Synthesis and *X*-Ray Crystal Structure of $[(C_5Me_5)_2Sm]_2C_4Ph_2$, A Samarium η^2-Complex derived from an Alkyne

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$(C_5Me_5)_2Sm(thf)_2$ (thf = tetrahydrofuran) reacts with PhC≡CC≡CPh to form $[(C_5Me_5)_2Sm]_2C_4Ph_2$ which is found by *X*-ray crystallography to have η^2-co-ordination of Sm^{3+} to the carbon–carbon multiple bonds.

Crystallographic evidence for η^2-co-ordination of unsaturated hydrocarbons to 4f elements is rare, a result which may be related to the ionic nature of these elements in their common oxidation states and the limited radial extension of their 4f valence orbitals.[1—3] Simple η^2-alkene or η^2-alkyne complexes of these elements have not been described in the literature. The closest related species are the η^2-co-ordination of a short C–N bond to Ln = Er and Y in the formimidoyl compounds $[(C_5H_5)_2Ln(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$[4,5] and the recently reported arene complex $(\eta^6\text{-}C_6Me_6)Sm(\eta^2\text{-}AlCl_4)_3$.[6] We report here the first structure in which η^2-co-ordination of a carbon–carbon multiple bond to samarium is observed.

We have previously reported that $(C_5Me_5)_2Sm(thf)_2$[7] (thf = tetrahydrofuran) reacts with PhC≡CPh to form the highly soluble $[(C_5Me_5)_2Sm]_2C_2Ph_2$, which does not readily form *X*-ray quality crystals.[8] Using the diyne PhC≡CC≡CPh, crystals suitable for an *X*-ray structure determination were obtained. $(C_5Me_5)_2Sm(thf)_2$ (0.58 mmol) reacts with PhC≡CC≡CPh (0.30 mmol) in thf overnight to form a red solution. Evaporation of the solvent *in vacuo* gives a solid which is washed with hexane leaving $[(C_5Me_5)_2Sm]_2C_4Ph_2$ in 60% yield. Recrystallization from toluene at −30 °C gives clear red crystals of $[(C_5Me_5)_2Sm]_2C_4Ph_2\cdot2PhMe$ (**1**) which was characterized by complexometric metal analysis, ^1H n.m.r. $[(C_4D_8O)$ δ 1.36 (s, C_5Me_5), 4.98 (m, *m*-H), 5.87 (br. t, *J* 5 Hz, *p*-H), 9.29 (d, *J* 7.5 Hz, *o*-H)], ^{13}C n.m.r. $[(C_4D_8O)$ δ 166.9 (s), 134.9 (s), 127.3 (d, *J* 157 Hz), 127.2 (d, *J* 157 Hz), 124.1 (d, *J* 160 Hz), 120.8 (d, *J* 160 Hz), 120.7 (s), 117.0 (s), 18.8 (q, *J* 125 Hz)], magnetic susceptibility $[10^6\chi_g$ (c.g.s. units) 2.96, $\mu_{eff.}$ (295 K) 1.8 $\mu_B]$, i.r. [(KBr) ν 2900 v br. s, 1575 w, 1450 s, 1380 s, 1250 w, 1150 m, 1060 s, 1020 s, 790 w, 750 m, 680 m cm^{-1}], and *X*-ray crystallography.†

A view of the molecule which resides on a crystallographic $2/m$ is site is given in Figure 1. The average Sm–C(C_5Me_5 ring) distance of 2.71(2) Å is in the range observed for other trivalent $(C_5Me_5)_2Sm(X)(Y)$ complexes.[10] This feature along with the magnetic susceptibility and the ^{13}C n.m.r. shift data indicate that the Sm bond distances should be evaluated as Sm^{3+} lengths. The Sm–C(1) distance of 2.48(1) Å is comparable to the Sm–C single bond distance in $(C_5Me_5)_2SmPh(thf)$, 2.511(8) Å.[11] The Sm–C(2) distance, 2.76(1) Å, is significantly longer. It is equivalent to the 2.77(2) Å Sm–C distance in the $\overline{Sm\text{–}OC(O)C}{=}C{=}O$ portion of $[(C_5Me_5)_4Sm_2(O_2CCCO)(thf)]_2$.[12] The Sm–C(2′) length of 3.03(1) Å is probably too large for a significant interaction.

