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Tetraphenylpentalenide organolanthanide complexes†

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The D_{2h} symmetrical 1,3,4,6-tetraphenylpentalenide is an excellent ligand for the stabilisation of strongly coloured bis(pentalenide) Ln^{III} sandwich complexes. These easily accessible compounds complement previously reported lanthanide organometallics and provide new opportunities to understand the roles of the f-orbitals in electronic structure and bonding.

Organometallic complexes have made major contributions to the understanding of electronic structure and bonding across the periodic table. Sandwich molecules such as ferrocene and bis(benzene) chromium have led the way and allowed for applications in organic spintronics and single molecule memory storage.¹ f-block compounds can display fascinating electronic properties at the quantum level including magnetism, Kondo behaviour, and superconductivity.^{2–6} Fundamental studies on f-block complexes with unusual electronic structures can help explain these phenomena, potentially providing transformative breakthroughs for quantum computing and future technologies at the nano-scale.^{7–12} Surprisingly, the range of organometallic ligands with the capacity to form bonding interactions with orbitals of many different symmetries is still small and limited mostly to monocyclic aromatic hydrocarbons such as 6π cyclopentadienide (C_5H_5^- , Cp^-)¹³ and 10π cyclooctatetraenide ($\text{C}_8\text{H}_8^{2-}$, COT^{2-})¹⁴ derivatives.¹⁵ The use of bicyclic 10π pentalenide ($\text{C}_8\text{H}_6^{2-}$, Pn^{2-} ; Fig. 1) in f-block organometallic chemistry has grown in popularity due to its D_{2h} symmetry

allowing for favorable bonding interactions involving δ -symmetry orbitals and the metal's d_{z^2} which are not available in the COT analogues due to their D_{8h} symmetry.¹⁶ Besides the parent Pn^{2-} synthesised by *in situ* deprotonation of unstable dihydropentalene,¹⁷ 1,4-disilylated derivatives (Pn^{\ddagger})^{2–} with increased stability and solubility have been reported.¹⁸ A hexamethylated pentalenide (Pn^*)^{2–} can also be accessed by a multi-step organic synthesis,¹⁹ and more recently 1,3,4,6-tetraphenyl pentalenide ($\text{Ph}_4\text{Pn}^{2-}$) has been reported to be accessible through the ring-closing condensation of Cp's with enones.^{20,21}

Bis(η^8 -pentalenide) sandwich compounds [$\text{M}(\eta^8\text{-C}_8\text{H}_n(\text{R})_{6-n})_2$] have been reported for Ti, Zr, Hf, Ce, Th, and U.¹⁸ These formal 20 electron complexes typically feature a staggered conformation with some degree of folding of the pentalenide around its bridgehead carbons (CB, $\text{C}_7\text{-C}_8$; Fig. 1).²² We were interested in the f-block chemistry of sandwich structures such as $\text{K}[\text{Ce}^{\text{III}}(\eta^8\text{-Pn}^*)]_2$,²³ and M^{IV} ($\text{M} = \text{Ce}, \text{U}, \text{Th}$) containing [$\text{M}(\eta^8\text{-Pn}^{\ddagger})_2$] (Fig. 2),^{24–26} because the ground state electronic structure of cerocene, and also the actinocenes, has been the subject of much debate.²⁷ In particular, comparison of the planar D_{8h} symmetrical COT^{2-} with the folded D_{2h} symmetrical Pn^{2-} in the stabilisation of f-block cations should offer further insight into the covalency in f-block bonding.^{28–30} The ground state electronic structure of [$\text{Ce}(\text{COT})_2$] is probably best viewed as a mixture of $\sim 80\%$ Ce^{III} with an isolated $4f^1$ cation coupled to an unpaired electron in the rings' π orbitals, and $\sim 20\%$

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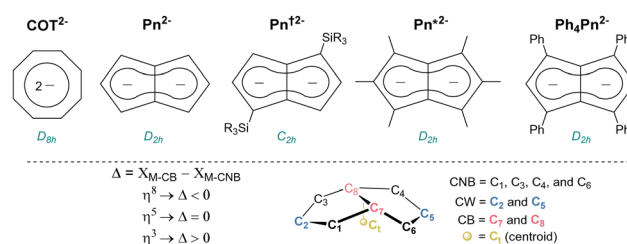


Fig. 1 Dianionic 10π ligands for organometallic complexes (upper) and positional numbering and hapticity definition of pentalenides (lower).



