Scandium, Yttrium, Uranium, and Thorium Derivatives of the 1,4-Bis(trimethylsilyl)cyclo-octatetraene Dianion; the *X*-Ray Crystal Structure of $[Sc_2(\eta\text{-}C_8H_6\{1,4\text{-}(SiMe_3)_2\})_2(\mu\text{-}Cl)_2(\mu\text{-thf})]$ (thf = tetrahydrofuran)

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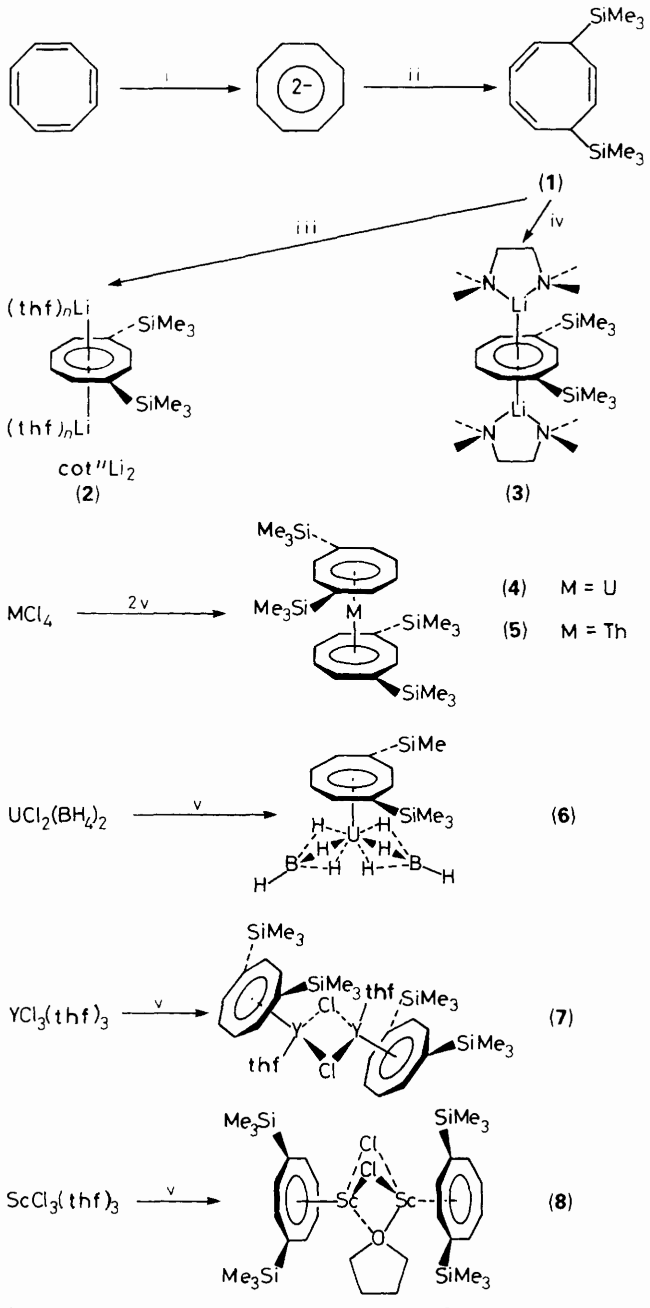
Deprotonation of 1,4-bis(trimethylsilyl)cyclo-octa-2,5,7-triene affords the 1,4-bis(trimethylsilyl)cyclo-octatetraene dianion, which reacts with $[UCl_4]$ or $[ThCl_4]$ to give the sandwich compounds $[M(\eta\text{-}C_8H_6\{1,4\text{-}(SiMe_3)_2\})_2]$, M = U or Th, with $[UCl_2(BH_4)_2]$ to give $[U(\eta\text{-}C_8H_6\{1,4\text{-}(SiMe_3)_2\})(\eta^3\text{-}BH_4)_2]$, and with $[ScCl_3(thf)_3]$ or $[YCl_3(thf)_3]$ (thf = tetrahydrofuran) to yield $[\{M(\eta\text{-}C_8H_6\{1,4\text{-}(SiMe_3)_2\})(\mu\text{-}Cl)\}_2\{thf\}_n]$, M = Sc, $n = 1$; M = Y, $n = 2$; *X*-ray crystallography shows the latter scandium compound to possess a novel semi-bridging thf ligand.

