Dimeric uranium complexes with bridging phospholyl ligands. Crystal structure of [{U(η^5-C$_4$Me$_4$P)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$]

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Abstract

In the symmetrical crystal structure of [{U(η^5-C$_4$Me$_4$P)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$], the U–P bond distances for the terminal and bridging η^5-phospholyl ligands are 2.945(3) and 2.995(3) Å respectively, and the U–P (η^1-phospholyl) bond length is equal to 2.996(3) Å; the tridentate borohydride ligands are *cis* to the (UP)$_2$ ring. The *cis* and *trans* isomers of [{U(Cp*)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$] (Cp* = η^5-C$_5$Me$_5$) are in equilibrium in toluene.

Key words: Uranium; Dinuclear; X-ray structure; Phospholyl complexes

1. Introduction

Phospholyl or phosphacyclopentadienyl ligands have been found to be capable of bridging two metals through the available lone pair on the P atom. Phospha- and diphospha-ferrocenes have been used as phosphorus ligands to build a series of polymetallic compounds in which the metal atoms are linked by one (μ-η^5, η^1-3,4-dimethylphospholyl) group (structure A) [1,2]. Although the geometry of the diphosphaferrocenes, with two parallel phospholyl rings, is not favourable for the formation of chelate derivatives, a complex, [{Fe(μ-η^5,η^1-C$_4$Me$_4$P)$_2$}$_2$Ag]$^+$ has been isolated [3]. Other chelate composites with structure B were obtained from [Zr(η^5-C$_4$Me$_4$P)$_2$Cl$_2$] [4]. In all these complexes, the aromaticity of the phospholyl

rings is not destroyed by coordination of the phosphorus atom.
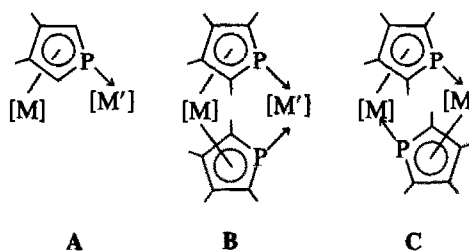
We recently reported the synthesis of [{U(η^5-C$_4$Me$_4$P)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$] (1), a unique example of a dimeric phospholyl compound [5]. The ^{1}H and ^{31}P NMR spectra revealed that in solution 1 adopts the symmetrical structure C, with one of the two phospholyl ligands of each monomeric unit in a bridging position. The complex would exist as isomers 1a or 1b, in which the borohydride ligands are *cis* or *trans* with respect to the U–P–U–P ring.

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L = η^5-C$_4$Me$_4$P, 1a
L = Cp*, 2a

L = η^5-C$_4$Me$_4$P, 1b
L = Cp*, 2b
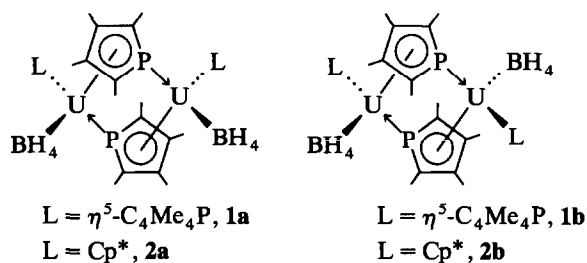
Here we present the crystal structure of this binuclear complex 1 which, in addition to exhibiting the new type of bonding C, is also a rare uranium compound with P donors and the sole uranium(III) phospholyl complex to have been crystallographically characterized. We also describe the synthesis and dynamic behaviour in solution of another uranium complex which adopts the structure C, [{U(Cp*)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$] (Cp* = η-C$_5$Me$_5$).

