The First Example of a Formal Scandium(I) Complex: Synthesis and Molecular Structure of a 22-Electron Scandium Triple Decker Incorporating the Novel 1,3,5-Triphosphabenzene Ring

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For a number of years considerable interest has been shown in the trimerization of 2,2-dimethylpropylidynephosphine (^tBuCP) to form a triphosphabenzene. Although the free ring is calculated to be thermodynamically stable, the few previous observations of trimerization on a metal center have resulted in the trimer binding as a Dewar-benzene form, and no η^6-metal bound complex has been structurally characterized to date.[1] Very recently, Binger *et al.*[2] have reported isolation of the free ring as a result of elimination of three phosphaalkyne units from $[Hf\{1,4\text{-}(SiMe_3)_2COT\}((^tBuCP)_3)]$. Cyclooligomerization reactions of ^tBuCP on $[Fe(\eta\text{-}PhMe)(C_2H_2)_2]$ (prepared by metal vapor synthesis) have been explored by Zenneck *et al.* and have led to the ligated 1,3 *di*phosphabenzene ring formed by cocyclization of ^tBuCP with terminal acetylenes.[3] We have been exploring the cyclooligomerization reactions of ^tBuCP *via direct* cocondensation with metal atoms, which result in the isolation of complexes such as $[(V(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]$,[4] $[Mo(\eta^4\text{-}P_2C_2{}^tBu_2)_3]$,[5] and $[Ni(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^3\text{-}PC_2{}^tBu_2)]$.[6] In this communication we report the synthesis of a triple decker complex which represents the first scandium(I) complex and incorporates a similarly unique, structurally characterized example of a ligated 1,3,5-triphosphabenzene ring.

Cocondensation of electron beam vaporized scandium with an excess of ^tBuCP at 77 K affords the forest-green complex $[\{\eta^5\text{-}P_3C_2{}^tBu_2)Sc\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_3C_3{}^tBu_3)]$, **1**, in 5−10% yield (based on scandium) after workup.[7] The molecular structure of **1** has been determined by X-ray crystallography and is depicted in Figure 1. (The compound crystallizes with one molecule of pentane, omitted for clarity.)[8]

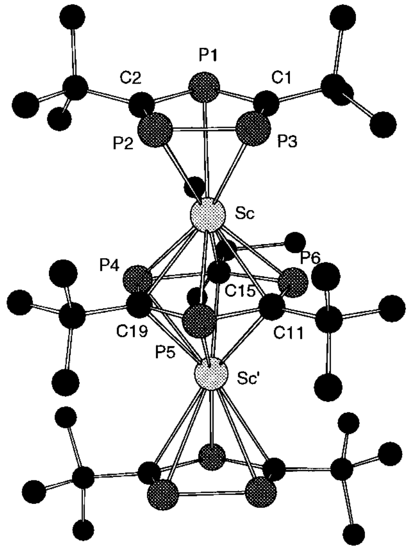

Figure 1. Molecular structure of **1**. Selected distances (Å) and angles (deg): Sc−C1 2.714(6), Sc−C2 2.771(6), Sc−P1 2.877(2), Sc−P2 2.802(2), Sc−P3 2.843(2), Sc−C11 2.450(5), Sc−C15 2.433(5), Sc−C19 2.404(5), Sc−P4 2.611(2), Sc−P5 2.630(2), Sc−P6 2.638(2), P1−C1 1.748(6), P1−C2 1.759(5), P3−C2 1.744(6), P2−P3 2.098(2), P4−C15 1.806(8), P4−C19 1.801(8), P5−C11 1.801(8), P5−C19 1.807(8), P6−C11 1.803(8), P6−C15 1.793(8), Sc−M_1 2.338(6), Sc−M_2 1.787(5), C11−P5−C19 104.1(4), P2−C1−P1 121.0(3), M_1−Sc−M_2 179.4(2), Sc−M_2−Sc′ 178.0(2). M_1 and M_2 are the centroids of rings $[P_3C_2]$ and $[P_3C_3]$, respectively.

