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Organometallic chemistry of the actinides
Part 4 [1] The chemistry of some tris(cyclopentadienyl) actinide complexes[2]

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Abstract

Four tris(cyclopentadienyl)thorium(IV) or uranium(IV) complexes have been prepared by the ready transmetallation between MCl_4 (M = Th or U) and the appropriate lithium cyclopentadienyl: $[ThCp''_3Cl]$1 **1**, $[ThCp^R_3Cl]$ **2**, $[ThCp^{tt}_3Cl]$ **3** and $[UCp''_3Cl]$ **7**. The treatment of $[ThCp''_2Cl_2]$ or $[ThCp^{tt}_2Cl_2]$ with the suitable lithium or potassium cyclopentadienyl yielded three mixed tris(cyclopentadienyl)thorium(IV) complexes: $[ThCp''_2(Cp^*)Cl]$ **4**, $[ThCp^{tt}_2(Cp)Cl]$ **5** and $[ThCp^{tt}_2(Cp^{B''})Cl]$ **6**. Compounds **1**–**7** have been characterised by C and H analyses, NMR spectra, EI mass spectra for **2**, **3**, **5** and **6**, and for compounds **1**–**4** and **7** single-crystal X-ray diffraction. [$Cp'' = \eta^5\text{-}C_5H_3(SiMe_3)_2$-1,3, $Cp^R = \eta^5\text{-}C_5H_4CH(SiMe_3)_2$, $Cp^{tt} = \eta^5\text{-}C_5H_3(SiMe_2Bu^t)_2$-1,3, $Cp^* = \eta^5\text{-}C_5Me_5$, $Cp = \eta^5\text{-}C_5H_5$, $Cp^{B''} = \eta^5\text{-}C_5H_3Bu^t_2$-1,3,$Cp''' = \eta^5\text{-}C_5H_2(SiMe_3)_3$-1,2,4]. © 1998 Elsevier Science S.A.

1. Introduction

The present paper is part of a study on new hydrocarbon-soluble, crystalline complexes of thorium and uranium, using bulky substituted cyclopentadienyl, 1-aza-allyl or β-diketiminate ligands.

In Part 1 of this series, we reported on the synthesis, spectroscopic properties and crystal structures of $[AcCp''_2Cl_2]$ (Ac = Th or U) and $[UCp''_2X_2]$ (X = Br, I or BH_4) [2]. In Part 2, we described two monocyclopentadienylthorium(IV) and seven bis(cyclopentadienyl)thorium(IV) complexes: $[\{(ThCp'''Cl_3)_2NaCl(OEt_2)\}_2]$, $[ThCp'''Cl_3(PMDETA)]$, $[ThCp'''_2Cl_2(OEt_2)]$, $[ThCp'''_2Cl_2]$, $[ThCp^*_2Br_2(THF)]$, $[ThCp^{tt}_2Cl_2]$, $[ThCp^{tt}_2Cl_2(DMPE)]$, $[ThCp^{tt}_2(Cl)\{CH(SiMe_3)_2\}]$ and $[ThCp^{tt}_2(acac)Cl]$ [3]. Part 3 dealt with the synthesis, spectroscopic properties and crystal structures of the heterobimetallic bis(1-aza-allyl)dichlorothorium(IV)–KCl complex $Th\{N(SiMe_3)C(BU^t)C(H)SiMe_3\}_2$-$(\mu-Cl)(\mu-Cl)_2K(OEt_2))_\infty]$ and the mononuclear bis(β-diketiminato)thorium(IV) chloride $[Th\{N(SiMe_3)C(Ph)C(H)C(Ph)N SiMe_3\}_2Cl_2]^2$ [1]. Earlier preliminary communications on organothorium chemistry concerned thorocene(IV) aryloxides [4] and the as yet sole X-ray-characterised thorium(III) complex $[ThCp''_3]$ [5] (obtained from $[ThCp''_2Cl_2]$ and K/Na) having a 6 d^1 (ESR-active at 300 K, g_{av} 1.9010 in methylcyclohexane) electronic ground state [6].

Herein we provide details on the synthesis, spectroscopic properties and structures of seven new lipophilic chlorotris(cyclopentadienyl)–thorium or –uranium complexes **1**–**7**, using the bulky substituted cyclopentadienyl ligands Cp''^-, Cp^{R-}, Cp^{tt-}, Cp^{*-}, and $Cp^{B''-}$ [7]. The thorium compounds, in particular, were sought as suitable substrates for elusive tricyclopentadienylthorium(III) complexes. No tris(η^5-cyclopentadienyl)thorium(IV) complexes or obvious analogues had previously been X-ray-characterised.

Abbreviations: $Cp = \eta^5\text{-}C_5H_5$; $Cp'' = \eta^5\text{-}C_5H_3(SiMe_3)_2$-1,3; $Cp^R = \eta^5\text{-}C_5H_4CH(SiMe_3)_2$; $Cp^{tt} = \eta^5\text{-}C_5H_3(SiMe_2Bu^t)_2$-1,3; $Cp^* = \eta^5\text{-}C_5Me_5$; $Cp^{B''} = \eta^5\text{-}C_5H_3Bu^t_2$-1,3

[*] Corresponding author.

[1] Part 3; Ref. [1].

[2] Dedicated to Peter Maitlis, a fine chemist and a good friend to MFL, to mark his 65th birthday.

2. Results and discussion

2.1. Synthesis and characterisation of new complexes

Seven new chlorotris(cyclopentadienyl)metal(IV) complexes of thorium and uranium are the subject of this paper: $[\mathrm{ThCp}^{x}_{3}\mathrm{Cl}]$ ($\mathrm{Cp}^{x} = \mathrm{Cp}''$ **1**, Cp^{R} **2** or Cp^{tt} **3**), $[\mathrm{ThCp}''_{2}(\mathrm{Cp}^{*})\mathrm{Cl}]$ **4**, $[\mathrm{ThCp}^{tt}_{2}(\mathrm{Cp}^{x})\mathrm{Cl}]$ ($\mathrm{Cp}^{x} = \mathrm{Cp}$ **5** or $\mathrm{Cp}^{B''}$ **6**) and $[\mathrm{UCp}''_{3}\mathrm{Cl}]$ **7**. Complex **1** had briefly been mentioned before [4], while the cyclopentadienes $\mathrm{Cp}^{R}\mathrm{H}$ and $\mathrm{Cp}^{tt}\mathrm{H}$ as well as the lithium complexes LiCp^{R}, LiCp^{tt} and $\mathrm{LiCp}^{b''}$ and the potassium complexes KCp^{R} and KCp^{tt} have recently been described [7].

