Synthesis and structural characterisation of lanthanide and actinide phosphaorganometallic complexes derived from the 3,5-di-*tert*-butyl-1,2,4-triphospholyl ring anion, $P_3C_2Bu_2^{t-}$: Crystal and molecular structures of $[M(\eta^5-P_3C_2Bu_2^t)_2(\eta^2-P_3C_2Bu_2^t)]$ (M = Sc, Y, Tm, and U)

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ARTICLE INFO

ABSTRACT

Treatment of MI_3 (M = Sc, Y, Tm, and U) with three equivalents of $KP_3C_2Bu_2^t$ in refluxing toluene led to the corresponding monomeric, formally eight coordinate, complexes $[M(\eta^5-P_3C_2Bu_2^t)_2(\eta^2-P_3C_2Bu_2^t)]$ in moderate yields. In the solid state the complexes, which are all iso-structural, display an interesting assembly of ligands comprising of one η^2-(bent) and two η^5-ligated triphospholyl rings. NMR studies indicate that the complexes are fluxional in solution.

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1. Introduction

Cyclopentadienyl derivatives of Group 3 elements (including scandium, yttrium, lanthanum and the lanthanides and actinides) have been extensively studied [1]. More recently the cyclopentadienyl ring system has been modified by the replacement of one or more ring carbon atoms by Group 15 elements to afford hetero-cyclopentadienyl complexes of these Group 3 elements. Typically pyrollyl, phospholyl and arsolyl ring systems involving one heteroatom; pyrazolyl rings involving two heteroatoms and 1,2,4-triphospholyl and 1,2,4-stibadiphospholyl rings containing three heteroatoms have been employed. A variety of novel bonding modes (in addition to the expected η^5-ligation) have been established for these hetero-cyclopentadienyl systems.

Thus, mono-substituted rings can ligate in both an η^1-(planar or bent) and μ-η^5-η^1 fashion, while the proximity of two heteroatoms in the 1,2,4-triphospholyl and 1,2,4-stibadiphospholyl rings offers the possibility for other coordination modes such as η^2-(planar or bent), as well as μ-η^2- and μ-η^1-ligation (see Scheme 1).

The field of Group 3 metal-hetero-cyclopentadienyl complexes has been comprehensively reviewed by Nief [2].

Previously, we have used the aromatic ring anion 3,5-ditertiarybutyl-1,2,4-triphospholyl, $P_3C_2Bu^t{}_2$ extensively for the synthesis of sandwich and half-sandwich complexes of several transition metals (e.g. Sc [3], Ti [4,5], V [6], Cr [17], Mn [18], Fe [7–13], Co [19], Ni [21–25], Ru [13–16], and Rh [16,20]) and main group elements (e.g. Ga [26], In [27–29], Tl [26], Sr [30], and Pb [31]). We have recently briefly reported [32] the synthesis of the first structurally characterised scandocene, "$[Sc(P_3C_2Bu_2^t)_2]$" by potassium graphite reduction of the corresponding Sc(III) complex. Unexpectedly, this "hexaphosphascandocene" has an unprecedented dimeric structure in the solid state and is perhaps best regarded as a mixed-valence compound containing both Sc(I) and Sc(III) centres.
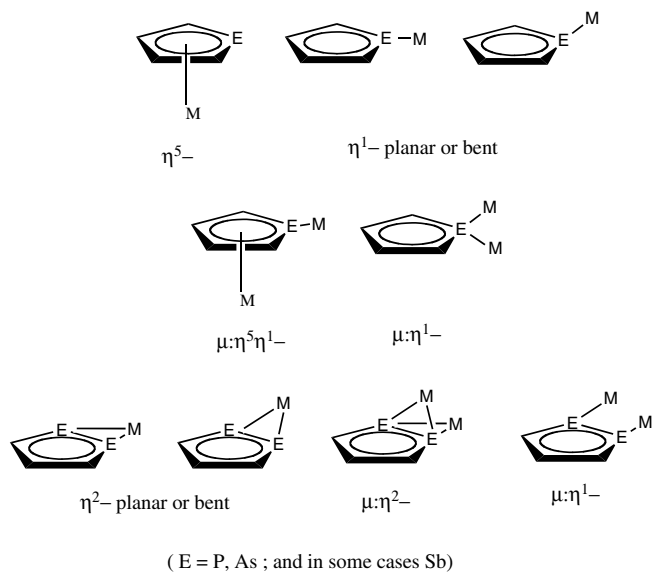
We now describe the extension of this work to the synthesis and structural characterisation of three other related trivalent metal 1,2,4-triphospholyl compounds of formula $[M(P_3C_2Bu^t{}_2)_3]$ (M = Y, Tm, U) drawn from both the lanthanide and actinide series, as well as fuller details of the Sc(III) compound.

