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Bis(trimethylsilyl)phosphido complexes

II *. Bis(trimethylsilyl)phosphidobis(tetrahydrofuran)lithium as a reducing agent; X-ray structure of $[UCp''_2(\mu\text{-Cl})_2Li(THF)_2]$ $[Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3;\ THF = OC_4H_8]$

Paul C. Blake, Evamarie Hey, Michael F. Lappert
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

Jerry L. Atwood and Hongming Zhang
Department of Chemistry, University of Alabama, University, Alabama 35486 (United States of America)

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Abstract

The lithium compound $[Li\{\mu\text{-}P(SiMe_3)_2\}(THF)_2]_2$ (I) in tetrahydrofuran (THF) under ambient conditions is an effective reducing agent for converting cyclopentadienyl-titanium(IV) or -uranium(IV) chlorides into the corresponding chlorocyclopentadienylmetal(III) complexes. Thus $[TiCp_2Cl_2]$, $[TiCpCl_3]$, and $[UCp''_2Cl_2]$ [Cp $= \eta\text{-}C_5H_5$, $Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$] were transformed in high yields into $[TiCp_2Cl(THF)]$, $[TiCpCl_2(THF)]$, and $[UCp''_2(\mu\text{-}Cl)_2Li(THF)_2]$ (II), respectively. The crystalline complex II is triclinic, space group $P\bar{1}$, with a 11.352(5), b 12.795(7), c 15.014(7) Å; α 101.63(7), β 90.34(4), γ 95.92(6)°, and $Z = 2$. Its X-ray structure was refined to $R_1 = 0.056$ and $R_2 = 0.072$. The compound is a monomer, with mean U–Cl and Li–Cl bond lengths of 2.730(1) and 2.46(6) Å, respectively; and Cl–U–Cl′, Cl–Li–Cl′, and U–Cl–Li 82.3(2), 94(2), and 91(1)°, respectively.

Introduction

In Part I we reported the X-ray structures of the bis(trimethylsilyl)phosphidolithium compounds $Li_4(\mu\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$ and $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (I), as well as their NMR spectra and those of a related compound $Li(PR_2)(PMDETA)$

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* For Part I, see ref. 1. No reprints available

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(R = $\mathrm{SiMe_3}$, THF = tetrahydrofuran, PMDETA = N,N,N',N',N''-pentamethyldiethylenetriamine) [1].

Compound I was first prepared by Fritz and Hölderich [2]. It has been extensively used as (i) a $\bar{\mathrm{P}}\mathrm{R}_2$ transfer reagent to metals other than lithium, and (ii) a source of various phosphorus-containing ligands by virtue of the facile loss of an $\mathrm{SiMe_3}$ (≡ R) group, e.g., as RCl, ROMe, or $\mathrm{PR_3}$ [1,3]. For (i) this is illustrated by the conversion of $[\mathrm{ZrCp_2Cl_2}]$ with I into $[\mathrm{Zr(Cp_2)Cl_{2-\mathit{n}}(PR_2)_{\mathit{n}}}]$ ($n = 1$ or 2, Cp = η-$\mathrm{C_5H_5}$) [4]; the latter compounds were used as substrates for the insertion into Zr–P bonds of $\mathrm{CS_2}$, $\mathrm{P_4}$, or $\mathrm{Ph_2CN_2}$ to afford $[\mathrm{ZrCp_2(Cl)(\eta^2\text{-}S_2CPR_2)}]$ [5], $[\mathrm{ZrCp_2\{P(PR_2)PP(PR_2)P\}}]$ [6], or $[\mathrm{ZrCp_2Cl\{\eta^2\text{-}N_2(PR_2)CPh_2\}}]$ [4], respectively.

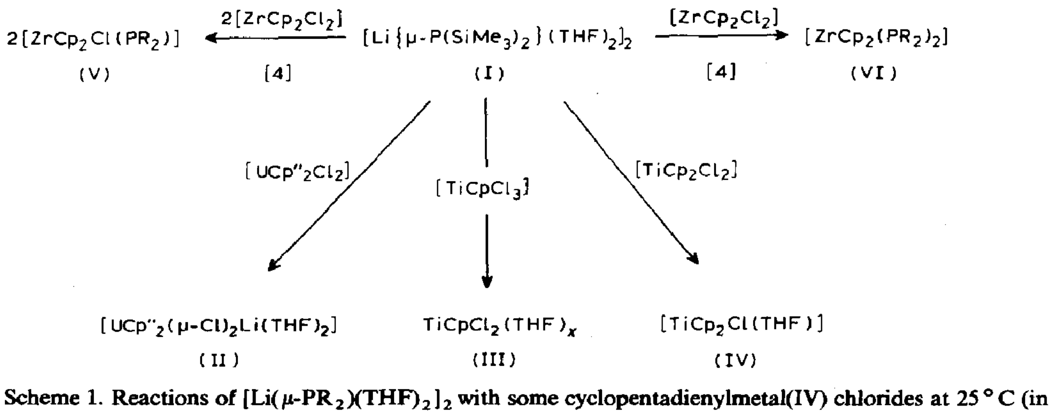
We now show that another aspect of the versatile chemistry of the lithium phosphide (I) is its capacity to function as a reducing agent.

