

The first structurally authenticated zerovalent heteroarene complex of a lanthanide; synthesis and X-ray structure of bis(2,4,6-tri-*tert*-butylphosphorin)holmium(o)

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Holmium vapour reacts with 2,4,6-tri-*tert*-butylphosphorin to afford the zerovalent $[\text{Ho}(\eta\text{-PC}_5\text{H}_2\text{Bu}^t\text{-2,4,6})_2]$, the first structurally characterised complex of this class.

The organometallic chemistry of the lanthanides has seen huge growth in recent years. Initial employment of ligands utilising purely electrostatic bonding was widespread, but recently the use of anionic and neutral π -ligands has emerged to encompass a wide range of complexes.^{1,2} The reports of binding of only neutral ligands still remain predominantly in the field of low-temperature matrix-isolation studies, since the highly electro-positive metal centre is difficult to stabilise in very low oxidation states.^{3–5} Examples of stable compounds where binding to the lanthanide can be regarded as covalent in nature are the bis(tri-*tert*-butylarene) zerovalent lanthanides.⁶ These complexes should not be considered as ‘metastable’ metal atoms isolated in the arene organic cavity, since thermochemical bond energy measurements supported by theoretical calculations have shown that the complexes which form are indeed thermodynamically stable with respect to their constituent metal atom and arenes, and that there is significant back bonding from the metal frontier orbitals.^{7,8} The members of the series of f-element bis(η -1,3,5-tri-*tert*-butylbenzene)metal(o) compounds that have not been isolated at room temperature are either those where the promotion energy from f^n to an $f^{n-1}d^1s^2$ configuration for bonding is prohibitively high, or those in which the atomic radius is presumably simply too large to allow kinetic stability through steric saturation.⁶ We have been interested in synthesising further examples of these sandwich compounds using a variety of new ligands to access remaining members of the series, and explore the reactivity thereof.

The replacement of a CH moiety by phosphorus is well documented, as is the effect on first-row transition-metal complexes synthesised from the resultant heteroarene.⁹ The use of tri-*tert*-butylphosphorin both constrains the mode of bonding interaction to a π -arene type by hindering access to the phosphorus lone pair, and satisfies the requirement of steric saturation at the metal centre for stabilisation of such an electropositive metal.^{10–13}

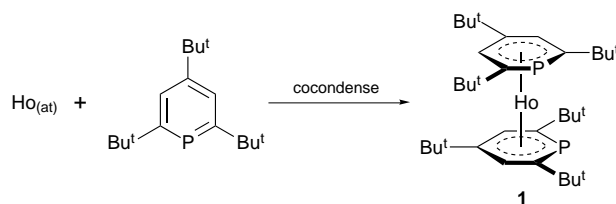
Cocondensation of holmium vapour with an excess of 2,4,6-tri-*tert*-butylphosphorin^{14,15} at -196°C leads to the formation of a dark purple matrix,¹⁶ from which extremely air- and moisture-sensitive purple iridescent crystals of bis(2,4,6-tri-*tert*-butylphosphorin)holmium(o) **1**, can be isolated in gram quantities (45% yield) after work-up and recrystallisation from pentane (Scheme 1).[†]

The UV–VIS spectrum of **1** shows one absorption at 489 nm, ascribed to ligand-to-metal charge transfer. This is in accordance with prior observations of bathochromic shifts that related heterocyclic systems show with respect to their carbocyclic analogues $\{\lambda_{\text{max}}[\text{Ho}(\eta\text{-C}_6\text{H}_3\text{Bu}^t\text{-1,3,5})_2] = 507\text{ nm}\}$.¹⁷ If the charge-transfer shift to higher energy is taken to imply stronger metal–ligand bonding, then this agrees well with

the observation of the capacity of a phospharene to act as a better π -electron acceptor but similar electron donor towards a metal.^{18,19}