2. Results and discussion

2.1. The crystal structure of [{U(η^5-C$_4$Me$_4$P)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$] (1)

The ORTEP drawing [6] of 1 is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The X-ray analysis confirms that 1 adopts the dimeric structure C in the solid state. The two monomeric units are crystallographically related by the two-fold axis of symmetry. The uranium atom is in a tetrahedral environment, if the phospholyl ligands are considered to be monodentate. This coordination geometry is quite simi-

lar to that invariably found in the series of monomeric compounds [M(Cp*)$_2$(X)(L)] [7] (M = lanthanoid or Group 3 metal, X = halide, alkyl or alkoxide, L = X or tetrahydrofuran). In particular, the ring centroid–U–ring centroid angle (131.0(3)°) and the B–U–P(1') angle (89.4(3)°) fall within the range normal for bent metallocene complexes of this type, and do not seem constrained by steric hindrance in the dimer. In contrast, the ring centroid–Zr–ring centroid angle in the chelate compound [Zr(Cl)$_2$(μ-η^5,η^1-C$_4$Me$_4$P)$_2$Fe-(CO)$_3$] (127° [4]) is smaller than in the free [Zr(η^5-C$_4$Me$_4$P)$_2$(Cl)$_2$] (131.6° [8]). The geometrical parameters of the terminal and bridging phospholyl ligands of 1 are not significantly different, further suggesting that the dimer is not subject to severe steric repulsions. Both phospholyl rings are planar within ±0.03(1) Å. The methyl carbons in the 3,4-positions of the rings (C(6), C(7), C(14) and C(15)) are bent away from uranium by an average distance of 0.16(4) Å, as it was observed in [Zr(η^5-C$_4$Me$_4$P)$_2$(Cl)$_2$] [8]. The average U–C bond length, the U–ring centroid and U–P bond distances for the terminal and bridging η^5-phospholyl ligands, are 2.86(3) and 2.83(3) Å, 2.56(1) and 2.54(1) Å, 2.945(3) and 2.995(3) Å respectively. The corresponding values determined in [U(η^5-C$_4$Me$_4$P)$_2$(BH$_4$)$_2$] are 2.81(4), 2.506(4) and 2.905(8) Å [5]. The slight differences between the bond distances in this UIV phospholyl complex and in 1, if significant, do not reflect the 0.11 Å difference between the ionic radii of UIV and UIII [9]. Such invariance of bond lengths in
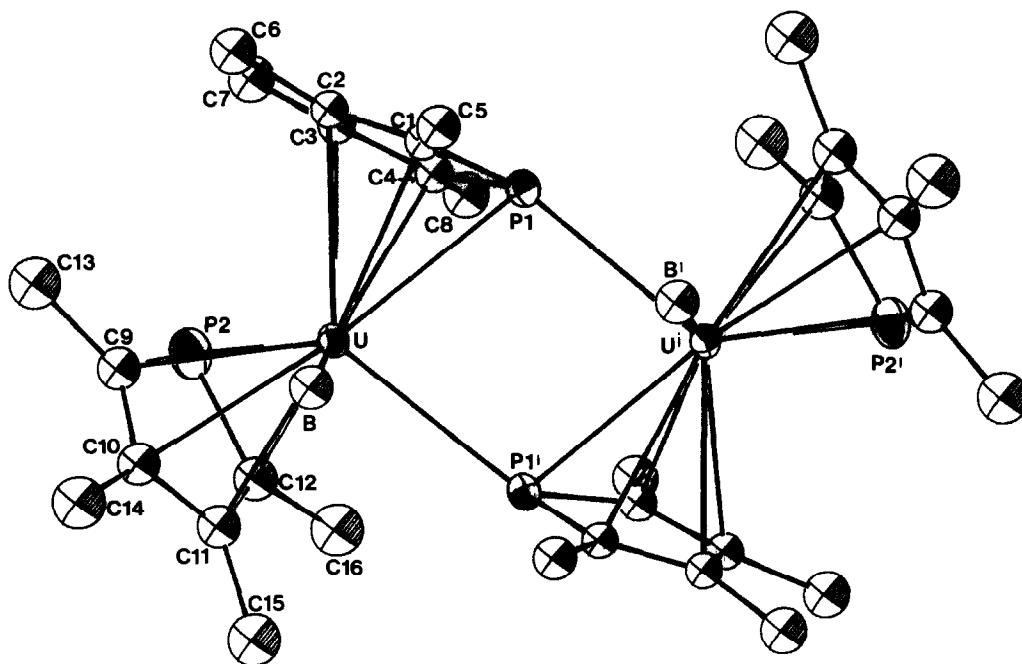
Fig. 1. Perspective view of the dimeric compound 1. Symmetry code: (i) $-x$, y, $1/2 - z$. The H atoms of the BH$_4$ ligand have been omitted for clarity.

