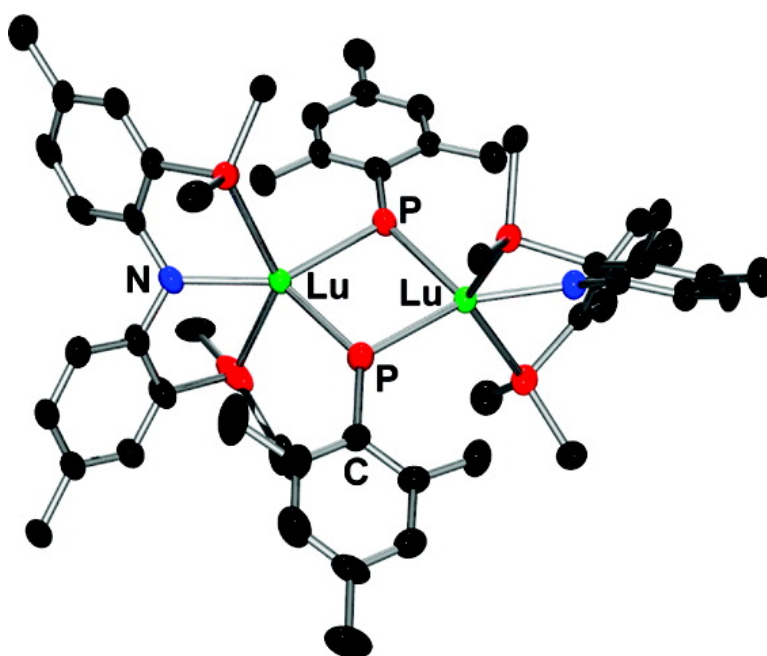


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A Lanthanide Phosphinidene Complex: Synthesis, Structure, and Phospha-Wittig Reactivity

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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: $(C_5Me_5)_2U(=PMe_3^*)(O=PMe_3)$ ($Me_3^* = 2,4,6\text{-}t\text{-Bu}_3\text{-C}_6H_2$),² featuring a terminal phosphinidene group, and $[(C_5Me_5)_2U(OCH_3)_2]_2PH$,³ possessing a bridging phosphinidene. Recently, highly reactive transition metal species such as group 4 alkylidenes, alkylidyne, 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 $Lu(CH_2SiMe_3)_3(THF)_2$ 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 TMS_2O 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 $^{31}P\{^1H\}$ NMR spectra at $\delta 14.5$ and -4.8 ppm, respectively, downfield from the resonances observed for the free ligands (**1**, $\delta -12.9$ ppm; **2**, $\delta -18.7$ ppm).⁵ Additionally, the ^{31}P NMR resonance of **3** compares favorably to the structurally related d^0 complex $(PNP^{iPr})ZrMe_3$ ($\delta 13.0$ 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^{*iPr*} 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– CH_2SiMe_3 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 $[\{2-(Ph_2P)C_6H_4\}_2N]Lu(CH_2SiMe_3)_2(THF)$ (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 $MesPH_2$ ($Mes = 2,4,6\text{-}Me_3\text{-C}_6H_2$) at 80 °C for 12 h afforded the Lu(III) phosphinidene complex **5** as a cherry red solid in 52% isolated yield. The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits a diagnostic quintet at $\delta 186.8$ ppm coupled to a triplet at $\delta 18.1$ ppm ($^2J_{P-P} = 14.6$ Hz) consistent with two bridging phosphinidene units between two $(PNP^{iPr})Lu$ fragments.