The sandwich complex sublimes (10^{-5} mbar) with around 90% recovery at 160°C . This remarkable thermal stability enabled single crystals suitable for X-ray structural determination to be grown by vapour-phase diffusion. A Chem 3D representation of the structure is depicted in Fig. 1.[‡] It is interesting that although the distortion of the arene from C_{3v} symmetry on inclusion of the large heteroatom is considerable, the *tert*-butyl groups dominate the orientations of crystal packing, thus throughout the molecules in the lattice the phosphorus atoms evenly show 1/3 occupancy and the CH moieties 2/3 occupancy. No preference for *syn* or *anti* conformation of the rings in a single molecule can be inferred. The high solubility of the transition-metal complexes $[\text{V}(\eta\text{-PC}_5\text{H}_2\text{Bu}^t\text{-2,4,6})_2]$ and $[\text{Cr}(\eta\text{-PC}_5\text{H}_2\text{Bu}^t\text{-2,4,6})_2]$ mentioned by Elschenbroich *et al.* frustrated attempts to grow crystals suitable for X-ray structural determination.¹³ Extensive disorder meant the data collected for single crystals of the titanium complex synthesised in our laboratory remained insoluble so no meaningful comparisons can be made. Elschenbroich *et al.* showed that in the phosphorus-expanded bis(arene) molecule, a smaller metal fits better if the rings have mutually *syn* rather than *anti* conformations. This is confirmed in our solution studies of the titanium complex, $[r_{\text{cov}}(\text{Ti}) = 1.32\text{ \AA}]$.²⁰ The greater size of this metal $[r_{\text{cov}}(\text{Ho}) = 1.58\text{ \AA}]$ ²¹ is possibly a factor in allowing ready access to all relative conformations of the rings.

It is of interest that twelve of the *tert*-butyl methyl groups are oriented towards the central metal atom providing considerable steric shielding, Fig. 1(c), however no significantly short metal–carbon or –hydrogen distances are seen. This geometry was equally noticeable in the structures of $[\text{M}(\eta\text{-C}_6\text{H}_3\text{Bu}^t\text{-1,3,5})_2]$ ($\text{M} = \text{Ho}, \text{Gd}, \text{Y}$)²² which are isostructural with each other and show little change in ring geometry apart from the expected slight ring C–C bond lengthening upon binding of the ligand. The phospharene bond lengths in **1** are consistent with retention of aromaticity in the heteroarene upon complexation, and the rings remain planar apart from the slight inclination of each phosphorus atom towards the metal, bending from the plane described by the five carbon atoms by an angle of $6.7(7)^\circ$.