substituted cyclopentadienyl groups coordinated either to UIV or UIII has already been pointed out and explained by the steric hindrance of these bulky ligands which cannot come in closer contact with the metal [10,11].

Special attention should be paid to the U ← P(1^i) bond. It has been demonstrated that the phosphorus lone pair lies in the plane of the phospholyl group [12], but the U atom in 1 is out of the plane of the bridging ligand. The U–P(1^i)–ring centroid angle (159.0(3)°) is similar to the Fe–P–ring centroid angles in [Zr(Cl)$_2$(μ-η^5,η^1-C$_4$Me$_4$P)$_2$Fe(CO)$_3$] (163° [4]) and smaller than the nearly linear Fe–P–ring centroid angle in the *mono*-bridged bimetallic compound [Fe(η^5-C$_5$H$_5$)(μ-η^5,η^1-C$_4$Me$_2$H$_2$P)Fe(CO)$_4$] (172° [2]). The deviations from linearity in the first two complexes are certainly related to the closure of the M(μ-η^5,η^1-C$_4$Me$_4$P)$_2$M ring. The U ← P(1^i) bond distance (2.996(3) Å) is at the lower limit of the range found for uranium–P(phosphine) bond lengths which range from 2.972(6) Å in [U(C$_5$H$_4$Me)$_3$(PMe$_3$)] [13] to 3.211(9) Å in [U(Cp*)$_2$-(H)(Me$_2$PCH$_2$CH$_2$PMe$_2$)] [14]. That a metal ← P-(phospholyl) bond is rather short in comparison to a classical metal ← P(phosphine) bond has already been noted in all the phospholyl-bridged polymetallic compounds possessing structures A or B. Because phosphametallocenes display strong accepting properties and are poorer donors than ordinary phosphines, this feature has been explained using the π back-bonding concept [2]. The U–P(1^i) and U–P(1) distances are equal, the U–P(1)–U^i and P(1)–U–P(1^i) angles are 100.65(8) and 77.31(9)°, respectively and the dihedral angle between the planes P(1)UP(1^i) and P(1)U^{i}P(1^i) is

160.57(4)°. The short U–B distance (2.59(1) Å) is characteristic of a tridentate BH$_4$ ligand [15]. The two borohydride groups (and the two terminal phospholyl ligands) are *cis* with respect to the U P(1) U^{i}P(1^i) ring. It is quite possible that this configuration 1a is also that preferentially adopted by the complex in solution [5].

2.2. Synthesis and structure in solution of [{U(Cp*)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$] (2)

The complex [{U(Cp*)(μ-η^5,η^1-C$_4$Me$_4$P)(BH$_4$)}$_2$] (2) was prepared in a manner similar to that of 1, by sodium amalgam reduction of [U(Cp*)(η^5-C$_4$Me$_4$P)-(BH$_4$)$_2$] in toluene [16]. By analogy with 1, it was expected that 2 would adopt the bridged structure C. The NMR spectra revealed that this compound exists in solution as two equilibrating isomers 2a and 2b. The ^{1}H NMR spectrum exhibited two homologous series of six signals, the intensities of which were in the ratio 15:4:3:3:3:3. These six resonances were easily attributed to the Cp*, BH$_4$ and the four non-equivalent Me groups of the phospholyl ligand in a U(Cp*)(η^5-C$_4$Me$_4$P)(BH$_4$) fragment. There are two resonances in the ^{31}P NMR spectrum in the intensity ratio 80:20. The same ratio between intensities was found for the corresponding signals in the two sets of six peaks in the ^{1}H NMR spectrum. These data indicated that at 30°C in toluene, 2a and 2b were present in this proportion 80:20, without it being possible to determine which isomer is preponderant. By lowering the temperature, the percentage of the less abundant isomer decreased progressively and was less than 5% at −90°C. This change was reversible. The equilibrium between 2a and 2b can be accounted for by dissociation of the U ← P

