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Permalink
https://escholarship.org/uc/item/37d2p0x7

Journal
European Journal of Inorganic Chemistry

ISSN
1434-1948

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Publication Date
2013-10-31

DOI
10.1002/ejic.201300225

Peer reviewed
P₄ Activation by Lanthanum and Lutetium Naphthalene Complexes Supported by a Ferrocene Diamide Ligand

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Keywords: P₄ activation / lanthanum and lutetium naphthalene complexes / ferrocene diamide ligand / Zintl-type polyphosphide

Two rare-earth metal (La and Lu) naphthalene complexes supported by a ferrocene diamide ligand activate P₄ under ambient conditions to form M₄P₄ species exclusively. The resulting complexes feature the Zintl type polyphosphide P₄³⁻ unit stabilized by three lanthanide ions supported by the ferrocene diamide ligand. Complexes were characterized by X-ray crystallography, multinuclear NMR spectroscopy, and elemental analysis.

Introduction

The Haber-Bosch process, which converts N₂ from air and H₂ from steam reforming to ammonia, consumes 1-2% of the world’s annual energy supply, 3-5% of the world’s natural gas production, in order to provide ammonia to the fertilizer industry. Like nitrogen, phosphorus is essential to life and widely used in fertilization. Unlike N₂, white phosphorus, P₄, is the common source of phosphorus in industry and is unstable. It self-ignites in air and converts to the more stable allotrope, red phosphorus, under light or heat. The high reactivity of P₄ is likely due to its weak P-P bond and geometric constraints of the tetrahedron structure.

Though easily activated, the activation of P₄ is not easily controlled.[5-7] P₄ activation by main group and transition metals has been of long-standing interest.[5-7] Alkali metals and late transition metals compose the majority of examples of direct P₄ activation.[5, 6, 10] On the contrary, early transition metal mediated P₄ activation is much less investigated and rare-earth examples are rare.[5, 10-13] Roessky et al. reported the formation of (Cp*Sm)₂P₄ from slow vapour transfer of P₄ into a toluene solution of Cp*Sm.[12] Our group recently reported a direct P₄ activation by well defined scandium and yttrium naphthalene or anthracene complexes under ambient conditions.[14] [(NN₅)Sc]₄P₄ (Sc₄P₄) and [(NN₅)Sc]₃P₅ (Sc₃P₅) formed in the scandium case, while [(NN₅)Y(THF)]₄P₇ (Y₃P₇) formed exclusively in the case of yttrium (NN₅⁺ = 1,1'-fc(NSiBuMe)₃, fc = ferrocenylenic). Herein we report the synthesis and characterization of [(NN₅)La(THF)]₄[(μ-C₈H₈)₂La] (La₄-naph) and [(NN₅)Lu(THF)]₄[(μ-C₈H₈)₂Lu] (Lu₄-naph) were included.

Results and Discussion

Synthesis and structural characterization. We previously reported the synthesis of [(NN₅)Sc]₄[(μ-C₈H₈)₂] (Sc₄-naph)[15] and [(NN₅)Y(THF)]₄[(μ-C₈H₈)₂] (Y₄-naph)[15] from the reaction of (NN₅)Sc(THF)₃, or (NN₅)Y(THF). With KC₈ and naphthalene, La₄-naph and Lu₄-naph were prepared by a similar protocol in moderate yield (Eq 1). Compounds La₄-naph and Lu₄-naph complete the series of diamagnetic lanthanide naphthalene complexes supported by NN₅ and allow us to compare their properties. For example, Sc₄-naph is a black solid, which is barely soluble in hexanes but soluble in aromatic solvents such as benzene and toluene. However, Y₄-naph is a dark-red solid, which is barely soluble in hexanes, aromatic solvents, or even diethyl ether and is only soluble in polar solvents such as THF. Lutetium, like yttrium, binds a molecule of THF and Lu₄-naph has similar physical properties to Y₄-naph: both are dark-red solids and show the same solubility in polar and non-polar solvents. However, lanthanum, with the largest ionic radius of all lanthanides, leads to La₄-naph, which has properties similar to Sc₄-naph: it is a black solid soluble in aromatic solvents and even slightly soluble in hexanes. The four examples indicate that it is difficult to predict the properties of rare-earth metal complexes based on their ionic radii as is commonly the practice.

