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A Lanthanide Phosphinidene Complex: Synthesis, Structure, and Phospha-Wittig Reactivity

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Although phosphinidene (M = P) complexes are quite common in transition metal chemistry, analogous lanthanide derivatives remain unknown.¹ The absence of bridging or terminal lanthanide phosphinidene complexes is striking since the related actinide series has two known structurally characterized examples belonging to uranium: $(C_5Me_5)_2U(=PMes^*)(O=PMe_3)$ (Mes* = 2,4,6-'Bu₃- C_6H_2),² featuring a terminal phosphinidene group, and [(C_5Me_5)₂U-(OCH₃)₂]₂PH,³ possessing a bridging phosphinidene. Recently, highly reactive transition metal species such as group 4 alkylidenes, alkylidynes, phosphinidenes, and imides have been stabilized using the robust pincer PNP ligand set.⁴ Herein we report the use of the PNP ligand **1** to prepare, isolate, and study the first example of a lanthanide phosphinidene complex.

Reaction of the PNP ligands 1 and 2 with Lu(CH₂SiMe₃)₃(THF)₂ at room temperature in pentane and toluene, respectively, gave the corresponding lutetium bis(alkyl) complexes 3 and 4, respectively, as yellow solids in good isolated yield (Scheme 1). Whereas **3** is highly soluble in ethers and hydrocarbons and is best purified by recrystallization from hot TMS₂O to give large yellow blocks, complex 4 must be triturated from pentane to yield an insoluble yellow powder. The most diagnostic feature in the ¹H NMR spectra for the two Lu(III) bis(alkyl) complexes are the methylene resonances at $\delta -0.33$ (3) and $\delta -0.08$ ppm (4). Both **3** and **4** also display signals in their ${}^{31}P{}^{1}H$ NMR spectra at δ 14.5 and -4.8 ppm, respectively, downfield from the resonances observed for the free ligands (1, δ -12.9 ppm; 2, δ -18.7 ppm).⁵ Additionally, the ³¹P NMR resonance of **3** compares favorably to the structurally related d⁰ complex (PNP^{*i*Pr})ZrMe₃ (δ 13.0 ppm).4a

The molecular structure of compound **3** is presented in Figure 1 and reveals a distorted square pyramidal geometry about the Lu-(III) metal center with one alkyl group in the apical position and the PNP^{*i*Pr} ligand and the other alkyl group forming the pyramid base. The Lu–C bond lengths (2.307(6), 2.322(6) Å) fall within the range typically observed for Lu–CH₂SiMe₃ bonds.⁶ The Lu–N (2.244(5) Å) and Lu–P bonds (2.8534(15), 2.8547(15) Å) are somewhat shorter than those reported for the structurally related [$\{2-(Ph_2P)C_6H_4\}_2N$]Lu(CH₂SiMe₃)₂(THF) (Lu–N = 2.342(3) Å; Lu–P = 2.9096(9), 2.9765(9) Å).⁷ This difference may be attributed to the lack of coordinated THF in **3**.

As shown in Scheme 1, reaction of a toluene solution of **3** with 1 equiv of MesPH₂ (Mes = 2,4,6-Me₃-C₆H₂) at 80 °C for 12 h afforded the Lu(III) phosphinidene complex **5** as a cherry red solid in 52% isolated yield. The ³¹P{¹H} NMR spectrum of **5** exhibits a diagnostic quintet at δ 186.8 ppm coupled to a triplet at δ 18.1 ppm (²J_{P-P} = 14.6 Hz) consistent with two bridging phosphinidene units between two (PNP^{iPr})Lu fragments.



Figure 1. Molecular structure of complex **3** with thermal ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (°): Lu(1)-N(1) 2.244(5), Lu(1)-C(5) 2.307(6), Lu(1)-C(1) 2.322-(6), Lu(1)-P(1) 2.8534(15), Lu(1)-P(2) 2.8547(15), Lu(1)-C(1)-Si(1) 126.2(3), Lu(1)-C(5)-Si(2) 127.6(3).