The neutral actinide sandwich compounds, $[M(\eta\text{-}C_8H_8)_2]$, M = U [1] or Th,[2] derived from the cyclo-octatetraene dianion, and their anionic lanthanide counterparts, $[M(\eta\text{-}C_8H_8)_2^-]$, M = Y, La, Ce, Pr, Nd, Sm, Gd, or Tb,[3] have been known for many years. Of more interest for exploratory synthetic chemistry are the corresponding half-sandwich complexes: $[M(\eta\text{-}C_8H_8)Cl_2(thf)_2]$, (thf = tetrahydrofuran), M = Th,[4] or U,[5] and $[M(\eta\text{-}C_8H_8)Cl(thf)_n]$, M = La, Ce, Pr, Nd, Sm, Er, or Lu.[3,6] The actinide derivatives $[M(\eta\text{-}C_8H_8)(N\{SiMe_3\}_2)_2]$, M = U, or Th,[7] have recently been reported; by contrast the lanthanide half-sandwich complexes have remained virtually unexplored, a reflection of their oligomeric nature and consequent poor solubility, although thermally unstable alkyl derivatives have been reported for lutetium.[6] Given the demonstrated influence of trimethylsilyl-substituted[8] cyclopentadienyl ligands on organo-f-element chemistry, we were encouraged to synthesise trimethylsilyl substituted cyclo-octatetraene derivatives of these elements, with the expectation that this would lead to well-defined, soluble complexes of low molecularity.



Scheme 1. *Reagents and conditions*: i, K/THF, −30 °C; ii, xs. $\mathrm{ClSiMe_3}$, −30 °C; iii, $\mathrm{Li^nBu/THF}$, −30 °C; iv, $\mathrm{Li^nBu/TMEDA}$, pentane, −30 °C; v, 1 equiv. $\mathrm{cot''Li_2/THF}$, −30 °C.

The synthesis of 1,4-bis(trimethylsilyl)cyclo-octa-2,5,7-triene (**1**) in 35% yield, from the reaction of $[\mathrm{Li_2C_8H_8}]$ with $[\mathrm{SiMe_3Cl}]$ in $\mathrm{Et_2O}$ at −50 °C, has been previously reported;[9] in our hands, the analogous reaction using $[\mathrm{K_2C_8H_8}]$ in THF at −30 °C afforded (**1**) as a white crystalline solid on a 20 g scale in *ca.* 80% yield, after recrystallisation from methanol (Scheme 1). The spectroscopic properties†‡ of (**1**) are identical to those reported previously.[9] Deprotonation of (**1**) with two equivalents of n-butyl-lithium in THF at −30 °C afforded the white, crystalline dilithium salt $[\{\mathrm{Li(thf)}_n\}_2\{\mathrm{C_8H_6(1,4\text{-}(SiMe_3)_2)}\}]$ (n = 1—2) (**2**) in high yield, after recrystallisation from hexane. Similarly, reaction of (**1**) with 2 equiv. of n-butyl-lithium in pentane in the presence of $[\mathrm{Me_2N(CH_2)_2NMe_2}]$, (TMEDA), afforded pale yellow, crystalline $[\{\mathrm{Li(tmeda)}\}_2\{\mathrm{C_8H_6(1,4\text{-}(SiMe_3)_2)}\}]$ (**3**) (Scheme 1). Compounds (**2**) and (**3**) are extremely air-sensitive, highly soluble in THF and moderately soluble in hexane or toluene. The upfield shifts in the ^{7}Li n.m.r. spectra[8] of (**2**) and (**3**) are characteristic of lithium symmetrically bound to an aromatic π-system,[10] and hence we assume they have the structure shown in Scheme 1. Compound (**2**) is hereafter abbreviated to $[\mathrm{cot''Li_2}]$, and the $[\eta\text{-}(\mathrm{C_8H_6\{1,4\text{-}(SiMe_3)_2\}})^{2-}]$ dianion to [cot″].