2. Results and discussion

Treatment of the 1,2,4-triphospholyl anion, $P_3C_2Bu^t{}_2$ (as its base free potassium salt), with MI_3 (M = Sc, Y, Tm, and U) in refluxing toluene leads to the corresponding heteroleptic tris-1,2,4-tri-

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η⁵– η¹– planar or bent

μ:η⁵η¹– μ:η¹–

η²– planar or bent μ:η²– μ:η¹–

(E = P, As ; and in some cases Sb)

Scheme 1.

|	Scandium	Yttrium	Thulium	Uranium
Formula	$C_{30}H_{54}P_9Sc$ (**1**)	$C_{30}H_{54}P_9Y$ (**2**)	$C_{30}H_{54}P_9Tm$ (**3**)	$C_{30}H_{54}P_9U$ (**4**)
M	738.4	782.37	862.39	931.49
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	11.066(2)	11.062(2)	11.0942(6)	11.0720(3)
b (Å)	16.014(2)	16.105(5)	16.1459(12)	16.2085(5)
c (Å)	22.193(3)	22.430(4)	22.4184(13)	22.5898(6)
α (°)	90	90	90	90
β (°)	102.99(2)	102.95(2)	102.938(3)	103.282(2)
γ (°)	90	90	90	90
V (Å³)	3832(1)	3894.3(16)	3913.8(4)	3945.56(19)
D (g cm⁻³)	1.26	1.33	1.46	1.57
Z	4	4	4	4
$F(000)$	1560	1632	1752	1844
μ (mm⁻¹)	0.59	1.89	2.65	4.50
Crystal size (mm)	$0.2 \times 0.2 \times 0.05$	$0.2 \times 0.1 \times 0.1$	$0.1 \times 0.05 \times 0.02$	$0.2 \times 0.05 \times 0.05$
$T_{min,max}$	0.82, 1.00	0.80, 1.00	0.832, 0.912	0.568, 0.750
Reflections collected	5622	7196	18484	39385
Independent (R_{int})	5315 (0.0555)	6828 (0.062)	6831 (0.081)	6925 (0.1047)
Reflections $I > 2\sigma I$	2929	3692	4154	5109
$R_1 I > 2\sigma I$	0.074	0.077	0.058	0.046
$wR_2 I > 2\sigma I$	0.150	0.144	0.119	0.092
R_1 all data	0.151	0.164	0.116	0.073
wR_2 all data	0.184	0.179	0.141	0.103

phospholyl metal (III) complexes $M(P_3C_2Bu^t_2)_3$ **1** M = Sc, **2** M = Y, **3** M = Tm, **4** M = U, in moderate yields (Eq. (1)).

The complexes were characterised by elemental analysis, multinuclear NMR spectroscopy and mass spectrometry and their solid-state structures were confirmed by single crystal X-ray diffraction studies. (*vide infra*).

$$MI_3 + 3KP_3C_2Bu^t_2 \rightarrow M(P_3C_2Bu^t_2)_3 + 3KI$$
1 M = Sc, **2** M = Y, **3** M = Tm, **4** M = U   (1)
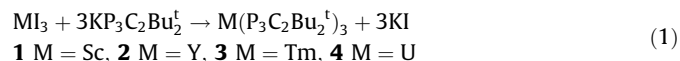
2.1. Structural studies

Single crystal X-ray diffraction studies were carried out on complexes **1–4** and the compounds were all found to be monomeric and iso-structural. Crystallographic data for **1–4** are summarised in Table 1. The molecular structure of each compound consists of a formally eight coordinate metal atom which is ligated to one 1,2,4-triphospholyl ring in an η²-(bent) fashion and to two 1,2,4-triphospholyl rings in an η⁵-coordination mode as shown below.

$$MI_3 + 3KP_3C_2Bu^t_2 \longrightarrow M(P_3C_2Bu^t_2)_3 + 3 KI$$
1 M = Sc, **2** M = Y, **3** M = Tm, **4** M = U
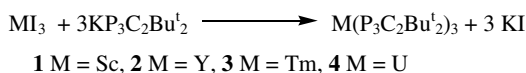
The molecular structures of compounds **1–4** are shown in Figs. 1–4 together with important bond length and bond angle information in Table 2. In all four complexes the rings are approximately planar, with the tertiary butyl groups orientated so as to minimise inter-ring interactions. There is very little variation in ring geometry within the three $P_3C_2Bu^t_2$ rings regardless of their mode of coordination nor is there significant variation in internal ring geometry with that of K or Mg salts of the free anionic ring [33,34].

