f-Block Phosphoryl and Arsyl Chemistry

David P. Mills* and Peter Evans[a]
1. Introduction

The f-block elements, the lanthanides (Ln) and actinides (An), exhibit remarkable physicochemical properties that have spurred numerous curiosity-driven investigations and technological applications.\(^1\) Organometallic f-block chemistry is predominated by cyclopentadienyl ligands (Cp, C\(_5\)H\(_5\)) and their derivatives (Cp\(^n\), C\(_n\)R\(_n\)), where one or more of the ring H atoms are substituted by a wide variety of alkyl, aryl or heteroatomic R groups; much of their success owes to: (i) straightforward ligand synthesis and installation at metals by well-developed and robust synthetic routes; (ii) occupation of the equivalent of three coordination sites at large f-block ions in their most common η\(^2\)-binding mode; and, (iii) facile tuning of ligand steric and electronic properties by R group variation to provide additional kinetic and thermodynamic stabilisation and fine-control of metal coordination spheres and redox chemistry.\(^3\) Cp and C\(_5\)R\(_n\) ligands have supported seminal examples of f-block chemistry in both a spectator ligand role and in controlling the physicochemical properties, including rare examples of f-block-metal (loid) bonds;\(^5\) and terminal unsupported multiple bonds between f-block and p-block elements;\(^6\) rich single-electron transfer (SET) chemistry;\(^7\) the discovery of hitherto unknown \(\pm 2\) oxidation states in solution for a wide range of Ln and An;\(^8\) and Ln single-molecule magnets (SMMs) with high blocking temperatures.\(^9\)

Given the huge influence of substituents in f-block Cp\(_5\) chemistry, the comparative dearth of examples of isoelectronic heterocyclopentadienyl f-block complexes, where one or more of the ring C atoms is substituted by other p-block atoms, is noteworthy.\(^8\) Of these related ligand families, phospholyls (C\(_5\)R\(_n\)-P\(_n\)) and arsnyl (C\(_5\)R\(_n\)-As\(_n\)) have proved popular, with the lighter congeners more widely investigated, and their group 3 and f-block metal chemistry was reviewed several times between 1998 and 2006.\(^3,8,9\) The relatively restricted development of f-block phospholyl and arsnyl chemistry compared with that of Cp and C\(_5\)R\(_n\) analogues is mirrored in the s-, p- and d-blocks.\(^5,8,9\) The reasons for this disparity are the same as for other heterocyclopentadienyls: the well-documented benefits of Cp and C\(_5\)R\(_n\) ligands summarised above, together with their widespread renown, make them natural primary choices for chemists in exploratory synthesis fields.\(^2\) However, for more nuanced and specific applications, the introduction of ring heteroatoms can provide electronic fine-tuning to maximise physicochemical properties, providing rich and diverse chemistry.\(^8\)

The relative popularity of phospholyls and arsnyls in f-block chemistry compared with other heterocyclopentadienyls can be attributed to both pragmatic (i–ii) and ligand design (iii–vi) considerations: (i) synthetic routes to monophospholyls and -arsnyls are mature and are relatively straightforward; (ii) \(1\)P nuclei are \(J = 1/2\) with \(100\%\) natural abundance (\(^3\)As \(J = 3/2\), \(100\%\) abundant), providing a useful NMR/EPR spectroscopic handle; (iii) phospholyl and arsnyl ligands are relatively soft compared with C\(_5\)R\(_n\) analogues and are thus well-suited for stabilising low oxidation state f-block ions; (iv) phospholyls and arsnyls are able to bind in a η\(^1\)-fashion through their P/As lone pairs but are more likely to exhibit an η\(^2\)-binding mode than lighter congeners with harder heteroatom donor atoms, for example, pyrrolyl (C\(_5\)R\(_2\)N) and pyrazolyl/imidazolyl (C\(_5\)R\(_2\)N\(_2\)), thus they more effectively mimic Cp\(^5\) ligands in occupying a large proportion of metal coordination spheres; (v) the P and As lone pairs provide a range of alternative binding modes over Cp\(^5\); for example, for monophospholyls \(\pi\)-\(\pi^*\), \(\pi\)-\(\pi^*\) and \(\mu\)-\(\pi\)-\(\pi^*\), binding modes increase the likelihood of formation of multinuclear complexes; and, (vi) phospholyls and arsnyls are poorer \(\pi\)-donors and stronger \(\pi\)-acceptors than analogous C\(_5\)R\(_n\) ligands, influencing metal reduction potentials and redox chemistry. Since the first rare earth phospholyl complexes were reported by Nieff and Mathey in 1989,\(^10\) \(< 100\) monophospholyl, monoarsnyl and polyphospholyl complexes of the group 3 metals, Ln and An (including benzannulated derivatives) have been structurally authenticated to date; this contrasts starkly with the corresponding Cp/Cp\(_5\) chemistry, where the first reported examples were by Birmingham and Wilkinson in 1954\(^11\) and there are now thousands of structurally characterised complexes.\(^12\) As noted above, various books and reviews have cov-
In the last 15 years, there have been significant discoveries that we believe now warrant a review solely dedicated to this topic. Here, we will firstly present an overview of the ligand design criteria and binding modes of phospholyls and arsols, followed by general synthetic routes to these ligands and metal complexes; we focus on selected examples for brevity as this material is covered in detail elsewhere. We then review all structurally authenticated group 3 and f-block metal phospholyl and arsyl chemistry prior to 2006 as part of wider subject areas. The phospholyl and arsyl ligands that have been employed in f-block chemistry to date are compiled in Figures 1 and 2; acronyms are provided for monophospholyls and -arsols, whereas polyphospholyls are labelled A–D. Monophospholyl and -arsyl ligands are variously substituted at the 2-, 3-, 4-,
| Complex | Molecular formula | Range M–P/As [Å] | $\delta_2$ [ppm] | Reference |
|---------|------------------|------------------|----------------|-----------|
| 19 | [Sm(1-Tmp)(OTf)] | 2.951(2)–3.026(2) | – | [30] |
| 20 | [Sm(Cp*)] | 3.153(1) | – | [31] |
| 21 | [Sm(Cp*)] | 3.265(1)–2.891(1) | – | [31] |
| 22-P | [Sm(Cp*)] | 2.886(1)–3.103(2) | – | [31] |
| 22-As | [Sm(Cp*)] | 2.9776(8)–3.1610(6) | – | [31] |
| 23 | [Sm(Cp*)] | 3.101(2)–3.274(1) | – | [31] |
| 24 | [Sm(Dsp)] | 2.948(4) | 148 | [25] |
| 25 | [Tm(1-Dtp)] | 2.869(1) | – | [25] |
| 26 | [Tm(1-Dtp)] | 2.875(7) | – | [25] |
| 27 | [Tm(1-Tmp)] | 2.889(5)–2.937(5) | 43.24, 46.75 | [28] |
| 28 | [Tm(1-Dtp)] | 2.825(2)–2.862(2) | – | [32] |
| 29 | [Tm(1-Dtp)] | 2.843(2)–2.844(2) | – | [32] |
| 30 | [Tm(1-Dtp)] | 2.841(2) | – | [32] |
| 31 | [Tm(1-Dtp)] | 2.813(5)–2.872(7) | – | [33] |
| 32 | [Sm(1-Tmp)] | 2.924(4)–2.953(3) | – | [34] |
| 33 | [Sm(1-Mhp)] | 2.9270(5)–2.9978(5) | 9.3 [h] | [34] |
| 34 | [Sm(1-Tmp)] | 2.905(2)–2.926(1) | 48.7 | [35] |
| 35 | [Sc(1-Tmp)] | 2.694(2)–2.718(2) | 99.8 | [36] |
| 36 | [Sc(1-Dtp)] | 2.6960(5) | 123.0 | [37] |
| 37-Dy | [Dy(1-Dtp)] | 2.9235(2) | – | [38] |
| 37-Tm | [Tm(1-Dtp)] | 2.8119(2)–2.8167(12) | – | [27] |
| 38 | [Tm(1-Htp)] | 2.906(2)–2.950(4) | – | [27] |
| 39 | [Dy(1-Dtp)] | 2.8500(7)–2.869(0) | – | [38] |
| 40 | [Sm(1-Dtp)] | 2.911(14) | 77.5 | [37] |
| 41 | [Dy(1-Dtp)] | 2.7880(8)–2.7981(8) | – | [39] |
| 42 | [K(18-crown-6)TFH][Nd(1-Tmp)] | 2.982(3)–2.995(3) | – | [41] |
| 43-La | [La(1-Htp)] | 3.089(5)–3.138(3) | 105.65 | [42] |
| 43-Sc | [Ce(1-Htp)] | 3.058(5)–3.099(4) | – | [42] |
| 43-Ne | [Nd(1-Htp)] | 3.019(1)–3.077(6) | – | [42] |
| 43-Sm | [Sm(1-Htp)] | 3.016(6)–3.054(4) | – | [42] |
| 44-La | [La(1-Htp)] | 3.1790(7)–3.1869(7) | 96.49 | [42] |
| 44-Sc | [Ce(1-Htp)] | 3.1456(13)–3.1533(14) | – | [42] |
| 45 | [Ce(1-Htp)] | 3.1488(13)–3.1682(12) | – | [42] |
| 46 | [Sc(1-Tmp)] | 3.071(2) | 119.2 | [36] |
| 47-Sc | [Sc(1-Dtp)] | 3.267(1) | 99.0 | [37] |
| 47-Y | [Y(1-Dtp)] | 3.298(1) | 88.9 | [37] |
| 47-Sm | [Sm(1-Dtp)] | 3.299(1)–3.176(1) | 62.9 | [37] |
| 48 | [La(1-mu1-Tmp)] | 3.0604(3)–3.1962(3) | 128.4 | [43] |
| 49 | [Nd(1-Tmp)] | 2.9252(1) | 444.0 | [43] |
| 50 | [Nd(1-Dsp)] | 2.897(3) | 484.1 | [43] |
| 51 | [Nd(1-Tmp)] | 2.9652(6) | 544 | [44] |
| 52 | [Nd(COT)] | 2.968(8) | – | [46] |
| 53 | [Nd(COT)] | 3.019(4) | – | [47] |
| 54-Y | [Y(COT)] | 2.8261(6) | 157.96 | [48] |
| 54-Tb | [Tb(COT)] | 2.8475(12) | – | [48] |
| 54-Dy | [Dy(COT)] | 2.8577(13) | – | [48] |
| 54-Er | [Er(COT)] | 2.7929(11) | – | [48] |
| 54-Tm | [Tm(COT)] | 2.7823(12) | – | [48] |

### 6.1. Ln$^{n}$ monophospholyl and -arsolyl complexes

| 55 | [U(1-Tmp)] | 2.945(3)–2.996(3) | 727, 3471 | [51] |
| 56-P | [UCl$_2$(SiPr$_2$)$_3$]$^{1,4}$ | 2.776(15)–2.9868(14) | 846.2 | [52] |
| 56-As | [UCl$_2$(SiPr$_2$)$_3$]$^{1,4}$ | 3.0781(7) | – | [52] |

### 6.2. An$^{n}$ monophospholyl complexes

| 57 | [U(1-Tmp)] | 2.905(1) | 960 | [49] |
| 58 | [U(1-Tmp)] | 2.927(4) | – | [53] |
| 59 | [U(1-Tmp)] | 2.926(4) | – | [54] |
| 60 | [U(1-Tmp)] | 2.970(8) | – | [55] |
| 61 | [UCl$_2$(SiPr$_2$)$_3$]$^{1,4}$ | 2.823(7)–2.862(7) | 199.2 | [56] |
| 62 | [UCl$_2$(SiPr$_2$)$_3$]$^{1,4}$ | 2.851(9)–2.861(6) | – | [56] |
or all four C-positions of the \( C_4 \) \( E = P, \text{As} \) rings, apart from the parent phospholyl \( C_2 \text{H}_2 \) \( P \), Hhp. Substituents include \( R = \text{Me}, \text{tBu}, \text{SiMe}_3 \), and \( \text{Ph} \), and benzannulated derivatives; the currently available selection and ring positions are intrinsically linked to the common synthetic routes to these ligands, as can be deduced from only \( \text{tBu} \) substituents being seen in the polyphospholys \( A-C \) (see Section 3). As stated previously, the introduction of \( P \) or \( \text{As} \) into carbycyclic rings influences both the strength of metal–ligand binding and the resultant redox properties of complexes.\[^{[3a,8]}\] As with \( \text{Cp}^8 \) chemistry,\[^{[2]}\] the substituents affect complex solubility and both the thermodynamic and kinetic stability of \( F \)-block complexes; the electron density of the rings is also influenced by donating (Me, \( \text{tBu} \)) and withdrawing (\( \text{SiMe}_3, \text{Ph} \), fused carbycyclic rings) \( R \) groups. Ligands with the largest \( R \) groups tend to give the most kinetically stable complexes, which are less likely to oligomerise owing to a combination of steric bulk around the metal coordination sphere and buttressing of the heteroatom lone pairs.