Results and discussion

1. Reactions of compound I with various cyclopentadienyl-titanium(IV) or -uranium(IV) chlorides

The reactions of $[\mathrm{Li(\mu\text{-}PR_2)(THF)_2}]_2$ (I) with some cyclopentadienyl-titanium(IV), -zirconium(IV), or -uranium(IV) chlorides are summarised in Scheme 1. This shows that the more readily reducible $\mathrm{U^{IV}}$ and $\mathrm{Ti^{IV}}$ chlorides are transformed into the novel uranocene(III) chloride $[\mathrm{UCp''_2(\mu\text{-}Cl)_2Li(THF)_2}]$ (II) and the known $\mathrm{Ti^{III}}$ complexes $[\mathrm{TiCp_{3-\mathit{n}}Cl_{\mathit{n}}(THF)}]$ {$n = 2$ (III) or 1 (IV)}, respectively. In contrast, the less easily reducible $[\mathrm{ZrCp_2Cl_2}]$ {$E_{1/2}^{\mathrm{red}}$ −1.70 V; cf., −0.75 V for Ti analogue [7]} underwent $\bar{\mathrm{Cl}}/\bar{\mathrm{P}}\mathrm{R}_2$ exchange to yield the appropriate zirconocene(IV) bis(trimethylsilyl)phosphide (V or VI), depending on the employed stoicheiometry [4]. Rather surprisingly, the $\mathrm{U^{III}}$ or $\mathrm{Ti^{III}}$ chlorides II–IV did not react further under mild conditions with an excess of $[\mathrm{Li(\mu\text{-}PR_2)(THF)_2}]_2$ to give $\mathrm{U^{III}}$ or $\mathrm{Ti^{III}}$ bis(trimethylsilyl)phosphides. On the other hand, treatment of $[\mathrm{ZrCp_2Cl_2}]$ with $2\mathrm{LiPR'_2}$ (R′ = Me, Et, or $\mathrm{Bu^n}$) gave $[\{\mathrm{ZrCp_2(\mu\text{-}PR_2)}\}_2]$ [8,9].

The uranocene(III) chloride (II) is the first example of a heterobimetallic $5f$ metallocene(III) complex in which two chloride ligands are bridging to an alkali metal, although $4f$ element (Ln) analogues, e.g., $[\mathrm{LnCp''_2(\mu\text{-}Cl)_2Li(THF)_2}]$, are well known [10]; as are simple homonuclear $\mathrm{U^{III}}$ complexes, such as $[\{\mathrm{UCp''_2(\mu\text{-}Cl)}\}_2]$ [11], obtained by reduction of $[\mathrm{UCp''_2Cl_2}]$ with Na/Hg in toluene.



Scheme 1. Reactions of $[\mathrm{Li(\mu\text{-}PR_2)(THF)_2}]_2$ with some cyclopentadienylmetal(IV) chlorides at 25 °C (in THF for II–IV, or PhMe for V or VI).