The C(1)–C(2) distance of 1.33(2) Å has enlarged from the 1.20—1.22 Å C≡C lengths typical in free diynes and the C(2)–C(1)–C(3) angle has decreased from 180° to 125°.[13] The C(2)–C(2′) distance of 1.29(2) Å may be somewhat shorter than the analogous 1.37—1.38 Å length in free diynes, suggesting that some multiple bond character may exist in this bond. This distance is comparable to the C=C lengths of 1.31 Å typically found in allenes,[14] yet the C(1)–C(2)–C(2′) angle of 154(1)° is significantly non-linear. The (C_5Me_5 ring centroid)–Sm–(C_5Me_5 ring centroid) angle of 133.9° is in the normal range for $(C_5Me_5)_2Sm(X)(Y)$ complexes,[7] but the eclipsed nature of the rings is unusual. Eclipsed arrangements have been observed previously when steric crowding is a problem[15] and indeed there are two Me · · · Me non-bonding contacts in (**1**) which are less than the van der Waals minimum of 4 Å. However, the smallest contact, 3.11(3) Å, between C(15) and C(15′), occurs owing to the eclipsed arrangement. Similarly, the other close contact of 3.64(3) Å between C(17) and C(18‴) could be reduced by staggering the rings. The observed arrangement may result because the methyl groups prefer not to reside over the C(1)—C(2) multiple bond.

This structure shows conclusively that trivalent lanthanide ions can co-ordinate within a significant bonding distance of a carbon–carbon multiple bond to form an η^2-complex.‡

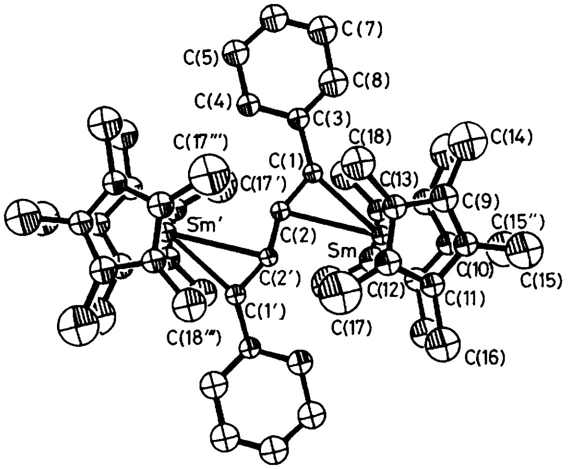

Figure 1. Molecular structure of $[(C_5Me_5)_2Sm]_2C_4Ph_2$ viewed perpendicular to carbon atoms 1—8 which reside on a crystallographic mirror plane which also contains the Sm atom. Thermal ellipsoids have been drawn at the 50% probability level.

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† *Crystal data* for (**1**) $C_{56}H_{70}Sm_2\cdot2C_6H_5CH_3$, monoclinic, space group $C2/m$, $a = 15.521(6)$, $b = 14.175(4)$, $c = 15.328(4)$ Å, $\beta = 114.55(3)°$, $U = 3067.5$ Å^3, $Z = 2$, $D_c = 1.33$ g cm^{-3}, $\mu = 19.68$ cm^{-1}, 2310 measured reflections, 1938 observed reflections, $2\theta_{max} = 46°$, $R = 0.047$, $R_w = 0.055$ [Mo-K_α radiation, $\lambda = 0.71069$ Å, $T = 295$ K]. Details of the data collection and refinement procedure are given in ref. 9. The structure was solved by the heavy atom method. An empirical absorption correction was applied based on ψ scans. Residues in the final difference Fourier ranged from 2 to −1.5 e Å^{-3}. Lattice toluene molecules were disordered. 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.

‡ *Note added in proof:* Since the submission of this manuscript, weakly interacting Lewis acid–base adducts of an alkyne and an alkene complex to $(C_5Me_5)_2Yb$ have been published: C. J. Burns and R. A. Andersen, *J. Am. Chem. Soc.*, 1987, **109**, 915, 941.

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