The most common binding modes of mono- and polyphospholys are compiled in Figure 3, with analogous hapticities seen for monoarsolys. The introduction of heteroatoms with lone pairs increases the flexibility of ligand coordination over the most common \( \eta^1, \eta^2 \), and \( \eta^1 \)-binding of \( \text{Cp}^8 \) ligands, where bridging modes are rare for the \( F \)-block.\[^{[2]}\] As stated previously, the \( \eta^1 \)-binding mode is the most common binding mode for phospholys and arsolys with \( F \)-block elements as \( P \) and \( \text{As} \) atoms are relatively soft. Substituents, available space at metal coordination spheres and ancillary ligands are all contributory factors as to whether or not the heteroatom lone pairs form dative bonds with \( F \)-block ions.\[^{[3a,8]}\] Although this review focuses on binding modes observed in solid-state structures, it must be appreciated that dynamic fluxional behaviour in solution is common, and the presence of \( ^{31}P \) or \( ^{75} \text{As} \) nuclei can provide an additional useful handle to study this behaviour by NMR or EPR spectroscopy.

![Table 1](image)

| Complex | Molecular formula | Range \( \text{M}–\text{P/As} \) (Å) | \( \delta_\text{p} \) [ppm] | Reference |
|---------|------------------|----------------|-----------|-----------|
| 63      | \([\text{Sc}(\eta^1\text{CtBuP}_3)_]_{[\mu\eta^1\eta^2\text{CtBuP}_3]}\] | 2.802(2)–2.877(2) | – | \[^{[57]}\] |
| 64-E    | \([\text{Sm}(\text{Cp}^8)_2]_{[\eta^1\text{CtBuP}_3]}_{[\text{THF}]}\) (\( E = \text{P, Sb} \)) | 3.135(2)–3.164(2) | – | \[^{[62]}\] |
| 65-E    | \([\text{Lu}(\text{THF})_2]_{[\eta^1\text{CtBuP}_3]}_{[\eta^1\text{CtBuP}_3]}\) (\( E = \text{P, Sb} \)) | 3.09(2) \[^{[62]}\] | – | \[^{[62]}\] |
| 66-Sc   | \([\text{Sc}(\eta^1\text{CtBuP}_3)]_{[\eta^1\text{CtBuP}_3]}\] | 2.762(3)–2.813(3) | 265.0, 296.5 | \[^{[63]}\] |
| 66-Y    | \([\text{Y}(\eta^1\text{CtBuP}_3)]_{[\eta^1\text{CtBuP}_3]}\] | 2.884(2)–3.059(3) | 263.9, 289.9 | \[^{[64]}\] |
| 66-Tm   | \([\text{Tm}(\eta^1\text{CtBuP}_3)]_{[\eta^1\text{CtBuP}_3]}\] | 2.853(2)–3.052(3) | – | \[^{[64]}\] |
| 66-U    | \([\text{U}(\eta^1\text{CtBuP}_3)]_{[\eta^1\text{CtBuP}_3]}\] | 2.968(2)–3.114(2) | 691.5 | \[^{[64]}\] |
| 67      | \([\text{Sc}(\eta^1\text{CtBuP}_3)_{[\mu\eta^1\eta^2\text{CtBuP}_3]}_{[\text{Sc}(\eta^1\text{CtBuP}_3)]}\] | 2.5627(14)–2.942(2) | – | \[^{[64]}\] |
| 68      | \([\text{Eu}(\text{diglyme})_{[\mu\text{CCPh}]}_{[\text{CtBuP}_3]}\] | – | – | \[^{[65]}\] |

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![Figure 1](image)

**Figure 1.** Monophospholyl and arsyl ligands in \( F \)-block chemistry, with acronyms used in this review that are commonplace in the literature.

![Figure 2](image)

**Figure 2.** Polyphospholyl ligands in \( F \)-block chemistry, labelled A–D.

![Figure 3](image)

**Figure 3.** Common binding modes (i–viii) of mono- and polyphospholyl ligands, shown for unsubstituted rings, where \( M = \) metal and \( E = \) P, As or Sb; arsyl binding modes are analogous.
3. Synthetic Routes to Phospholyls and Arsolyls

Monophospholyl and -arsolyl pro-ligands are typically prepared from the corresponding alkyne starting materials (R’CR=CR’’3) by the synthetic routes outlined in Scheme 1, or by variations of these methods. Alkynes are first reductively coupled with a zirconocene species “ZrCp2” to generate the corresponding metallacycles [Zr(Cp)2(η5-CH2CHC(=C)-2,5-R’2-R’’2-3,4)] in which the less sterically demanding ammetal species are selectively placed in the positions (R’’2 > R’2 with respect to steric bulk). The zirconocene species is typically generated in situ, historically from Negishi’s reagent “[Zr(Cp)2(η5-CH2CHC(=C)-2,5-R’2-R’’2-3,4)]”; however, Rosenthal’s reagent [Zr(Cp)2(η5-2,5-Me2SiCCSiMe3)(py)] (py = pyridine) offers multiple advantages over species generated in situ, such as: significantly greater thermal stability in the solid state, solubility in non-donor solvents and generally provides higher yields of the targeted metallacycle. Alternatively, low oxidation state titanium reagents, such as Ti(O-iPr)4(η5-propene), may be used as reductive coupling reagents but these tend to exhibit lower functional group tolerances than zirconocene-based reagents.

The zirconium metallacycles [Zr(Cp)2(η5-2,5-R’2-R’’2-3,4)] are treated with diiodine to liberate [Zr(Cp)2(0)] and the respective 1,4-diiodobutadienes. Following work-up and recrystallisation, the dienes are then subjected to ammetal-halogen exchange reaction with nBuLi, and the dilithio salt generated in situ is treated with ClEX (E = P, As; X = Cl, Ph) to yield the respective cyclic phenyl- or chloro-substituted phosphate or arsole EX[CE(=C)(η5-2,5-R’2-R’’2-3,4)] by a salt metathesis reaction. In some cases, these heterocycles may be prepared more directly by an η5-bond metathesis reaction of the zirconium metallacycles [Zr(Cp)2(η5-2,5-R’2-R’’2-3,4)] with parent ECl (E = P, As). The P/As-η5 bond in the substituted phosphorus or arsole is cleaved with at least two equivalents of an alkali metal to generate the corresponding alkali metal monophospholyl or -arsolyl salts [M(E(=C)2-R’2-R’’2-3,4)] (M = Li, Na, K), which are used as ligand transfer reagents to generate f-element complexes.

Owing to the synthetic ease of functionalising alkynes, the relatively low cost of starting materials, and the high functional group tolerance of the alkyne coupling reactions, a diverse range of monophospholyl and -arsolyl ligands can be readily obtained and have been installed at f-block metals (Figure 1). There are significantly fewer reported examples of f-block complexes featuring polyphospholyl ligands A-D (Figure 2). This can be attributed to A–C being prepared by multistep syntheses with hazardous reagents such as P(SiMe3)3 and tBuCP (e.g., Scheme 2). The synthesis of P(SiMe3)3 from red phosphorus, sodium and Me3SiCl can be disconcerting, and this is prohibitively expensive to purchase in bulk; removing the reliance on tBuCP could thus facilitate the rapid development of polyphospholyl chemistry. The cyclo-P3 ring (D) is typically assembled directly at the metal from white phosphorus, which also presents significant hazards.

4. Synthetic Routes to Complexes

A number of synthetic strategies have been developed for the synthesis of f-block phospholyl, arsole and polyphospholyl complexes, with the route depending upon the nature of both the metal and ligand employed, as well as the metal oxidation state. The four most common strategies to monophospholyls and -arsolyls and practical considerations will be briefly outlined in this section, in decreasing order of their frequency of application; examples will be provided throughout Sections 5–6. Various synthetic routes to f-block polyphospholyl complexes will be discussed separately with dedicated schemes in Section 7.

4.1. Salt metathesis

Salt metathesis reactions between Ln and An halides or pseudo-halides with alkali metal ligand transfer agents are by far the most common route for synthesising f-block phospholyl and arsole complexes. This is typically due to the commercial availability and facile synthetic routes to anhydrous and donor-olvent coordinated trihalides for all the Ln (with
the exception of PrM(X)₃, which can be used to prepare pseudo-
halide complexes, for example, Ln(BH₄)₃(THF)₃ and Ln(AlMe₃)₃; some Ln diiodides are also readily available (Sm, Eu, Tm and Yb here; although DyI₃ and NdI₃ are known, they have not been utilised successfully in Ln³⁺ phospholyl chemistry to date). Conversely, the two An with lowest radiological hazard and highest natural abundancies, thorium and uranium, have well-developed synthetic routes to readily solvated halide (e.g., AnCl₃, Ul₃) and pseudo-halide (e.g., U(BH₄)₃, n = 3, 4) precursors from nitrate (Th), and oxide and metallic (U) starting materials. Most f-block halide and borohydride precursors can be converted to donor solvent adducts, typically THF or DME, to endow improved solubility, which facilitates their salt metathesis reactions, but the presence of these solvents can also lead to unwanted side-products, for example, dipyrotonation and ring-opening reactions of THF.

The choice of ligand transfer reagent and reaction solvent are crucial for determining the composition of products because of the highly electropositive nature of the f-block elements. In the majority of cases where lithium phospholyls are used as transfer reagents salt-occluded complexes tend to form, where Li is trapped in the coordination sphere through contacts with several Ln-/An-bound halides. A combination of Ln or An di-/tri-iodides and sodium or potassium transfer reagents often yields discrete f-block complexes by assisting the precipitation of alkali metal iodide by-products; potassium iodide is only sparingly soluble in THF and is therefore a desirable by-product. Although the occlusion of such salts is suppressed with these reagents, a handful of potassium ‘ate’ f-block phospholyl complexes have been isolated and are included in this review. The high affinity of f-block ions for binding ethereal solvents can make it challenging to synthesise donor solvent-free phospholyl and arseryl complexes as diethyl ether or THF are typically used as the reaction solvents for solubility reasons. Whilst some metal-bound solvent molecules can be removed from f-block complexes upon exposure to vacuum, the elevated temperatures often required to facilitate the dissociation of strongly bound N- and O-donor solvents can be greater than the temperature of complex decomposition. As a consequence, some solvent-free f-block phospholyl and arseryl complexes are synthesised by reacting binary Ln or An halides with sodium or potassium ligand transfer agents in toluene at reflux for extended periods to circumvent the low solubility of the reactants in aromatic solvents. These reactions are moderate- to high-yielding and have facilitated numerous studies of the resultant rare earth phospholyl complexes.

4.2. Redox transmetallation

Whilst salt metathesis is often the most convenient synthetic strategy for preparing f-block phospholyl and arseryl complexes, several alternative approaches have been developed, which in some cases can be more suitable. Redox transmetallation reactions using ligand transfer reagents of readily reducible metal ions such as Tl and Pb have proved useful for concomitant ligand installation and f-block metal ion oxidation, in cases where the Ln or An ions have suitable redox potentials, for example, Sm³⁺ and U⁴⁺.