The most interesting aspect of the structure is the asymmetric Lu_2P_2 core. The Lu–Lu distance of 3.9353(5) Å is longer than the sum of their ionic radii (1.722 Å).⁸ The two shorter bonds of the core, Lu(1)-P(3) (2.6031(16) Å) and Lu(2)-P(4) (2.5973(15) Å), are on average ~0.06 Å shorter than Lu(1)-P(4) (2.6724(14) Å) and Lu(2)-P(3) (2.6527(16) Å) as well as shorter than the Lu–P bond distances reported for the few known lutetium phosphide complexes (e.g., $[Me_2Si(C_5Me_4)(\mu-PPh)Lu(CH_2SiMe_3)]_2$, Lu-P = 2.826(1), 2.786(1) Å; $[Me_2Si(C_5Me_4)(\mu-PCy)Lu(CH_2SiMe_3)]_2$, Lu-P

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Figure 2. Molecular structure of complex 5 with thermal ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (°): Lu(1)-P(3) 2.6031(16), Lu(1)-P(4) 2.6724(14), Lu(2)-P(3) 2.6527(16), Lu(2)-P(2) 2.5973(15), Lu(1)-N(1) 2.296(4), Lu(2)-N(2) 2.295(4), Lu(1)-P(3)-Lu(2) 96.96(5), Lu(1)-P(4)-Lu(2) 96.61(5), P(3)-Lu(1)-P(4) 82.90(5), P(4)-Lu(2)-P(3) 83.40(5).

= 2.817(1), 2.789(1) Å; $[Me_2Si(C_5Me_4)(PPh)Lu(\mu-H)]_2(THF)_3$, $Lu-P = 2.788(2), 2.861(2) \text{ Å}; [Me_2Si(C_5Me_4)(PMes^*)Lu(\mu-H) (THF)]_2$, Lu-P = 2.683(1) Å; $[Cp_2Lu\{\mu-PPh_2\}_2Li(tmeda)]$, Lu-P $= 2.782(1), 2.813(2) \text{ Å}).^{6a,9}$

Interestingly, the mesityl rings are nearly planar with the Lu₂P₂ core, with Lu(1)-P(4)-C(10)-C(11) and Lu(2)-P(3)-C(1)-C(2)dihedral angles of 7.11 and 5.81°, respectively. This likely minimizes unfavorable interactions between the ortho-CH₃ groups on the mesityl rings and the ⁱPr groups on the PNP ligand. Finally, the sum of the angles around P(3) and P(4) are 358.9 and 356.5°, respectively, allowing for π -donation of the phosphorus lone pairs to the Lu atoms. All of these combined structural features are consistent with the formulation of complex 5 as an asymmetric dimer of the terminal phosphinidene, (PNP^{iPr})Lu=PMes, with a bond order greater than 1 in the Lu(1)-P(3) and Lu(2)-P(4) interactions.

Preliminary reactivity studies demonstrate that 5 behaves similarly to known nucleophilic phosphinidene systems such as [(N₃N)-Ta=PR] (R = Ph, Cy, 'Bu; N₃N = $(Me_3SiNCH_2CH_2)_3N)^{10}$ and Cp₂Zr(=PMes*)(PMe₃) (Figure 2).¹¹ Complex 5 reacts smoothly as a phospha-Wittig reagent with aldehydes and ketones to give the corresponding phosphaalkenes. For example, reaction of 5 with pivalaldehyde affords (E)-MesP=C(H)^tBu (48% yield, ³¹P NMR δ 227.1 ppm)¹² and with benzophenone yields MesP=CPh₂ (72% yield, ³¹P NMR δ 234.0 ppm).¹³ Concomitant formation of $[(PNP^{iPr})LuO]_x$ is likely, but to date, we have not been able to ascertain the fate of the lutetium byproduct.

Attempts to disrupt the dimer and stabilize a terminal phosphinidene using Lewis bases were unsuccessful (PMe₃, tmeda, DMAP, or bipyridines) or resulted in decomposition (O=PMe₃). Kinetic stabilization was also explored using the sterically demanding phosphine, Mes*PH₂. Reaction of a toluene- d_8 solution of 3 or 4 with Mes*PH₂ at 80 °C for 7-12 h resulted in quantitative formation of the phosphaindole 6 as determined by ³¹P NMR spectroscopy (eq 1).



For transition metals, the production of **6** signals the generation of a transient phosphinidene complex,1c,f which reacts with a C-H bond on the Mes* ortho-'Bu group to give the phosphaindole.^{14,15}

In summary, the first lanthanide complex featuring a phosphinidene functional group has been prepared and isolated. Although the large ionic radii of the lanthanide ions make it challenging to introduce enough steric saturation to stabilize a terminal phosphinidene, these results demonstrate that the formation of lanthanide phosphinidenes is possible and that the phosphinidene dimer 5 behaves as a nucleophilic phosphinidene transfer reagent. Efforts focused on stabilizing a terminal lanthanide-based phosphinidene complex by modifying both the supporting ligand and the substituent on the phosphorus atom are currently underway in our laboratory.

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Supporting Information Available: Full experimental and characterization details for all new compounds. Crystallographic data for 3 and 5. This material is available free of charge via the Internet at http:// pubs.acs.org.

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