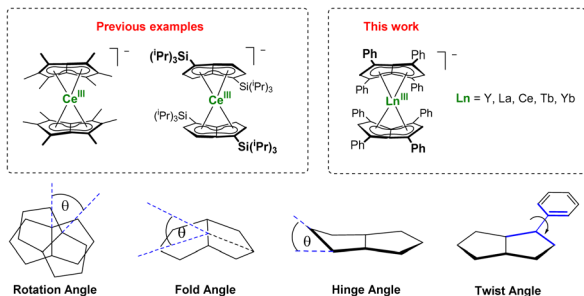


Fig. 2 F-block bis(pentalenide) sandwich complexes (upper) and geometric definitions of relevant structural parameters (lower).

of a state containing the Ce^{IV} ion sandwiched by two aromatic 10π dianions with significant Ce 4f–ring covalency.^{31–33} Pentalenides have also been shown to support pianostool f-block complexes with interesting properties. For example, [(η⁸-Pn⁺)Dy^{III}(η⁵-Cp*)] behaves as a single molecule magnet with an energy barrier of 245 cm⁻¹.³⁴ In related U^{III} complexes the fold of the Pn²⁻ ligand was noted as important for subsequent reactivity such as dinitrogen reduction to form (N₂)[U(η⁵-Cp*)(η⁸-Pn⁺)]₂.^{35,36}

Here we explore the organometallic lanthanide chemistry of 1,3,4,6-tetraphenylpentalenide **Ph₄Pn**²⁻ with a range of 4f cations and study the metal–ligand bonding both experimentally and computationally.

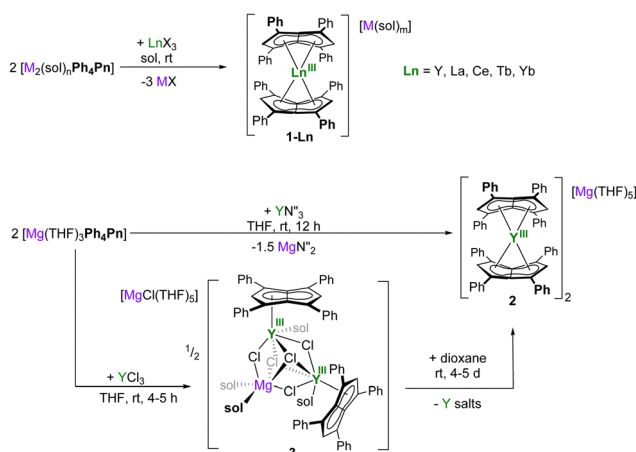
Salt metathesis reactions between dilithium, disodium, or dipotassium salts of **Ph₄Pn**²⁻ reacted cleanly with half an equivalent of anhydrous lanthanide(III) halides in THF or DME to afford the pentalenide Ln sandwich ‘ate’ complexes [M(sol)_m][Ln^{III}(Ph₄Pn)₂]₂ (**1-Ln**) for Ln = Y (orange), La (bright orange), Ce (rust-orange), Tb (bright red), Yb (red-orange) (Scheme 1). These are a good representation of the size and Lewis acidity range for the rare earths, with *r*_{covalent}(6-coordinate Ln^{III}) = 0.900 Å (Y), 1.032 Å (La), 1.01 Å (Ce), 0.923 Å (Tb),

0.868 Å (Yb).³⁷ The reactions proceed most cleanly for the largest Ln, with isolated yields of 76% for **1-La**, 87% for **1-Ce**, and 77% for **1-Tb**, but only a few single crystals could be isolated from the reaction that afforded **1-Yb**. ¹H NMR spectroscopic analysis of the crude product solution of the latter suggested the formation of a mixture of products, so further efforts to isolate pure material were not pursued. We have also crystallographically characterized the new DME adducts of Li₂[Ph₄Pn], K₂[Ph₄Pn], and **1-Ln** (Fig. S12 and S22, ESI[†]).