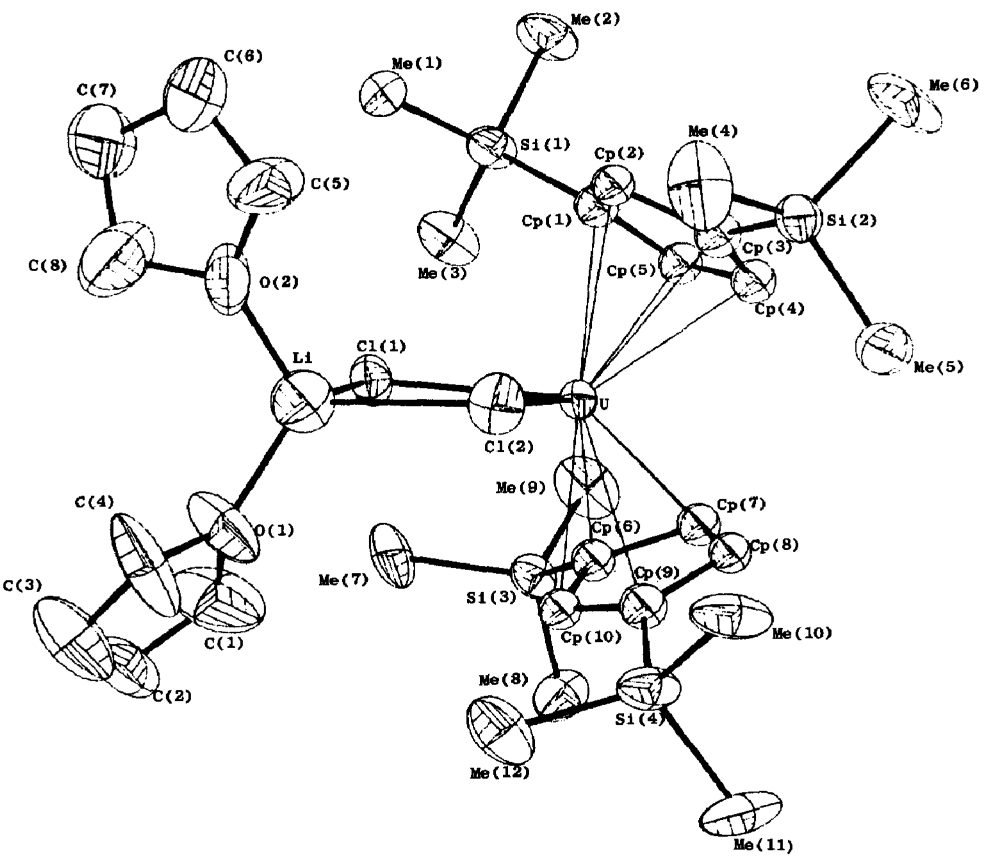


Fig. 1. The molecular structure and atom numbering scheme for $[\mathrm{UCp}_2''(\mu\text{-Cl})_2\mathrm{Li(THF)}_2]$.

Table 1

Selected intramolecular distances (Å) and angles (degrees), with estimated standard deviations in parentheses for $[\mathrm{UCp}_2''(\mu\text{-Cl})_2\mathrm{Li(THF)}_2]$

Atoms	Distance	Atoms	Distance
(a) Bonds (Å)			
U–Cl(1)	2.729(6)	U–Cl(2)	2.730(7)
U–Cp(1)	2.80(2)	U–Cp(2)	2.81(2)
U–Cp(3)	2.77(2)	U–Cp(4)	2.76(2)
U–Cp(5)	2.77(2)	U–Cp(6)	2.78(2)
U–Cp(7)	2.74(2)	U–Cp(8)	2.74(2)
U–Cp(9)	2.78(2)	U–Cp(10)	2.79(2)
Cl(1)–Li	2.44(6)	Cl(2)–Li	2.48(6)
Li–O(1)	1.86(7)	Li–O(2)	1.83(6)
(b) Angles (°)			
Cl(1)–U–Cl(2)	82.3(2)	U–Cl(1)–Li	92(1)
U–Cl(2)–Li	91(1)	Cl(1)–Li–Cl(2)	94(2)
Cl(1)–Li–O(1)	104(3)	Cl(2)–Li–O(1)	119(3)
O(1)–Li–O(2)	115(3)	Cl(1)–Li–O(2)	113(3)
Cl(2)–Li–O(2)	110(3)		

That steric effects play a role in the potentially competing reactions of $\bar{P}R'_2$ ligand-transfer and reduction, has already been demonstrated in Zr^{IV}–Zr^{III} chemistry; the former reaction pathway was favoured by use of bulky R′ substituents and low temperatures. Thus, $[ZrCp_2Cl_2]$ gave $[ZrCp_2(PR'_2)_2]$ when R′ = Ph or cyclo-C_6H_{11}, but the Zr^{III} compound $[\{ZrCp_2(\mu\text{-}PR'_2)\}_2]$ was obtained when R′ = Me; at 80 °C, however, $LiPEt_2$ gave the Zr^{IV} product $[ZrCp_2(PEt_2)_2]$ [12]. On the other hand, the bulky dialkylphosphidolithium reagent $[Li\{\mu\text{-}P(CHR_2)_2\}]_2$ (R = $SiMe_3$) even reduced $SnCl_2$ or Bu^tCl (to Sn or $^{\bullet}Bu^t$, respectively), consistent with its having a low first ionisation potential, 7.5 eV [13].