4.3. Bond insertion

Biphospholes and biarsoles containing E–E bonds, and phospholes and arsoles containing E–X bonds (e.g., X = halide, Ph), may react directly with metallic Ln and An by a formal bond insertion with metal oxidation and ligand reduction. This has proved most useful to date for Ln³⁺ phospholyl and arsaryl chemistry for Sm and Yb.

4.4. Redox

As phospholyl and arsyl ligands have proven utility for stabilising metals in low oxidation states it is unsurprising that when these ligands have been installed on f-block metals in intermediate oxidation states, the resultant complexes can often be straightforwardly oxidised or reduced, for example, Ln⁴⁺ to Ln³⁺ or U⁴⁺ to U³⁺, and vice versa.

5. Lanthanide Monophospholyl and -arsoly Complexes

5.1. Ln³⁺ complexes

In 1991, Nief and Mathey communicated the synthesis of the first Ln³⁺ phospholyl complexes [Ln(Tmp)₂(THF)]₃ (Ln = Sm, Yb), by the salt metathesis reactions of the respective LnI₂, precursor with two equivalents of K(Tmp), or the oxidative insertion reactions ofLn powders with the parent biphosphole. In a full paper published two years later, the corresponding bis(arsoyl) analogues [Ln(Tmas)₂(THF)]₃ (Ln = Sm, Yb) were reported to form by analogous methods, and the related Ln³⁺ complexes [Ln(n⁻⁵-Dpp)₂(THF)]₃ (Ln = Sm; Yb, 1) were prepared by adapted procedures where a trace amount of HgCl₂ was added to promote the reactions of Ln powders with a phenyl-functionalised biphosphole (Scheme 3). The Dpp-substituted complexes did not appear to desolate upon exposure to vacuum, but the Tmp- and Tmas-substituted complexes were found to rapidly lose THF in vacuo to give donor solvent-free variants; this provides a juxtaposition to the sluggish removal of THF from [Sm(Cp*)₂(THF)]₂ (Cp* = C₅Me₅) under dynamic vacuum. [Ln(Tmp)₂(THF)]₃, [Ln(Tmas)₂(THF)]₃ and [Ln(n⁻⁵-Dpp)₂(THF)]₃ were variously characterised by microanalysis and H and ¹³C NMR spectroscopy in THF, with some derivatives additionally probed by ³¹P NMR spectroscopy (δ₃¹P: [Ln(Tmp)₂(THF)]₃).
The solid-state structure of Sm(THF)\(_3\) (2) or oxidative insertion (3) strategies in THF in 1994.[20] A broad signal was observed at −694 ppm in the \(^{31}\)P NMR spectrum of 2, and a combination of variable-temperature NMR experiments indicated \(\eta^1\)-binding of Bdmp ligands in THF solution. This arrangement of ligands was confirmed in the solid state by single-crystal XRD, with the structure of 2 analogous to that of 1,[18] but with a longer Ln–P distance (3.0775(1) Å)[20] owing to Sm being larger than Yb.[14] The Sm–P distance of 3 is even longer at 3.1908(6) Å, owing to the mutually trans-Bdp ligands adopting \(\eta^1\)-binding modes, which allow for the coordination of two additional THF molecules, leading to a distorted octahedral geometry. The authors attributed the alternative \(\eta^1\)-cooordination of the Bdp ligands in 3 to the bis-benzanulated system having reduced aromaticity about the phospholyl ring, by analysis of the degree of pyramidalisation of the P atom and intra-ring distances.

Also in 1994, Nief and Ricard reported the syntheses of the heteroleptic dinuclear Yb\(^3\) complexes \([\text{Yb}(\eta^1\text{-Tmp})_2(\eta^1\text{-Cl})(\text{THF})_2]_2\) (4) and \([\text{Yb}(\eta^1\text{-Tmp})(\mu\text{-Cl})(\eta^1\text{-Cl})(\text{THF})_2]_2\) (5) (Figure 5) by the oxidative insertion reactions of Yb powder with the respective reagent XPCMe\(_2\) (X = Cl or SPh) in THF with a trace amount of HgCl\(_2\). Complex 4 could also be prepared by the ligand scrambling reaction of \([\text{Yb}(\text{Tmp})(\text{THF})_2]_2\) with YbCl\(_3\) in THF; the salt elimination reaction of 4 with two equivalents of NaSPh in THF also gave 5.[21] Complexes 4 and 5 exhibit similar geometries in the solid state, with half-sandwich motifs at Yb with \(\eta^1\)-Tmp ligands (Yb–P: 2.911(1) Å for 4; 2.931(4) Å for 5), Yb–X, and each Yb coordination sphere completed by two bound THF molecules. The \(^{31}\)P NMR spectra of 4 (81.4 ppm) and 5 (82.5 ppm) each exhibited one signal, with no \(J_{\text{pp}}\) coupling constants reported.

Nief reported the synthesis of the benzannulated Sm\(^3\) phospholyl complexes \([\text{Sm}(\eta^1\text{-Bdp})(\text{THF})_2]_2\) (2) and \([\text{Sm}(\eta^1\text{-Bdp})(\text{THF})_2]_2\) (3; Figure 4) by salt metathesis from Sml\(_2\)(THF)\(_3\) (2) or oxidative insertion (3) strategies in THF in 1994.[20] A broad signal was observed at −694 ppm in the \(^{31}\)P NMR spectrum of 2, and a combination of variable-temperature NMR experiments indicated \(\eta^1\)-binding of Bdmp ligands in THF solution. This arrangement of ligands was confirmed in the solid state by single-crystal X-ray crystallography, showing a bent metalloocene-type geometry with staggered \(\eta^1\)-Tmp rings (Yb–P: 2.959(1) Å and 2.986(1) Å) and mutually cis-THF molecules; the phenyl groups of the Dpp ligands of 1 are co-planar with the phospholyl rings.[18]

Figure 4. Complexes 2 and 3.[22]
ing low oxidation state metals, whilst the incorporation of bulkier substituents in the α-positions in Dtp, Dsp and Dsas compared with Tmp provides additional kinetic stabilisation; however, 7 and 8 slowly decompose at room temperature under argon.[25] The solid-state structures of 7 and 8 were obtained, with both complexes adopting similar pseudo-bent metallocene geometries in the solid state with two η¹-Dtp/DSas ligands and a single THF molecule coordinated to the thulium centre; as expected the Tm–P distances of 7 (2.943(1) and 2.967(1) Å) are overall shorter than the Tm–As distances of 8 (2.968(1) and 2.9759(8) Å). The Tm⁴⁺ phospholyl complexes in this paper were also characterised by ¹¹B NMR spectroscopy (δ₈: –338.33 for L = Dtp, 7, and –265.75 ppm for L = Dsp).

In 2003, Nief and co-workers reported the synthesis of donor solvent-free [Sm(η¹-Dtp)(μ:η¹,η¹-Dtp)]₉, [Sm(η¹-Dsp)(μ:η¹,η¹-Dsp)]₁₀ and [Sm(η¹-Dtp)]₁₁ (Figure 6), and solvated [Sm(Dsp₂)(OEt)₂], by performing salt metathesis reactions in diethyl ether using the parent Ln₃ and two equivalents of K(Dtp) or K(Dsp).[26] The coordinated diethyl ether was easily removed under vacuum in all cases apart from [Sm(Dsp₂)(OEt)₂], as this solvent does not bind as strongly as THF. A combination of ligand effects and the size of the Ln³ centre influences both the tendency of the complexes to desolvate and whether or not oligomerisation occurs. In the solid state, 9 and 10 exhibit dinuclear structures with two η¹- and two μ:η¹,η¹-bound ligands owing to their relatively large Sm³ centres, with the longest Sm–P distances arising from the η¹-bound P atoms (Sm–P: 3.045(1), 3.148(1) and 3.197(1) Å for 9; and 3.023(1), 3.113(1) and 3.168(1) Å for 10). In contrast with the bent metallocene THF adduct 7,[23] complex 11 adopts a near-linear geometry (DtpC₀-DspC₀-DtpC₀: 170°), exhibiting almost eclipsed C₈P rings but with staggered P atoms (Tm–P: 2.867(2) and 2.875(1) Å)[25] (Figure 7). As both [Tm(Cp₃)₂]²⁺[27] and [Sm(Cp₃)₂]²⁺[28] redox couple pyridine, the lack of SET chemistry of 11 and [Sm(Tmp)]₃ towards this substrate showcases how the weaker π-donor properties of phospholyl ligands versus Cp³ makes metal centres less reducing. However, the next section shows that the SET chemistry of Ln³ phospholyl complexes is still rich and can exhibit considerable reduction potentials.

In follow-up papers in 2005 and 2007, Nief and co-workers reported crystallographic characterisation of the solvated Tm⁴⁺ mononuclear complexes [Tm(Htp)(THF)]₁₂ and [Tm(Hsp)₂(THF)]₁₃.[26] and the solvent-free dinuclear Tm⁴⁺ complex [[(η¹-Htp)Tm(μ:η¹,η¹-Htp)]₂]₁₄[27] (Figure 6), as part of investigations to compare the donor properties of Cp³ and phospholyl ligands in Tm⁴⁺ chemistry. Complexes 12 and 13 were synthesised by analogous salt metathesis methods²⁶b to those used for 7–11,[25] whilst 14 was prepared by reduction of the Tm⁴⁺ precursor ([Tm(η¹-Htp)(μ:η¹)]) with KC₈ in hexanes.[27] The monomeric complexes exhibited broad ¹³B NMR spectra (δ₈: –290 for 12, –235 ppm for 13)[26] and no signal was seen for 14 in C₆D₆ unless THF was added, whereby a ¹³B NMR spectrum identical to that of solvated 12 was observed.[27] The pseudo-bent metallocene structures of mononuclear 12 and 13 in the solid state are similar to those of 7 and 8,[24] with the lack of Me groups at the β-positions leading to larger C₈P centroid–Tm–C₈P centroid angles and shorter mean Tm–P distances (2.941(2) Å for 12 and 2.921(1) Å for 13).[26] The solid-state structure of dinuclear 14 is analogous to 9 and 10[20] with shorter Ln–P distances for 14 (2.954(2), 3.028(2) and 3.002(2) Å)[27] owing to the smaller size of Tm⁴⁺ versus Sm³⁺.[24]

Simultaneously to the disclosure of the solid structure of 14, Nief and co-workers stated that treatment of 11 with pyridine gave NMR spectra consistent with the formation of an adduct [Tm(Dtp₂)(NC₃H₇)],[27] but this product was not structurally authenticated. In 2012, Labouille et al. showed that [Sm(Tmp)]₂ reacted with pyridine to give the adduct [Sm(η¹-Tmp)(py)₂] (15-Sm)[28] the corresponding Yb³⁺ complex 15-Yb was reported in 2015 by Nocton, Auffrant and Cheisson, together with the structures of several similar substituted Yb³⁺ bis-phospholyl complexes coordinated by substituted pyridines, [Yb(Tmp)₂(L)] (L = CH₃N(CH₂NH₂)₂; 26; R = Et, 16; Cy, 17; Ph, 18)[29] (Figure 7). As both [Tm(Cp₃)₂][27] and [Sm(Cp₃)₂][28] reductively couple pyridine, the lack of SET chemistry of 11 and [Sm(Tmp)]₃ towards this substrate showcases how the weaker π-donor properties of phospholyl ligands versus Cp³ makes metal centres less reducing. However, the next section shows that the SET chemistry of Ln³ phospholyl complexes is still rich and can exhibit considerable reduction potentials.