Magnesium pentalenides may also be used to make rare earth pentalenide sandwich complexes.³⁸ A metathesis reaction between Mg[Ph₄Pn] and Y(N[′])₃ (N[′] = bis(trimethylsilyl)amide, Scheme 1) gave the magnesium congener of **1-Y**, orange [Mg(THF)₅][Y^{III}(Ph₄Pn)₂]₂ (**2**) in 40% isolated yield plus Mg(N[′])₂ as a by-product. An orange slurry of equimolar YCl₃ and Mg[Ph₄Pn] in THF at room temperature immediately turns red, and work-up after four hours yields the trimetallic [(Mg^{II})₂Y^{III}] halide bridged complex [MgCl(THF)₅][(Y^{III}Ph₄Pn)₂(μ-Cl)₅Mg(THF)₄] (**3**, Scheme 1). The same reaction with group 1 pentalenide salts gave similar results (Fig. S1, ESI[†]), suggesting the formation of halide-bridged mono-pentalenide clusters to be characteristic of the harder Y^{III} cation.³⁹ Attempts to break up the halide bridges to access monomeric pianostool Y^{III} complexes by addition of AgPF₆, B(C₆F₅)₃, or AlCl₃ led to decomposition into unidentifiable mixtures, but **3** could be converted to the bis(pentalenide) sandwich [Mg(THF)₅][Y^{III}(Ph₄Pn)₂]₂ (**2**) congener to **1-Y** by addition of dioxane, as confirmed by NMR and XRD (Fig. S2, ESI[†]). All these reactions support the expectation that the bis-η⁸ sandwich complexes are the thermodynamically favored products for the rare earth cations.

The ¹H NMR spectra of the diamagnetic **1-Ln** and **2** show diagnostic resonances for the pentalenide wingtip protons *H_w* which are sensitive reporters for the degree of shielding of the 10π system (Fig. 1).⁴⁰ Spectra of **1-La** in THF show a single resonance for the two equivalent *H_w* at 6.39 ppm and a corresponding *C_w* resonance at 122.5 ppm. Comparatively, the NMR spectra of **2** in THF contained a single ¹H resonance for *H_w* at 7.20 ppm and a ¹³C resonance for *C_w* at 124.1 ppm. The latter is 8.6 ppm higher frequency than in Mg[Ph₄Pn] which exists as a solvent-separated ion pair in ethereal solution.³⁸ The NMR spectra of the cluster complex **3** also show a *D*_{2h} symmetrical pentalenide with one sharp set of equivalent *H_w* at temperatures down to -60 °C in THF, while DOSY analysis suggests the cluster anion of **3** remains intact in solution (*D* = 6.325 × 10⁻¹⁰ m² s⁻¹ corresponding to 1462 g mol⁻¹ compared to MW = 1484 g mol⁻¹; Fig. S3, ESI[†]). These observations support the presence of strong Mg–Cl–Y interactions in the trinuclear cluster with rapid ring slippage of the η⁵ pentalenide on Y^{III}.⁴¹

The *D*_{2h} symmetry of 1,3,4,6-**Ph₄Pn**²⁻ greatly facilitates structural analysis of the new sandwich complexes in solution and in the solid state, as it eliminates the formation of *meso*, *rac*, and twist isomers seen with the *C*_{2h} symmetrical 1,4-bis(silyl)-substituted (Pn⁺)²⁻ (Fig. 1).¹⁸ **1-Ln** crystallize as either solvent-separated ion pairs (SSIP) or contact ion pairs (CIP) depending on the solvent and counteraction. In each case, the Ln^{III} ion sits on a crystallographic *C*₂ axis positioned centrally