TABLE 1. Selected bond distances (Å) and angles (°) with estimated standard deviations for 1 [a]

Uranium environment					
U–P(1)	2.995(3)	U–C(1)	2.882(9)	U–C(2)	2.87(1)
U–C(3)	2.86(1)	U–C(4)	2.82(1)	U–1	2.56(1)
U–P(2)	2.945(3)	U–C(9)	2.79(1)	U–C(10)	2.84(1)
U–C(11)	2.85(1)	U–C(12)	2.83(1)	U–2	2.54(1)
U–B	2.59(1)	U–P(1^i)	2.996(3)		
1–U–2	131.0(3)	1–U–P(1^i)	106.8(3)	2–U–P(1^i)	104.2(4)
B–U–P(1^i)	89.4(3)	B–U–1	108.9(4)	B–U–2	108.4(4)
U–P(1)–U^i	100.6(4)	P(1)–U–P(1^i)	77.3(4)	1–P(1)–U^i	159.0(3)
Phospholyl ligands					
P(1)–C(1)	1.78(1)	P(1)–C(4)	1.78(1)	C(1)–C(2)	1.38(1)
C(2)–C(3)	1.44(1)	C(3)–C(4)	1.39(1)		
P(1)–C(1)–C(2)	111.0(8)	P(1)–C(4)–C(3)	109.6(8)	C(1)–P(1)–C(4)	91.9(5)
C(1)–C(2)–C(3)	113.0(9)	C(2)–C(3)–C(4)	114.2(9)		
P(2)–C(9)	1.75(1)	P(2)–C(12)	1.75(1)	C(9)–C(10)	1.38(2)
C(10)–C(11)	1.42(2)	C(11)–C(12)	1.38(2)		
P(2)–C(9)–C(10)	112.3(9)	P(2)–C(12)–C(11)	111.9(9)	C(9)–P(2)–C(12)	90.4(6)
C(9)–C(10)–C(11)	112(1)	C(10)–C(11)–C(12)	113(1)		

[a] 1 and 2 are the centroids of the bridged and terminal phospholyl ligands; atoms labelled *i* are related to corresponding unlabelled atoms by the two-fold axis of symmetry.

bond, followed by rotation around the bridging phospholyl–U axis and recombination. Such a mechanism was proposed to explain the fluxional behaviour of 1 [5].

The evidence of the two isomers 2a and 2b led us to examine the ^{1}H NMR spectra of 1 with more attention. These spectra exhibit eight resonances of equal intensities corresponding to the eight non-equivalent methyl groups, and a broad signal at δ 165 attributed to the BH_4. Under forcing recording conditions other small signals could be detected, which would correspond to the minor isomer of 1 (ca. 5%). In particular, a broad BH_4 resonance was observed at δ 140. The other eight peaks corresponding to the methyl groups were more difficult to find because of overlapping with the methyl resonances of the major isomer.

As observed for 1, cleavage of the phospholyl bridges of 2 occurred in tetrahydrofuran (THF), giving the Lewis base adduct $[U(Cp^*)(\eta^5\text{-}C_4Me_4P)(BH_4)(THF)]$ which was characterized by its ^{1}H NMR spectrum.