Addition of three equivalents of LiCp'' to ThCl_4 in diethyl ether, followed by removal of solvent, extraction of the residue into hexane and concentration and cooling of the extract afforded $[\mathrm{ThCp}''_{3}\mathrm{Cl}]$ **1** in good yield (Table 1). This complex had originally been prepared by oxidation of $[\mathrm{ThCp}''_{3}]$ with 2-chloro-2-methylpropane [4]. The present method is not only more direct but employs readily available starting materials. Moreover, **1** is a convenient precursor for $[\mathrm{ThCp}''_{3}]$ [5]. In a similar fashion, from ThCl_4 and three equivalents of KCp^{R} or KCp^{tt}, good yields of $[\mathrm{ThCp}^{R}_{3}\mathrm{Cl}]$ **2** or $[\mathrm{ThCp}^{tt}_{3}\mathrm{Cl}]$ **3** were obtained (Table 1).

The crystalline compounds **1** and **2** were extremely soluble in hydrocarbons and air- and moisture- sensitive, while colourless **3** was much less lipophilic and also less sensitive to air or moisture. Complex **3** (like **1**, m.p. 270–272°C) was remarkably thermally stable; crystals were obtained by sublimation of the crude product at high vacuum at a bath temperature of 280–300°C. This robustness is attributed to the considerable steric shielding of the metal centre by the particularly bulky Cp^{tt-} ligands. The colourless compounds **1**–**3** were characterised by carbon and hydrogen elemental analysis (Table 1), ^{1}H (and for **2** $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$) NMR spectra (Table 2) and single crystal X-ray diffraction studies (see 2.2). Additionally, EI mass spectra for **2** or **3** showed the parent molecular ion as the highest m/z species (Table 1). The ^{1}H NMR spectra of **1**, **2** or **3** gave the appropriate signals and signal intensities for the organic ligands, which for **1** and **3** were similar to those for the corresponding thorocene(IV) chloride $[\mathrm{ThCp}''_{2}\mathrm{Cl}_{2}]$ and $[\mathrm{ThCp}^{tt}_{2}\mathrm{Cl}_{2}]$ [3], except for minor variations in the chemical shift data (Table 2). The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of **2** showed the characteristic features of the Cp^{R-} ligand.

A reason for undertaking the preparation of the mixed tris(cyclopentadienyl)thorium(IV) chlorides $[\mathrm{ThCp}''_{2}(\mathrm{Cp}^{*})\mathrm{Cl}]$ **4** or $[\mathrm{ThCp}^{tt}_{2}(\mathrm{Cp}^{x})\mathrm{Cl}]$ ($\mathrm{Cp}^{x} = \mathrm{Cp}$ **5** or $\mathrm{Cp}^{B''}$ **6**) was to make them available as useful substrates for the synthesis of new tris(cyclopentadienyl)-thorium(III) complexes (which will be reported in part 5 of this series). A feature of complexes **4**–**6** is that they have an analytical advantage over the symmetrical analogues **1**–**3** in that integration of the ^{1}H NMR spectral signals provides a measure of their purity.

Each of the colourless, crystalline compounds **4**–**6** was conveniently prepared in good yield (Table 1) from $[\mathrm{ThCp}''_{2}\mathrm{Cl}_{2}]$ [3] and LiCp^{*} for **4**, or $[\mathrm{ThCp}^{tt}_{2}\mathrm{Cl}_{2}]$ [3] and NaCp for **5** or $\mathrm{LiCp}^{B''}$ for **6**, in diethyl ether (**4** or **5**) or tetrahydrofuran **6**. The compounds were characterised by microanalysis (Table 1) and ^{1}H NMR spectra (Table 2). Although each of the compounds **4**–**6** is prochiral, which in principle makes the Cp'' groups in **4** or Cp^{tt} groups in **5** or **6** magnetically inequivalent, this was experimentally observed only for **4** and **5** (Table 2). The EI mass spectra of **5** and **6** showed (Table 1) the parent molecular ion as the highest m/z peak.

As part of our study of 1,3-bis(trimethylsilyl)cyclopentadienyl ($\equiv \mathrm{Cp}''$) complexes of the *f*-elements (initiated as long ago as 1981 [8]), we also now describe the new crystalline, dark red high melting (m.p. 287–289°C) complex $[\mathrm{UCp}''_{3}\mathrm{Cl}]$ **7**, obtained in good yield (Table 1) from UCl_4 and three equivalents of LiCp'' in diethyl ether. It gave satisfactory carbon and hydrogen analysis (Table 1) and ^{1}H NMR spectra (Table 2). Being an f^{2} complex, the chemical shifts were paramagnetically shifted: $\delta - 3.18$ for the SiMe_3 protons and $\delta + 24.7$ ($\varpi_{1/2} > 35$ Hz) for the cyclopentadienyl ring protons; the latter were observed as a single broad signal using a sweep width of 16,000 Hz (200 ppm). The single crystal X-ray diffraction data for

Table 1
Yields, mass spectra and analytical data for compounds **1**–**7**

Compounds	Yield[a] (%)	m/z for M^{+} in the E.I. mass spectra	Analysis[b] (%)
1	89	*c*	C 44.0 (44.2); H 7.0 (7.1).
2	82	937	C 46.0 (46.1); H 7.47 (7.42).
3	69	1147	C 53.1 (53.3); H 8.7 (8.7).
4	82	*c*	C 46.7 (46.8); H 7.0 (7.0).
5	81	918	C 49.3 (50.9); H 7.5 (7.8).
6	70	1031	C 54.5 (54.7); H 8.4 (8.5).
7	87	*c*	C 43.4 (44.0); H 6.97 (7.00).

[a] These refer to pure crystalline products and were not optimised. [b] Calculated values in parentheses. [c] Not determined.