Scheme 1 Synthesis of [M(sol)_m][Ln^{III}(Ph₄Pn)₂]₂ (**1-Ln**) for Ln = Y, La, Ce, Tb, Yb from group 1 pentalenide salts (for Ln = Y, M = Li, *n* = 4, X = Cl, sol = THF, M(sol)_m = Li(DME)₃; for Ln = Ce, M = K, *n* = 2, X = Br, sol = DME, M(sol)_m = K(DME)₄; for Ln = Yb, M = Na, *n* = 6, X = Cl, sol = THF, M(sol)_m = Na(THF)₅), synthesis of the Mg analogue of **1-Y**, [Mg(THF)₅][Y^{III}(Ph₄Pn)₂]₂ (**2**) from a magnesium pentalenide, and a half-sandwich cluster [MgCl(THF)₅][(Y^{III}Ph₄Pn)₂(μ-Cl)₅Mg(THF)₄] (**3**).



Time-dependent DFT calculations of the electronic excitation spectra of **1-Ln** reproduced the observed spectral patterns in gas phase calculations as well as with the use of a solvent model, although at the chosen level of broadening the computed bands are more intense in the low-energy regions than the experimental spectra (Fig. S31, S33 and S36, ESI†). The natural transition orbital (NTO) analysis of **1-La** (Fig. 4 and Fig. S32, ESI†) shows low-energy bands around 1.6 eV/780 nm and 2.5 eV/500 nm. The calculated spectrum also features comparatively intense bands at energies of 3.1 eV and higher/400 nm and below. According to the NTO analysis, an intense transition calculated around 375 nm has mixed intra-ligand, MLCT, and metal 5d to 6p character, the latter being possible because of the donation into 5d in the ground state. The most intense transition in the 500 nm peak is mixed LMCT and 5d–5d, with the acceptor NTO of the dominant contribution to the transition having approximate δ symmetry about the C_t –Ln– C_t axis. The donor ('hole') NTO in both cases corresponds closely to the HOMO–1. The band at lowest energy is assigned as HOMO to ligand π^* with weak metal contributions in the acceptor NTO (Fig. 4). The peak assignment is qualitatively similar for the corresponding absorptions of **1-Ce** (Fig. S33–S35, ESI†) and **1-Tb** (Fig. S36–S37, ESI†). In contrast to the analogous COT^{2-} complexes, participation of the phenyl substituents is clearly noticeable in the NTOs. Furthermore, the pentalenides induce mixing of rotational symmetries of σ , π , δ , and φ where the metal and ligand fragment orbitals are similar in energy (Fig. 4 and Fig. S38–S43, ESI†).

In conclusion, the $\text{Ph}_4\text{Pn}^{2-}$ ligand is highly suited for stabilising f-block organometallics giving access to both half-sandwich as well as sandwich complexes of the rare earths. Its ease of synthesis, high symmetry and ready crystallisation facilitate NMR and XRD analysis and promises access to the first homologous series of f-block pentalenide sandwich complexes to investigate fundamental aspects of electronic structure and bonding. In comparison to unsubstituted Pn^{2-} and COT^{2-} we find $\text{Ph}_4\text{Pn}^{2-}$ to be a better acceptor, *i.e.* the order of ligand-to-metal electron donation (primarily into 5d orbitals) is $\text{Pn} > \text{COT} > \text{Ph}_4\text{Pn}$. This will prove useful for the stabilisation of electron-rich f-block organometallics where the comparatively low symmetry offers positive overlap of ligand frontier orbitals with the metal ion's d_{z^2} orbital which is not possible in the COT^{2-} complexes.

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Data availability

Crystallographic datasets are available from the CCDC deposition numbers 2332849, 2357823–2357832 and other analytical data can be retrieved via DOI: <https://doi.org/10.5061/dryad.sxksn03bf>.

Conflicts of interest

There are no conflicts of interest to declare.

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