The unusual η²-(bent) bonding of one of the $P_3C_2Bu^t_2$ rings observed in complexes **1–4** is of interest and is similar to that reported by Deacon et al. [35] for both the triphospholyl compound $[Sm(η⁵-C_5Me_5)_2(η²-P_3C_2Bu^t_2)THF]$ and the stibadiphospholyl salt $[Li(THF)_4][Yb(η⁵-P_2SbC_2Bu^t_2)_2(η²-P_2SbC_2Bu^t_2)]$. These authors attributed the structural differences between the triphospholyl and stibadiphospholyl complexes and the corresponding Ph_2(pyrazolyl) compounds (which involves largely σ-ring bonding) to the increasingly diffuse nature of the lone pairs of the heavier hetero-atoms in the sequence N, P, Sb which makes
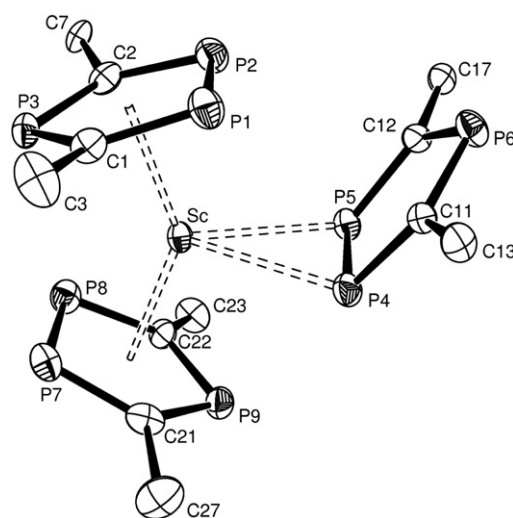

Fig. 1. Molecular structure of **1** (Me groups omitted for clarity; ellipsoids at 50% probability). Selected bond lengths (Å) and angles (°) Sc–M(1) 2.326(9), Sc–M(2) 2.371(9), Sc–C(1) 2.743(9), Sc–C(2) 2.731(9), Sc–C(21) 2.822(8), Sc–C(22) 2.790(8), Sc–P(1) 2.813(3), Sc–P(2) 2.806(3), Sc–P(3) 2.870(3), Sc–P(4) 2.762(3), Sc–P(5) 2.796(3), Sc–P(7) 2.793(3), Sc–P(8) 2.773(3), Sc–P(9) 2.773(3), P(1)–C(1) 1.754(8), P(1)–P(2) 2.117(4), P(2)–C(2) 1.751(8), P(3)–C(1) 1.744(8), M(1)–Sc–M(2) 140.2(2), M(1)–Sc–P(4) 114.10(8), M(1)–Sc–P(5) 112.75(7), M(2)–Sc–P(4) 102.70(8), M(2)–Sc–P(5) 103.85(7), C(1)–P(1)–P(2) 98.6(3), C(2)–P(2)–P(1) 98.8(3), C(2)–P(3)–C(1) 98.9(4), P(1)–C(1)–P(3) 121.8(5), P(2)–C(2)–P(3) 121.9(5). (M(1) and M(2) refer to the centroids of the two η⁵-ligated rings).

the latter less suitable for electrostatic interactions with the hard Ln^{3+} ions, thereby causing a steady change from σ- via σ/π to π interactions.