Table 2
NMR spectral chemical shifts (δ) with assignments (the number of hydrogen atoms refers to relative, rather than absolute, values) for complexes **1**–**7** at 305 K[a]

Compound	^{1}H	Solvent
1[b]	$SiMe_3$ 0.33 (54H, s); Ring 6.57 (3H, s), 6.73 (6H, s).	C_7D_8
2[c]	$SiMe_3$ 0.21 (36H, s); CH 2.19 (2H, s); Ring 6.26 (4H, t), 5.18 (4H, t).	C_6D_6
3[d]	$SiBu^t$ 0.71 (54H, s); $SiMe_2$ 0.56 (36 H, s); Ring 6.30 (3H, s), 6.55 (6H, s).	C_7D_8
4	$SiMe_3$ 0.45 (18H, s), 0.42 (18H, s); Ring 6.45 (4H, b),[e] 6.62 (2H, b);[e] Cp* 2.17 (15 H, s).	C_6D_6
5	$SiBu^t$ 0.71(18H, s), 0.68 (18H, s); $SiMe_2$ 0.57 (6H, s), 0.53 (6H, s), 0.43 (6H, s), 0.41 (6H, s); Ring 6.79 (2H, b),[e] 6.53(4H, b),[e] 6.35 (5H, s).	C_7D_8
6	Bu^t 1.01 (18H, s); $SiBu^t$ 0.90 (36H, s); $SiMe_2$ 0.24 (12H, s); Ring 6.92 (1H, s), 6.86 (4H, s), 6.83 (2H, s), 6.59 (2H, s).	C_6D_6
7	$SiMe_3$ −3.18 (54H, s); Ring 24.70 (9H, bs).	C_6D_6

[a] At 360.1 MHz for ^{1}H NMR. [b] *Cf*. [$ThCp''_2Cl_2$]: 0.35, 7.32, 6.93. [c] $^{13}C\{^1H\}$ (62.9 MHz): δ$SiMe_3$ 1.91; CH 20.59; Ring 117.40, 118.40, 139.74. [d] *Cf*. [$ThCp^{tt}_2Cl_2$]: 0.44, 0.45, 0.70, 6.92, 7.23. [e] Due to prochiral Cp″.

7 (2.2) confirmed its identity as a mononuclear complex.

2.2. X-ray structures of **1**–**4** and **7**

The X-ray structures of a number of tris(cyclopentadienyl)uranium(IV) chlorides have been determined [9], including those of [UCp_3Cl] [10] and [$U(C_5Me_4H)_3Cl$] [11]. However, no thorium analogues have similarly been characterised, although such data are available for three tris(indenyl)chlorothorium(IV) complexes, which showed the indenyl rings to be η^3-bound to the metal [12–14].

The structures of complexes **1**–**4** and **7** have been determined by X-ray crystallography. Their molecular structures, with atom numbering schemes, are shown in

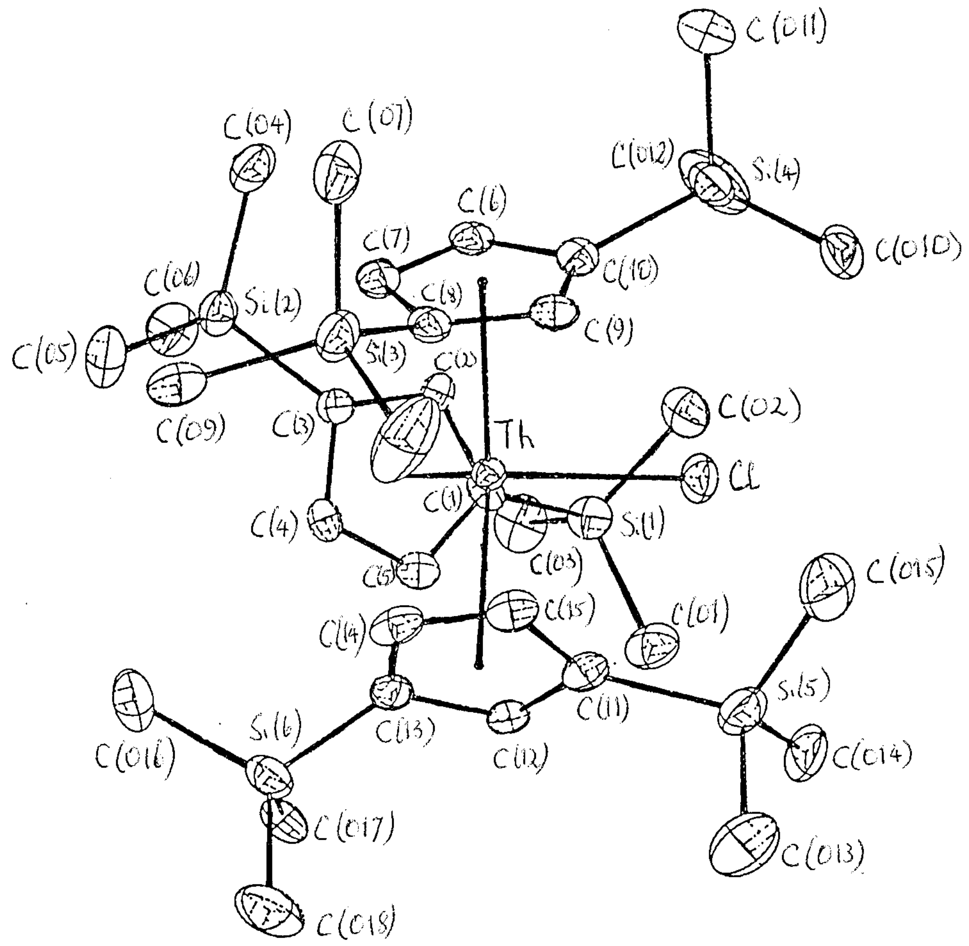

Fig. 1. Molecular structure and atom numbering scheme for **1**.