3. Experimental details

3.1. General methods

All experiments were carried out under argon (less than 5 ppm oxygen) using standard Schlenk vessel and vacuum line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated over Na/K, and distilled immediately before use. $[U(Cp^*)(\eta^5\text{-}C_4Me_4P)(BH_4)_2]$ was prepared as described [16]. The ^{1}H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual solvent proton resonances relative to tetramethylsilane (δ 0). The ^{31}P NMR spectrum was recorded on a Bruker WP 80 instrument, the external reference being 85% H_3PO_4.

3.2. X-ray crystal structure of $[\{U(\eta^5\text{-}C_4Me_4P)(\mu\text{-}\eta^5, \eta^1\text{-}C_4Me_4P)(BH_4)\}_2]$ (1)

Complex 1 was recrystallized from toluene-pentane at 4°C. A selected single crystal was introduced into a thin-walled Lindeman glass tube in the glove box. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator ($\lambda = 0.71073$ Å). The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standards reflections were measured after each hour: a decay was observed (5% in 27 h) and was corrected linearly. The data were corrected for Lorentz polarization effects and absorption based on Ψ scans [17]. The structure was solved by the heavy-atom method and refined by full-matrix least-squares on F with anisotropic thermal parameters for U and P atoms. H atoms of the phospholyl ligands were introduced at

TABLE 2. Crystallographic data and experimental details for compound 1

Crystal data	
Formula	$C_{32}H_{56}B_2P_4U_2$
M	1062.38
Crystal dimensions(mm)	$0.60 \times 0.40 \times 0.20$
Colour	dark brown
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	16.566(3)
b (Å)	14.418(3)
c (Å)	17.552(4)
β (°)	109.27(2)
V (Å^3)	3957(2)
Z	4
D_{calc} (g cm^{-3})	1.783
μ (Mo–Kα) (cm^{-1})	79.298
$F(000)$	2008
Data collection	
θ limits (°)	1, 20
Scan type	$\omega, 2\theta$
Scan width	$0.8 + 0.35 \tan \theta$
Range of abs. trans.	0.400, 0.999
Range h, k, l	0 to 15, 0 to 13, −16 to 16
Reflections collected	
total	2115
unique	1849
with $I > 3\sigma(I)$	1505
No. of parameters	96
$R = \Sigma\|Fo\| - \|Fc\|/\Sigma\|Fo\|$	0.027
$Rw = [\Sigma w\|Fo\| - \|Fc\|^2/\Sigma w(\|Fo\|)^2]^{1/2}$	0.038
p in weighting scheme	0.04
$w = 1/(\sigma F)^2 = 4F^2/[\sigma I^2 + (pF^2)^2]^{1/2}$	
Max. residual electron density (e Å^{-3})	0.5

calculated positions (C–H = 0.95 Å and B = 6 Å^2); they were not refined but constrained to ride on their C atom. H atoms of the borohydride ligand were found in the last ΔF Fourier map and introduced in the refinements at fixed positions. All calculations were performed on a VAX 4200 computer with the Enraf-Nonius MolEN system [18]. Analytical scattering factors for neutral atoms [19] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 2. Final positional and thermal parameters are listed in Table 3. Full lists of atomic coordinates, bond lengths, angles, and thermal parameters are available from the Cambridge Crystallographic Data Centre.

3.3. Synthesis of $[\{U(Cp^*)(\mu\text{-}\eta^5,\eta^1\text{-}C_4Me_4P)(BH_4)\}_2]$ (2)

A 50 ml round bottom flask was charged with $[U(Cp^*)(\eta^5\text{-}C_4Me_4P)(BH_4)_2]$ (569.2 mg, 1.05 mmol) and 2% Na(Hg) (2017 mg, 1.75 mmol of Na) and toluene (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 14 h at

TABLE 3. Fractional atomic coordinates, thermal parameters and their e.s.d.s. for compound 1