The solid-state structures of 15-Ln for both Sm²⁸ and Yb²⁹ reveal bent metallocene-type motifs, with two eclipsed η¹-Tmp ligands with staggered Cp³ rings (Sm–P: 3.043(1) and 3.046(1) Å; Yb–P: 2.903(8) and 2.941(2) Å) and two equatorially coordinated pyridine molecules. The structures of 16–18 differ according to the identity of L³, with 16 and 17 containing k¹-coordinated L³ ligands to enforce one η¹-bound Tmp (Yb–P: 2.9723(8) Å for 16 and 3.0231(1) Å for 17) and one η¹-Tmp (Yb–P: 3.027(1) Å for 16 and 2.925(1) Å for 17)[29]. Only one of the iminophosphoranyl arms are bound in the k²-L⁵ ligand of 18, thus both Tmp ligands are able to bind in an η¹-fashion (Yb–P: 2.9480(8) and 2.947(1) Å). One broad signal was observed in the ¹³B NMR spectrum of paramagnetic 15-Sm (δ₈: –624 ppm, δ₀ = 550 Hz),[28] whereas coupling to ¹⁷Yb is observed in diamagnetic 15-Yb (δ₈: 79.5 ppm, δ₀ = 105.5 Hz).[28] Similarly, only one signal was observed in the ¹³B NMR spectra of 16 (δ₈: 77.9 ppm, δ₀ = 434.7 Hz) and 17 (δ₈: 79.8 ppm, δ₀ = 491.4 Hz) at 298 K, which the authors assigned to the Tmp ligands both being η¹-bound at this temperature owing to the large coupling constants. Variable-temperature studies showed that these signals decoalesce at ~90°C, whereas the k²-bind-

Chem. Eur. J. 2021, 27, 6645 – 6665 www.chemeurj.org © 2021 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH
ing mode of L₈ persisted in solution for 16 and 17 at all temperatures investigated. In contrast, the ³¹P NMR spectrum of 18 exhibits a signal at 79.0 ppm with a coupling constant more in line with η¹-Tmp (ΔJ₉₀ = 172.3 Hz), and the asymmetrically-bound κ²-L₈ showed two phosphorus environments.

5.2. Ln³⁺ complexes

5.2.1. Ln³⁺ complexes derived from Ln³⁺ precursors

Redox reactions of Ln³⁺ complexes over the last two decades have furnished a number of structurally authenticated Ln³⁺ monophospholyl products, which we cover here. In 2001, Barbier-Baudry et al. reported the reaction of [Sm(Tmp)₂(THF)] with half an equivalent of tert-butylperoxide to give [Sm(η¹-Tmp)₂(OrBu)(THF)] (19) by an SET reaction in a toluene/THF mixture (Scheme 5).[30] Orange crystals of 19 were studied by XRD to reveal a pseudo-bent metallocene geometry at the Sm³⁺ centre with staggered η¹-Tmp rings (Sm−P: 2.951(2) and 3.026(2) Å) and both a tert-butoxide and a THF molecule coordinating at the equatorial positions. Complex 19 was shown to be an effective initiator for the ring-opening polymerisation of ε-caprolactone in the same publication.

Also in 2001, Nief and Ricard reported the syntheses of a series of bis-Cp⁺ Sm³⁺ complexes bound by phospholyl or arsanyl ligands: [Sm(Cp⁺)(η¹-Htp)] (20), [Sm(Cp⁺)(η¹-Tmp)] (21), [Sm(Cp⁺)(μ₆-η¹,η¹-Mhp)(Sm(Cp⁺)(η¹-Mhp))] (22-P), [Sm(Cp⁺)(μ-η¹,η¹-Mhas)Sm(Cp⁺)(η¹-Mhas)] (22-As) and [[Sm(Cp⁺)(μ-η¹,η¹-C₄H₄P)]₂ (23; Figure 8).[31] Complexes 20–22 were synthesised by the separate SET reactions of [Sm(Cp⁺)₃] or [Sm(Cp⁺)(OEt)₃] with the parent biphosphole or biarssole, whereas 23 was most straightforwardly prepared from [Sm(Cp⁺)(OEt)₃] and [Tlig₃H₄P]. The solid-state structures of 20–23 vary with the steric requirements of the various phospholyl and arsanyl ligands. Complexes 20 and 21 are monomeric, with an η¹-Htp in the former (Sm−P: 3.153(1) Å) and an unsymmetrically bound η¹-Tmp in the latter, with two independent molecules in the asymmetric unit showing different Sm−P distances (2.856(1) and 2.891(1) Å). Complexes 22-E and 23 are dinuclear with bridging phospholyl or arsanyl ligands; for the former examples, these asymmetric dimers each contain one μ-η¹,η¹-Mhp (Sm−P: 3.0132(8) and 3.1032(8) Å) or μ-η¹,η¹-Mhas (Sm−As: 3.0671(6) and 3.1610(6) Å), and one η¹-Mhp (Sm−P: 2.886(1) Å) or η¹-Mhas (Sm−As: 2.9776(8) Å) bound to the less congested Sm³⁺ centre. Complex 23 is a symmetric dimer with two μ-η¹,η¹-C₄H₄P bridges (Sm−P: 3.101(2) and 3.274(1) Å), with each Sm³⁺ centre showing identical coordination spheres.

In 2003, Nief and co-workers treated 9–11 separately with azobenzene to give mononuclear Ln³⁺ complexes bound by azobenzyl radicals following SET; single-crystal XRD data were obtained for [Sm(η¹-Dsp)₃(N₆Ph₃)] (24) and [Tm(η¹-Dtp)₃(N₆Ph₃)] (25; Figure 9), but not for [Sm(Dtp)₃(N₆Ph₃)].[32] Complexes 24 and 25 exhibit similar open-metallocene type structures with η¹-bound phospholyl ligands (Ln−P: 2.9484(6) Å for 24 and 2.869(1) Å for 25) and equatorially bound η¹-N₆Ph₃ radicals, with the expected differences in metrical parameters arising from varying Ln³⁺ ionic radii and ring substitution. The ³¹P NMR spectra for 24 (δₚ: 148 ppm) and [Sm(Dtp)₃(N₆Ph₃)] (δₚ: 46 ppm) showed vastly different chemical shifts owing to paramagnetic effects. In the same paper, 9–11 were treated separately with half an equivalent of triphenylphosphine sulfide, but an SET reaction was only observed for the Tm analogue to afford the dinuclear Tm³⁺ complex [[Tm(η¹-Dtp)₃(μ-S)] (26; Figure 9), with concomitant loss of triphenylphosphine. The solid-state structure of 26 revealed mean Tm−P distances of 2.875(7) Å for the η¹-Dtp ligands, with a bent Tm-S-Tm motif (165.3(2)°).

Several other Ln³⁺ phospholyl complexes have been shown to form via SET reactions of Ln³⁺ precursors (Figure 10). In 2012, Labouille et al. showed that the dinuclear Sm³⁺ complex [[Sm(η¹-Tmp)₃(μ-NC₅H₅C₅H₅N)] (27) formed from the reductive coupling of acridine by [Sm(Tmp)₃]²⁺. Complex 27 exhibits asymmetrical Sm³⁺ coordination spheres (range Sm−P:...
The first report of LnIII halides being used to synthesise phosphanyl complexes was by Nief and Mathey in 1989, where the authors presented the salt metathesis reactions of LnCl3 (Ln = Y, Lu) with two equivalents of Li(Temp) in ethereal solvents to give [Ln(Temp)]2(μ-Cl)Li(Sol)] (Ln = Y, Sol = DME; Ln = Lu, Sol = OEt2). These diamagnetic LnIII complexes were characterised by multinuclear NMR spectroscopy, with each showing one signal in their 31P NMR spectra (δP: 84.0 ppm, 1JPP = 6.4 Hz for Ln = Y; δP: 78.6 ppm for Ln = Lu), with 19F NMR data used to corroborate the coupling in the former complex and assign η5-bound Tmp ligands, but no solid-state structures were obtained. In 1995, Nief and co-workers reported the synthesis of the SmIII phosphanyl complexes ([Sm(η5-Tmp)(μ-η5,η7-Tmp)]2(μ-Cl)K(C5H5)2)32 (32) and ([Sm(η5-Mhp)(μ-η5,η7-Mhp)])33 (33); Figure 11) by the reactions of SmCl3 with three equivalents of the respective group 1 ligand transfer agents K(Temp) and K(Mhp) in toluene at reflux.14 The solid-state structure of salt-occluded 32 revealed two crystallographically distinct SmIII centres, each with one terminal η5-Tmp (Sm–P: 2.953(3) Å), a μ-η5,η7-Tmp that is η5-bound to Sm (Sm–P: 2.924(4) Å) and a μ-η5,η7-Tmp that is η7-bound to Sm (Sm–P: 2.931(4) Å); a chloride completes the Sm coordination spheres that also bridge to K, which are in turn η5-bound by toluene and η5-bound by bridging phosphonyls to give a net-like structure. The SmIII centres in salt-free dincular 33 are each η5-bound to three Mhp ligands and η7-bound to a fourth, as a consequence of two asymmetrically bound μ-η5,η7-Mhp ligands (Sm–P: 2.927(5), 2.986(5) and 2.997(5) Å). The 31P NMR spectrum of 32 in Cs2D6 exhibited six broad signals (δP: 34.1, 41.4, 44.5, 47.7, 50.1 and 52.3 ppm; W1/2 range: 12–109 Hz), indicating that a number of different species are present in solution of varying aggregation, whereas the 31P NMR spectrum of 33 in Cs2D6O showed one signal (δP: 9.3 ppm, W1/2 = 120 Hz), indicating that monomeric [Sm(η5-Mhp)(Cs2D6O)] formed in solution.

Several other heteroleptic LnIII Temp chloride complexes have been reported in the interim (Figure 12). In 1999, Nief and co-workers prepared the ‘ate’ complexes [Ln(Temp)2Cl2K] (Ln = Nd, Sm) by the separate reactions of parent LnCl3(THF) with two equivalents of K(Temp) in THF; recrystallisation of the Sm ana-
logue from diethyl ether allowed the solid-state structure of \([\text{Sm}(\eta^3 \text{-Tmp})\{\mu_3\eta^1 \text{-Tmp}\}{\mu_2 \text{-Cl}}\text{(Et,O)}]_n\) (34) to be determined. Complexes \([\text{Ln}(\text{Tmp})\text{Cl}_2\text{K}]\) were characterised by \(^{31}\text{P}\) NMR spectroscopy (\(\text{Ln} = \text{Nd}, \delta_p: 459 \text{ppm}; \text{Ln} = \text{Sm}, \delta_p: 49.7 \text{ppm}\)). In the solid state, the \(\text{Sm}^\text{III}\) centres of polymeric 34 exhibit open metalocene-type motifs with two \(\eta^1\)-Tmp ligands (\(\text{Sm} = \text{Nd}: 2.905(2)\) and 2.926(1) Å), one of which is also \(\eta^1\)-bound to \(\text{K}\), with two chlorides bridging to multiple \(\text{K}\) atoms, which are capped with a single diethyl ether molecule. In 2006, Tilley and co-workers reported the synthesis of \([\text{Sc}(\eta^1 \text{-Tmp})\{\mu_3 \text{-Cl}\}{\text{Li}(\text{TMEDA})}]\) (35, \(\text{TMEDA} = N,N',N,N'$'$-tetramethylethlenediamine) by the reaction of \(\text{ScCl}_3(\text{THF})\), with two equivalents of \(\text{Li}(\text{Tmp})(\text{TMEDA})\) in toluene. The \(^{31}\text{P}\) NMR spectrum of 35 exhibits one signal at 9.98 ppm, and the local structure about \(\text{Sc}^\text{III}\) in the solid state is comparable to the \(\text{Sm}^\text{III}\) centre in 34, although the alteration of coordinating solvent, alkali metal and \(\text{Ln}^\text{III}\) ion enforces a monomeric structure at 35 (\(\text{Sc} = \text{P}: 2.694(2)\) and 2.718(2) Å). The separate reactions of 35 with \(\text{LiCP}^*\) or \(\text{Sc(CP}^*)\text{(Cl)}\), with \(\text{Li}(\text{Tmp})(\text{TMEDA})\) both gave reaction mixtures with signals in their \(^{31}\text{P}\) NMR spectra at 100.2 ppm, which the authors ascribed to the mixed \(\text{CP}^*/\text{Tmp}\) complex \([\text{Sc(CP}^*)(\text{Tmp})(\mu_3 \text{-Cl})\text{Li(\text{TMEDA})}]\), although this product was not structurally authenticated. Finally, in 2007, Nief, Hou and co-workers reported the synthesis of dinuclear \([\text{Sc}(\eta^1 \text{-Dtp})\{\mu_3 \text{-Cl}\}(\text{Cl}(\text{py}))]\) (36) from the equimolar reaction of \(\text{ScCl}_3\) and \(\text{K(Dtp)}\) in a mixture of toluene and pyridine (5:1). Complex 36 exhibits a single peak in its \(^{31}\text{P}\) NMR spectrum (123.0 ppm), and single-crystal XRD revealed each \(\text{Sc}^\text{III}\) centre is bound by a molecule of pyridine, a terminal chloride and two bridging chlorides, and is capped by one \(\eta^1\)-Dtp (\(\text{Sc} = \text{P}: 2.6960(5)\) Å).