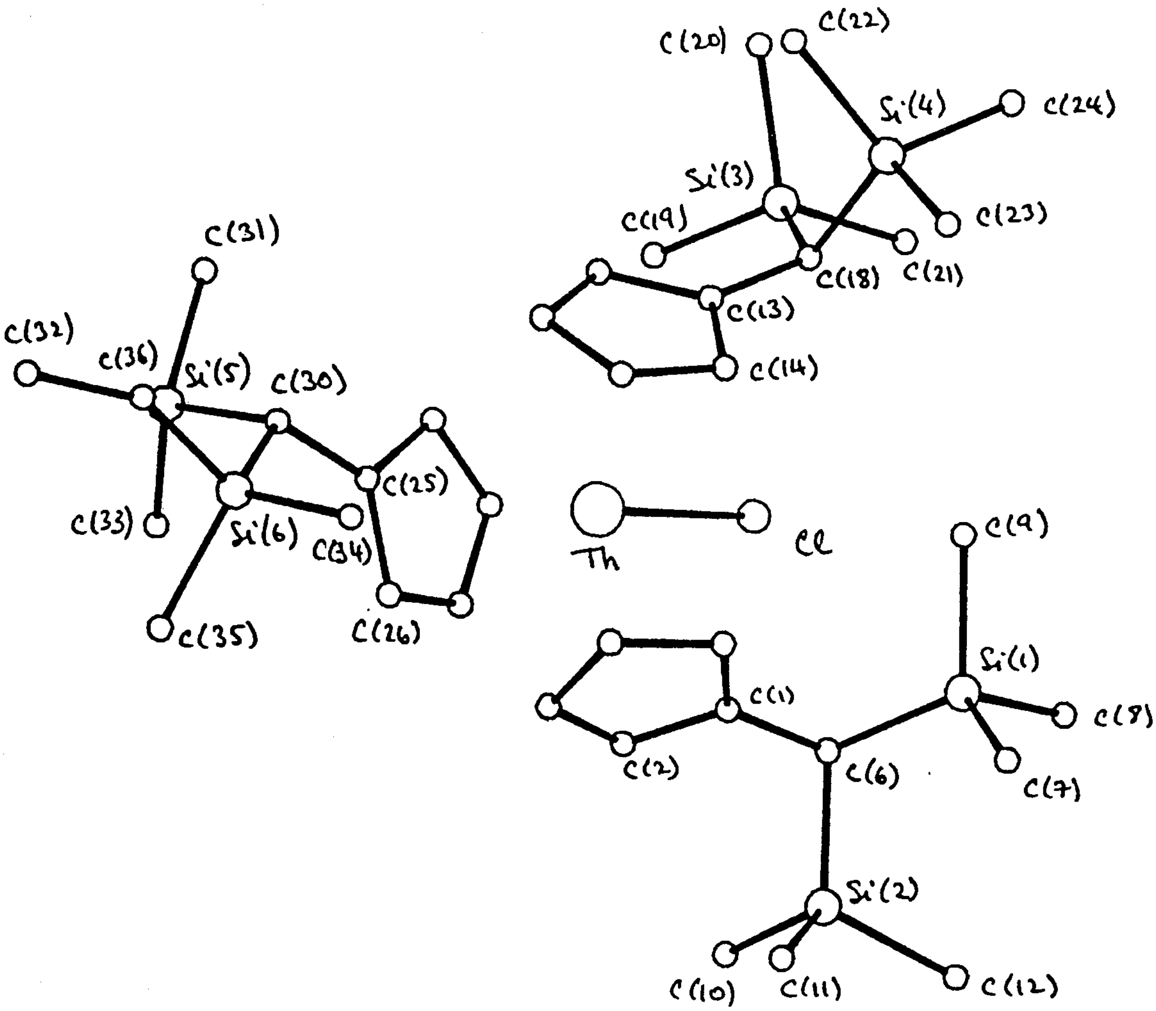

Fig. 2. Molecular structure and atom numbering scheme for **2**.

Figs. 1–5, respectively. Selected bond lengths and angles are listed in Table 3 (**1**) and Table 4 (**2**), Table 5 (**3**), Table 6 (**4**) and Table 7 (**7**), while Table 8 summarises some key structural parameters. All five complexes are monomeric with similar gross overall structures. In particular, they have a distorted tetrahedral coordination environment around the metal if the Cp^x rings are assumed to occupy a single coordination site. The isoleptic and isotypic [AcCp$''_3$Cl] (Ac = Th **1** or U **7**) have the most closely related crystal and molecular

Table 3
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [ThCp$''_3$Cl] **1**

Th–Cp(1)	2.562	Th–C(7)	2.806(9)
Th–Cp(2)	2.564	Th–C(8)	2.862(9)
Th–Cp(3)	2.568	Th–C(9)	2.840(9)
Th–Cl	2.651(2)	Th–C(10)	2.860(9)
Th–C(1)	2.87(1)	Th–C(11)	2.874(9)
Th–C(2)	2.863(9)	Th–C(12)	2.877(8)
Th–C(3)	2.86(1)	Th–C(13)	2.860(9)
Th–C(4)	2.786(9)	Th–C(14)	2.785(8)
Th–C(5)	2.770(9)	Th–C(15)	2.797(9)
Th–C(6)	2.805(9)		
Cl–Th–Cp(1)	99.5	Cp(1)–Th–Cp(2)	116.7
Cl–Th–Cp(2)	100.8	Cp(1)–Th–Cp(3)	117.6
Cl–Th–Cp(3)	100.0	Cp(2)–Th–Cp(3)	116.6

Cp(1), Cp(2) and Cp(3) are the centroids of the rings C(1) to C(5), C(6) to C(10) and C(11) to C(15), respectively.