Atom	x	y	z	B_{eq} (Å²)
U	0.04651(2)	0.22104(3)	0.13985(2)	2.531(8) *
P(1)	−0.1135(2)	0.2484(2)	0.1810(2)	3.16(6) *
P(2)	0.0998(2)	0.3679(2)	0.0500(2)	4.69(7) *
C(1)	−0.1276(5)	0.1606(7)	0.1068(5)	2.9(2)
C(2)	−0.1264(5)	0.1977(7)	0.0346(5)	3.2(2)
C(3)	−0.1119(6)	0.2966(7)	0.0386(5)	3.2(2)
C(4)	−0.0985(5)	0.3349(7)	0.1147(5)	3.1(2)
C(5)	−0.1477(6)	0.0603(7)	0.1170(6)	4.2(2)
C(6)	−0.1480(6)	0.1439(8)	−0.0424(6)	5.1(3)
C(7)	−0.1218(6)	0.3554(8)	−0.0358(6)	4.9(2)
C(8)	−0.0857(6)	0.4359(7)	0.1344(6)	4.9(2)
C(9)	0.1217(6)	0.2566(7)	0.0221(6)	4.0(2)
C(10)	0.1875(6)	0.2139(7)	0.0819(6)	4.2(2)
C(11)	0.2172(6)	0.2695(7)	0.1526(6)	4.3(2)
C(12)	0.1750(6)	0.3529(7)	0.1459(6)	4.2(2)
C(13)	0.0808(7)	0.2164(8)	−0.0607(7)	5.9(3)
C(14)	0.2257(7)	0.1222(9)	0.0701(7)	6.8(3)
C(15)	0.2921(8)	0.2424(9)	0.2274(8)	6.6(3)
C(16)	0.1969(7)	0.4277(9)	0.2096(7)	6.7(3)
B	0.0768(7)	0.045(1)	0.1613(7)	4.4(3)
H(1)	0.037	0.064	0.197	6.0
H(2)	0.128	0.086	0.187	6.0
H(3)	0.054	0.069	0.100	6.0
H(4)	0.0810	−0.0303	0.1670	6.0

* $B_{eq} = 4/3 \Sigma_i \Sigma_j \beta_{ij} a_i a_j$

20°C. The solution was filtered and evaporated, leaving a black powder of 2 (371 mg, 67%). The product was contaminated by a diamagnetic impurity which could not be eliminated by recrystallization from toluene-pentane. The NMR signals of this impurity contributed to ca. 5% of the total intensity of the spectrum. ^{1}H NMR of 2, δ (toluene d_8, 30°C); major isomer: 138 (4H, $w_{1/2}$ = 270 Hz, BH$_4$), 19.51, −35.43, −44.60 and −60.92 (4 × 3H, s, C$_4$Me$_4$P), −0.36 (15H, s, Cp*); minor isomer: 109 (4H, $w_{1/2}$ = 360 Hz, BH$_4$), 2.86 (15H, s, Cp*), −5.82, −31.93, −38.77 and −44.81 (4 × 3H, s, C$_4$Me$_4$P). The two isomers were in the ratio 80:20. The ^{31}P NMR of 2 (toluene, 30°C) exhibited two resonances at δ 3886 ($w_{1/2}$ = 1130 Hz) and 3672 ($w_{1/2}$ = 1600 Hz) in the ratio 80:20.

Compound 2 was dissolved in THF and after evaporation of the solvent, the adduct [U(Cp*)(η^5-C$_4$Me$_4$P)(BH$_4$)(THF)] was obtained in quantitative yield. ^{1}H NMR δ (toluene d_8, 30°C): 83.4 (4H, $w_{1/2}$ = 435 Hz,

BH$_4$), 19.04, 11.26, −13.82 and −30.93 (4 × 3H, s, C$_4$Me$_4$P), −2.32 (15H, s, Cp*) −11.84 (4H, s, β-THF), −36.06 (4H, s, α-THF); δ (THF d_8, 30°C): 82.3 (4H, $w_{1/2}$ = 350 Hz, BH$_4$), 16.33 and −22.97 (6H + 6H, s, C$_4$Me$_4$P), −2.31 (15H, s, Cp*).

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