A handful of \(\text{Ln}^\text{III}\) phosphoryl iodide complexes have also been structurally authenticated (Figure 13). In 2007, Nief and co-workers reported the synthesis of mononuclear \([\text{Sm}(\eta^1 \text{-Dtp})\{\mu_3 \text{-Cl}\})\] (37-\(\text{Tm}\)) and dinuclear \([\text{Sm}(\eta^1 \text{-Htp})\{\mu_2 \text{-Cl}\}]\) (38) by the reaction of \(\text{TmI}_3\) with two equivalents of \(\text{K(Dtp)}\) or \(\text{K(Htp)}\) in toluene at reflux. In 2009, a \(\text{Dy}^\text{III}\) homologue 37-\(\text{Dy}\) and a related dinuclear complex \([\text{Dy}(\eta^1 \text{-Dsp})\{\mu_3 \text{-Cl}\}]\) (39) were reported to form by analogous methods. Complexes 37–39 all contain two \(\eta^1\)-bound phosphoryl ligands at each metal centre; for mononuclear 37-\(\text{Ln}\) (\(\text{Ln} = \text{P}: 2.9235(2)\) Å for \(\text{Dy}\); 2.8119(12) and 2.8167(12) Å for \(\text{Tm}\)) the metals are also bound by a single iodide ligand, whereas dinuclear 38 (\(\text{P}: 2.9062(12)\) and 2.9504(14) Å) and 39 (range \(\text{Dy} = 2.8500(7)–2.8690(7)\) Å) each exhibit two bridging iodides, which saturate their metal coordination spheres. Finally, in 2007, Nief, Hou and co-workers disclosed the synthesis of the mono-ring \(\text{Sm}^\text{III}\) complex \([\text{Sm}(\eta^1 \text{-Dtp})\{\mu_2 \text{-Cl}\}]\) (40) by the reaction of \(\text{SmI}(\text{THF})_2\) with equimolar \(\text{K(Dtp)}\). Complex 40 exhibits one signal in its \(^{31}\text{P}\) NMR spectrum at 77.5 ppm and has a typical half-sandwich structure in the solid state, with mutually trans-\(\text{THF}\) and iodide ligands and a single \(\eta^1\)-Dtp (\(\text{Sm} = \text{P}: 2.9112(14)\) Å) coordinated to Sm.

The homoleptic mononuclear \(\text{Dy}^\text{III}\) complex \([\text{Dy}(\eta^1 \text{-Dtp})\] \(\text{[Al(\text{OC}(\text{CF}_3)_2)_2]\})\) (41) was synthesised in 2019 by Chilton, Mills and co-workers by the sequential salt metathesis and protonolysis reaction of \(\text{Dy}^\text{III}\) with allyl magnesium chloride and \(\text{[NEt}_3\text{H]}\text{[Al(\text{OC}(\text{CF}_3)_2)_2]\})\), with the respective elimination of magnesium dialdehydes, triethylamine and propylene providing thermodynamic driving forces (Scheme 6). The installation of a sufficiently weakly coordinating anion provided an isolated bent \([\text{Dy}(\eta^1 \text{-Dtp})]\) cation in the solid state, with \(\text{Dy} = \text{P}\) distances of 2.7880(8) and 2.7981(8) Å. The axial ligand field and rigidity of the aromatic ligands of 41 are both conducive to enhance the SMM properties for \(\text{Dy}^\text{III}\), and the effective barrier to magnetic reversal (1760 K) and maximum hysteresis temperature (48 K) for 41 are both competitive with leading \(\text{Cp}^\text{V}\) \(\text{Ln}\) SMMs.

Scheme 6. Synthesis of 41 by the sequential reaction of 37-\(\text{Dy}\) with \(\text{Mg(C}_5\text{H}_5\text{Cl})\) and \(\text{[NEt}_3\text{H]}\text{[Al(\text{OC}(\text{CF}_3)_2)_2]\})\).
rated anion contains a pseudo-tetrahedral Nd
centre with two borohydride and two \( \eta^1 \)-Tmp ligands (Nd–P: 2.982(3) and 2.995(3) Å).\[^{41}\] In 2020, Mills and co-workers reported a series of salt metathesis reactions of THF solvates of light Ln\(^{III}\) borohydrides with K(Htp) in a range of stoichiometries and solvents to afford the polynuclear heteroleptic Ln\(^{III}\) phospholyl borohydride complexes [\( \text{[Ln(\eta^1-Htp)_2(\mu-\text{BH}_2)_2]} \)] (43-Ln; Ln = La, Ce, Nd, Sm) and [\( \text{[Ln(\eta^1-Htp)_2(\mu-\text{BH}_2)_2]} \)] (44-Ln; Ln = La, Ce, Nd, Sm = 2 DME, n = 2; 45, Ln = Ce, Sol = Et\(_2\)O and THF, \( n = \infty \)).\[^{42}\] The varying but similar local pseudo-tetrahedral coordination spheres of [\( \text{[Ln(\eta^1-Htp)_2(\text{BH}_2)_2]} \)] fragments in 43–45 were established by single-crystal XRD (Ln–P: 3.089(5) and 3.138(3) Å, 43-La; 3.058(5) and 3.099(4) Å, 43-Ce; 3.019(11) and 3.077(6) Å, 43-Nd; 3.016(6) and 3.054(4) Å, 43-Sm; 3.1790(7) and 3.1869(7) Å, 44-La; 3.1456(13) and 3.1534(13) Å, 44-Ce; 3.1488(13) and 3.1682(12) Å, 45). The paramagnetism of the majority of 43–45 precluded the collection of reliable \( ^{31}P \) NMR spectra in most cases, but signals were observed for diamagnetic 43-La (\( \delta_P : 105.65 \) ppm) and 44-La (\( \delta_P : 96.49 \) ppm).

5.2.2.3. Complexes containing alkyl co-ligands

A handful of structurally authenticated heteroleptic Ln\(^{III}\) phospholyl alkyl complexes have been reported (Figure 15). In 1999, Nief et al. reported the synthesis of the bis-phospholyl complexes [\( \text{[La(\eta^1-\text{Htp})]}(\text{CH(SiMe}_3)_2)] \) (Ln = Nd, Sm), with the most efficient synthetic route being the sequential salt metathesis reactions of parent LnCl\(_2\)(THF), with two equivalents of K(Tmp) followed by one equivalent of Li(CH(SiMe\(_3\))\(_2\)) in THF.\[^{35}\] Al-

Figure 14. Complexes 42–45.\[^{40–42}\]

Figure 15. Complexes 46 and 47-Ln (Ln = Sc, Y, Sm).\[^{50–57}\]

Figure 16. Complexes 48–51.\[^{50–54}\]

though these products were not characterised by single-crystal XRD, they each exhibited two signals in their \( ^{31}P \) NMR spectra (\( \delta_P : 456 \) and 501 ppm for Ln = Nd; 43.4 and 46.7 ppm for Ln = Sm). Hydrogenolysis reactions of [\( \text{[Ln(Tmp)](CH(SiMe}_3)_2)} \)] gave products with formulations consistent with reduction for Sm to form \("\text{[Sm(Tmp)]} \)\), and with \( \alpha \)-bond metathesis for Nd to give \("\text{[Nd(Tmp)](H)} \)\). Two Sc\(^{III}\) ‘ate’ complexes [\( \text{[Sc(Tmp)](Me)(\text{Li(TMEDA)})]} \) (X = Cl, Me) were reported in 2006 by Tilley and co-workers, together with the first structurally characterised Ln\(^{III}\) phospholyl alkyl complex, [\( \text{[Sc(\eta^1-Tmp)(CH(SiMe}_3)_2](\mu-\text{Cl})(\text{Li(TMEDA)})]} \) (46).\[^{36}\] These complexes were prepared by salt metathesis reactions of 35 with MeLi or Li(CH(SiMe\(_3\))\(_2\)). Complexes [\( \text{[Sc(Tmp)](Me)(\text{Li(TMEDA)})]} \) (X = Cl, Me) could not be isolated but were assigned to signals in the \( ^{31}P \) NMR spectra of reaction mixtures (\( \delta_P : 88.1 \) ppm for X = Cl, 82.9 for X = Me), whilst 46 exhibits \( \delta_P : 119.2 \) ppm. Single-crystal XRD revealed a piano-stool geometry about Sc, with the two chlorides bridging to Li, and \( \eta^1 \)-Tmp (Sc–P: 2.712(2) Å). A family of heteroleptic Ln\(^{III}\) phospholyl complexes containing substituted benzyl ligands, [\( \text{[Ln(\eta^1-Dsp)(CH)(C}_6\text{H}_5\text{Me}_2)_2)] \) (47-Ln, Ln = Sc, Y, Sm), were reported by Nief, Hou and co-workers in 2007 by sequential salt metathesis reactions of parent LnCl\(_2\) with K(Dtp) and two equivalents of [\( \text{[K(C}_6\text{H}_5\text{Me}_2)_2)) \]) \(^{37}\). Complexes 47-Ln exhibited signals in their \( ^{31}P \) NMR spectra at 99.0 (Sc), 88.9 (Y) and 62.9 (Sm) ppm, and similar solid-state structures with the benzyl ligands additionally coordinating with pendant NMe\(_2\) groups in a mutually trans-fashion, and \( \eta^1 \)-coordinated Dtp (Ln–P: 2.769(1), 2.928(1) and 3.009(1) Å for Sc, Y and Sm, respectively). When activated with [\( \text{[CP}_2\text{Li}][\text{B(C}_6\text{H}_5\text{F}_3)_2)] \) (47-Sc was shown to be efficient in promoting the formation of syndiotactic polystyrene, with 47-Y less efficient and 47-Sm unreactive towards styrene under identical conditions.

A handful of heteroleptic Ln\(^{III}\) phospholyl aluminolate complexes have been synthesised by Anwander and co-workers (Figure 16).\[^{43, 44}\] In 2007, the mono-ring complexes [\( \text{[La(\eta^1-\text{Htp})]}(\text{AlMe}_2)_2)] \) (48, \[\text{[Nd(\eta^1-\text{Htp})]}(\text{AlMe}_2)_2) \) (49), [\( \text{[La-(Dsp)](AlMe}_2)_2)] \) and [\( \text{[Nd(\eta^1-Dsp)](AlMe}_2)_2)] \) (50) were reported to
form via salt metathesis reactions of Ln(AlMe₃)₃ precursors with K(Tmp) or K(Dsp). Complexes 48 and 49 were attributed to differing Ln³⁺ charge densities, with the former complex exhibiting both η¹-(La–P: 3.1962(3) Å) and η¹'- (La–P: 3.6064(3) Å) binding modes of the bridging Tmp rings. Complexes 49 (Nd–P: 2.9252(10) Å) and 50 (Nd–P: 2.8972(3) Å) exhibited mononuclear half-sandwich motifs with η³-bound phospholys; a crystal structure was not obtained for [La(Dsp)(AlMe₃)₃]. In follow-up work in 2012, 48–50 and [La(Dsp)(AlMe₃)₃] were reacted with silica, and the resultant materials were investigated as catalysts in isoprene polymerisation. As part of this work, [Nd(η¹-Tmp)(AlMe₃)(OSi(OBu)₃)(AlMe₃)] (51) was synthesised by the protonolysis reaction of 49 with HOSi(OBu)₃ to provide a molecular complex that models the surface species formed on silica. Complex 51 exhibits a signal at 544 ppm in its ³¹P NMR spectrum, and its solid-state structure is comparable to that of 49, with a Nd–P distance of 2.9652(6) Å.

