Synthesis of Bis(η-1,3,5-tri-t-butylbenzene) Sandwich Complexes of Yttrium(0) and Gadolinium(0); the *X*-Ray Crystal Structure of the First Authentic Lanthanide(0) Complex, $[Gd(\eta\text{-}Bu^t_3C_6H_3)_2]$

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The vapours of yttrium and gadolinium react with 1,3,5-tri-t-butylbenzene to afford the metal(0) complexes $[(M(\eta\text{-}Bu^t_3C_6H_3)_2]$, M = Y, Gd; the *X*-ray crystal structure of the gadolinium complex shows the molecule to possess the parallel ring sandwich structure.

There are few known π-arene complexes of the f-block elements,[1,2] and only one such complex, $[Sm(\eta\text{-}C_6Me_6)(AlCl_4)_3]$,[2] contains a lanthanide ion.[2] In all of these complexes, the metal is in a high oxidation state (M^{3+} or M^{4+}), and the bonding can be viewed as an electrostatic attraction between the positively charged metal centre and the π-electron density of the arene ring.[2]

Recently we described the use of the bulky 1,3,5-tri-t-butylbenzene ligand to synthesise the 16-electron bis(η-arene) sandwich complexes of Zr^0 and Hf^0.[3] With less sterically demanding arenes such as benzene, toluene, or mesitylene, the latter are highly unstable.[4] We were therefore interested to examine the reactions of atoms of other electropositive elements with this ligand, and in particular those of the f-block metals.

Cocondensation of electron-beam vapourised yttrium with an excess of 1,3,5-tri-t-butylbenzene (at 77 K), using a type of apparatus described previously,[5] gave a deep purple matrix whose colour persisted on warm-up to room temperature (in a similar reaction using toluene, the purple colour was rapidly discharged on warm-up and only bulk metal and free toluene could be recovered from the reactor). Extraction of the product with hexane, removal of excess of 1,3,5-tri-t-butylbenzene by sublimation, and low temperature recrystallisation of the residue from pentane afforded deep purple crystals of $[Y(\eta\text{-}Bu^t_3C_6H_3)_2]$† (**1**) (yield *ca.* 50%, 2 g). Similarly, gadolinium vapour reacted with 1,3,5-tri-t-butylbenzene to give deep purple crystalline $[Gd(\eta\text{-}Bu^t_3C_6H_3)_2]$† (**2**), in similar yield after work-up.

Compounds (**1**) and (**2**) are highly soluble in hydrocarbon solvents and extremely sensitive to minute traces of air or moisture. They are thermally stable at room temperature, and may be sublimed at *ca.* 100 °C and 10^{-4} mbar with partial decomposition.

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† Satisfactory microanalysis has been obtained.

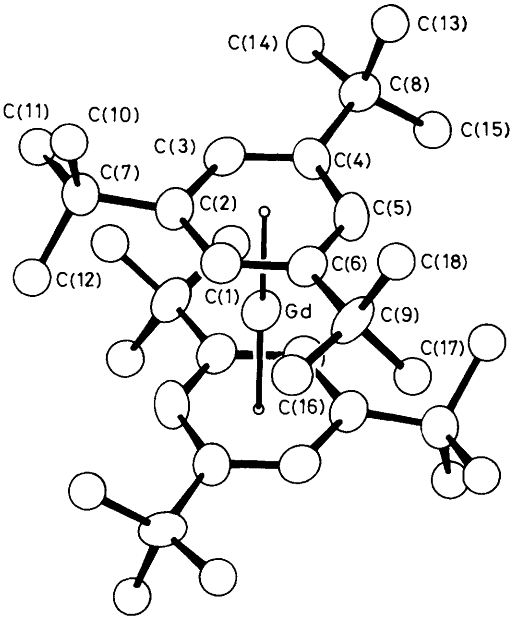

Figure 1. ORTEP view of $[Gd(\eta\text{-}Bu^t{}_3C_6H_3)_2]$. Selected bond lengths (Å): C(1)–C(2), 1.426(5); C(2)–C(3), 1.419(6); C(3)–C(4), 1.407(6); C(4)–C(5), 1.419(5); C(5)–C(6), 1.411(6); C(1)–C(6), 1.400(6); Gd–C(1), 2.626(4); Gd–C(2), 2.640(4); Gd–C(3), 2.638(4); Gd–C(4), 2.634(4); Gd–C(5), 2.585(4); Gd–C(6), 2.660(4); Gd–ring centroid, 2.219.

