η-Arene Complexes of Scandium(0) and Scandium(II)

F. Geoffrey N. Cloke,*[a] **Karl Khan**[a] **and Robin N. Perutz**[b]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK*
[b] *Department of Chemistry, University of York, Heslington, York YO1 5DD, UK*

Cocondensation of scandium vapour with 1,3,5-tri-*tert*-butylbenzene affords the first example of a scandium(0) complex, the sandwich compound bis(η-1,3,5-tri-*tert*-butylbenzene)scandium; ESR and UV studies also the reveal the presence of a second compound from this reaction, formulated as a similarly unique example of scandium(II) arising from activation of one of the methyl groups of a *tert*-butyl ring substituent.

We have previously described the reactions of yttrium and lanthanide metal vapours with the bulky arene 1,3,5-tri-*tert*-butylbenzene, which afforded the bis(η-arene) sandwich complexes as the first examples of stable metal(0) complexes of this class of elements.[1,2,3] We now report the reaction of scandium atoms with this ligand, which yields not only the bis(η-arene) complex but also a product arising from C–H activation of one of the ring substituents of the ligand.

Cocondensation of electron-beam vapourised scandium with an excess of 1,3,5-tri-*tert*-butylbenzene at 77 K, using apparatus previously described,[4] gave a deep-red matrix whose colour persisted on warm-up to room temperature (in a similar reaction using toluene, the red colour was rapidly discharged on warm-up and only bulk metal and free toluene could be recovered from the reactor). Extraction of the products from the reactor with hexane, removal of solvent and excess 1,3,5-tri-*tert*-butylbenzene *in vacuo* and final sublimation (100 °C/10^{-4} mbar) of the residue afforded deep orange–green (dichroic), crystalline $[\mathrm{Sc}(\eta\text{-}^1\mathrm{Bu^t{}_3C_6H_3})_2]$,† **1**, in *ca.* 20% yield. Compound **1** displays an intense absorption ($\varepsilon = 2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) in the visible region at 495 nm in pentane solution, which we assign to a charge-transfer transition. The analogous 15-electron yttrium compound $[\mathrm{Y}(\eta\text{-}\mathrm{Bu^t{}_3C_6H_3})_2]$ has been shown to possess a ^{2}E ground state by ESR and magnetic measurements.[3] Like the yttrium complex, **1** is ESR silent at room temperature but exhibits an intense ESR spectrum at 77 K (Fig. 1). The spectrum of a frozen toluene solution is axial with $g_\perp = 2.004$ and $g_\parallel = 2.03$. There is prominent hyperfine coupling to ^{45}Sc ($I = 7/2$, 100%) revealing a clear octet for the perpendicular features ($A_\perp$ = 19.4 G) and the three parallel components to lowest fields ($A_\parallel$ = 29 G). The absence of an ESR spectrum at room temperature together with the g values of the low-temperature spectrum are indicative of a ^{2}E $(\mathrm{d}_{xy,x^2-y^2})^3$ ground state (contrast vanadocene with a d^3, ^{4}A ground state). The proximity of the g values to g_e shows that the orbital angular momentum is largely quenched probably by reduction from ideal D_{3d} symmetry.[1]

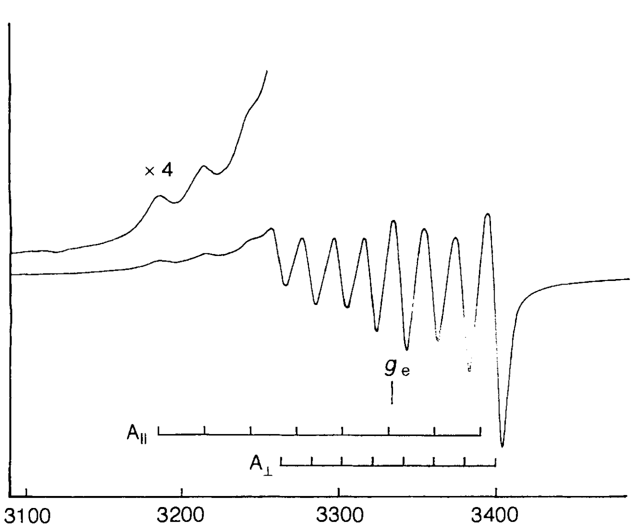

Fig. 1 ESR spectrum of **1** $[\mathrm{Sc(Bu^t{}_3C_6H_3)_2}]$, in frozen toluene at 77 K (ν = 9.3442 GHz). The inset shows a 4× expansion of the low-field region. The ESR parameters are given in the text.

During the work-up of **1**, as described above, we noticed a distinct purple tint to solutions of the products from the reactor prior to the sublimation step, which we reasoned might be due to a second product, which is unstable to the sublimation conditions. Thus, a modified work-up procedure was employed, in which the residue obtained after removal of solvent and excess 1,3,5-tri-*tert*-butylbenzene was recrystallised from pentane at −80 °C. This afforded a red–purple crystalline solid, which displayed two bands in the visible region of the spectrum in pentane solution, one at 495 nm due to **1** and a band due to a second product **2** at 555 nm ($\varepsilon = 10^4$ dm^3 mol^{-1} cm^{-1}). This solution exhibited a complex, but well resolved ESR spectrum at room temperature [Fig. 2(*a*)]. The analysis of this spectrum as an octet (g = 2.004, A (Sc) = 13.45 G) of doublets ($A[\mathrm{H}^1]$ = 8.9 G) of triplets ($A[\mathrm{H}^2]$ = 3.3 G) is supported by the simulation [Fig. 2(*b*)].