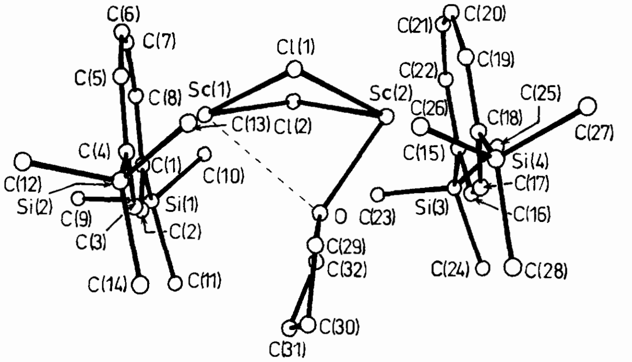


Figure 1. The *X*-ray structure of (**8**). Selected bond lengths (Å): Sc(1)–Cl(1), 2.518(3); Sc(1)–Cl(2), 2.513(3); Sc(2)–Cl(1), 2.590(3); Sc(2)–Cl(2), 2.583(3); Sc(1) · · · O, 3.056(9); Sc(2)–O, 2.324(7); Sc(1)–ring centroid(1), 1.535; Sc(2)–ring centroid(2), 1.550. Selected bond angles (°): Cl(1)–Sc(1)–Cl(2), 81.0(1); Cl(1)–Sc(2)–Cl(2), 78.34(9); Sc(1)–Cl(2)–Sc(2), 94.4(1); Sc(1)–Cl(1)–Sc(2), 94.1(1); Cl(1)–Sc(2)–O, 75.8(2); Cl(2)–Sc(2)–O, 76.1(2).

The reaction of 2 equiv. of $[\mathrm{cot''Li_2}]$ with $[\mathrm{MCl_4}]$, M = U, or Th, in THF gave high yields of the substituted uranocene and thorocene derivatives, blue-green $[\mathrm{U(cot'')_2}]$, (**4**), and yellow $[\mathrm{Th(cot'')_2}]$, (**5**), respectively (Scheme 1). Compounds (**4**) and (**5**) have similar spectroscopic†‡§ and physical properties to

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† A parent ion was observed in the mass spectrum.

‡ Satisfactory microanalysis has been obtained.