Scheme 1

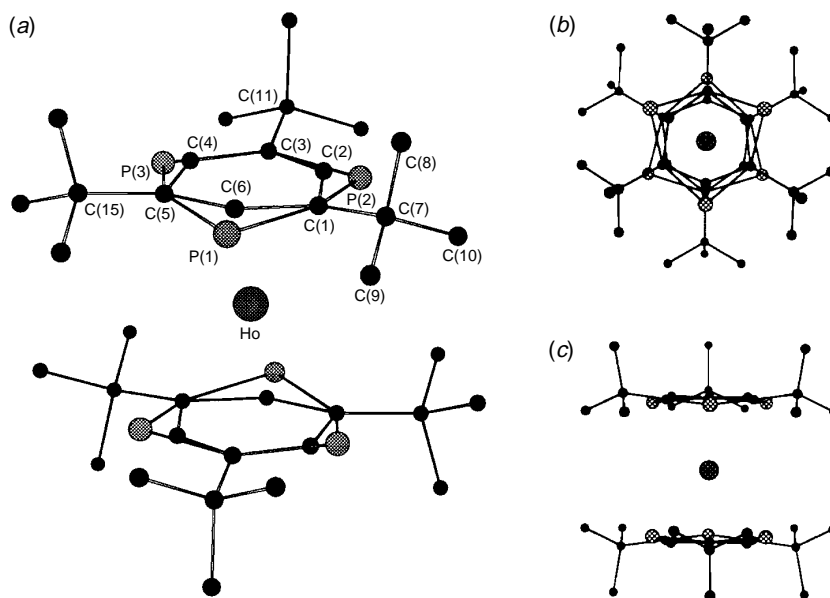


Fig. 1 (a) Chem 3D Representation of the crystal structure of **1**. (a) All orientations of P and C have been included, as refined in the structure, allowing for the three-fold disorder: Selected distances (Å) and angles (°): Ho–C(1) 2.649(7), Ho–C(2) 2.587(14), Ho–C(3) 2.633(10), Ho–C(6) 2.58(2), P(1)–C(1) 1.797(10), P(2)–C(1) 1.785(10), P(2)–C(3) 1.760(8), C(1)–C(2) 1.42(2), C(1)–C(6) 1.45(12), C(1)–C(7) 1.495(13), C(2)–C(3) 1.44(2), C(3)–C(4) 1.44(2), C(3)–C(11) 1.52(2), C(7)–C(8) 1.44(2), C(7)–C(9) 1.43(2), C(7)–C(10) 1.39(2); C(1)–P(1)–C(5) 94.1(7), C(1)–P(2)–C(3) 95.9(6), C(2)–C(1)–C(7) 126.1(10), C(2)–C(1)–P(1) 125.8(9), C(7)–C(1)–P(1) 107.8(6), C(1)–C(2)–C(3) 134.0(13), C(4)–C(3)–C(2) 105(2). (b) Top view, all disordered atoms refined are included. (c) Side view.

The rings are mutually parallel with perfectly staggered *tert*-butyl groups, bent slightly away from the metal (8.8°).

Repeated determinations of the magnetism of a toluene solution of **1** (Evans' method) reproducibly yield an effective magnetic moment of 8.9 μ_B , the solution displaying Curie–Weiss paramagnetism over the temperature range studied (205–355 K) with a value of $\theta = -10.6$ K. This value of the moment is lower than that calculated for the case where spin–spin coupling is small compared to kT (10.75 μ_B), and lower than that found in $[\text{Ho}(\eta\text{-C}_6\text{H}_3\text{Bu}^t\text{-1,3,5})_2]$ (10.10 μ_B) or atomic holmium (9.58 μ_B). The lowering of symmetry of the frontier orbitals inflicted by the heteroatom conceivably allows more extensive degree of distribution of the unpaired electron density away from the metal *via* enhanced spin–orbit coupling; this would lead to the observed lower value for μ_{eff} in **1** as compared with $[\text{Ho}(\eta\text{-C}_6\text{H}_3\text{Bu}^t\text{-1,3,5})_2]$.

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Footnotes

† Holmium (0.65 g, 3.9 mmol) was vaporised by resistive heating (alumina crucible, 250 W) and cocondensed with an excess of 2,4,6-tri-*tert*-butylphosphorin (20 g, 76 mmol) at -196 °C. The dark purple matrix was extracted from the vessel at ambient temperature under an argon atmosphere. Removal of free metal by filtration through a bed of Celite and recovery of excess ligand after removal of volatiles under reduced pressure, yielded a dark solid from which extremely air- and moisture-sensitive purple iridescent crystals of bis(2,4,6-tri-*tert*-butylphosphorin)holmium(o) **1**, could be isolated in 45% yield, 1.2 g after recrystallisation from pentane. UV–VIS: λ_{max} 489 nm (ϵ 1.2×10^4 dm³ mol⁻¹). MS (EI): m/z 693 (69%) (M⁺). Elemental analysis: Found C, 56.65; H, 8.47%. C₃₄H₅₈HoP₂ requires: C, 58.87; H, 8.43%. The low measured carbon percentage is also found for other complexes of this class, and is attributed to incomplete combustion.

‡ *Crystal data* for **1**: C₃₄H₅₈HoP₂, $M = 639.7$, monoclinic, space group C2/m (no. 12), $a = 10.279(3)$, $b = 17.758(3)$, $c = 10.293(2)$ Å, $\beta = 109.70^\circ$, $U = 1768.9(7)$ Å³, $T = 293(2)$ K, $Z = 2$, $D_c = 1.30$ g cm⁻³, $2 < \theta < 25^\circ$, $\mu(\text{Mo-K}\alpha) = 2.35$ mm⁻¹. Dark purple block, crystal size 0.20 \times 0.20 \times 0.15 mm. Refinement on F^2 using SHELXL-93. $R_1 = 0.048$ for 1547 reflections with $I > 2\sigma(I)$, $wR_2 = 0.126$ for all 1621 unique reflections. The molecule lies on a site of $2/m$ symmetry and the PC₅ rings show threefold disorder. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request

to the CCDC for this material should quote the full literature citation and the reference number 182/363.

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