The central 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene ring in the triple decker structure lies on a crystallographic mirror plane and is planar with no significant variation in ring P−C bond lengths, indicative of binding as a $\mu,\eta^6{:}\eta^6$ aromatic ligand. In comparison to the free ligand,[9] the ring in **1** shows lengthening of the P−C ring bonds by 0.064−0.089 Å and an expansion of the P−C−P angles by 4.3−4.4°. Further comparisons are difficult due to the almost complete lack of related analogues, although we note that the metal-"arene" ring centroid distance of 1.787(5) Å in **1** is considerably shorter than that in $[Sc(\eta\text{-}C_6{}^tBu_3MeH_2)_2]$ (1.983 Å).[10] This is presumably partially a reflection of the formal oxidation state difference {(I) and (0), respectively}, but may also be attributed to the larger size and stronger binding of the phosphorus-containing ring system, as has been observed in $[V(\eta^6\text{-}PC_5H_5)_2]$ *vs* $[V(\eta^6\text{-}C_6H_6)_2]$.[11] The outer 3,5-di-*tert*-butyl-1,2,4-triphosphacyclopentadienyl rings display structural features essentially analogous to those found in simple metallocenes containing this ligand, *e.g.* $[(V(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]^4$ and $[Ni(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^3\text{-}PC_2{}^tBu_2)]$.[6] The P_3C_2-ring centroid distance of 2.338(6) Å in **1**, however, is unusually long compared with those in the metallocenes (*cf.* 1.972 Å in $[(V(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]^4$).

Complex **1** is very air sensitive and soluble in pentane and other nonpolar solvents; it sublimes at 250 °C at 10^{-5} mbar with minimal decomposition. The compound displays temperature dependent paramagnetism with a solution magnetic moment (determined by the NMR method) of 3.98 μB at 295 K, which decreases monotonically with temperature to a value of 3.69 μB at 208 K. These values are clearly somewhat lower than the value predicted for four unpaired electrons by the spin only formula (4.47 μB), and the temperature dependence suggests either ground or excited state orbital contribution. A dilute solution of **1** in toluene is EPR silent at temperatures down to 77 K. The magnitude of the extinction coefficient for the band in the UV−visible spectrum[7] of **1** is indicative of a

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[7] Cocondensation of scandium vapor with ^tBuCP (M:L ratio 1:10) at 77 K afforded a dark brown matrix. After it warmed up to room temperature under an argon atmosphere, excess ^tBuCP was recovered under reduced pressure, and the product was washed from the reactor with hexane. The hexane extract was filtered through a bed of Teflon powder (20 μm) and evaporated to dryness. The resultant solid was flash sublimed to remove a scandium-containing purple oil and phosphaalkyne oligomerization products. The purple product is currently under further investigation. Careful cold washing (−78 °C) of the sublimant with pentane to remove remaining brown residues yielded a forest-green solid which was recrystallized from pentane to afford **1**. UV−vis: λ_{max} 426 nm (ϵ 1.2×10^4). MS (EI): *m/z* 852 (56%) (M^+). Elemental analysis: Found C, 50.50; H, 7.70. Calculated for $[C_{35}H_{63}P_9Sc_2{\cdot}(C_5H_{12})_{0.4}]$: C, 50.42; H, 7.75.

[8] Crystal data for **1**: Orthorhombic, dark green block, FW 924.7, in the space group *Pnma* (No. 62); $a = 20.131(6)$ Å, $b = 16.868(2)$ Å, $c = 14.425(4)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$. Final residual wR2 (all data) = 0.165 (R = 0.062, with goodness of fit, 1.036 on F^2).

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charge-transfer transition, a feature also observed in other low oxidation state scandium complexes.[12]

The very low formal electron number of 22 for **1** is particularly notable. From construction of frontier molecular orbital schemes from individual fragments, Hoffmann *et al.*[13] have proposed the 30/34 valence electron (VE) rule to account for the stability of a triple decker. No triple decker complex of scandium has previously been reported, and the complex [{Ti(η^5-C_5H_5)}$_2$(μ-η^6:η^6-P_6)] has, to date, the lowest recorded electron count (24 VE).[14] Interestingly, the middle ring in the latter is puckered, as is the geometry predicted for the C_6H_6 analogue, but the 28 VE complex [{Mo(η^5-C_5Me_5)}$_2$(μ-η^6:η^6-P_6)] exhibits a planar μ-η^6:η^6 bridging mode for the central ring.[14] In the case of the 26 VE complexes [{V(η^5-C_5Me_4Et)}$_2$(μ-η^6:η^6-P_6)][14] and [{V(η^5-C_5H_5)}$_2$(μ-η^6:η^6-C_6H_6)],[15] the central rings are again planar, but there is an in-plane distortion toward a bis-allylic system with unequal bond lengths within the rings. This is not the case for **1**, and theoretical and detailed magnetic studies are in progress in order to rationalize the geometry and electronic structure.

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Supporting Information Available: Experimental details for the preparation of **1**; X-ray data and figures giving additional atom labeling (12 pages). See any current masthead page for ordering and Internet access instructions.

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