§ *N.m.r. data:* spectra were recorded at probe temperature on Bruker WH360 or WP80 instruments. Coupling constants are in Hz. For ^{1}H and ^{13}C, δ is relative to internal solvent; ^{7}Li is referenced to 1.0 M LiCl in $\mathrm{D_2O}$. (**1**) ^{1}H ($\mathrm{CDCl_3}$): δ 5.84—5.79 (2H, m, ring =C*H*), 5.57—5.50 (4H, m, ring =CH), 2.82 (2H, m, ring –C*H*$\mathrm{SiMe_3}$), 0.027 [18H, s, $\mathrm{Si(CH_3)_3}$]; ^{13}C{^{1}H} ($\mathrm{CDCl_3}$): 128.69, 125.24, 124.63 (ring =CH), 33.82 (ring –*C*H$\mathrm{SiMe_3}$), −2.60 [$\mathrm{Si(CH_3)_3}$]. (**2**) ^{1}H ($\mathrm{C_6D_6}$): δ 6.46 (2H, m, ring CH), 6.33 (4H, m, ring CH), 2.80 (m, thf), 1.03 (m, thf), 0.71 [18H, s, $\mathrm{Si(CH_3)_3}$]; ^{13}C{^{1}H} ($\mathrm{C_4D_8O}$): δ 95.90, 94.48, 89.64 (ring CH), 86.66 (ring *C*–$\mathrm{SiMe_3}$), 68.22 (co-ord. thf), 26.39 (co-ord. thf), 2.28 [$\mathrm{Si(CH_3)_3}$]; ^{7}Li ($\mathrm{C_6D_6}$): δ −11.70. (**3**) ^{1}H ($\mathrm{C_6D_6}$): δ 6.68 (2H, s, ring CH), 6.32 (4H, m, ring CH), 1.58 (24H, s, $\mathrm{CH_3}$ of tmeda), 1.20 (8H, s, $\mathrm{CH_2}$ of tmeda), 0.70 [18H, s, $\mathrm{Si(CH_3)_3}$]; ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): δ 96.86, 93.68, 88.29 (ring CH), 86.24 (ring *C*–$\mathrm{SiMe_3}$), 55.95 ($\mathrm{CH_2}$ of tmeda), 44.63 ($\mathrm{CH_3}$ of tmeda), 2.77 [$\mathrm{Si(CH_3)_3}$]. ^{7}Li ($\mathrm{C_6D_6}$): δ −9.0. (**4**) ^{1}H ($\mathrm{C_6D_6}$): δ −9.54 [18H, s, $\mathrm{Si(CH_3)_3}$], −24.62 (2H, s, ring CH), −38.74 (2H, s, ring CH), −45.04 (2H, s, ring CH). (**5**) ^{1}H ($\mathrm{C_6D_6}$): δ 6.90 (4H, m, ring CH), 6.70 (2H, m, ring CH), 0.58 [18H, s, $\mathrm{Si(CH_3)_3}$]; ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): δ 117.3 (ring C–$\mathrm{SiMe_3}$), 113.8, 112.4, 110.6 (ring CH), 1.07 [$\mathrm{Si(CH_3)_3}$]. (**6**) ^{1}H ($\mathrm{C_6D_6}$): δ 122.5 (8H, br. m, $\mathrm{BH_4}$), −7.78 [18H, s, $\mathrm{Si(CH_3)_3}$], −29.85 (2H, s, ring CH), −30.66 (2H, s, ring CH), −32.62 (2H, s, ring CH). (**7**) ^{1}H ($\mathrm{C_6D_6}$): δ 6.80 (2H, s, ring CH), 6.55 (4H, m, ring CH), 3.45 (4H, m, thf), 1.30 (4H, m, thf), 0.51 [18H, s, $\mathrm{Si(CH_3)_3}$]; ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): δ 101.61 (d, J_{CY} 2.2, ring *C*–$\mathrm{SiMe_3}$), 101.04 (d, J_{CY} 2.6, ring C–H), 100.18 (d, J_{CY} 2.2, ring C–H), 97.77 (d, J_{CY} 2.5, ring C–H), 71.15 (thf), 25.50 (thf), 0.91 [$\mathrm{Si(CH_3)_3}$]. (**8**) ^{1}H ($\mathrm{C_6D_6}$): δ 7.01 (2H, s, ring CH), 6.86 (4H, m, ring CH), 3.15 (2H, m, thf), 1.15 (2H, m, thf), 0.47 [18H, s, $\mathrm{Si(CH_3)_3}$]; ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): δ 107.68 (ring C–$\mathrm{SiMe_3}$), 104.76, 103.36, 100.56 (ring CH), 71.19 (thf), 25.35 (thf), 0.50 [$\mathrm{Si(CH_3)_3}$].

the unsubstituted analogues, $[\mathrm{U}(\eta\text{-}\mathrm{C_8H_8})_2]$[1] and $[\mathrm{Th}(\eta\text{-}\mathrm{C_8H_8})_2]$,[2] with the notable difference that the latter only dissolve with difficulty in hot THF and toluene, whereas (**4**) and (**5**) are highly soluble, even in saturated hydrocarbons. The reaction between $[\mathrm{U(BH_4)_2Cl_2}]$[11] and 1 equiv. of $[\mathrm{cot''Li_2}]$ afforded red crystals of the half-sandwich complex $[\mathrm{U}(\eta^3\text{-}\mathrm{BH_4})_2\,(\mathrm{cot''})]$ (**6**).†‡

