Subvalent Scandium Complexes

Stabilization of Low-Oxidation-State Early Transition-Metal Complexes Bearing 1,2,4-Triphosphacyclopentadienyl Ligands: Structure of [{Sc(P_3C_2tBu$_2$)$_2$}$_2$]; Sc^{II} or Mixed Oxidation State?

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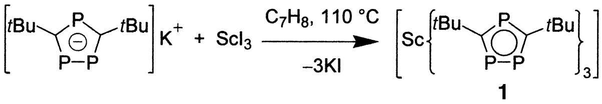
The prevalence of the tervalent oxidation state for complexes of the rare-earth elements is both well understood and amply documented.[1] Traditionally, bivalent lanthanide chemistry has been limited to just Eu^{II}, Yb^{II}, and Sm^{II},[2,3] however, quite recent work has detailed the syntheses of well-characterized Tm^{II},[4–6] Nd^{II},[5] and Dy^{II}[7] complexes and has reported their impressive and unprecedented reactivity towards otherwise unreactive small molecules.[4,7,8] Parallel development of bivalent chemistry for the earlier, larger lanthanides might seem an impossible task by comparison. The Ln^{III}/Ln^{II} couple, already high for the late series lanthanides (≥ -2.5 V versus NHE),[3] might prove to be of prohibitively high magnitude for the larger, earlier members. Nevertheless, under special conditions, for instance those operating in metal vapor synthesis (MVS) experiments,[9] zero-, uni-,[10] and bivalent[11] metal centers can be accessed even for the electropositive Group 3 metals. The volatile and reactive phosphaalkyne, *t*BuC≡P, has proved to be an important feedstock in such MVS reactions, as it is able to undergo cyclization reactions in the MVS reactor to give a variety of heterocyclic ligands capable of supporting oxidation states that were hitherto unknown for these highly Lewis-acidic metals.[12] The presence of phosphorus atoms in the ring lowers the energy of the unoccupied orbitals and promotes δ back-bonding from the metal, thus stabilizing the d electrons of reduced oxidation states.[13] The work reported here describes the application of the aromatic triphospholyl ring P_3C_2tBu$_2$ to the chemistry of the smallest Group 3 metal, namely scandium, but without resort to the MVS technique. Treatment of ScI$_3$ with the 1,3-P_3C_2tBu$_2$ anion, as its base-free potassium salt,[14] gives the homoleptic, tervalent complex [Sc(P_3C_2tBu$_2$)$_3$]. This proves to be a convenient entry point for subvalent scandium chemistry, as the P_3C_2tBu$_2$ ring is a much poorer electron donor than either Cp* or Cp″ (Cp* = $C_5Me_5^-$, Cp″ = 1,3-$C_5H_3(SiMe_3)_2^-$), and is capable of acting as a leaving group. Here the solid-state and solution structures of a reduced, formally bivalent Sc complex stabilized by the 1,2,4-triphosphacyclopentadienyl ring are presented, along with details of its parent Sc^{III} complex. In addition, we describe the results of DFT calculations on both new Sc complexes, which are in excellent agreement with the experimental findings.

Prolonged heating of base-free K[P_3C_2tBu$_2$] and ScI$_3$ in toluene or mesitylene at reflux gives rise to a deep red solution from which red crystals may be isolated upon workup. The mass spectrum of the red product (*m*/*z* 738) suggests its formulation as [Sc(P_3C_2tBu$_2$)$_3$] (**1**) [Eq. (1)].