Table 2

Final atomic coordinates, with estimated standard deviations in parentheses, for $[UCp''_2(\mu\text{-}Cl)_2Li(THF)_2]$

Atom	*x/a*	*y/b*	*z/c*
U	0.16072(9)	0.20354(8)	0.21513(7)
Cl(1)	0.3363(6)	0.3565(5)	0.2943(5)
Cl(2)	0.0239(6)	0.3265(6)	0.3334(5)
Si(1)	0.4370(6)	0.1009(6)	0.3454(6)
Si(2)	−0.0779(6)	−0.0084(6)	0.3126(5)
Si(3)	0.3809(6)	0.2646(6)	0.0003(5)
Si(4)	−0.1044(6)	0.3330(7)	0.0890(6)
Cp(1)	0.285(2)	0.064(2)	0.293(2)
Cp(2)	0.175(2)	0.075(2)	0.345(1)
Cp(3)	0.080(2)	0.021(2)	0.280(2)
Cp(4)	0.124(2)	−0.017(2)	0.197(2)
Cp(5)	0.253(2)	0.009(2)	0.202(2)
Cp(6)	0.232(2)	0.237(2)	0.046(1)
Cp(7)	0.160(2)	0.130(2)	0.031(1)
Cp(8)	0.042(2)	0.149(2)	0.050(1)
Cp(9)	0.033(2)	0.263(2)	0.079(2)
Cp(10)	0.150(2)	0.316(2)	0.075(1)
Me(1)	0.431(2)	0.194(2)	0.460(2)
Me(2)	0.500(2)	−0.028(2)	0.366(2)
Me(3)	0.541(2)	0.158(2)	0.262(2)
Me(4)	−0.117(3)	0.094(3)	0.420(2)
Me(5)	−0.179(2)	−0.005(2)	0.213(2)
Me(6)	−0.106(3)	−0.147(3)	0.339(3)
Me(7)	0.471(3)	0.385(2)	0.082(2)
Me(8)	0.364(2)	0.297(3)	−0.113(2)
Me(9)	0.464(3)	0.142(3)	−0.010(3)
Me(10)	−0.224(2)	0.264(3)	0.152(2)
Me(11)	−0.165(3)	0.314(3)	−0.035(2)
Me(12)	−0.069(3)	0.480(2)	0.144(2)
Li	0.196(5)	0.462(5)	0.385(4)
O(1)	−0.209(2)	0.410(2)	0.656(2)
O(2)	0.224(2)	0.476(2)	0.508(1)
C(1)	−0.274(5)	0.386(4)	0.734(3)
C(2)	−0.283(5)	0.271(4)	0.726(3)
C(3)	−0.219(4)	0.229(3)	0.642(4)
C(4)	−0.156(4)	0.315(3)	0.610(4)
C(5)	0.172(3)	0.413(4)	0.569(3)
C(6)	0.271(6)	0.420(4)	0.637(3)
C(7)	0.350(4)	0.506(4)	0.634(4)
C(8)	0.313(5)	0.551(5)	0.559(3)

A similar contrast between $\mathrm{Ti^{IV}}$ and $\mathrm{Zr^{IV}}$ chemistry to that now revealed in Scheme 1 has previously been noted in the reactions of $[\mathrm{MCp_2Cl_2}]$ with $\mathrm{LiCHR_2}$ ($\mathrm{R = SiMe_3}$). For M = Ti, the ultimate product was $[\mathrm{TiCp_2(CHR_2)}]$ with $[\{\mathrm{TiCp_2}(\mu\text{-}\mathrm{Cl})\}_2]$ as an isolable intermediate; whereas for M = Zr, $[\mathrm{ZrCp_2(CHR_2)Cl}]$ was obtained [14]. Lithium alkyls are not as powerful reducing agents as the phosphides. For example, $\mathrm{LiCHR_2}$ gave $\mathrm{Sn_2(CHR_2)_4}$ with $\mathrm{SnCl_2}$ [15]. Lithium amides are still weaker; e.g., $[\mathrm{TiCp_2Cl_2}]$ and $\mathrm{LiNR_2}$ gave an amido-$\mathrm{Ti^{IV}}$ product $[\mathrm{TiCp_2[NRSiMe_2CH_2)}]$ [16]. After the synthesis reported here of complex II from $[\mathrm{UCp''_2Cl_2}]$, it was shown that $\mathrm{LiBu^n}$ provides an alternative reagent to the bis(trimethylsilyl)phosphidolithium compound I [17]; complex II was also obtained from $[\{\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})\}_2]$ [11] and 2LiCl in THF. However, $[\mathrm{UCp''_2Cl_2}]$ and 2LiR or $\mathrm{2LiNMe_2}$ at −80 °C furnished $[\mathrm{UCp''_2R'_2}]$ ($\mathrm{R' = CH_2SiMe_3}$ or $\mathrm{CH_2Ph}$) or $[\mathrm{UCp''_2(NMe_2)_2}]$, respectively [18].

