The first stable scandocene: synthesis and characterisation of bis(η-2,4,5-tri-*tert*-butyl-1,3-diphosphacyclopentadienyl)scandium(II)

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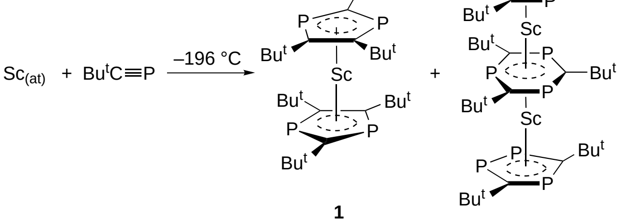
The first isolable example of a molecular scandium(II) complex, the dark purple scandocene [Sc(η^5-$P_2C_3Bu^t{}_3$)] 1, has been isolated from the cocondensation of scandium vapour with *tert*-butylphosphaalkyne, Bu^tCP at 77 K.

To date the only stable divalent lanthanoid metallocenes are those of the elements Sm, Eu and Yb for reasons which have been well documented.[1] These metallocenes are all highly reactive, showing strong reducing properties and consequent unusual reaction chemistry.[2] Very recently, two lanthanum species that are intermediates in the potassium reduction of $[La(Cp'')_3]$ $\{Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2\}$ have been observed and characterised, by EPR spectroscopy, as containing a La^{II} centre; one of the latter has been shown to be a dme solvated metallocene, $La(Cp'')_2(dme)$.[3]

In recent years metal vapour synthetic techniques have afforded a variety of novel and reactive low valent organometallic complexes of group 3 and the lanthanides directly from the elements; the technique remains the only route to zero-valent molecular lanthanide complexes.[4] Cyclisation reactions undergone by 2,2-dimethylpropylidynephosphine (*tert*-butylphosphaalkyne, Bu^tCP) at metal atoms during cocondensation reactions are of considerable current interest since the choice of metal clearly dictates the nature of ring or rings formed.[5] The most common cyclisation observed to date is the combination of five phosphaalkyne units resulting in the isolation of sandwich complexes such as $[(V(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$.[6] Here, we report the synthesis of $[Sc(\eta^5\text{-}P_2C_3Bu^t{}_3)_2]$ **1**, which represents only the second reported scandium(II) complex. The first example, also described by our laboratory, resulted from ligand metallation during the cocondensation of scandium vapour with tri-*tert*-butylbenzene; this product was unfortunately not separable from the admixture with $[Sc(\eta\text{-}C_6H_3Bu^t{}_3\text{-}1,3,5)_2]$.[7] The present work is thus the first instance in which we have been able to isolate, and thus fully characterise, a complex of scandium in this oxidation state.

Cocondensation of electron beam vaporised scandium with an excess of Bu^tCP at 77 K affords a dark brown matrix which is soluble in hexanes. Two products are separable from the dark solution by flash sublimation (220 °C, 10^{-5} mbar), Scheme 1.‡ The dark purple microcrystalline $[Sc(\eta^5\text{-}P_2C_3Bu^t{}_3)_2]$ **1** may be obtained from the sublimate by repeated sublimation and removal of by-product volatile oils. The forest-green triple-decker complex $[(\eta^5\text{-}P_3C_2Bu^t{}_2)Sc(\mu\text{-}\eta^6:\eta^6\text{-}P_3C_3Bu^t{}_3)Sc(\eta^5\text{-}P_3C_2Bu^t{}_2)]$, can be extracted from the sublimant and has been the subject of a recent communication.[8]



Scheme 1 Synthesis of **1**

The 1,2,4-triphospha-3,5-di-*tert*-butylcyclopentadienyl ring is regularly formed in conjunction with the 1,3-diphospha-2,4,5-di-*tert*-butylcyclopentadienyl ring in cyclisation reactions at a number of both transition elements and main group metal centres.[5b] Since the yield of **1** is approximately the same as that of the scandium(I) triple-decker complex $[(\eta^5\text{-}P_3C_2Bu^t{}_2)Sc(\mu\text{-}\eta^6:\eta^6\text{-}P_3C_3Bu^t{}_3)Sc(\eta^5\text{-}P_3C_2Bu^t{}_2)]$, which contains a greater proportion of ligated phosphorus, the number of phosphaalkyne monomers is preserved between the two complexes. This leads us to believe, at least in this case, that the fusion of a number of Bu^tCP molecules around the metal does not simply involve one metal centre.