(1)

Crystals suitable for an X-ray diffraction experiment were grown from heptane and the structure of **1** is presented in Figure 1. The scandium atom of compound **1** is η^5-bound to two of the P_3C_2tBu$_2$ rings and coordination is completed by a third P_3C_2tBu$_2$ ring bound in an η^2 fashion to two adjacent phosphorus centers. The Sc–M distances (M = ring centroid) are 2.326(9) and 2.371(9) Å, respectively, and the η^2-bound phosphorus atoms are coordinated symmetrically (Sc–P4 2.762(3), Sc–P5 2.792(3) Å). Although there are no other examples of [M(P_3C_2tBu$_2$)$_3$] compounds in the literature, we have in unpublished work synthesized and structurally characterized the homologous Y^{III}, Tm^{III}, and U^{III} derivatives that are all isostructural, but have longer Ln/Ac–M and Ln/Ac–(η^2-P_2) bond lengths.[15] The corresponding Ce, Sm, and

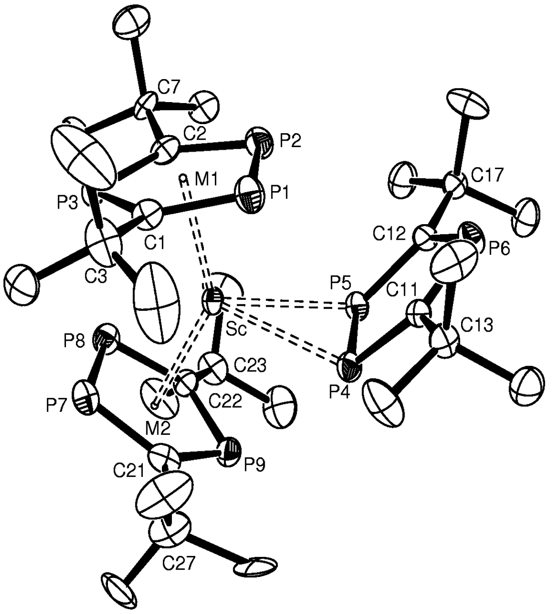


Figure 1. Structure of [Sc(η^5-P_3C_2tBu$_2$)(η^2-P_3C_2tBu$_2$)] (**1**) (ORTEP view). Selected bond lengths [Å] and angles [°]: Sc-M1 2.326(9), Sc-M2 2.371(9), P1-P2 2.117(4), Sc-P4 2.762(3), Sc-P5 2.796(3); M1-Sc-M2 140.2(2), M2-Sc-P4 102.70(8), M2-Sc-P5 103.85(7), M1-Sc-P4 114.10(8), M1-Sc-P5 112.75(7).[23]

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Th derivatives of the cyclopentadienyl ring $C_5H_3(SiMe_3)_2$, which is arguably similar in steric properties to $P_3C_2t\mathrm{Bu}_2$, each show η^5-bound rings exclusively, and it seems likely therefore that the η^5/η^2 bonding motif observed for the Sc–U series above is electronic rather than steric in origin. The presence of phosphorus centers on the ring demonstrably allows more versatile binding modes than its carbocyclic equivalent.[16]

Density functional calculations on $[Sc(P_3C_2H_2)_3]$ as a model for **1** gave an optimized geometry in good agreement with the crystal structure of **1**. Sc–M ring distances were calculated as 2.20 and 2.21 Å and the Sc–P distances to the η^2 ring as 2.76 and 2.74 Å. The model calculation thus results in smaller distances for the metal to ring centroid distances.

The alternative C_{3h} structure, in which all three rings are bound in an η^5 fashion, allows a formal symmetry match between the metal and all possible combinations of π-donor orbitals. However, the a′ combination formed by the π_3 orbitals would have three angular nodes and thus have effectively no overlap with the metal d orbitals. Distortion of one ligand to an η^2-coordination mode should enhance the electron donation to the electrophilic Sc center.

Interestingly, although the solid-state structure of **1** shows the $P_3C_2t\mathrm{Bu}_2$ rings to be coordinated in two different modes, the compound exhibits fluxional behavior in solution and all three rings are equivalent in the solution ^1H and $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectrum displays only a singlet at $\delta = 1.67$ ppm, and the $^{31}P\{^1H\}$ NMR spectrum comprises a symmetric $[AX_2]_3$ coupling pattern ($\delta_{A,X} = 296.5$, 265.0 ppm; Figure 2). Fluxional equilibrium between η^5 and η^2 modes of coordination in solution must therefore be rapid and the variable-temperature $^{31}P\{^1H\}$ NMR spectrum of **1** in [D$_8$]toluene loses resolution before the limiting spectrum is reached.