Interestingly, the analogous tris(cyclopentadienyl) lanthanide complexes exhibit one of three structural motifs (each of which is oligomeric or polymeric) so as to maximise the coordination num-
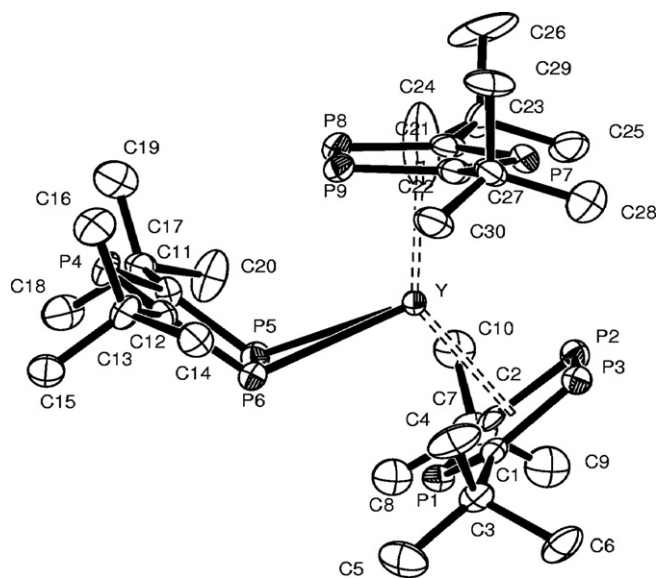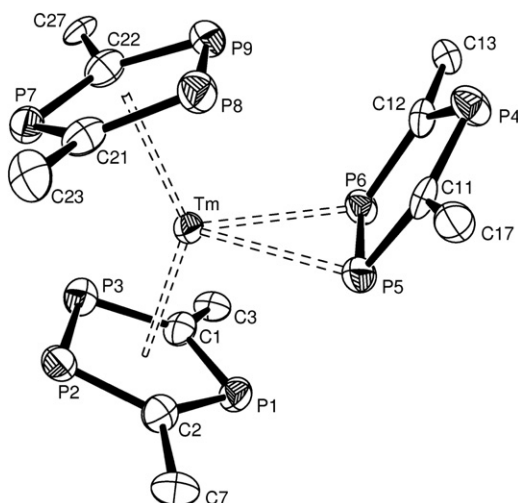
Fig. 2. Molecular structure of Y(P$_3$C$_2^t$Bu$_2$)$_3$ (**2**).

Fig. 3. Molecular structure of Tm(P$_3$C$_2^t$Bu$_2$)$_3$ (**3**) (Me groups are omitted for clarity; ellipsoids at 50% probability).
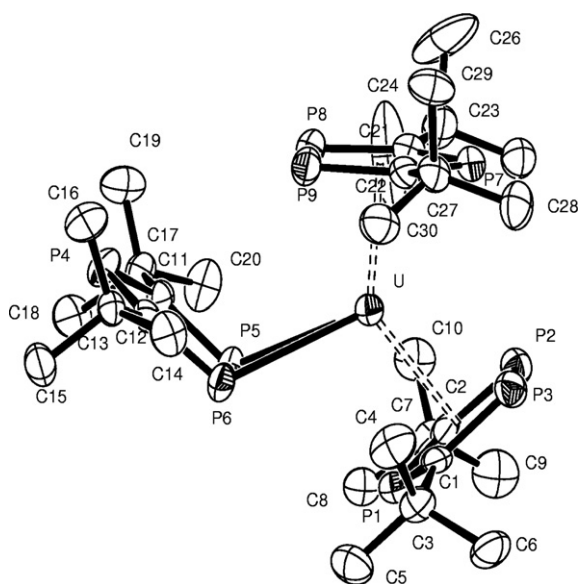

Fig. 4. Molecular structure of U(P$_3$C$_2^t$Bu$_2$)$_3$ (**4**).

Table 2
Bond lengths (Å) and angles (°) for M(P$_3$C$_2^t$Bu$_2$)$_3$ (**1–4**) (M = Sc, Y, Tm, and U)

Bond/angle	Sc	Y	Tm	U
M–M(1)	2.326(9)	2.478(8)	2.488(9)	2.577(7)
M–M(2)	2.371(9)	2.508(8)	2.451(9)	2.580(7)
M–P(4)	2.762(3)	2.884(2)	2.853(2)	2.9675(19)
M–P(5)	2.796(3)	2.912(2)	2.891(2)	2.9950(18)
P(4)–P(5)	2.099(3)	2.111(3)	2.118(3)	2.118(3)
P(1)–P(2)	2.117(4)	2.120(4)	2.116(3)	2.126(3)
P(1)–C(1)	1.754(8)	1.759(9)	1.765(8)	1.761(7)
P(2)–C(2)	1.751(8)	1.766(8)	1.779(8)	1.765(7)
P(3)–C(1)	1.744(8)	1.760(8)	1.751(8)	1.754(8)
P(3)–C(2)	1.740(8)	1.743(9)	1.742(9)	1.764(7)
M(1)–M–M(2)	140.2(2)	139.4(2)	139.49(2)	136.7(2)
C(1)–P(1)–P(2)	98.6(3)	99.3(3)	99.0(3)	98.9(3)
C(2)–P(2)–P(1)	98.8(3)	99.0(3)	98.8(3)	99.5(3)
C(1)–P(3)–C(2)	98.9(4)	99.8(4)	99.5(4)	99.8(3)
P(1)–C(1)–P(3)	121.8(5)	120.7(5)	121.4(5)	121.3(4)
P(2)–C(2)–P(3)	121.9(5)	121.1(5)	121.2(4)	120.4(4)