The reaction sequence in the $\mathrm{M^{IV}} \rightarrow \mathrm{M^{III}}$ reduction for the $[\mathrm{MCp_2Cl_2}] \xrightarrow{\mathrm{LiPMe_2}} \frac{1}{2}[\{\mathrm{MCp_2}(\mu\text{-}\mathrm{PMe_2})\}_2]$ (M = Ti and Zr) systems has been further examined [9]. Use of an equimolar portion of $\mathrm{LiPMe_2}$ (presumably at ambient temperature) yielded $\frac{1}{2}[\{\mathrm{TiCp_2}(\mu\text{-}\mathrm{Cl})\}_2]$ (with $\frac{1}{2}\mathrm{P_2Me_4}$) and $\frac{1}{2}[\mathrm{ZrCp_2Cl_2}] + \frac{1}{2}[\{\mathrm{ZrCp_2}(\mu\text{-}\mathrm{PMe_2})\}_2]$, respectively; while with $\mathrm{2LiPMe_2}$, the product was $\frac{1}{2}[\{\mathrm{MCp_2}(\mu\text{-}\mathrm{PMe_2})\}_2]$ in each case.

2. *X-Ray crystal structure of* $[\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(THF)_2}]$ *(II)*

The molecular structure and atom numbering scheme for complex II are shown in Fig. 1, selected bond distances and angles are in Table 1, and final fractional coordinates in Table 2.

The uranocene(III) complex II is the first $\mathrm{U^{III}}$-dichloro-bridged alkali metal complex to be structurally characterised, although data for a related compound $[\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(PMDETA)}]$ (VII), having five-coordinate lithium, are now available [17]. A sodium derivative was suggested to have the structure $[\mathrm{UCp^{\star}_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Na(THF)}_x]$ ($\mathrm{Cp^{\star}} = \eta\text{-}\mathrm{C_5Me_5}$, $x = 1.5–2$) on the basis of its analysis and IR and NMR spectra [19]. Among compounds of the 4*f* elements, the following $[\mathrm{LnCp^{x}_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{LiL_2})$ complexes have been characterised by X-ray diffraction: Ln =

Table 3

Selected structural parameters for some lithium derivatives of f^3-metallocene(III) dichlorides and $[\{\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})\}_2]$

Compound	M–Cl (Å)	Li–Cl (Å)	Cent–M (Å)	Cl–M–Cl (°)	Cent–M–Cent (°)	Cl–Li–Cl (°)	Ref.
$[\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(THF)_2}]$	2.729(6) 2.730(7)	2.44(6) 2.48(6)	2.48 2.50	82.3(2)	124	94(2)	This work
$[\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(PMDETA)}]$	2.69(2) 2.72(1)	2.52(4) 2.51(4)	2.51 2.58	84.6(5)	124	93(1)	17
$[\mathrm{NdCp''_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(THF)_2}]$	2.744av.	2.405av.	2.48 2.49	82.1	126	97.2(9)	10
$[\{\mathrm{UCp''_2}(\mu\text{-}\mathrm{Cl})\}_2]$	2.818(4) 2.802(4)	–	2.496 2.494	78.5(1)	131	[ClUCl 101.5(1)]	11

Nd, $Cp^x = Cp''$, and L = THF [10]; Ln = Nd, $Cp^x = Cp^\star$, and L = THF [20]; Ln = Yb, $Cp^x = Cp^\star$, and $L = OEt_2$ [21] (also the di-iodo analogue); and Ln = Yb, $Cp^x = \eta\text{-}C_5H_4SiMePh_2$, and $L = OEt_2$ [22]. Of these, the first, a $4f^3$ complex, is isostructural with the $5f^3$ title compound II.

Some comparative structural data are given in Table 3.

Experimental

General procedures

These have been described previously [1].