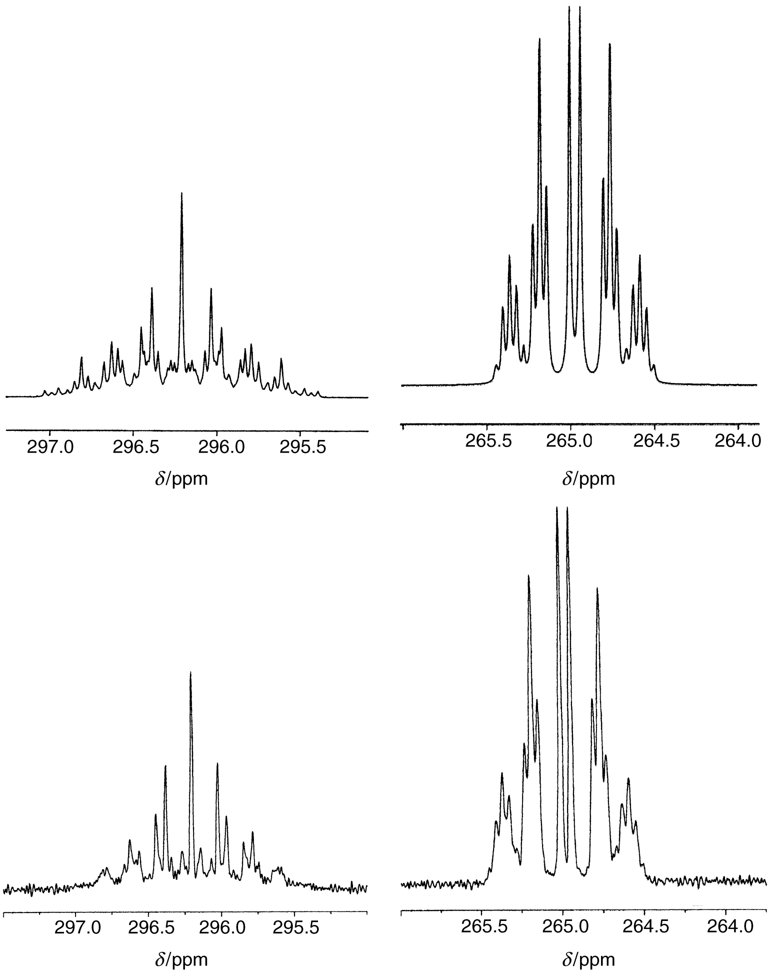


Figure 2. Simulated (top) and experimental (bottom) $^{31}P\{^1H\}$ NMR spectrum of **1**.

Although the metal center of **1** is sterically congested, one way of promoting reactivity is to designate one of the heterocyclic rings as a leaving group.[17] Such an approach has been used in the synthesis of bivalent lanthanides from coordinatively saturated triscyclopentadienyllanthanide(III) species such as $[Ln(\eta^5\text{-}Cp'')_3]$ (Ln = Ce, Yb; Cp″ = 1,3-$C_5H_3(SiMe_3)_2$).[18] In the case of **1** the $P_3C_2t\mathrm{Bu}_2$ rings are much poorer electron donors than a corresponding carbocyclic ring and should therefore in principle be much better leaving groups. Furthermore the presence of three phosphorus atoms in the ring makes the unsaturated rings better acceptors for the d electrons of any reduced species. Accordingly, treatment of **1** with one equivalent of KC_8 in toluene at low temperature (−78 °C) produces a very deep blue solution whose color persists upon warming to room temperature. Sublimation (170–180 °C, 1×10^{-5} bar) of the residue after removal of the volatiles, and recrystallization from hexane gives very dark blue crystals of **2**, whose mass spectrum (*m*/*z* 550) indicates a formulation of $[Sc(P_3C_2t\mathrm{Bu}_2)_2]$ [Eq. (2)].

$$[Sc(\eta^5\text{-}P_3C_2t\mathrm{Bu}_2)_2(\eta^2\text{-}P_3C_2t\mathrm{Bu}_2)] + KC_8 \xrightarrow{C_7H_8,\ -78\,^\circ C} [Sc(P_3C_2t\mathrm{Bu}_2)_2]_n + K[P_3C_2t\mathrm{Bu}_2] \qquad (2)$$

The single-crystal X-ray structure of **2** (Figure 3) reveals an unusual dimer containing two Sc centers bridged by a $(\mu\text{-}\eta^2{:}\eta^5)\text{-}P_3C_2t\mathrm{Bu}_2$ ring.