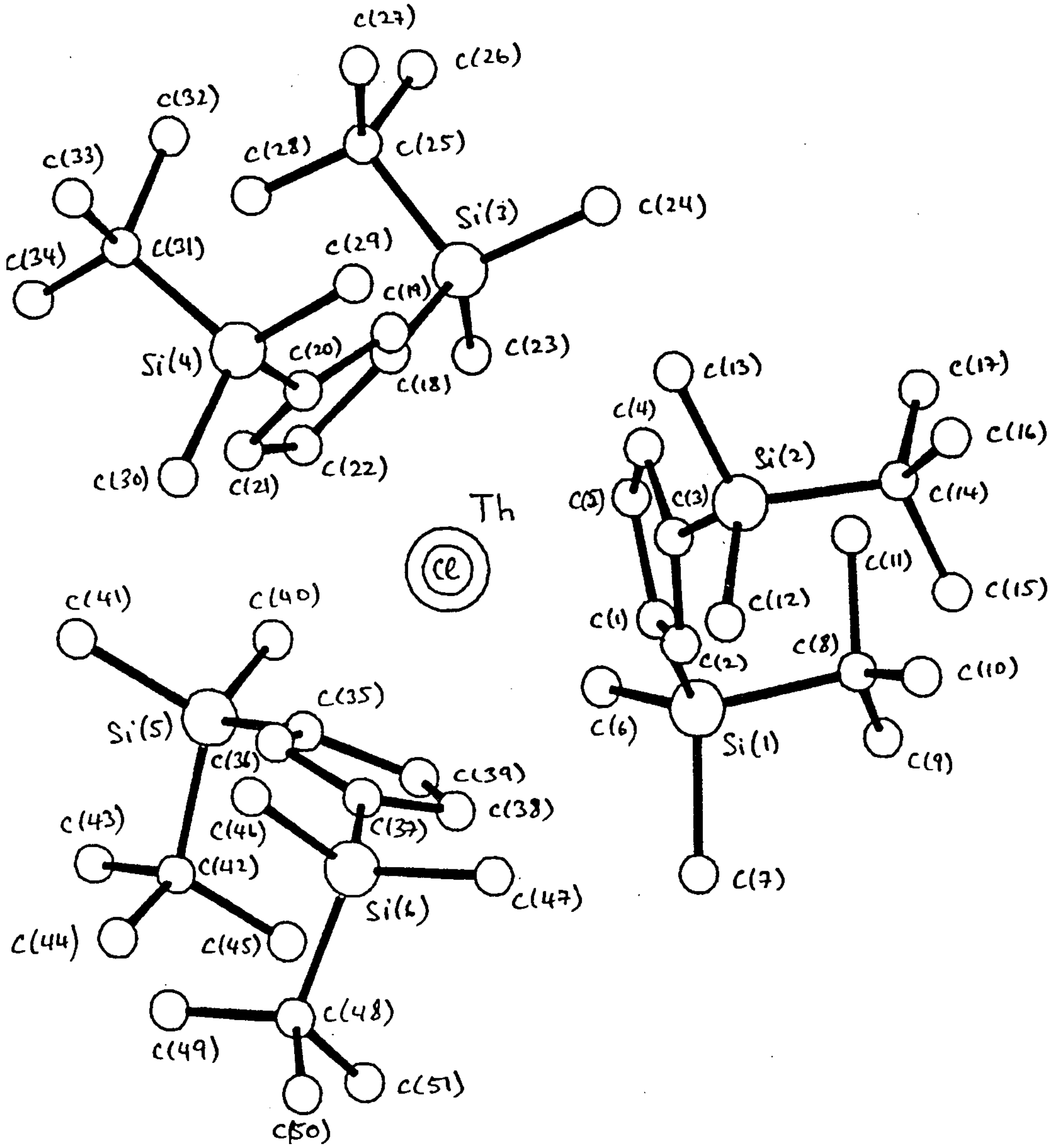

Fig. 3. Molecular structure and atom numbering scheme for **3**.

Table 4
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [ThCp$^R_3$Cl] **2**

Th–Cp(1)	2.557	Th–C(14)	2.816(9)
Th–Cp(2)	2.568	Th–C(15)	2.746(10)
Th–Cp(3)	2.562	Th–C(16)	2.768(10)
Th–Cl	2.664(3)	Th–C(17)	2.878(10)
Th–C(1)	2.944(10)	Th–C(25)	2.935(10)
Th–C(2)	2.811(9)	Th–C(26)	2.852(11)
Th–C(3)	2.732(10)	Th–C(27)	2.748(12)
Th–C(4)	2.748(10)	Th–C(28)	2.728(12)
Th–C(5)	2.869(10)	Th–C(29)	2.838(12)
Th–C(13)	2.957(9)		
Cp(1)–Th–Cp(2)	119.0	Cp(2)–Th–Cl	100.7
Cp(1)–Th–Cp(3)	116.0	Cp(3)–Th–Cl	101.6
Cp(2)–Th–Cp(3)	116.6	Cp(1)–Th–Cl	97.0

Cp(1), Cp(2) and Cp(3) are the centroids of the rings C(1) to C(5), C(11) to C(15) and C(22) to C(26), respectively.

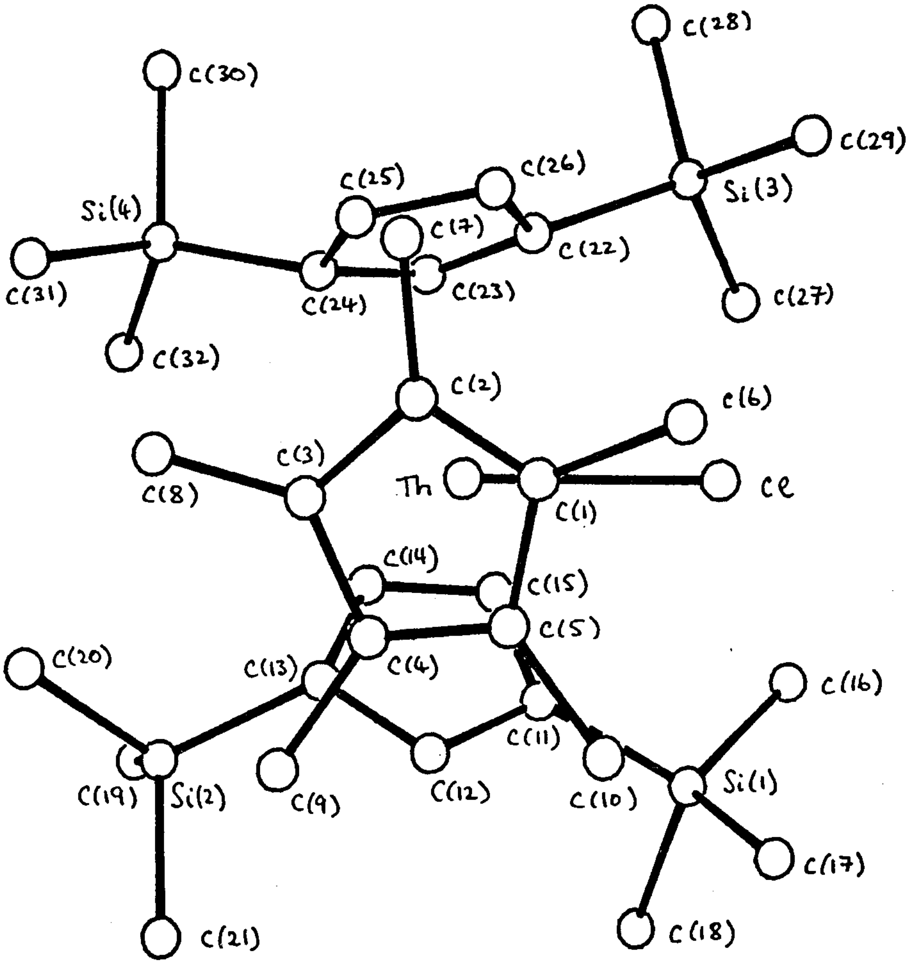

Fig. 4. Molecular structure and atom numbering scheme for **4**.