These results strongly suggest that the purple product **2** from the metal atom reaction is the 17-electron Sc$^{\mathrm{II}}$ complex $\mathrm{Sc}(\eta\text{-}\mathrm{Bu^t{}_3C_6H_3}(\eta^6,\eta^1\text{-}\mathrm{Bu^t{}_2[CMe_2CH_2]C_6H_3})\mathrm{H}$ shown in

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† Satisfactory microanalytical and mass spectral data have been obtained.

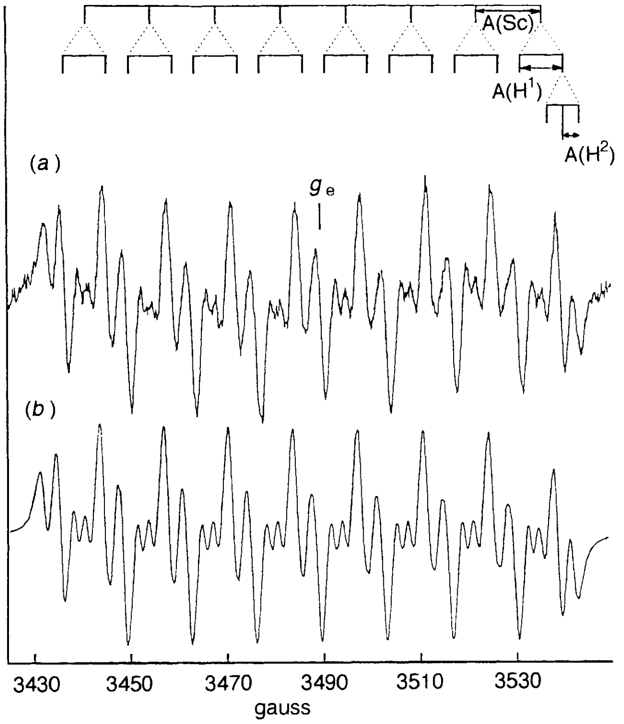
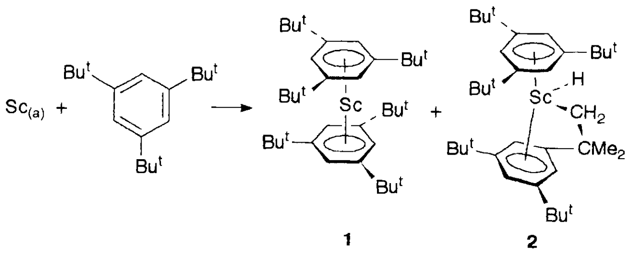


Fig. 2 (*a*) ESR spectrum of **2** at ambient temperature in toluene solution (v = 9.7785 GHz). The sloping background has been subtracted. The coupling pattern is indicated by the stick diagram. (*b*) Simulated spectrum with parameters as given in text.

Scheme 1, arising from C–H activation of a methyl group of a *tert*-butyl substituent on the 1,3,5-tri-*tert*-butylbenzene ring. Related intramolecular activation of ring substituents in η-C_5Me_5 complexes of Mo, W and Re has been previously observed by us.[5] The ESR spectrum arises from coupling to the scandium (octet), the hydridic proton (large doublet) and the CH_2 protons. We have been unable to separate **1** and **2**; the thermal instability of **2** precludes fractional sublimation (see above) whilst their high and very similar solubility in hydrocarbon solvents makes fractional crystallisation impracticable. Attempted low-temperature chromatography on deactivated alumina resulted in rapid decomposition.

Attempts to effect the interconversion of **1** and **2**, which we anticipated should be reasonably facile, by photolysis or careful thermolysis were unsuccessful. Thermolysis of a mixture of **1** and **2** in toluene at 80 °C or pentane at 45 °C resulted in the gradual disappearance of **2** and no concomitant increase in the amount of **1**, as monitored by UV–VIS spectroscopy. UV photolysis of a mixture of **1** and **2** under a variety of conditions had no effect on their relative concentrations. Thus, it appears that **2** is formed during the cocondensation experiment, and is the product of insertion of a naked scandium atom into a C–H bond of 1,3,5-tri-*tert*-butylbenzene. This is supported by the fact that when the cocondensation experiment is performed at 77 K the product ratio (as determined by UV–VIS spectroscopy) is *ca.* 8 : 1 in favour of the sandwich compound **1**, whereas cocondensation at 195 K significantly increases the relative amount of the C–H activation product **2**, to almost equimolar amounts. This is to be expected, since activation energy considerations mean that bond-breaking processes will be favoured at higher cocondensation temperatures. Metal atom induced C–H activation of the ring substituents of alkylbenzenes has also been previously observed, although in the products of the latter reactions, involving rhenium atoms, the π system of the activated alkylbenzene is not coordinated to the metal centre.[6]



Scheme 1

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