Remarkably, the Sc1 atom lies in a coordination environment whose metrical parameters are virtually indistinguishable from those of the parent molecule **1**. On the other hand, the Sc2 metal center is sandwiched between two η^5-bound heterocycles with two quite distinct Sc2–M distances (Sc2–M1 2.046(4), Sc2–M(4) 2.253(4) Å). The $\mu\text{-}\eta^2{:}\eta^5$ ring shows slight deviation from the geometry of the η^5 rings, with longer P–C distances observed (P1–C1 1.832(4), P2–C2 1.831(4) Å) and a longer P1–P2 distance of 2.21 Å. The M1-Sc1-M4 angle is slightly bent at 168.27(16)°.

DFT geometry optimizations were carried out on the dimer $[Sc_2(P_3C_2H_2)_4]$ in two different spin states, that is, with $S = 0$ and $S = 1$. The crystal structure data were used for the initial calculations and the $S = 0$ structure was found to be 0.47 eV lower in energy. Both calculations gave an optimized geometry in good general agreement with that found for **2**, however the distances for the bridging ring were in better accord with the $S = 0$ structure (Table 1). The calculations therefore support a diamagnetic ground state in the solid state.

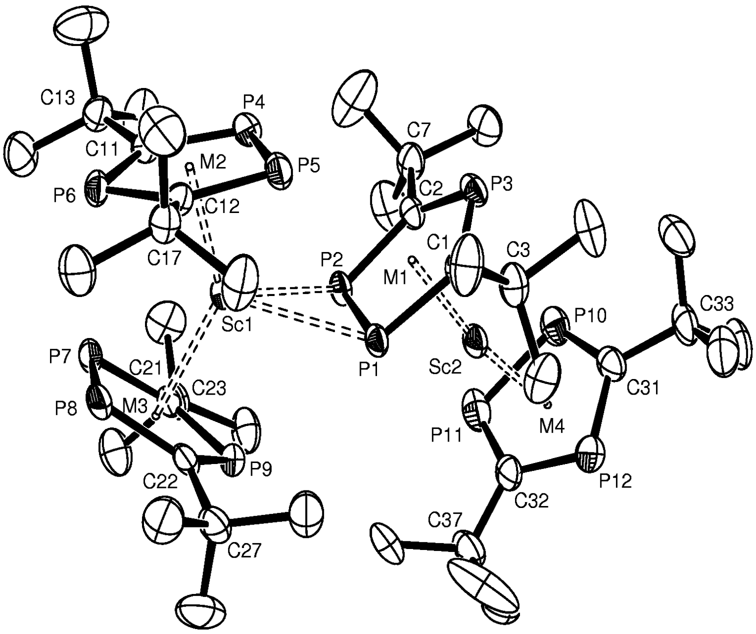


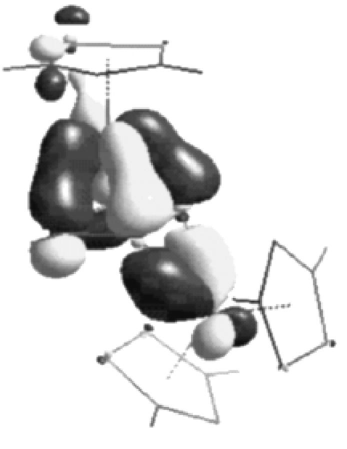
Figure 3. Structure of [Sc(η^5-P$_3$C$_2$$tBu_2$)($\mu$-$\eta^2$:$\eta^5$-P$_3C_2$$tBu_2$)Sc($\eta^5$-P$_3C_2$$tBu_2$)] (**2**) (ORTEP view). Selected bond lengths [Å] and angles [°]: Sc1-M2 2.322(4), Sc1-M3 2.360(4), P1-P2 2.2146(16), Sc1-P1 2.7646(13), Sc1-P2 2.7904(13), Sc2-M1 2.046(4), Sc2-M4 2.253(4); M2-Sc-M3 136.62(13), M1-Sc2-M4 168.27(16).[23]