structures; the smaller radius of U(IV) is consistently evident from the noticeably shorter Ac–C and Ac–Cl bonds in the uranium complex **7** (Table 8). Each of the cyclopentadienyl ligands in **1**–**4** is η^5-bound to thorium, thus providing a contrast with the substituted indenyl analogues which have η^3-bound ligands [12–14]. Comparing **1**–**4** (Table 8), [ThCp$^{tt}_3$Cl] **3** has the longest average Th–C(Cp) and the shortest Th–Cl bond length, which reflects the fact that the Cp^{tt-} ligands are the most bulky of the presently used substituted cyclopenta-

Table 5
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [ThCp$^{tt}_3$Cl] **3**

Th–Cp(1)	2.578	Th–C(19)	2.883(9)
Th–Cp(2)	2.582	Th–C(20)	2.894(9)
Th–Cp(3)	2.583	Th–C(21)	2.813(9)
Th–Cl	2.648(2)	Th–C(22)	2.780(8)
Th–C(1)	2.885(9)	Th–C(35)	2.890(8)
Th–C(2)	2.906(9)	Th–C(36)	2.894(9)
Th–C(3)	2.903(9)	Th–C(37)	2.895(8)
Th–C(4)	2.799(10)	Th–C(38)	2.799(8)
Th–C(5)	2.761(9)	Th–C(39)	2.771(8)
Th–C(18)	2.876(8)		
Cp(1)–Th–Cp(2)	117.2	Cp(1)–Th–Cl	99.4
Cp(1)–Th–Cp(3)	116.7	Cp(2)–Th–Cl	99.7
Cp(2)–Th–Cp(3)	117.2	Cp(3)–Th–Cl	100.9

Cp(1), Cp(2) and Cp(3) are the centroids of the cyclopentadienyl rings C(1) to C(5), C(18) to C(22) and C(35) to C(39), respectively.

Table 6
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [ThCp$''_2$(Cp*)Cl] **4**

Th–Cp(1)	2.544	Th–C(12)	2.93(2)
Th–Cp(2)	2.589	Th–C(13)	2.89(2)
Th–Cp(3)	2.579	Th–C(14)	2.76(2)
Th–Cl	2.657(5)	Th–C(15)	2.78(2)
Th–C(1)	2.80(2)	Th–C(22)	2.86(1)
Th–C(2)	2.83(2)	Th–C(23)	2.89(1)
Th–C(3)	2.83(2)	Th–C(24)	2.85(1)
Th–C(4)	2.79(1)	Th–C(25)	2.79(2)
Th–C(5)	2.82(2)	Th–C(26)	2.84(2)
Th–C(11)	2.91(2)		
Cp(1)–Th–Cp(2)	122.1	Cl–Th–Cp(1)	97.8
Cp(1)–Th–Cp(3)	117.4	Cl–Th–Cp(2)	97.3
Cp(2)–Th–Cp(3)	114.4	Cl–Th–Cp(3)	99.8

Cp(1), Cp(2) and Cp(3) are the centroids of the rings C(1) to C(5), C(11) to C(15) and C(22) to C(26), respectively.

dienyls. For [UCp$''_3$Cl] **7**, the Cp$''^-$ ligands are η^5-bound to the uranium centre, and the overall structure is directly comparable with those of [UCp$_3$Cl] [10], [U(C$_5$Me$_4$H)$_3$Cl] [11] and [U(C$_5$H$_4$CH$_2$C$_6$H$_5$)$_3$Cl] [15].

3. Experimental details

3.1. Materials and procedures

All manipulations were carried out under argon using a high vacuum manifold and conventional Schlenk techniques. Solvents were distilled over appropriate drying agents and were thoroughly degassed prior to use. NMR spectra were recorded on a Bruker WM 360 or AC-250SY instrument, and mass spectra were obtained with a Fisons VG Autospec instrument. Elemental analyses were determined by Medac, Brunel University. The compounds Cp$''$H [16], Cp$^{B''}$H [17], LiCp$''$[8], KCp^R [7], KCp^{tt} [7], NaCp [18] and [ThCp$''_2$Cl$_2$] [3] were prepared by literature procedures. LiCp$^{B''}$ was prepared from Cp$^{B''}$H and LiBu^n in hexane; LiCp* was prepared similarly from Cp*H, THF and LiBu^n in hexane.

3.2. Synthesis of [ThCp$''_3$Cl] **1**

Solid LiCp$''$ (5.80 g, 26.9 mmol) was added to a stirred slurry of ThCl4 (3.34 g, 8.9 mmol) in diethyl ether (ca. 100 ml) at ca. −50°C. The reaction mixture was warmed to room temperature and was then stirred for a further 24 h. The diethyl ether was removed in vacuo to yield a white solid which was extracted into hexane (ca. 50 ml). The extract was filtered, the volume of the filtrate was reduced to ca. 25 ml, and cooling to −30°C yielded clear, colourless crystals of compound **1** (7.1 g, 89%).

3.3. Synthesis of [ThCp$^R_3$Cl] **2**

A solution of KCp^R (9.0 g, 34.4 mmol, 20% excess) in diethyl ether (100 ml) was added to a stirred mixture

Table 7
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [UCp$''_3$Cl] **7**

U–Cp(1)	2.48	U–C(7)	2.800(9)
U–Cp(2)	2.49	U–C(8)	2.812(8)
U–Cp(3)	2.49	U–C(9)	2.752(8)
U–Cl	2.614(2)	U–C(10)	2.757(8)
U–C(1)	2.81(1)	U–C(11)	2.81(1)
U–C(2)	2.787(9)	U–C(12)	2.818(8)
U–C(3)	2.75(1)	U–C(13)	2.787(8)
U–C(4)	2.718(8)	U–C(14)	2.733(7)
U–C(5)	2.72(1)	U–C(15)	2.72(1)
U–C(6)	2.795(9)		
Cl–U–Cp(1)	99.7	Cp(1)–U–Cp(2)	116.6
Cl–U–Cp(2)	101.0	Cp(1)–U–Cp(3)	118.0
Cl–U–Cp(3)	99.6	Cp(2)–U–Cp(3)	116.4

Cp(1), Cp(2) and Cp(3) are the centroids of the rings C(1) to C(5), C(6) to C(10) and C(11) to C(15), respectively.