5.2.2.4. Complexes containing a cyclooctatetraenyl co-ligand

Mixed sandwich Ln³⁺ phospholyl complexes are rare, and apart from the Cp³ examples in prior sections there are several other structurally authenticated complexes containing cyclooctatetraenyl ligands (C₈H₈, COT) (Figure 17). In 2002, Cendrowski-Guillaumee et al. reported that the reaction of [Nd(COT)(THF)] with K(Tmp) gave a powder formulated as [(Nd(COT))[Tmp](THF)]⁻; exposure of this powder to vacuum removed the THF and the residue was formulated as a dinuclear complex, [(Nd(COT)[Tmp])]. The same solvent-free reaction was later obtained by the reaction of [Nd(COT)(THF)] with [BPH₃] with K(Tmp), and subsequent reaction with hexamethylphosphoramide (HMPA) gave green crystals of [Nd(COT)(η¹-Tmp)(HMPA)] (52). Complex 52 exhibits an open metalloocene-type geometry with a Nd–P distance of 2.9688(8) Å; this structure is analogous to a complex reported the previous year by Visseaux and co-workers, [Nd(COT)(η³-Dsp)(THF)] (53), although this exhibits a longer Nd–P distance (3.1095(4) Å). Complex 53 was synthesised from the reaction of [Nd(COT)(μ-Cl)(THF)] with two equivalents of K(Tmp); the 5m⁹⁻ complexes [Sm(COT)(Tmp)(THF)] and [Sm(COT)(Dsp)] were accessed by similar methods and although these were not structurally authenticated, the Tmp analogue was found to exhibit a signal in its ³¹P NMR spectrum at 134.1 ppm. In 2018, Chen et al. adapted these methods to synthesise [La(COT)(η³-Dsp)] (54–Ln, Ln = Y, Tb, Dy, Er, Tm) from [Ln(COT)(THF)] precursors. Complexes 54–Ln do not contain a coordinated THF molecule as late Ln have smaller ionic radii; these mixed metalloocene complexes exhibit Ln–P bonds lengths of 2.8261(6) Y, 2.8745(12) Tb, 2.8577(13) Dy, 2.7929(11) Er and 2.7823(12) Tm) Å. The Y(III) complex 54-Y exhibits a doublet in its ³¹P NMR spectrum at 157.96 ppm (J_P = 12.1 Hz), whilst the Er(III) analogue 54-Er has a favourable geometry for enhanced SMM properties, and was found to exhibit a competitive barrier to magnetic reversal of 367 K.

6. Actinide Monophospholyl and -arsolyl Complexes

6.1. An³⁺ complexes

There are only a handful of examples of An monophospholyl complexes, and only one monarsolyl complex, that have been structurally authenticated to date, and to the best of our knowledge all reported An examples are of uranium. Baudry, Nief and co-workers reported the first An monophospholyl complexes in 1990, where it was disclosed that the salt metathesis reaction of [UC₈H₇Me₂-1,3,5(BH₄)] with two equivalents of K(Tmp) in THF yielded the ‘ate’ complex [(U(Tmp))(BH₄)]PK; subsequent removal of THF and addition of tolune to the reaction mixture gave the dinuclear U⁵⁺ complex [U(η¹-Tmp)(μ-η¹-Tmp)(BH₄)] (55; Scheme 7). Complex 55 exhibited two broad signals in its ³¹P NMR spectrum at δ_p = 727 (W_p = 150 Hz) and 3471 (W_p = 1000 Hz), and reacted separately with THF and OPPh₃ to give the monomeric Lewis base adducts [(U(Tmp)(BH₄)(THF)) and (U(Tmp)(BH₄)(OPPh₃)), respectively. No U⁶⁺ complexes were structurally authenticated in this initial report.

In a follow-up full paper in 1992, Gradoz et al. presented an alternative synthetic route to obtain 55 by Na/Hg amalgam reduction of the U⁶⁺ precursor [U(Tmp)(BH₄)] in toluene (see Section 6.2). Two U⁶⁺ ‘ate’ complexes, [Na(15-crown-5)] [U(Tmp)(BH₄)] and [Na(15-crown-5)][U(Tmp)(BH₄)], were also reported in this paper to form from analogous Na/Hg reductions of the respective U⁵⁺ precursors [U(Tmp)(BH₄)] and [U(Tmp)(BH₄)] in the presence of 15-crown-5, but these products were characterised by elemental analysis only. The
1H NMR spectrum of 55 was investigated in additional detail, and variable-temperature experiments were performed to determine that a cis/trans-isomerisation equilibrium is in operation in solution owing to fluxional 1η-binding of the Tmp ligand. The solid-state structure of dinuclear pseudo-tetraedral 55 was eventually disclosed in 1994, with U–P distances of the 1η-bound Tmp of 2.945(3) and 2.995(3) Å, and, for the 1η-bound Tmp of 2.996(3) Å. This remains the only report of a structurally authenticated U1 monophosphoryl complex to date. The syntheses of [U(Cp*)&(Tmp)(BH4)] by Na/Hg reduction of [U(Cp*)&(Tmp)(BH4)] was also reported in the same paper; although no structural authentication was presented for this mixed Cp*/Tmp U1 complex, its 1H and 31P NMR spectra (δH: 3672 ppm, δP = 1600 Hz; 3886 ppm, δP1/2 = 1130 Hz) indicated similar dynamic solution behaviour to that shown by 55. Addition of THF to [U(Cp*)&(Tmp)(BH4)] allowed the characterisation of [U(Cp*)&(Tmp)(BH4)(THF)] by NMR spectroscopy.

It is noteworthy that, in 2002–2003, Cendrowski-Guillaume et al. reported that the mixed sandwich U1 complex [U(COT)&(Tmp)(HMPA)] could be synthetised by the Na/Hg reduction of the UIV precursor [U(COT)&(Tmp)(HMPA)][BH4] (see Section 6.2). Although this U1 complex was not structurally authenticated at the time, the presence of an additional coordinated molecule of HMPA over the analogous Nd1 complex 52 (see Section 5.3) was assigned by the authors, based on elemental analysis and 1H NMR spectroscopy data. The reaction of [U(COT)&(Tmp)(HMPA)] with NET3&HPB6 gave a 1H NMR spectrum that was consistent with the formation of the UIV complex [U(COT)&(HMPA)][BH4] by concomitant protonolysis of Tmp and oxidation of U1 to UIV; the mechanism of this reaction was not discussed. In 2015, Croke and co-workers reported the one-pot stoichiometric salt metathesis reactions of UI1, [K3(C8H12(SiPr3)2)·1,4] and either K(Tmp) or K(Tmas) in THF to give the respective U1 monophosphoryl complexes [U(C8H12(SiPr3)2·1,4)1η-Tmp][THF] (56-P), or arsolly complex [U(C8H12(SiMe3)2·1,4)1η-Tmas][THF] (56-As), following work-up and recrystallisation (Scheme 8). Complexes 56-E were characterised by mass spectrometry, elemental analysis, single-crystal XRD and 1H and 29Si NMR spectroscopy, and by 31P NMR spectroscopy for 56-P (δP: 846.2, δP1/2 = 411 Hz); no 31As NMR spectrum was reported for 56-As. The solid-state structures of 56-E revealed similar bent metalloocene-like arrangements with an equatorial molecule of THF, 1η-bound (C8H12(SiPr3)2·1,4) and 1η-bound Tmp/Tmas, with disorder of the Tmp ligand giving two U–P (2.776(15) and 2.9868(14) Å) and two U–Tmp centroid (2.542(2) and 2.592(2) Å) distances for 56-P; complex 56-As is the only structurally authenticated An arsoly complex to date and exhibits a U–As bond length of 3.0781(7) Å and a U–Tmas centroid distance of 2.5962(4) Å. The coordinated THF in 56-E can be removed upon exposure of powdered samples to vacuum, and the reaction of desolvated 56-P with CO2 gave the dinuclear U1V phosphacarbonyl complex [[U(C8H12(SiMe3)2·1,4)][u,k2-O2(CP2Me3)](μ-O)]. The authors monitored the corresponding reaction of 56-P with 13CO2 by 13C NMR spectroscopy, and proposed a U1V μ-oxo intermediate "[[U(C8H12(SiMe3)2·1,4)(PC2Me3)](μ-O)]" forms first by the reduction of CO2 to CO and oxidation of the two UIV centres, followed by isomerisation of two molecules of CO2 to form the observed product; analogous CO2 activation chemistry was observed for a homologous pyrrole complex 56-N.

6.2. AnIV complexes

The first structurally authenticated AnIV phosphorolyl complex, [U(1η-Tmp)(BH4)] (57), was reported in 1990 by Baudry, Nief and co-workers to form from the salt metathesis reaction of U(BH4) with two equivalents of K(Tmp) in THF (Scheme 9) or the oxidation of 55 with TiBH4. Single-crystal XRD revealed that the UIV centre of 57 exhibits a pseudo-tetrahedral geometry in the solid state, with 1η-bound Tmp rings and U–P distances of 2.905(1) Å. Complex 57 was also characterised by elemental analysis, and 1H and 31P NMR spectroscopy (δH: 960; δP1/2 = 200 Hz). These data are comparable to those of a second UIV monophosphoryl borohydride complex that was not structurally authenticated, [U(Tmp)(BH4)] (δH: 923; δP1/2 = 44 Hz), which was reported in a follow-up paper in 1992. [U(Tmp)(BH4)] was synthesised directly from U(BH4) and one equivalent of K(Tmp) in toluene, with ligand scrambling of this complex occurring in THF solutions to afford 57 and [U(BH4)(THF)].

In 1992, Ephritikhine and co-workers reported the salt metathesis reaction of UCl3 with three equivalents of K(tmp) in toluene to yield [U(1η-Tmp)(Cl)] (58, Figure 18); the corresponding reaction with stoichiometric K(tmp) gave [U(Tmp)(Cl)]35. Several derivatives of 58 were synthesised by salt metathesis protocols with various reagents: (i) KBEt3H yielded the hydride [U(Tmp)(H)]; (ii) MeLi gave the alky1 [U(Tmp)(Me)]; and, (iii) NaOPr afforded the alkoxide [U(Tmp)(OPr)]. All U1 complexes in this paper were characterised by 1H NMR spectroscopy and elemental analysis, but only 58 was structurally authenticated, showing an approximate trigonal planar arrangement of the three 1η-bound phospholyls with respect to the ring centroids.
were assigned by $^1$H NMR spectroscopy and elemental analysis, although a solid-state structure was determined for 60 to reveal a U$^{IV}$ centre coordinated by $\kappa^2$-BH$_4$, THF, $\eta^1$-COT and $\eta^1$-Tmp, with a typical U–P distance of 2.970(8) Å.

The only other U$^{IV}$ monophospholyl complexes that have been structurally authenticated to date, $[\text{U(Cl)}_2(\mu^1\cdot\eta^1\cdot\text{Tmp})]\text{Ni}(\mu^1\cdot\eta^1\cdot\text{Tmp})]_2$ (61) and $[\text{U(Cl)}_2(\mu^1\cdot\eta^1\cdot\text{Tmp})]\text{Ni}(\mu^1\cdot\eta^1\cdot\text{Tmp})]_2$, were reported in 1996 by Ephritikhine and co-workers to form by the respective Na/Hg reductions of 2:1 mixtures of either $[\text{U(Tmp)}_2(\text{Cl})]_2$ and NiCl$_2$, or $[\text{U(Tmp)}_2(\text{Cl})]_2$ and $[\text{Ni(\eta^1\cdot\text{Tmp})}_2(\mu^1\cdot\text{Tmp})]_2$. Single-crystal X-ray diffraction studies of 61 and 62 revealed that the pseudo-tetrahedral U$^{IV}$ centres were bound by two terminal cis-chlorides and two Tmp ligands in an $\eta^1$-binding mode in each case (61: range U–P: 2.823(7)–2.862(7) Å; 62: U–P: 2.851(9) and 2.86(1) Å). The assignment of U$^{IV}$ centres in 61 and 62 is made through analysis of Ni–P distances in the former complex being in line with Ni$^{II}$ tetrakis-phosphines, and a short Ni–Ni distance in the latter complex (2.546(9) Å) being consistent with the presence of a metal–metal bond and formal Ni$^{IV}$ centres; long mean U–Ni distances in these complexes (e.g., 3.38(2) Å for 61) are not in line with 5f/3d metal–metal bonds. The $^1$H and $^{31}$P NMR spectra of 61 provided additional characterisation data ($\delta_{\text{H}}$: 199.2 ppm), whilst those of 62 were broad and could not be interpreted; crystals of 62 could not be separated easily from the NaCl by-product, hence no additional characterisation data were obtained.