Atom numbering is based on that of Sc(P$_3$C$_2^t$Bu$_2$)$_3$. (M(1) and M(2) refer to the centroids of the two η^5-ligated rings).

ber of the central metal atom. The use of cyclopentadienyl ligands with bulky substituents such as (1,3-(TMS)C$_5$H$_3$) has facilitated the isolation and characterisation of monomeric tris(cyclopentadienyl) complexes of cerium, samarium and thorium [36–38]. However, these compounds differ from the M(P$_3$C$_2^t$Bu$_2$)$_3$ compounds reported above, in that all the three (1,3-(TMS)C$_5$H$_3$) rings are η^5-coordinated and are equally disposed around the metal centre. The P$_3$C$_2^t$Bu$_2$ and 1,3-(TMS)(C$_5$H$_3$) ring systems bear substituents of similar steric bulk and the longer P–C bonds make the P$_3$C$_2^t$Bu$_2$ rings more sterically demanding, but it is difficult to conclude whether steric or electronic effects play the most significant role in determining the structures of compounds **1–4**.

Figs. 2–4 show the molecular structures of complexes [M(η^5-P$_3$C$_2$Bu$^t_2$)$_2$(η^2-P$_3$C$_2$Bu$^t_2$)] (**2–4**) (M = Y, Tm, and U).

A comparison of selected bond lengths and bond angles for all the [M(P$_3$C$_2^t$Bu$_2$)$_3$] metal complexes **1–4** is presented in Table 2. The similarity for a series of compounds containing metals of considerably different sizes strongly suggests that the ligand system is the dominating factor in determining structure.

2.2. ^{31}P NMR studies

As previously mentioned in our preliminary publication, [32] the ^{31}P{^{1}H} NMR spectrum of a solution of the scandium(III) tris-1,2,4-triphospholyl complex **1** consists of two symmetric but highly complex multiplets at 296.2 and 265.0 ppm in the ratio of 1:2. The presence of only two resonances suggests that on the NMR timescale the three 1,2,4-triphospholyl rings are rapidly inter-converting in solution in contrast to the solid-state structure discussed earlier, in which two distinct bonding modes are observed for the 1,2,4-triphospholyl ligands. The complexity of the multiplets in the ^{31}P{^{1}H} NMR spectrum suggests that there is significant inter-ring coupling which causes the resonances to deviate from a simple AX$_2$ spin system and it was successfully simulated as an AA′A″X$_2$X′$_2$X″$_2$ spin system involving coupling constants $J_{AX} = J_{A'X'} = -50.7$ Hz; $J_{AX'} = J_{AX''} = J_{A'X} = J_{A'X''} = J_{A''X} = J_{A''X'} = +21.5$ Hz; $J_{XX'} = J_{XX''} = J_{X'X''} = \pm 5.0$ Hz; $J_{AA'} = J_{AA''} = J_{A'A''} = 0$ Hz (signs of the couplings are relative, not absolute). A comparison of the simulated and experimental spectra is illustrated in Fig. 5 and shows excellent agreement between the two.