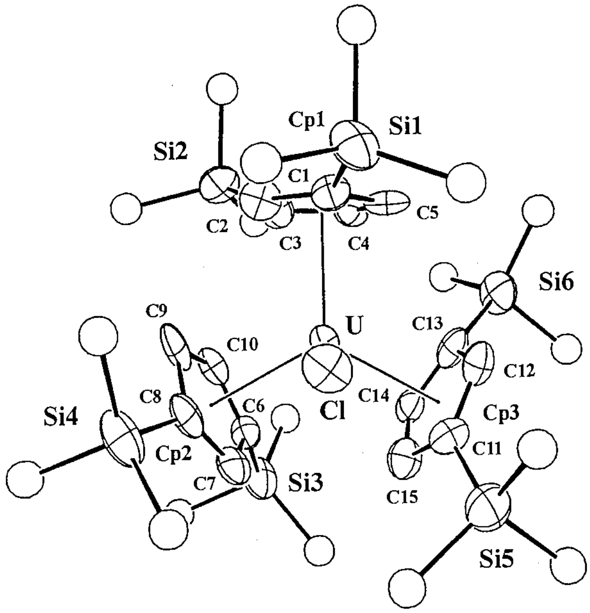

Fig. 5. Molecular structure and atom numbering scheme for **7**.

of $ThCl_4$ (3.5 g, 9.4 mmol) in diethyl ether (250 ml) at −78°C. The mixture was allowed to warm to room temperature and was stirred for 3 d and refluxed for 12 h, leaving a slightly yellow solution and a white precipitate, which was filtered off. Solvent was removed from the filtrate in vacuo. The white solid residue was extracted with pentane (200 ml) and filtered. The pentane filtrate was concentrated and the volume was reduced to ca. 20 ml. Cooling to −30°C afforded colourless needles of compound **3** (7.2 g, 81.8%).

3.4. Synthesis of [ThCp$^{tt}_3$Cl] **3**

A white suspension of KCp^{tt} (2.4 g, 7.2 mmol) in diethyl ether (100 ml) was added to a stirred suspension of $ThCl_4$ (0.88 g, 2.36 mmol) in diethyl ether (200 ml) at −78°C. The suspension was allowed to warm to room temperature and was stirred for 2 d and further refluxed for 8 h, leaving a slightly cloudy solution and a white precipitate, which was filtered off. Solvent was removed from the filtrate in vacuo and the solid residue was sublimed at 280–300°C/10^{-2} mm Hg to yield the colourless crystalline compound **4** (1.94 g, 68.8%).

3.5. Synthesis of [ThCp$''_2$(Cp*)Cl] **4**

Solid LiCp*(THF) (0.45 g, 2.1 mmol) was added to a cooled (−70°C) stirring solution of [ThCp$''_2$Cl$_2$] (1.44 g, 2.0 mmol) in diethyl ether (ca. 50 ml). The mixture was stirred for 12 h at room temperature and then heated under reflux for ca. 4 h. The Et_2O was removed in vacuo. The residual white solid was extracted into hexane (ca. 50 ml). The extract was filtered and the volume of the filtrate reduced to ca. 25 ml. Cooling to −30°C yielded clear, colourless crystals of compound **4** (1.35 g, 82%).

3.6. Synthesis of [ThCp^{tt}(Cp)Cl] **5**

Solid NaCp (0.16 g, 1.81 mmol) was added to a cooled (0°C) stirred solution of [ThCp$^{tt}_2$Cl$_2$] (1.62 g, 1.81 mmol) in diethyl ether (ca. 100 ml). The reaction mixture was allowed to warm to room temperature and was stirred for 2 d. The diethyl ether was removed in vacuo to yield a white solid which was extracted into toluene (ca. 100 ml); the extract was filtered. Volatiles were removed from the filtrate in vacuo and the solid residue was recrystallised from hexane to yield the colourless crystalline compound **5** (1.35 g, 81%).

3.7. Synthesis of [ThCp$^{tt}_2$(Cp$^{B''}$)Cl] **6**

Solid LiCp$^{B''}$ (0.33 g, 1.81 mmol) was added to a cooled (0°C) stirred solution of [ThCp$^{tt}_2$Cl$_2$] (1.62 g, 1.81 mmol) in THF (ca. 100 ml). The mixture was allowed to warm to room temperature and was stirred for 2 d. The THF was removed in vacuo to yield a white solid. Toluene (ca. 100 ml) was added and the mixture was heated to ca. 60°C for 2 d, then filtered, and the filtrate concentrated to yield the colourless crystalline compound **6** (1.31 g, 70%).

Table 8
Selected bond lengths (Å) for some tris(cyclopentadienyl)actinide(IV) chlorides

Compound	M–C(Cp)$_{av.}$	M–Cent$_{av.}$	M–Cl	Ref.
[ThCp$''_3$Cl]	2.833	2.565	2.651(2)	This work
[ThCp$^R_3$ Cl]	2.825	2.562	2.664(3)	This work
[ThCp$^{tt}_3$Cl]	2.850	2.882	2.648(2)	This work
[ThCp$''_2$Cp* Cl]	2.838	2.571	2.675(5)	This work
[UCp$''_3$Cl]	2.771	2.485	2.614(2)	This work
[UCp$_3$Cl]	2.74		2.559(16)	[10]
[U(C$_5$Me$_4$H)$_3$Cl]	2.791	2.520	2.637	[11]
[U(C$_5$H$_4$CH$_2$C$_6$H$_5$)$_3$Cl]	2.733	2.472	2.627(2)	[13]

Table 9
X-ray crystal structure details for complexes **1–4**, **7**[a]

