Table S-1. Crystallographic information

	1	**3**	**4**	**5**
Empirical formula	$C_{22}H_{34}Cl_2KO_6Ti$	$C_{79}H_{167}K_2O_{12}Si_{16}Ti_2$	$C_{63}H_{129}K_2O_{15}Si_9Ti$	$C_{190}H_{349}K_6O_{36}Si_{24}Ti_3$
M_w	552.39	1932.57	1505.57	4262.15
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Size [mm]	0.38x0.30x0.22	0.32x0.25x0.18	0.46x0.33x0.20	0.37x0.30x0.20
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	P2(1)/c	P-1	P2(1)/n	C2/c
a [Å]	11.410(2)	13.606(3)	11.572(2)	25.623(5)
b [Å]	11.789(2)	19.608(4)	34.572(7)	24.455(5)
c [Å]	19.048(4)	21.586(4)	21.520(4)	40.583(8)
α [°]	90	74.40(3)	90	90
β [°]	94.45(3)	79.95(3)	102.46(3)	106.02(3)
γ [°]	90	89.22(3)	90	90
V [$Å^3$]	2554(9)	5458(2)	8407(3)	24443(8)
Z	4	2	4	4
ρ_{calc} [gcm^{-3}]	1.436	1.176	1.190	1.158
Absorption coefficient [mm^{-1}]	0.742	0.446	0.383	0.375
F(000)	1156	2086	3252	9172
θ range	1.79<θ<25.00	1.25<θ<25.00	1.13<θ<26.38	1.04<θ<24.00
Reflections collected/unique	18001/4495	19068/19068	65949/17177	80407/19181

Completeness to θ [%]	100	99.1	99.9	99.9
Data/restraints/parameters	4495/0/289	19068/0/1012	17177/0/829	19181/37/1160
Goodness of fit on F^2	1.03	1.02	1.03	1.02
Final R indices [$I>2\sigma(I)$]	R1=0.053,	R1=0.075,	R1=0.058,	R1=0.123,
	*w*R2=0.107	*w*R2=0.160	*w*R2=0.120	*w*R2=0.299
R indices (all data)	R1=0.075,	R1=0.120,	R1=0.096,	R1=0.1642,
	*w*R2=0.118	*w*R2=0.178	*w*R2=0.134	*w*R2=0.333
Largest diff. Peak/hole [e^-/ $Å^3$]	1.02/-0.85	2.11/-0.42	1.03/-0.59	2.11/-1.19

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-705716 (**1**), 705717 (**3**), 705719 (**4**), and 705718 (**5**). Copies of the data can be obtained free of charge at: http://www.ccdc.cam.ac.uk/products/csd/request/.

Compound **1** was crystallized from a mixture of pentane and toluene at low temperature (-60 to -70). The compound can be obtained in almost quantitative yield when Cp_2TiCl_2 is reacted with 0.5 equiv of the 18-rown-6 adduct of 1,4-di-potassio¬1,1,4,4-tetrakis¬(trimethylsilyl)¬tetramethyl¬tetra¬silane. The crown ether part of the structure of **1** contains some disorder.

The asymmetric unit of the structure of compound **3** contains two independent molecules of **3**. While in one of these molecules the potassium ion is located exactly centered above a Cp unit this is not true for the second molecule, where the potassium is located above one of the Cp carbons. In addition the asymmetric unit contains a poorly resolved benzene molecule which is distributed over two sites and can not be refined anisotropically.

The asymmetric unit of the structure of compound **4** contains an isolated anionic $[Cp_2Ti\{Si(SiMe_3)_2SiMe_2\}_2]$ fragment, a cationic $[Cp(18\text{-crown-}6\cdot K)_2]$ unit and in addition a 18-crown-6 crown ether molecule.

The crystal quality of compound **5** was poor. This is reflected by a value for R1 of 0.12 (at 48 degrees for 2θ). The asymmetric unit contains two independent units of $[Cp_2Ti\{Si(SiMe_3)(SiMe_2)_2\}_2]$, three $[Cp(18\text{-crown-}6\cdot K)_2]$, a Cp^-, a benzene and a toluene molecule. The crown ethers are strongly disordered so that 37 restraints were used to treat this disorder. The fact that the measurement was carried out at 100K indicates that the nature of the disorder is statistical and not dynamic.