The corresponding ^{31}P{^{1}H} NMR spectrum for the yttrium complex **2** is significantly different from that of **1**. At room temperature two broad resonances are observed at 289.9 and 263.9 ppm in the ratio of 1:2. As the sample is warmed, the signals gradually begin to resolve somewhat although they remain slightly broadened
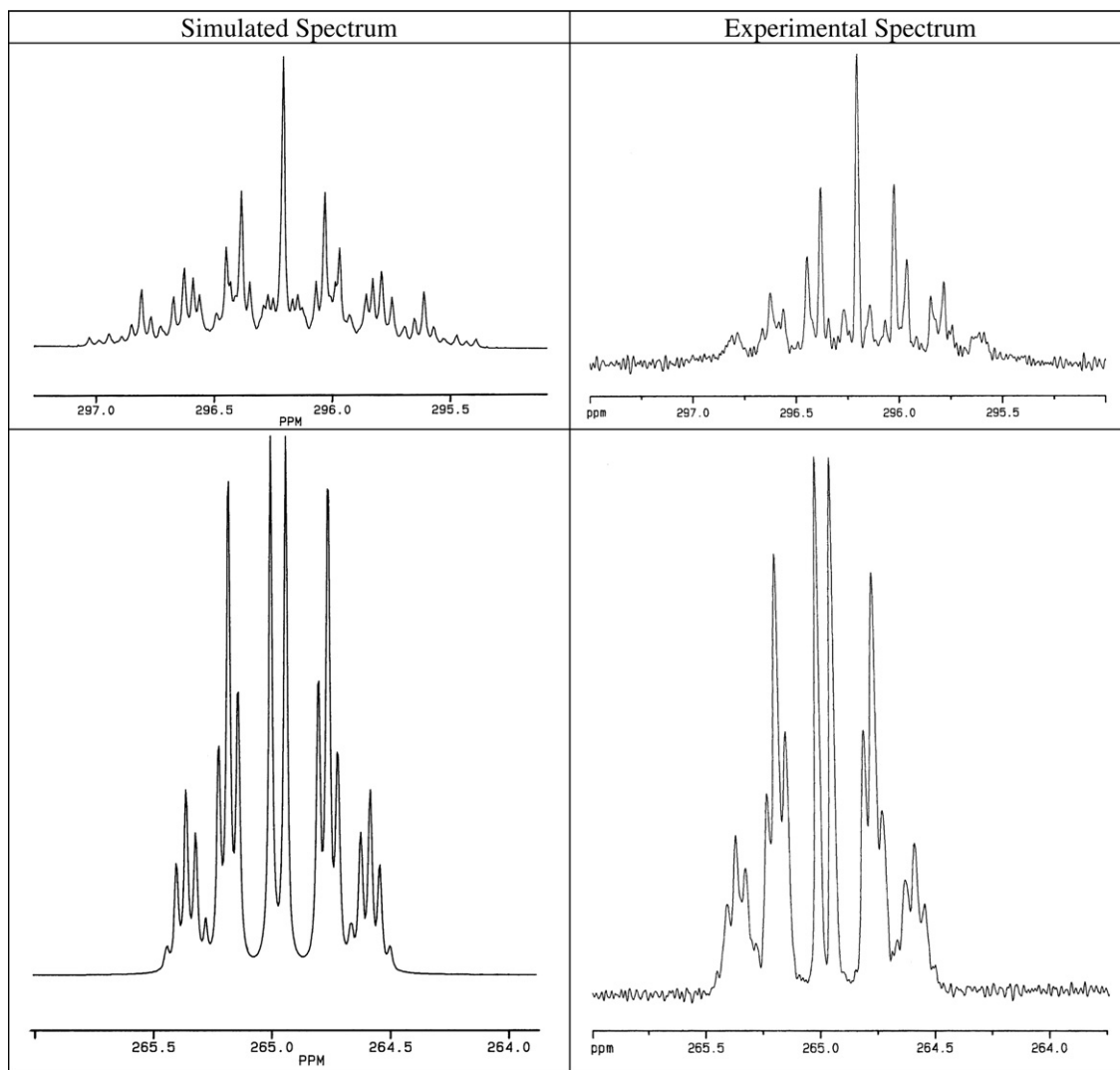
Fig. 5. Experimental and simulated ^{31}P{^{1}H} NMR spectrum of [Sc(η^5-P$_3$C$_2$Bu$^t_2$)$_2$(η^2-P$_3$C$_2$Bu$^t_2$)] (**1**).

and at 70 °C the higher field signal becomes a doublet from which a typical $^2J_{PP}$ coupling of 49.3 Hz can be measured. At this temperature the lower field resonance also begins to show evidence of resolution into the expected doublet but the coupling cannot be clearly deduced from this signal. The absence of any other couplings in this system suggests that, unlike the scandium case, there is smaller coupling between rings in the yttrium complex, perhaps because the larger size of yttrium reduces any significant 'through-space' coupling. The ^{31}P{^{1}H} NMR spectra of **3** (4f^{12}) and **4** (5f^3) were both very broad as expected.