Complex **1** is extremely air- and moisture-sensitive and is soluble in pentane and other non-polar solvents; a solution in thf decomposes immediately giving no tractable products, precluding electrochemical studies. Unfortunately, single crystals of **1** suitable for X-ray structural determination could not be obtained owing to its extreme solubility in solvents with which it does not react. The intense purple colour of **1**, due to an absorption maximum observed at 571 nm in the UV–VIS spectrum, is characteristic of a charge transfer band and appears to be a common feature in low- and zero-valent group 3 and lanthanide complexes.[4a]

Magnetic and EPR studies have been employed to study the d^1 electronic configuration of **1**. The EPR spectrum of **1** in toluene at 295 K is broad and shows coupling only to the ^{45}Sc nucleus, presumably due to rapid relaxation at this temperature, characterised by g_{iso} 1.9823 and $A_{iso}(^{45}Sc)$ 3.757 mT (I = 7/2, 100%). Upon cooling the sample to a glass at 120 K, well resolved coupling to scandium is observed, accompanied by further hyperfine coupling to the four phosphorus nuclei ($I = \frac{1}{2}$, 100%) which are equivalent on the EPR timescale at this temperature, Fig. 1. The resonance is characterised by $g_\perp$ 2.0098 with a calculated value of $g_\parallel$ 1.9273 and is well simulated using values of $A_\perp(^{45}Sc)$ 2.99 mT, $A_\parallel(^{45}Sc)$ 5.29 mT and $A(^{31}P)$ 0.72 mT. The solution magnetic moment is found to be 1.70 μ_B at room temperature,[9] showing no evidence for any orbital contribution to the spin only value (μ_{eff} = 1.73 μ_B).

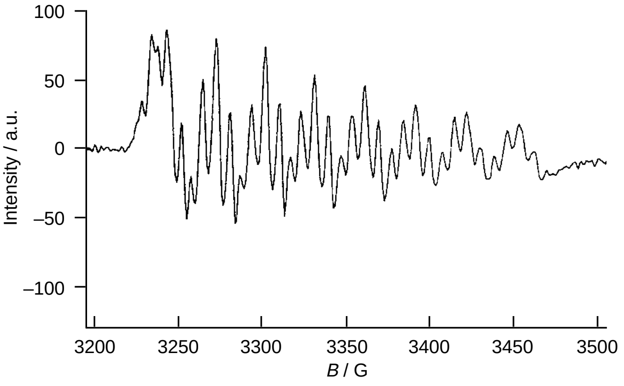


Fig. 1 EPR spectrum of **1** (toluene glass, 120 K)

Warren has suggested,[10] in a review of the ligand field theory for pseudo-axially symmetric metallocenes that a distortion and subsequent lowering to C_{2v} symmetry occurs since the degenerate ground state is necessarily Jahn–Teller unstable. The majority of d^1 metallocene systems extant in the literature are bent from pseudo-axial symmetry and the resulting quenching of any orbital contribution results in isotropic *g* values close to 2.00 and near spin-only values of the magnetic moment.[11] A similar argument is appropriate here since **1** is not modelled well as axial, owing to the unsymmetric substitution of the cyclopentadienyl rings.[12] The phosphorus atom in the diphosphatri-*tert*-butylcyclopentadienyl ligands provides a second magnetic nucleus, thus the resolution of coupling to the ligand nuclei by the electron, particularly at lower temperatures when the relaxation processes are slowed, strongly suggests that the single electron resides in the degenerate d_{xy} or $d_{x^2-y^2}$ orbitals (rather than the d_{z^2} orbital), as predicted.

The existence and stability of **1**, which thus completes the series of divalent metallocenes for the 3d elements, presumably result from a combination of steric shielding of the diphospha-tri-*tert*-butylcyclopentadienyl rings and the increased π-electron accepting properties of the rings induced by phosphorus incorporation.

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Notes and References

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‡ Scandium (0.30 g, 0.66 mol) was vaporised (power input 200 W) and cocondensed with Bu^{t}CP (10 g, 0.1 mol, M : L ratio 1 : 10) at 77 K.[1] The dark brown matrix formed over a period of 2.5 h persisted on warming to room temperature under an inert atmosphere. The product was washed from the reactor with hexanes (2 l), filtered through a bed of Teflon powder (20 μm), and evaporated to dryness. Flash sublimation (by introduction of the sublimer into a tube furnace pre-heated to 220 °C) at 10^{-5} mbar of the resultant solid yielded a purple oil. From this, **1** is obtained pure in 5–10% yield, *ca*. 30 mg (based on scandium) after resublimation. UV–VIS for **1**: λ_{max}/nm (pentane) 571 (ε/dm^3 mol^{-1} cm^{-1} 15 000). MS (EI): *m/z* 583 (90%, M$^+$), 269 (43, $P_2C_3Bu^t{}_3{}^+$); HRMS: *m/z* found 583.273922. $C_{30}P_4H_{54}Sc$ requires 583.273519. Solution state magnetism (Evans method, [$^2H_8$]toluene): μ_{eff} = 1.70 μ_B.

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