### 7. Lanthanide and Actinide Polyphospholyl Complexes

#### 7.1. C$_p$P$_2$ and C$_p$P$_3$ complexes

A handful of examples of Ln and An polyphospholyl complexes have been reported, whilst there have been no reports to date of corresponding polyarsolyls. The first structurally characterised rare earth polyphospholyl complex, $[\text{Sc(\eta^1\cdot\text{C}_7\text{Bu}_3\text{P}_3)}_2(\mu^1\cdot\eta^1\cdot\eta^1\cdot\text{C}_7\text{Bu}_3\text{P}_3)]_2$ (63), was reported in 1996 by Cloke, Nixon and co-workers to form in 5–10% isolated yield from the cyclooligomerisation reaction of $\text{fBuCP}$ with Sc vapour in a 10:1 ratio (Scheme 12). This noteworthy triple decker complex represented the first structurally authenticated example of formal Sc$^{IV}$ centres, together with a novel instance of ligated 1,3,5-triphosphabenzene in the solid state; f-block

![Scheme 10. Synthesis of 60 from [U(COT)(BH$_4$)$_2$(THF)] with 1 equivalent of K(Tmp)](53)]

**Figure 18.** Complexes 58$^{[52]}$ and 59$^{[54]}$.

**Figure 19.** Complexes 61 and 62$^{[56]}$.
complexes with Ln or An centres in formal +1 oxidation states are unknown to date. The total valence electron count of 63 is only 22 e−, which is also remarkably low for a triple-decker sandwich complex. The reaction mixture that yielded 63 was further investigated by Cloke, Nixon and co-workers, and the sandwich complex [Sc(C₅tBu₄P)₃] was isolated in 5–10% crystalline yield after sublimation (Scheme 11).[58] Unfortunately, this complex could not be structurally authenticated, but all characterisation data were in line with a ScI formulation. To the best of our knowledge, no Ln and An diporphospholyl complexes have been structurally authenticated to date, but it is noteworthy that [Yb(C₅tBu₄P)₃] was made by analogous procedures and has been spectroscopically characterised.[59] The diuranium complex [([UHC(SiMe₃)₃C(H-Me-4)])₂μ-η⁵,η⁵-

C₅tBu₂P]₃, reported by Liddle and co-workers in 2014 to form from the reductive coupling of two molecules of tBuCP by a U⁴ precursor, is also worthy of mention at this point as the sole example of a Ln/An complex containing a cyclo-C₅P₂ ring that has been structurally characterised to date.[59] Liddle has recently found f-block complexes containing diionic four-membered aromatic rings.[61]

The solid-state structure of 63 revealed that the planar bridging 1,3,5-triporphosphabenzenes has elongated ring P–C bonds compared with unbound 1,3,5-C₅tBu₄P, together with remarkably short Sc–C₅P₂Distances of 1.787(5) Å; this contrasts with the relatively long Sc–C₅P₂Distances to the capping anionic C₅tBu₂P₁-3 rings of 2.338(8) Å (Sc–P: 2.802(2), 2.843(2) and 2.877(2) Å).[53] These unusual metrical parameters indicate that significant charge transfer is present in 63, making the formal oxidation state a moot point, but the assignment of Sc³ centres is a useful formalism to rationalise experimental data. Crystals of 63 exhibit a forest-green colour, and the intense absorption in the UV/Vis spectrum of a dilute toluene solution (λmax = 426 nm, ε = 12000 dm³ mol⁻¹ cm⁻¹) was assigned to a metal to ligand charge transfer band, which is typical of low oxidation state scandium;[57] a pentane solution of dark-purple [Sc(C₅tBu₂P)₃] similarly exhibits a maximum absorbance at 571 nm and ε = 15000 dm³ mol⁻¹ cm⁻¹.[58]

Solutions of 63 were determined to be EPR silent between 298 K and 77 K,[37] whilst a toluene glass of [Sc(C₅tBu₂P)₃] at 120 K was shown to exhibit a rich and well-resolved EPR spectrum with hyperfine coupling of the Sc-based unpaired electron to a 100% abundant I = 7/2 Sc nucleus and additional splitting by four equivalent ³¹P nuclei (100% abundance, I = 1/2); these features were simulated with g⊥ = 2.0098, g∥ = 1.9273, A(⁴⁴Sc) = 29.9 G, A(⁴⁴Sc) = 52.9 G and A(³¹P) = 7.2 G.[58] A solution of 63 was additionally probed by Evans method magnetic susceptibility, where the value at 295 K (3.98 μB) is lower than the predicted value of 4.47 μB for four unpaired electrons arising from two isolated Sc I centres.[53] In contrast, the magnetic susceptibility measured at room temperature for a toluene solution of [Sc(C₅tBu₂P)₃] (1.70 μB) is fully in accord with the expected value of 1.73 μB for a 3d⁷ system with no orbital contribution, and a more clear-cut Sc I centre; however, the stability of this complex was attributed to the capability of the diporphospholyl ligands to accept electron density from the metal.[58]

In 2000, Deacon et al. reported the syntheses of co-crystallised [Sm(Cp*)₂(η⁵-C₅tBu₂P, E)(THF)] (64-E, E = P, Sb; Figure 20), in 10% yield from the SET reaction of [Sm(Cp*)₂(THF)] with [Tl(C₅tBu₂P, E)], where the Sb/P ratio of E in the Tl I precursors was approximately 4:1.[52] In the same paper, a mixture of [Tl(C₅tBu₂P, E)] and Yb metal in THF was sonicated for 48 h, and upon work-up co-crystals of [Yb(η⁵-C₅tBu₂P, E), (η⁵-

C₅tBu₂P, E)] (65-E, E = P, Sb; Figure 20) were isolated, with the Tl I precursor presumably contaminated with a significant amount of Li-containing compounds.[62] The authors made valiant efforts to determine the Sb/P ratios of E in 64-E and 65-E by 1H and ³¹P NMR spectroscopy, and found that for the former mixture P was in excess, whereas for the latter the Sb/P ratio was 2:1. This indicates that if pure [Tl(C₅tBu₂P, E)] could be obtained then it may react with [Sm(Cp*)₂(THF)] to give 64-P cleanly, but there are more variables to explore for the synthesis of pure 65-P in the future.

Recrystallisation of 64-E gave several crystals of antimony-free 64-P, which were analysed by single-crystal XRD, whereas the SC-XRD dataset for 65-E showed the presence of both Sb and P, as well as other products containing C₅tBu₂P rings.[62] The Sm⁴ centre in 64-P is coordinated by two η⁵-Cp* ligands, a molecule of THF, and the 1,2,4-C₅tBu₂P, ring in an η⁵-fashion, with relatively long Sm–P distances of 3.135(2) and 3.164(2) Å attributed to steric buttressing. The angle between Sm, the P, as well as the other products containing C₅tBu₂P rings.

![Scheme 11. Synthesis of 63 from Sc vapour and tBuCP](image1)

![Figure 20. Complexes 64-E and 65-E (E = P, Sb)](image2)
component of the \( \eta^2 \)-bound ring exhibiting an angle of 112.8° between the Yb–Sb–P(bridged) vector and the ring mean plane. The authors attributed this observation to inter-ligand steric repulsion preventing \( \eta^2 \)-coordination of the third ring; crystallographic disorder prevented the extraction of reliable Yb–Sb (3.24(3) Å) and Yb–P (3.09(2) Å) distances from these data.\(^{[62]}\)

In 2003, Cloke, Green and Nixon communicated the synthesis of the Sc\(^{4+}\) complex \([\text{Sc}(\eta^2\text{-C}_5\text{BuCP})_2(\eta^2\text{-C}_7\text{BuCP})_2])\) (66-Sc), by the reaction of ScI\(_3\) with three equivalents of K(C\(_2\text{BuCP}\)) in toluene under reflux (Scheme 12).\(^{[63]}\) In a follow-up full paper in 2008, Clentsmith et al. reported the analogous synthesis and solid-state structures of the homologous Ln\(^{III}\) and An\(^{III}\) complexes 66-M for \( M = \text{Y, Tm and U} \) (Scheme 12).\(^{[64]}\) The metrical parameters in the solid-state structures of 66-M vary according to \( M^{III} \) ionic radii but all exhibited two \( \eta^1 \)- and one \( \eta^2 \)-bound triphospholyl ligands: \( M \equiv \text{P} \) distances to the former are 2.773(3)–2.813(3) Å (66-Sc), 2.928(3)–3.059(3) Å (66-Y), 2.896(2)–3.052(2) Å (66-Tm) and 2.998(2)–3.114(2) Å (66-U); \( M \equiv \text{P} \) distances to the latter are 2.762(3) and 2.796(3) Å (66-Sc), 2.884(2) and 2.912(2) Å (66-Y), 2.853(2) and 2.891(2) Å (66-Tm) and 2.968(2) and 2.995(2) Å (66-U).\(^{[63,64]}\) The variable-temperature \(^{31}\)P NMR spectra of 66-Sc showed an approximate (AX)\(_3\) pattern at all temperatures investigated (although a simulation of an AA'X,X',X'' system showed there is slight deviation owing to inter-ring coupling), suggesting that a more symmetrical arrangement of ligands exists in solution for this complex, with signals at 296.5 (A) and 265.0 (X) ppm, and coupling constants of \( J_{AX} = -50.7 \text{ Hz}, J_{AX} = +21.5 \text{ Hz}, J_{AX} = \pm 5.0 \text{ Hz} \) and \( J_{AX} = 0 \text{ Hz} \). The \(^{31}\)P NMR spectra for 66-Y were not as well-resolved (\( J_{AX} = 289.9 \text{ (br, 1P), 263.9 (br, 2P) ppm} \)), but at 70 °C the high field signal resolved to a doublet with a splitting of 49.3 Hz, typical of a \( J_{AX} \) coupling constant; the authors attributed the smaller inter-ring coupling in this system to the rings being further apart.\(^{[64]}\) The signals in the \(^{31}\)P NMR spectra of paramagnetic 66-Tm and 66-U were broader, with the former indistinguishable from the baseline and a single observable signal for the latter at 691.5 ppm (W\(_{1/2} = 200 \text{ Hz} \).