Table 1: Calculated distances for Sc$_2$(P$_3$C$_2$H$_2$)$_4$ with $S=0$ and $S=1$. Experimental distances are given for comparison.

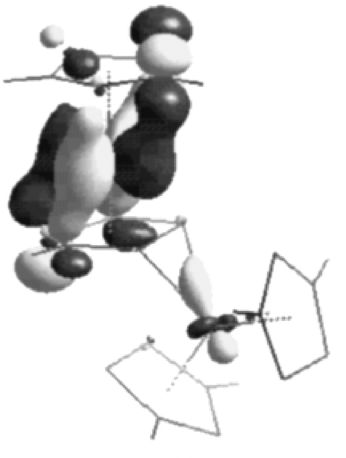
	[Sc$_2$(P$_3$C$_2$H$_2$)$_4$] $S=0$	[Sc$_2$(P$_3$C$_2$H$_2$)$_4$] $S=1$	**2**
Sc1–M1	3.31	3.36	
Sc1–M2	2.16	2.17	2.32
Sc1–M3	2.18	2.19	2.36
Sc2–M1	1.99	2.06	2.04
Sc2–M4	2.16	2.11	2.25
P–P ring 2	2.12	2.18	2.12
P–P ring 2	2.18	2.18	2.12
P–P ring 3	2.16	2.16	2.12
P–P ring 1 ring1	2.25	2.19	2.21
P1–C1	1.82	1.78	1.832
P2–C2	1.82	1.79	1.831
Sc1–P1	2.75	2.81	2.76
Sc1–P2	2.75	2.75	2.79

The orbitals occupied by the two d electrons in both magnetic states are of interest (Figure 4). With $S=0$, both electrons occupy orbital A61, which is back-bonding from Sc2 to the bridging ring and can be seen to be responsible for the lengthening of the P–P, P1–C1, and P2–C2 bonds. On the other hand with $S=1$, one of the unpaired electrons occupies a similar orbital, while the other, A62, is back-bonding from Sc2 to both rings. In both cases, the description of **2** as a mixed oxidation state Sc^{I}/Sc^{III} complex is more appropriate than two Sc^{II} centers.

The X-ray crystal structure and theoretical calculations thus both support the formulation of **2** as a mixed-valence Sc^{I}/Sc^{III} complex. Indeed, SQUID magnetometry performed upon a solid sample of **2** indicates diamagnetic material. In solution in benzene or toluene, however, **2** exhibits a magnetic moment as measured by Evans' method ($\mu_{eff}=1.7$ μ_B per Sc atom), which is fully consistent with a d^1 metal center. This suggests that in solution a monomer/dimer equilibrium may operate, in which the hypothetical monomer [Sc(P$_3$C$_2$$tBu_2$)$_2$] is responsible for the observed magnetic moment. In cyclohexane solution, a molecular weight determination by cryoscopy gave a value consistent with the dimer (900 g mol^{-1}); the corresponding experiment in benzene was inconclusive. On the basis of these experiments, it would appear that the aromatic solvent facilitates dissociation of the dimer and a concomitant change in spin state. The ESR spectrum of **2** in toluene did not reveal a signal attributable to [Sc(P$_3$C$_2$$tBu_2$)$_2$]; presumably, association of the monomer occurs to give the diamagnetic system before the ESR spectrum of monomeric **2** is resolved. By contrast, [Sc(P$_2$C$_3$$tBu_3$)$_2$] exhibits a septet of binomial quintets in its ESR spectrum, attributable to a monomeric complex, in frozen toluene.[11] The difference in molecularity between **2** and [Sc(P$_2$C$_3$$tBu_3$)$_2$] is likely to be a result of the greater steric demand of the P$_2$C$_3$$tBu_3$ ring.