Reaction of $[\mathrm{YCl_3\,(thf)_3}]$ with 1 equiv. of $[\mathrm{cot''Li_2}]$ in THF gave white $[\{\mathrm{Y(cot'')(\mu\text{-}Cl)(thf)}\}_2]$ (**7**),‡ after recrystallisation from toluene. Compound (**7**) is readily soluble in hydrocarbon solvents, and dimeric in solution; we assume the molecule to have the doubly chloride-bridged structure shown in Scheme 1. Compound (**7**) thus represents the first well defined, soluble monocyclo-octatetraene half-sandwich yttrium complex, one which should be a useful precursor to a wide range of derivatives of this class. The analogous reaction between $[\mathrm{ScCl_3(thf)_3}]$ and $[\mathrm{cot''Li_2}]$ afforded yellow crystals of a complex of stoicheiometry $[\mathrm{Sc(cot'')Cl(thf)_{1/2}}]$ (**8**),‡§ which is also dimeric in solution. The structure of (**8**) has been determined by single crystal *X*-ray diffraction,¶ and is shown in Figure 1, together with significant bond lengths and angles.

The molecule is dimeric in the solid state, the two scandium centres being doubly chloride-bridged, although somewhat asymmetrically (*vide infra*). The most interesting feature of the structure concerns the thf ligand, which is also in a bridging position. Consideration of the two scandium–oxygen distances [Sc(1)–O, 3.056(9); Sc(2)–O, 2.324(7) Å] suggests that the thf is best regarded as a 'semi-bridging' ligand. The latter is also presumably associated with the asymmetry in the chloride bridges: the Sc(2)–Cl distances are *ca.* 0.07 Å longer than the Sc(1)–Cl distances. The only other example of a crystallographically characterised bridging thf ligand is that found in $[\mathrm{Mg_2Br_2(thf)_2(\mu\text{-}N{:}CPh_2)_2(\mu\text{-}thf)}]$,[12] although in the latter compound the thf adopts a totally symmetric bridging position [Mg–O distance 2.453(3) Å]. The distortion of the thf ligand in (**8**) towards scandium(2) is presumably a reflection of the high oxophilicity of the electron deficient $\mathrm{Sc^{III}}$ centre. However, there was no evidence for any agostic interactions between the trimethylsilyl groups and the electron-deficient scandium centres in (**8**), either from low temperature solution n.m.r. studies, or from consideration of the Sc · · · H contacts in the solid state structure, which are all greater than 3 Å.

The results demonstrate that cot″ should be a useful ligand for preparing soluble, well-defined complexes of low molecularity for these and other elements, and further studies, particularly with the lanthanide series, are in progress.

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¶ *Crystal data:* $\mathrm{C_{32}H_{56}Cl_2OSc_2Si_4}$, $M = 730.0$, monoclinic, space group $P2_1/n$, $a = 11.859(3)$, $b = 13.871(2)$, $c = 23.924(4)$ Å, $\beta = 96.65(2)°$, $U = 3908.9$ Å^3, $Z = 4$, $D_c = 1.24\ \mathrm{g\ cm^{-3}}$, $F(000) = 1552$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 6.3\ \mathrm{cm^{-1}}$.

Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ-2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min, using a crystal *ca.* 0.4 × 0.25 × 0.1 mm sealed in a capillary under argon. A total of 3852 unique reflections were measured for $2 < \theta < 20°$ and $+h\ +k\ \pm l$, and 1782 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/4$. There was no crystal decay and no absorption corrections were applied.

The Sc and Cl atoms were located by MULTAN[13] and the remaining non-hydrogen atoms located on difference maps. Refinement was by full matrix least squares with anisotropic temperature factors. Hydrogen atoms were fixed at calculated positions with $B_{\mathrm{iso}} = 1.3B_{\mathrm{eq}}$ of the C atom to which they were bonded. The weighting scheme was $\sigma = 1/\omega^2(F)$ and the final residuals were $R = 0.052$, $R' = 0.053$. A final difference map showed no feature which could be interpreted as an atom. Programs from the Enraf-Nonius SDP-Plus package were run on a MicroVax computer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.