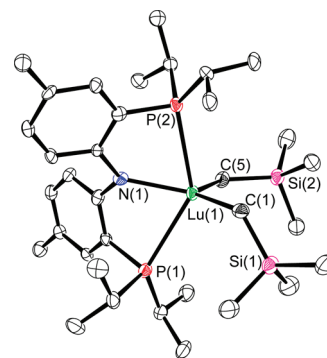
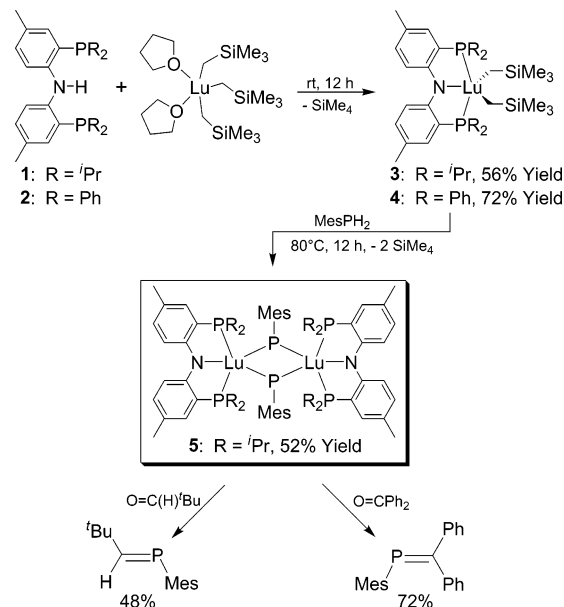


Figure 1. Molecular structure of complex **3** with thermal ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (°): Lu(1)–N(1) 2.244(5), Lu(1)–C(5) 2.307(6), Lu(1)–C(1) 2.322(6), Lu(1)–P(1) 2.8534(15), Lu(1)–P(2) 2.8547(15), Lu(1)–C(1)–Si(1) 126.2(3), Lu(1)–C(5)–Si(2)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

Scheme 1



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., $[Me_2Si(C_5Me_4)(\mu\text{-PPH})Lu(CH_2SiMe_3)_2]$, Lu–P = 2.826(1), 2.786(1) Å; $[Me_2Si(C_5Me_4)(\mu\text{-PCy})Lu(CH_2SiMe_3)_2]$, Lu–P =

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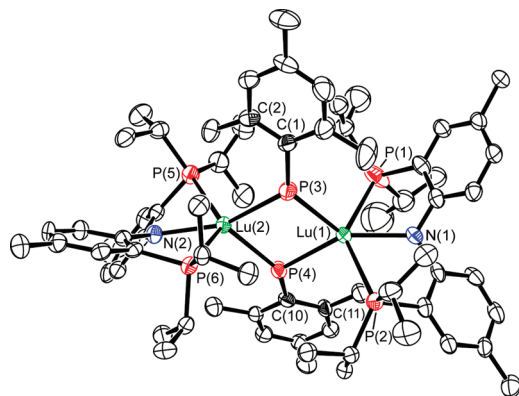


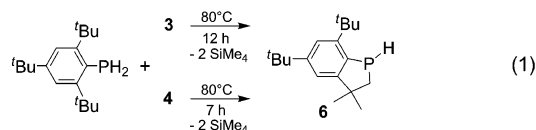
Figure 2. Molecular structure of complex **5** with thermal ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (°): Lu(1)–P(3) 2.6031(16), Lu(1)–P(4) 2.6724(14), Lu(2)–P(3) 2.6527(16), Lu(2)–P(2) 2.5973(15), Lu(1)–N(1) 2.296(4), Lu(2)–N(2) 2.295(4), Lu(1)–P(3)–Lu(2) 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; [Me₂Si(C₅Me₄)(PPh)Lu(μ -H)]₂(THF)₃, Lu–P = 2.788(2), 2.861(2) Å; [Me₂Si(C₅Me₄)(PMes*)Lu(μ -H)-(THF)]₂, Lu–P = 2.683(1) Å; [Cp₂Lu{ μ -PPh₂}₂Li(tmeda)], Lu–P = 2.782(1), 2.813(2) 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 *i*Pr 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^{*i*Pr})Lu=PMe₃, 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, ^tBu; N₃N = (Me₃SiNCH₂CH₂)₃N)¹⁰ and Cp₂Zr(=PMe₃)(PMe₃)(Figure 2).¹¹ Complex **5** reacts smoothly as a phospho-Wittig reagent with aldehydes and ketones to give the corresponding phosphalkenes. 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^{*i*Pr})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*-^tBu 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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