3. Experimental

3.1. General procedures

Since all the compounds described are highly air and moisture sensitive, manipulations were carried out under an atmosphere of high purity argon using conventional Schlenk or glove box techniques. The solvents toluene, mesitylene, hexane and pentane were refluxed over Na/K alloy for at least 36 h and were distilled and freeze-thaw degassed before use. NMR solvents were refluxed over potassium and were vacuum distilled into greaseless Schlenk tubes and stored under argon. NMR spectra were recorded on a Bruker AMX-500 or DPX-300 instrument and were referenced to the resid-ual ^{1}H resonances of the solvent or to external 85% H$_3$PO$_4$ (δ = 0.00, ^{31}P{^{1}H} NMR). EI mass spectra were recorded on a VG Autospec instrument at 70 eV. Microanalyses were conducted by Labor Pascher, Remagen, Germany or by the Canadian Microanalytical Services Ltd. The anhydrous metal iodides UI$_3$, YI$_3$ and TmI$_3$ were prepared according to the general method described by Corbett [39], in which the metal (in the form of turnings) is heated with an excess of HgI$_2$ in a sealed tube at ca 320 °C.

3.2. Synthesis of uranium triiodide

Uranium turnings were treated with concentrated nitric acid then washed with de-ionised water to give them a silver metallic finish. The turnings were then washed with methanol followed by acetone and dried *in vacuo*. A thick-walled ampoule with two con-striction points was then charged with the dry uranium turnings (2.28 g, 9.58 × 10^{-3} mol) and HgI$_2$ (8.71 g, 19.16 × 10^{-3} mol). The ampoule was then evacuated to 10^{-6} mbar, sealed under vacuum at the first constriction point and fully immersed vertically in a tube furnace at 315 °C for 3 days. The furnace was then placed in a hor-izontal position with the empty end of the ampoule protruding from the furnace to allow Hg and unreacted HgI$_2$ to condense and sublime out, respectively. This was left for a further 2 days at 315 °C. The sealed tube was taken into the glove box and snapped

at the constriction; the UI_3 was collected and ground up with a mortar and pestle. The purple powder was transferred to a tantalum boat, which was placed in a sublimation tube. The tube was evacuated to 10^{-6} mbar and heated in a furnace to 200 °C for 2 h, 300 °C for 1 h and 400 °C for 30 min to remove any remaining Hg and HgI_2. The purple solid in the tantalum boat was then collected and stored under dinitrogen in the glovebox (5.63 g, 9.09 mmol, 95% yield). YI_3 and TmI_3 were prepared in a similar fashion.

3.3. Synthesis of $[Sc(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ (1)

ScI_3 (0.254 g, 0.597 mmol) and $KP_3C_2Bu^t$ (0.5 g, 1.85 mmol) were placed in an ampoule and toluene (40 mL) was added. The ampoule was evacuated, the mixture sonicated for ten minutes and then heated at 110 °C for 40 h during which time a deep red color developed. The reaction mixture was filtered to remove salts and the solvent removed in vacuo to afford the crude product as a red solid. This was recrystallised at −40 °C from hexane yielding pure $[Sc(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ as a dark red crystalline solid (0.240 g, 54 %). ^{1}H (300 MHz; C_7D_8): δ 1.67 (s, 54H, Bu^t). $^{31}P\{^1H\}$ (121 MHz; C_7D_8): δ 296.2 (m, C**P**C), 265.0 (m, C**PP**C); both multiplets are complex, see Section 2 for analysis of the couplings and a spectral simulation. MS (70 eV, EI) m/z (%): 738 (35) $[M]^+$, 681 (21) $[M−Bu^t]^+$, 57 (100) $[Bu^t]^+$. Anal. Calc. for $C_{30}H_{54}P_9Sc$ (738.4): C, 48.79; H, 7.37. Found: C, 48.54; H, 7.21%. Single crystals suitable for X-ray analysis were grown from a slowly cooled (to −40 °C) hexane solution.

