated positions. *Special features and exceptions:* **Complex [(thf)K( $\mu$ - $\eta^5$ : $\eta^5$ -PdI')]<sub>∞</sub>**: Data were recorded at 130(2) K because the crystals disintegrate at 100 K. The space group is  $P2_12_12_1$ , but the structure was refined as a racemic twin (Flack parameter 0.49(2)), and the symmetry is close to  $Pnma$  (with  $b$  and  $c$  axes exchanged). However, the refinement in this space group proceeded to the unsatisfactory  $wR2$  value of 0.2, and some  $U$  values were high. Using the program suite PLATON (A. L. Spek, University of Utrecht, Netherlands) the mean deviation of the  $P2_12_12_1$  positions from  $Pnma$  was calculated to be 0.17 Å, with maximum deviation 0.30 Å for some atoms of the THF. Furthermore, around 100 reflections that should be systematically absent in  $Pnma$  displayed significant intensity. We therefore prefer the structure model with the lower symmetry. **Complex 3:** Each of the THF molecules is disordered over two positions with an (assumed) common oxygen atom position. Similarity restraints were employed, but the C-O bond lengths remain significantly different. It is possible that the oxygen positions are also slightly disordered, but a suitable model could not be refined. Dimensions of the THF ligands should be interpreted with caution.

**Table S1** Crystallographic details.

Complex	$[(\text{thf})\text{K}(\mu\text{-}\eta^5\text{:}\eta^5\text{-PdI}^{\prime})]_{\infty}$	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	$\text{C}_{17}\text{H}_{31}\text{KO}$	$\text{C}_{30}\text{H}_{54}\text{CaO}$	$\text{C}_{30}\text{H}_{54}\text{SrO}$	$\text{C}_{34}\text{H}_{62}\text{BaO}_2$
Formula Mass	290.52	470.81	518.35	640.18
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
$a/\text{\AA}$	10.1190(2)	9.9014(2)	9.7948(5)	9.5411(3)
$b/\text{\AA}$	10.7148(6)	21.7075(4)	14.1834(5)	12.0829(3)
$c/\text{\AA}$	16.4367(9)	14.4003(3)	23.3962(10)	15.6171(5)
$\alpha/^{\circ}$	90.00	90.00	88.549(3)	96.320(2)
$\beta/^{\circ}$	90.00	105.501(2)	79.821(2)	97.530(3)
$\gamma/^{\circ}$	90.00	90.00	71.131(2)	98.661(3)
Unit cell volume/ $\text{\AA}^3$	1782.11(14)	2982.56(10)	3025.4(2)	1748.97(9)
Temperature/K	130(2)	100(2)	100(2)	100(2)
Space group	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
No. of formula units per unit cell, $Z$	4	4	4	2
Radiation type	CuK $\alpha$	CuK $\alpha$	MoK $\alpha$	MoK $\alpha$
Absorption coefficient, $\mu/\text{mm}^{-1}$	2.526	1.923	1.800	1.160
No. of reflections measured	18651	78853	132306	92321
No. of independent reflections	3697	6171	15422	10431
$R_{int}$	0.1075	0.0475	0.1111	0.0306
Final $R_I$ values ( $I > 2\sigma(I)$ )	0.0498	0.0296	0.0544	0.0222
Final $wR(F^2)$ values ( $I > 2\sigma(I)$ )	0.1245	0.0785	0.0724	0.0493
Final $R_I$ values (all data)	0.0572	0.0306	0.1022	0.0262
Final $wR(F^2)$ values (all data)	0.1304	0.0794	0.0825	0.0514
Goodness of fit on $F^2$	1.015	1.050	1.037	1.053

### 3. References

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