The yttrium complex (**1**) is paramagnetic, but is e.s.r. silent at room temperature; this is in accord with a bis(η-arene) sandwich structure with a ^2E ground state, in which the large *g*-value anisotropy would be expected to make an e.s.r. signal hard to detect. However, (**1**) displays an e.s.r. spectrum in frozen methylcyclohexane at 77 K, exhibiting coupling to ^{89}Y (100%, $I = \frac{1}{2}$): $g_{\parallel} = 2.085$, d, $A = 3.0$ mT; $g_{\perp} = 2.005$. The ^1H n.m.r. spectrum of the gadolinium complex (**2**) in $[^2H_8]$toluene shows only one very broad resonance centred at *ca.* δ 21 ($\nu_{\frac{1}{2}}$ 1600 Hz). The structure of (**2**) has been determined by single crystal *X*-ray diffraction and is shown in Figure 1, together with significant bond distances.‡

The gadolinium atom lies on a centre of symmetry, with the essentially planar arene rings eclipsed, presumably to minimise t-butyl group interactions; the t-butyl groups are bent out of the plane of the arene rings by 6—10°. Two of the three methyl groups of each t-butyl substituent are located between the planes defined by the arene rings; the metal centre is thus surrounded by twelve methyl groups, presumably accounting for the kinetic stability of the complex. The Gd–C distances range from 2.585(4) to 2.660(4) Å [average 2.630(4) Å], significantly shorter than the average M–C distance, 2.89(5) Å, found in $[Sm(\eta\text{-}C_6Me_6)(AlCl_4)_3]$.[2] Given the vastly different nature of the bonding in these two compounds, a discussion of the relatively short Gd–C distance would be premature. The Gd–C distance is, however, consistent with the observed M–C distances in other η-arene complexes such as $[Cr(\eta\text{-}C_6H_6)_2]$ [2.142(2) Å][6] or $[Mo(\eta\text{-}C_6H_3Me_3)(CO)_3]$ [2.372(5) Å],[7] given the relative sizes of the metals and the presumed strengths of the metal arene bonds. The bond angles in the arene rings are not perturbed (within standard deviation) from those of the free ligand,[8] but the average C–C bond distance appears to be slightly longer; this effect has been observed previously in the structure of $[Cr(\eta\text{-}C_6H_6)_2]$.[6] The ring C–C distances are sufficiently accurate to show that the alternating long and short C–C bonds, suggested for $[Cr(\eta\text{-}C_6H_6)_2]$,[6] are not present in (**2**). Preliminary *X*-ray studies show that the yttrium analogue (**1**) is isostructural with (**2**).

A discussion of the bonding in these complexes would be purely speculative at this point; the reaction between ytterbium atoms and 1,3,5-tri-t-butylbenzene gave only colloidal metal and free ligand. We are currently examining the remaining lanthanide and actinide elements to determine whether a necessary criterion for complex stability is a ground state or low-lying electronic configuration which contains d-electrons.[9]

Compounds (**1**) and (**2**) thus represent the first examples of bis(η-arene) complexes and the first unambiguous examples of metal(0) complexes of these elements.

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‡ *Crystal data* for (**2**): $C_{36}H_{60}Gd$, triclinic, space group $P\bar{1}$, a = 10.387(6), b = 10.579(5), c = 9.847(6) Å, α = 72.46(5), β = 61.78(4), γ = 66.14(4)°, U = 863.8 Å^3, Z = 1, D_c = 1.250 g cm^{-3}. Data were collected on a modified Picker FACS-1 diffractometer at 296 K using graphite monochromated Mo-K_α radiation. Scan type θ–2θ, 2967 independent reflections, $4.2° < 2\theta < 50.5°$. Corrections were made for Lorentz and polarisation effects, but not for absorption, μ(Mo-K_α) = 19.47 cm^{-1}. Standard intensities were checked every 250 reflections. Intensities were found to decrease by *ca.* 10% over 2 weeks and were adjusted accordingly. Scattering factors for neutral Gd, C, and H were taken from the International Tables for *X*-ray Crystallography. The structure was solved by the heavy atom method and parameters were refined by full matrix least squares with refinement on F (local unpublished programs and ORTEP 2). $R = 0.033$, $R_w = 0.037$, $w = 4F_o{}^2/[\sigma^2F_o{}^2 + (0.04F_o{}^2)^2]$. The final difference density range was 1.1 to −0.7 e Å^{-3}.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Preliminary crystal data for (**1**): $C_{36}H_{60}Y$, triclinic, space group $P\bar{1}$, a = 10.425(6), b = 10.547(5), c = 9.862(5) Å, α = 72.53(4), β = 61.70(4), γ = 66.07°, U = 864.80 Å^3, D_c = 1.117 g cm^{-3}.