Reduction of 66-Sc with KC\(_8\) in toluene at −78 °C gave a dark-blue solution with elimination of K(C\(_2\text{BuCP}\)) and graphite, and following work-up and sublimation at 170–180 °C and 1 × 10\(^{-5}\) bar, crystals of dinuclear \([\{\eta^1\text{-C}_7\text{BuCP}\}_2\text{Sc}[\mu-\eta^2\eta^2,\eta^1-\text{C}_7\text{BuCP}])\) (67) were obtained (Scheme 13).\(^{[60]}\) The coordination spheres of the two Sc centres in 67 differ, with one almost identical to that seen in 66-Sc, with a range of Sc–P distances (2.750(4)–2.942(2) Å) and Sc–C\(_{P(bound)} \) distances of 2.322(4) and 2.360(4) Å to the \( \eta^1 \)-bound rings. The second Sc exhibits a sandwich motif (range Sc–P: 2.5627(14)–2.842(2) Å), with short Sc–C\(_{P(bound)} \) distances of 2.046(4) Å to the bridging ring and 2.253(4) Å to the terminal ring. This asymmetry led the authors to propose that in the solid state, Sc\(^{III}\) and Sc\(^{II}\) formalisms can be assigned to describe the electronic structure of 67 rather than two Sc\(^{II}\) centres; this is in accord with DFT calculations and powdered samples of 67 being diamagnetic by SQUID magnetometry, which led to the authors proposing an \( S = 0 \) closed-shell ground state. Intriguingly, the magnetic susceptibility of 67 was determined to be 1.7 \( \mu_B \) per Sc atom in toluene solution;\(^{[65]}\) these data are analogous to \([\text{Sc}(\eta^2\text{-C}_7\text{BuCP})_2])\) (see above).\(^{[58]}\) The authors proposed that in aromatic solvents a monomeric complex \([\text{Sc}(\eta^2\text{-C}_7\text{BuCP})_2])\) with a Sc\(^{III}\) centre in equilibrium with 67.\(^{[66]}\) No signal was observed in the EPR spectrum of a toluene solution of 67, which was ascribed to the dimer being more favoured than for bulkier \([\text{Sc}(\eta^2\text{-C}_7\text{BuCP})_2])\) which exhibited a rich EPR spectrum (see above).\(^{[58]}\) The strong absorption in the visible region of the electronic spectrum of a dark-blue \( n \)-heptane solution of 67 provides further evidence of the presence of a low valent Sc centre (\( \lambda_{max} = 613 \text{ nm, } \epsilon = 15000 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1} \)).\(^{[58]}\)

Finally, in 2006, Deacon and co-workers reported that the dinuclear Eu\(^{III}\) complex \([[\text{Eu}(\text{diglyme})_2(\mu-\text{CCPh})_2]]([\text{C}_7\text{BuCP}])\) (68) formed as a minor product from the reaction of Eu(CCPH\(_2\)) with 1.2 equivalents of tBuCP in THF, followed by the addition of diglyme and toluene (Scheme 14).\(^{[59]}\) Only a small crop of yellow crystals of 68 formed from the reaction mixture, and the authors postulated that oxidative dimerisation of half of the alkynyl groups to form (CCPh\(_2\)) had occurred. Crystals of the cage P\(_6\)C\(_8\)Bu were also identified in the reaction mixture, thus the authors posited that \([\text{C}_7\text{BuCP}])_2\) and \([\text{C}_7\text{BuCP}])_4\) anions had both initially formed via phosphalkyne oligomerisation, maintaining the +2 oxidation state of Eu. Despite the low yield of 68, this complex was characterised by single-crystal XRD, IR spectroscopy and mass spectrometry. The dinuclear Eu\(^{III}\) dication features eight-coordinate Eu centres with bicapped trigonal prismatic geometries; the diglyme ligands are tri-
dentate and the two alkylnyl ligands bridge to form an asymmetric Eu$_2$C$_3$ core. From the context of this review, the most interesting structural feature of 68 is that the two [C$_7$Bu$_4$P$_3$]$^-$ anions do not bind to the Eu$^2$ centres; isolated [C$_7$Bu$_4$P$_3$]$^-$ rings had not previously been observed in the solid state. Remarkably, 68 is the only Eu phospholyl or arslyl complex that has been structurally authenticated to date.

7.2. Planar cyclo-$P_5$ complexes

Although pentaphospholyls form a unique family of complexes that are somewhat independent of the organophosphorus derivatives in the rest of this review, we include them here for completeness; there have been no reports to date of Ln or An cyclo-$P_5$ complexes. Metal cyclo-$P_5$ complexes are typically synthesised via the direct activation of white phosphorus or reactions with various $P_5^-$transfer agents; aromatic cyclo-$P_5$ anions are one of a number of potential outcomes of these reactions along with a range of $P_5^-$-bound fragments, including Zintl clusters and related aromatic cyclo-$P_5$ dianions. To the best of our knowledge only one Ln and one An complex that contain planar cyclo-$P_5$ ligands have been structurally authenticated to date (Figure 21). The sole example of a structurally authenticated Ln complex containing a planar cyclo-$P_5$ ring, [[(Sm(Cp*)$_2$($μ$-$η^1,η^2$-cyclo-$P_5$))Mo(Cp)(CO)$_2$]] (69), was reported in 2015 by Roeksy and co-workers to form a minor product from the reduction of the $P_5$ unit in [[(Mo(Cp)(CO)$_2$)$_2$($μ$-$η^1,η^2$-P$_5$)]$^-$] by [Sm(Cp*)$_2$(THF)]. Owing to disorder the metrical parameters from the single-crystal X-ray diffraction data for 69 are unreliable, but the connectivity is clear-cut, with the planar cyclo-$P_5$ ring $η^1$-bound to two Mo centres and $η^2$-bound to a third, with one of the P atoms additionally $η^1$-bound to a single Sm centre (Sm–P: 2.978(11) Å). Unfortunately, owing to the low yield of 69 and co-crystallisation with another reaction product, no additional characterisation data could be obtained.

Also in 2015, Liddle and co-workers reported the synthesis of the dinuclear inverted sandwich uranium complex [[UN[NC$_8$H$_6$NSiPr$_3$]$^-$]$^2$[[μ-$η^1,η^3$-cyclo-$P_5$]$^-$]] (70) from the reduction of $P_5$ by the $U^6$ precursor [[UN[NC$_8$H$_6$NSiPr$_3$]$^-$]] in a 1:1 U/$P_5$ ratio. The planar cyclo-$P_5$ ring is disordered over two positions in the solid-state structure of 70, which again prevents meaningful analysis of P–P distances, and the U–P distances (range 3.250(6)–3.335(6) Å) are relatively long owing to the bulky ancillary ligands. Surprisingly, the U–N distances in the ancillary ligands are in line with the presence of two identical U$^6$ centres rather than the expected mixed U(III/IV) system for a cyclo-$P_5$ anion. All other analytical data for 70 (NMR and UV/Vis/NIR spectroscopy, SQUID magnetometry) are also consistent with the formal presence of two U$^6$ ions and a cyclo-$P_5$ dianion, although such formalisms are often moot in systems with significant covalency. DFT studies of 70 showed significant $δ$-donation from filled uranium 5f orbitals of appropriate symmetry to the vacant $π^*$ $e_1$ orbitals of cyclo-$P_5$, which were again in line with significant charge transfer from uranium to the cyclo-$P_5$ ring. This is a consequence of both the ability of uranium to donate $δ$-electron density using 5f orbitals and the superior electron accepting capability of cyclo-$P_5$ over Cp; the isolation of 70 versus the absence of Cp from the family of bridging cyclo-C$_n$R$_n$ ligands ($n$ = 4, 6–8) in inverted sandwich An chemistry is significant.

It is noteworthy that non-planar cyclo-$P_5$ fragments were observed as part of $P_5$ moieties in the Sm complexes [[Sm(C$_5$Me$_3$R)$_2$][Fe(Cp*)$_2$($μ$-$η^1$-$η^2$,$η^2$-$η^3$-P$_5$)]$^-$] (R = Me, Pr), where a P–P single bond connects the two $P_5$ sub-units that are $η^2$-bound to Sm and $η^1$-bound to Fe; these complexes were prepared in 2013 by Scheer, Roeksy and co-workers from the reactions of parent [[Sm(C$_5$Me$_3$R)$_2$(THF)]$^-$] with [Fe(Cp*)$_2$(P$_5$)]. Planar aromatic cyclo-$E_4$ dianions ($E$ = P, As) have also been observed in f-block chemistry, and structurally characterised examples have been shown to exhibit a range of binding modes when bridging between metal centres, with the steric effects of ancillary ligands dictating how these rings coordinate.

8. Summary and Outlook

Although group 3 and f-block metal phospholyl and arslyl chemistry is immature compared with cyclopentadienyls and their derivatives, some differences between the families of complexes are already evident, which provide perspectives for future exploration. Firstly, the ability of monophospholyls to stabilise low oxidation states has been demonstrated by the isolation and reactivity studies of rare examples of molecular Tm$^3$ complexes; given the crucial role of Cp$^5$ ligands in the development of low oxidation state Ln and An chemistry, the further exploitation of monophospholyl and -arslyl ligands in synthesis and reactivity studies of analogous complexes is an obvious pathway to explore. Fine-tuning of reduction potentials by multiple heteroatom substitution in polyphospholyl and -arslyl complexes could be a useful tool in stabilising more exotic low oxidation state group 3 and f-block complexes, as has been demonstrated in the isolation of a Sc$^3$ complex. Polyphospholyl substituents are limited to tert-butyl groups to date owing to the current reliance on RBUCP to generate these ligands; the development of facile synthetic routes to a wide range of polyphospholyl and -arslyl ligands would be transformative in developing their f-block chemistry to the same degree as monosubstituted analogues. Second, some interesting SMM properties have already been reported for Ln monophospholyl complexes; in view of recent reports of...
high blocking temperature Ln SMMs containing Cp8 ligands, it is unsurprising that Ln SMMs containing polyphospholyl ligands have already been predicted and are targets for the synthetic community. The optical properties of Ln phospholyl and arsosyl complexes will also vary from Cp8 derivatives and one can speculate that these can also be tuned by variation of the ligand field to suit specific applications.

There is considerable chemical space to explore in An phospholyl and arsosyl chemistry. Currently, there are only structurally characterised examples of such complexes for An = U; the lack of Th complexes to date is surprising given the relatively low radiological hazard of Th, the similarity of ThIV and UIV chemistry, and that solvated ThIV starting materials are readily synthesised from commercially available precursors.[27] For transuranic elements, the increasing radiological hazard across the An series limits investigations to specialist facilities,[16] but the recent extension of Cp8 chemistry to a structurally authenticated AmIV complex[27] indicates that phospholides and arsosyls can also find success for Np, Pu, Am and even beyond. Investigations into An phospholyl and arsosyl redox chemistry is also currently limited to U4+ and U6+ examples, where there are a wide range of An oxidation states to explore;[22] for example, for U, Cp8 complexes have been structurally authenticated from the +2 to the +6 oxidation state.[24-29] There are also pathways for future exploration that are of relevance to both Ln and An phospholyl and arsosyl chemistry, which have not yet been fully exploited. Firstly, we speculate that the heteroatom lone pairs in phospholyl and arsosyl rings in n1-bound complexes could be actively involved in reactivity profiles. Ln and An Cp and Cp8 complexes have well-established applicability in a wide range of hydroelementation and polymerisation reactions, including catalytic processes,[27] and low oxidation state Ln and An complexes of these ligands have shown rich small molecule activation chemistry.[24-29] We anticipate that future investigations with analogous Ln and An phospholyl and arsosyl complexes will furnish results that complement and contrast with established Cp/Cp8 chemistry, with the possible involvement of P and As lone pairs in these reactions an exciting prospect. Secondly, the presence of 100% abundant spin-active 31P and 77As nuclei in phospholyl and arsosyl rings provides new opportunities for quantification of f-block covalency by NMR[28] and pulsed EPR[27] spectroscopy. In the latter case, this has already been achieved for Th and U Cp8 complexes with 1.1% abundant 113Cd nuclei, thus the presence of 31P or 77As would provide improved sensitivity, as has been shown in NMR spectroscopy covalency measurements for heterooatom-containing ligands.[26] Taking into consideration the importance of minor differences in covalency between f-block elements to their technological applications, obtaining such data is crucial for future developments.[28]

To conclude, although the field of f-block phospholyl and arsosyl chemistry is in its relative infancy it has already provided important results that juxtapose with those of derivatised cyclopentadienyl f-block complexes. Given these past successes and the potential for wide variations in chemistry with heteroatom substitution, we realistically anticipate that other exciting results will surely follow in future investigations.

Acknowledgements

We would like to thank the European Research Council (CoG-816268 for D.P.M.), the UK Engineering and Physical Sciences Research Council (EP/R002605X/1 for P.E.), and the University of Manchester for support. B. L. L. Réant is thanked for helpful comments.

Conflict of interest

The authors declare no conflict of interest.

Keywords: actinides · arsosyl · lanthanides · phospholyl · rare earths

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