A61 HOMO



A62 LUMO

Figure 4. Isosurfaces of orbitals A61 (HOMO) and A62 (LUMO) calculated for [{Sc(P$_3$C$_2$H$_2$)$_2$}$_2$].

In summary, isolation of a homoleptic complex of tervalent scandium bearing 1,2,4-triphosphacyclopentadienyl ligands has allowed access to a subvalent or nonclassical Sc complex.[17] Although formally bivalent with respect to scandium, **2** is best described as a mixed oxidation state complex containing both Sc^{I} and Sc^{III} centers. DFT calculations show that the d electrons retained by the Sc^{I} center are stabilized by δ bond formation with the heterocyclic rings. Evidence for the solution-state structure of **2** is ambiguous, the choice of saturated or aromatic solvent apparently influencing its molecularity. Details of the solid-state structure are unequivocal and represent only the second unambiguously subvalent Sc complex and the first such complex to be isolated by conventional means.

Experimental Section

1: Under argon, K[P$_3$C$_2$$tBu_2$] (500 mg, 1.85 mmol) and ScI$_3$ (254 mg, 0.597 mmol) were placed in an ampoule and slurried in toluene (50 mL). The ampoule was evacuated and then heated at 110 °C for 48 h during which time a dark red color developed. The reaction mixture was filtered and the toluene was removed by suction to leave a red solid. Recrystallization from heptane (20 mL) at −40 °C gave dark red crystals (254 mg, 54 %). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): $\delta = 1.67$ ppm (s, tBu); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]benzene, 20 °C): $\delta_{A,X} = 296.5$, 265.0 ppm ([AX$_2$]$_3$, J(A,X) = −50.7 Hz; J(A′,X) = 21.5 Hz; J(X,X′) = 5.0 Hz; J(A,A′) = 0 Hz); MS (70 eV): m/z (%): 738 (35) [M^+], 681 (21) [$M^+ - t$Bu], 57 (100) [tBu$^+$]; elemental analysis (%) calcd for C$_{30}$H$_{54}$P$_9$Sc (738.48): C 48.79, H 7.37; found: C 48.54, H 7.21.

2: Under 99.999 % argon, **1** (100 mg, 0.14 mmol) and KC$_8$ (25 mg, 0.18 mmol) were placed in a sublimation tube and slurried in cold (−78 °C) toluene (10 mL). An intense blue color rapidly developed and the mixture was warmed to room temperature. The volatiles were removed by suction and the crude product was sublimed (170 °C, 1×10^{-5} mbar). Recrystallization of the sublimate from pentane (2.5 mL) at 4 °C yielded dark blue crystals (50 mg, 65 %). μ_{eff} (25 °C) = 1.7 μ_B; MS (70 eV): m/z (%): 507 (65) [M^+], 450 (26) [$M^+ - t$Bu], 57 (100) [tBu$^+$]; UV/Vis (n-heptane): $\lambda_{\max}$ (ε) = 613 (15 000); molecular weight in solution (C$_6$H$_{12}$): 900 g mol^{-1}; elemental analysis (%) calcd for C$_{20}$H$_{36}$P$_6$Sc (507.30): C 47.35, H 7.15; found: C 47.34, H 7.41.

DFT calculations were carried out using the Amsterdam Density functional code version 2002.2.[19] Type IV basis sets were used with triple ζ accuracy sets of Slater type orbitals, with a single polarization function added to the main-group atoms. The cores of the atoms were frozen up to 2p for Sc, 1s for C, and 2p for P. The local density approximation of Vosko,[20] Wilk and Nusair was used with the nonlocal exchange corrections of Becke,[21] and nonlocal correlation corrections by Perdew.[22]

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[23] CCDC-196035 (**1**) and CCDC-196036 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).