Preparation of $[UCp''_2(\mu\text{-}Cl)_2Li(THF)_2]$ (II)

A solution of $[Li(\mu\text{-}PR_2)(THF)_2]_2$ ($R = SiMe_3$) (I) (0.84 g, 2.56 mmol) in THF (30 cm^3) was added dropwise with stirring to a solution of $[UCp''_2Cl_2]$ [$Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$] (1.84 g, 2.53 mmol) in THF (10 cm^3) at 0 °C. There was rapid colour change from orange-brown to deep green. The mixture was stirred for 30 min at 0 °C, then at ca. 25 °C for 12 h and volatiles were then removed in vacuo. The residue was extracted with n-pentane and the extract was filtered and cooled to −30 °C to yield green di-η-[1,3-bis(trimethylsilyl)cyclopentadienyl]-(μ-dichloro)-uranium(III)-bis(tetrahydrofuran)lithium (II) (1.50 g, 68%). Found: C, 41.2; H, 6.80. $C_{30}H_{58}Cl_2LiO_2Si_4U$ calc.: 41.0; H, 6.66%. Compound I had m.p. 105–107 °C; it was found to be soluble in THF, toluene, or pentane, and to be air-sensitive. The ^1H NMR spectrum in toluene-d_8 at 25 °C showed signals (assignment, integration) at δ −33.15 (H_4, H_5; 4), −5.00 (CH_3, 36), 1.68 (THF, 8), 3.35 (THF, 8), and 37.54 (H_2). The ^7Li NMR spectrum in benzene-d_6 at 25 °C showed a singlet signal at 0.91 ppm (rel. to aqueous $Li[NO_3]$).

Preparation of $TiCpCl_2(THF)_x$ (III)

A solution of $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (1.86 g, 5.66 mmol) in THF (25 cm^3) was added dropwise with stirring to a suspension of $[TiCpCl_3]$ (1.20 g, 5.47 mmol) in THF (10 cm^3) at ca. 25 °C. The colour changed from yellow to green and then to deep blue. The mixture was stirred for ca. 1 h and then filtered. The filtrate was cooled to −30 °C to yield purple crystals of $TiCpCl_2(THF)_x$ ($x < 1$) (III) (0.80 g). The product was identified by comparing its EPR [23] and IR [24] spectra with those of authentic specimens.

When the reaction of the lithium reagent (0.67 g, 3.04 mmol) and $[TiCpCl_3]$ (0.66 g, 3.01 mmol) was carried out in n-hexane (25 cm^3) the product was the purple $TiCpCl_2$.

Preparation of $[TiCp_2Cl(THF)]$ (IV)

A solution of $[Li(\mu\text{-}PR_2)(THF)_2]_2$ (2.54 g, 7.73 mmol) in THF (25 cm^3) was added dropwise with stirring to a suspension of $[TiCp_2Cl_2]$ (1.96 g, 7.87 mmol) in THF (10 cm^3) at ca. 25 °C. There was rapid colour change from red to deep green. The mixture was stirred for 48 h, and the volatiles were then removed in vacuo. The residue was extracted with toluene, and the extract was filtered, then cooled to −30 °C to give sky-blue crystals of di-η-cyclopentadienyl(chloro)(tetrahydrofuran)titanium(III) (1.10 g), which had an IR spectrum identical with that of an authentic specimen [25].

When the reaction of the lithium reagent (0.85 g, 3.86 mmol) and $[TiCp_2Cl_2]$ (0.96 g, 3.86 mmol) was carried out in n-hexane (30 cm^3) the product was the blue $[\{TiCp_2(\mu\text{-Cl})\}_2]$.

X-Ray data collection, structure determination, and refinement for $[UCp''_2(\mu\text{-}Cl)_2Li(THF)_2]$

Crystalline $C_{30}H_{58}Cl_2LiO_2Si_4U$ $M = 879.0$, is triclinic, with a 11.352(5), b 12.795(7), c 15.014(7) Å; α 101.63(7), β 90.34(4), γ 95.92(6)°; U 2123.8 $Å^3$, $Z = 2$, D_c 1.37 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ 49.5 cm^{-1}, space group $P\bar{1}$. The lattice parameters were determined from a least-squares refinement of the angular settings of 25 reflections ($2\theta > 30°$), accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions $0.22 \times 0.20 \times 0.15$ mm was sealed in a thin-walled capillary under an atmosphere of argon. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ technique in a manner similar to that described previously [26]. All unique reflections out to $2\theta \leqslant 40°$ were measured; of the total of 3929 reflections, 2682 were considered as observed ($I \geqslant 3\sigma(I)$).

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