3.4. Synthesis of $[Y(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ (2)

YI_3 (1 mmol) and $KP_3C_2Bu^t$ (3 mmol) were placed in an ampoule and toluene (50 mL) was added. The ampoule was evacuated and the mixture heated at 110 °C for 48 h during which time a deep red color formed. The reaction mixture was filtered to remove salts and the filtrate evaporated in vacuo to afford the crude product as a dark red solid. This was recrystallised from hexane at −85 °C to afford pure $[Y(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ as a dark red crystalline solid (0.220 g, 28%). $^{31}P\{^1H\}$ (343 K, 121 MHz, C_6D_6) δ 291.4 (m, C**P**C), 264.9 (d, $^2J_{PP}$= 49.3 Hz, C**PP**C). MS (70 eV, EI) m/z (%) 782 (12) $[M]^+$, 552 (100) $[M−P_3C_2Bu^t_2]^+$. Anal. Calc. for $C_{30}H_{54}P_9Y$ (782): C, 46.05; H, 6.96. Found: C, 46.32; H, 6.96%. Single crystals suitable for X-ray analysis were grown from a slowly cooled (to −40 °C) pentane solution.

3.5. Synthesis of $[Tm(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ (3)

TmI_3 (0.328 g, 0.598 mmol) and $KP_3C_2Bu^t_2$ (0.5 g, 1.85 mmol) were placed in an ampoule and mesitylene (30 mL) was added. The ampoule was evacuated, the mixture sonicated for 10 min and then heated at 160 °C for 48 h during which time an orange color developed. The mixture was then filtered to remove salts and the filtrate evaporated in vacuo to yield the crude product as a dark orange solid. This was recrystallised from hexane at −40 °C to afford pure $[Tm(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ as an orange crystalline solid (0.110 g, 21%). MS (70 eV, EI) m/z (%): 862 (12) $[M]^+$, 631 (100) $[M−P_3C_2Bu^t_2]^+$. Anal. Calc. for $C_{30}H_{54}P_9Tm$ (862): C, 41.80; H, 6.31. Found: C, 41.09; H, 6.93%.

In a slightly modified procedure, a mixture of the solids TmI_3 and $KP_3C_2{}^tBu_2$ was placed in an ampoule, toluene was added and, after brief sonication to break up the solids, the mixture heated to 110 °C for 72 h. Filtration followed by recrystallisation from hexane at −45 °C yielded (3) in 20% yield.

3.6. Synthesis of $[U(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ (4)

UI_3 (0.764 g, 1.2 mmol) and $KP_3C_2Bu^t_2$ (1.0 g, 3.7 mmol) were stirred in toluene (60 mL) in an ampoule. The ampoule was evacu-

ated and the mixture heated to 110 °C for 48 h during which time it became a dark brown color. The reaction mixture was filtered to remove salts and the filtrate evaporated in vacuo to afford a brown solid. Sublimation at 220 °C (10^{-6} mm Hg) afforded pure $[U(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ as a dark brown crystalline solid (0.420 g, 36%). Alternatively the crude product could be purified by recrystallisation from pentane at −40 °C. ^{1}H (300 MHz, C_6D_6) δ −8.54 (s, 54H, Bu^t). $^{31}P\{^1H\}$ (121 MHz; C_6D_6): δ 691.5 (broad, $W_{1/2} \approx$ 200 Hz). MS (70 eV, EI) m/z (%): 931 (27) $[M]^+$, 700 (100) $[M−P_3C_2Bu^t_2]^+$. Anal. Calc. for $C_{30}H_{54}P_9U$ (931.5): C, 38.68; H, 5.84. Found: C, 38.69; H, 5.72%. Single crystals suitable for X-ray analysis were grown from a slowly cooled (to −40 °C) pentane solution.

3.7. Structure determinations

X-ray quality crystals of all complexes were grown from slowly cooled saturated hexane or pentane solutions. Reflection data were measured on a Kappa CCD area detector at 172(3) K using Mo Kα radiation (λ = 0.71073 Å). The structure of the yttrium complex is disordered 0.96:0.04 about a mirror plane perpendicular to the coordination plane going through Y and P(6). Only the P atoms of the lower occupancy orientation were located and were refined with a common isotropic thermal parameter. One t-butyl group of the major orientation was disordered in a 50:50 ratio. Non-H atoms were anisotropic, except for the disordered t-butyl group and the alternative P atom sites. H's were included in riding mode with U_{iso}(H) equal to $1.5U_{eq}$(C). In the thulium complex there is a very low occupancy (0.02) alternative mirror image ligand arrangement, sharing a common P(4) site, for which only the P atom sites could be located. The C(8), C(9) and C(10) carbon atoms of the methyl group were disordered equally over two sets of positions which were refined isotropic and with distance constraints.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.03.030.

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