Parameter	**1**	**2**	**3**	**4**	**7**
Formula	$C_{33}H_{63}ClSi_6Th$	$C_{36}H_{69}ClSi_6Th$	$C_{51}H_{99}ClSi_6Th$	$C_{32}H_{57}ClSi_4Th$	$C_{33}H_{63}ClSi_6U$
M	895.9	938.0	1148.4	821.6	901.9
Size of crystal	0.2 × 0.2 × 0.15	0.4 × 0.4 × 0.15	0.3 × 0.3 × 0.1	0.2 × 0.15 × 0.10	0.3 × 0.4 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a/Å	13.256(8)	15.145(6)	15.820(4)	17.528(4)	13.195(3)
b/Å	19.271(6)	14.658(10)	20.125(7)	13.447(2)	19.245(3)
c/Å	17.826(10)	21.557(9)	21.160(6)	18.363(3)	17.770(2)
$\beta/°$	91.32(6)	97.78(3)	108.80(2)	114.81(2)	91.42(2)
$U/Å^3$	4552.3	4741.6	6377.2	3928.7	4511.1
Z	4	4	4	4	4
$D_{calc}/g\ cm^{-3}$	1.31	1.31	1.20	1.39	1.33
$\mu(Mo–K_\alpha)/cm^{-1}$	44.28	34.8	26.0	41.3	36.5
θ_{max} for data/°	21	25	22	25	30
Reflections measured	5310	8978	8404	7429	18506
Unique reflections	5115	8654	8075	7200	13064
Reflections observed	3329 $[I > 3\sigma(I)]$	4483 $[I > 2\sigma(I)]$	5049$[I > 2\sigma(I)]$	2854 $[I > 3\sigma(I)]$	7301 $[I > 2\sigma(I)]$
R^b	0.027	0.050	0.040	0.051	0.072
R'^c	0.031	0.056	0.047	0.062	0.043

[a] All data are collected at 298 K.
$R = \Sigma\|Fo| - |Fo\|/\Sigma|Fo|$.
$R' = ((\Sigma w(|Fo| - |Fc|)^2/\Sigma w(|Fo|^2))^{1/2}$.

3.8. Synthesis of [UCp$''_3$Cl] ***7***

LiBu^n (1.6 M in hexane, 13.15 ml, 21.05 mmol) was added at ca. 0°C via a cannula to Cp$''$H (4.42 g, 21.05 mmol) in diethyl ether (ca. 100 ml) and the mixture was stirred for ca. 12 h. UCl_4 (2.66 g, 7 mmol) was added to the resultant mixture, which was stirred for a further 15 h; the colour changed from lime green to golden brown. The diethyl ether was removed in vacuo to yield a brown red solid which was extracted into hexane (ca. 100 ml); the extract was filtered. The volume of the filtrate was reduced to ca. 50 ml and cooling to −30°C yielded red brown crystals of compound **7** (5.48 g, 87%).

3.9. X-ray structure determination of crystalline ***1–4*** *and* ***7***

The structures of **2–4** were solved by routine heavy-atom methods of SHELXS-86 [19] and all non-H atoms were refined anisotropically by full-matrix least-squares methods using the Enraf-Nonius Molen package [20]. For **1** and **7**, the structure determination was carried out using SHELX-76 [21]. Data were corrected for Lorentz and polarization effects (Lp) and also for absorption using DIFABS [22] for **1–4** and ψ scan data for **7** ($I_{min} = 0.68$, $I_{max} = 1.00$). Decay correction was applied to **2**, **3** and **7**. The weighting schemes were $w = \sigma^{-2}(F)$. Hydrogen atoms were placed at calculated positions ($U_{iso} = 1.3\ U_{eq}$) for **2**, **3** and **4**. Further details are given in Table 9. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, atom co-ordinates, Fo/Fc Tables and remaining bond lengths and angles.

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References

[1] P.B. Hitchcock, J. Hu, M.F. Lappert, S. Tian, J. Organomet. Chem., 536–537 (1997) 473.
[2] P.C. Blake, M.F. Lappert, R.G. Taylor, J.L. Atwood, W.E. Hunts, H. Zhang, J. Chem., Soc., Dalton Trans., (1995) 3335.
[3] M.A. Edelman, P.B. Hitchcock, J. Hu, M.F. Lappert, New J. Chem. 19 (1995) 481.
[4] P.C. Blake, M.F. Lappert, R.G. Taylor, J.L. Atwood, H. Zhang, Inorg. Chim. Acta 139 (1987) 13.
[5] P.C. Blake, M.F. Lappert, J.L. Atwood, H. Zhang, J. Chem. Soc., Chem. Commun., (1986) 1148.
[6] W.K. Kot, G.V. Shalimoff, N.M. Edelstein, M.A. Edelman, M.F. Lappert, J. Am. Chem. Soc. 110 (1988) 986.
[7] M.A. Edelman, P.B. Hitchcock, M.F. Lappert, D.-S. Liu, S. Tian, J. Organomet. Chem., 550 (1997) 323.
[8] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, J. Chem. Soc., Chem. Commun., (1981) 1190.
[9] F.T. Edelmann, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 4 (M.F. Lappert, Ed.), Pergamon, Oxford, 2nd edn. 1995, Chap. 2.

[10] C.-H. Wong, T.-M. Yen, T. Lee, Acta Crystallogr. 18 (1965) 340.
[11] F.G.N. Cloke, S.A. Hawkes, P.B. Hitchcock, P. Scott, Organometallics 13 (1994) 2895.
[12] M.R. Spirlet, J. Rebizant, J. Goffart, Acta Crystallogr. Sect. A 37 (1981) C223.
[13] M.R. Spirlet, J. Rebizant, J. Goffart, Acta Crystallogr. Sect. B 38 (1982) 2400.
[14] M.R. Spirlet, J. Rebizant, S. Bettonville, J. Goffart, Acta Crystallogr. Sect. C 46 (1990) 1234.
[15] J. Leong, K.O. Hodgson, K.N. Raymond, Inorg. Chem. 12 (1973) 1329.
[16] E.W. Abel, S. Moorhouse, J. Organomet. Chem. 29 (1971) 227.
[17] C.G. Venier, E.W. Casserly, J. Am. Chem. Soc. 112 (1990) 2808.
[18] R.B. King, F.G.A. Stone, Inorg. Synth. 7 (1967) 99.
[19] G.M. Sheldrick, SHELXS-86, Program for Solution of Crystal Structures, University of Göttingen, 1985.
[20] C.K. Fair, MOLEN, Structure Determination System, Enraf-Nonius, Delft, 1990.
[21] G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.
[22] N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.