Compounds La₄-naph and Lu₄-naph were characterized by ¹H and ³¹C NMR spectroscopy and elemental analysis. While the proton chemical shifts of Lu₄-naph were close to the corresponding proton chemical shifts of Y₄-naph and Sc₄-naph, the proton chemical shifts of the naphthalene fragment in La₄-
The molecular structure of La\textsubscript{naph} (Figure 1) was determined by X-ray crystallography. La\textsubscript{naph} crystallized in the space group P\textbar 1, while Y\textsubscript{naph} crystallized in P\textbar 2\textbar 1/n. The C-C distances within the naphthalene fragment were closer in value to each other than in the case of Y\textsubscript{naph}, ranging from 1.374 to 1.451 Å in La\textsubscript{naph} compared to 1.376 to 1.470 Å in Y\textsubscript{naph}.[14] The two lanthanum fragments are η\textsuperscript{2}-coordinated to opposite sides of the naphthalene ligand. The distances between lanthanum and the four coordinating carbon atoms were similar, ranging from 2.827 to 2.891 Å. Noteworthy, the La-Fe distance is 3.266 Å, which is 0.12 Å shorter than the sum of the metal covalent radii. On the contrary, the corresponding Y-Fe distance in Y\textsubscript{naph} was 3.20 Å, which is close to the sum of metal covalent radii (3.22 Å). Interestingly, the THF free Sc\textsubscript{naph} had a Sc-Fe distance of 2.83 Å, which is about 0.19 Å shorter than the sum of the metal covalent radii.[10] We previously proposed that the electron-rich iron in the ferrocene-based ligand could serve as a Lewis base to a highly Lewis acidic rare-earth metal centre.[15, 17-21] This Lewis acid-base interaction is weak and may be disrupted by strong Lewis bases such as THF, as was the case in Y\textsubscript{naph}, where the extra THF molecule cancelled the weak M-Fe interaction and resulted in a long Y-Fe distance. However, in the case of La\textsubscript{naph}, the La-Fe interaction is maintained even with one extra THF molecule coordinated to lanthanum.

Figure 1. Molecular structure of La\textsubscript{naph} with thermal ellipsoids drawn at the 50% probability level. Only one of the two crystallographically independent molecules is shown here. Hydrogen atoms were omitted for clarity. Lanthanum in green, nitrogen in blue, oxygen in red, silicon in light blue, and carbon in grey. Selected distances [Å] and angles [°]: La1-N1 2.382(2), La1-N2 2.3672(2), La1-O1 2.354(2), La1-Fe1 3.2609(4), La1-C30 2.891(2), La1-C31 2.841(2), La1-C32 2.827(2), La1-C33 2.865(2), C29-C29A 1.451(5), C29-C30 1.418(3), C30-C31 1.433(4), C31-C32 1.374(4), C32-C33 1.437(4), N1-La-N2 120.28(7), C29A-C29-C30 121.00(22), C30-C31-C32 119.45(24), C31-C32-C33 119.76(23), C32-C33-C29A 120.55(22).

With La\textsubscript{naph} and Lu\textsubscript{naph} in hand, we tested their reactivity toward P\textsubscript{3}. Regardless of the stoichiometry of P\textsubscript{3} vs. M\textsubscript{naph}, La\textsubscript{P} and Lu\textsubscript{P} were formed exclusively. This behaviour was analogous to that of Y\textsubscript{naph} but different from that of Sc\textsubscript{naph}, which led to two different products, ([NN\textsuperscript{6}Sc\textsubscript{3}P\textsubscript{5} (Sc\textsubscript{3}P\textsubscript{5})] and ([NN\textsuperscript{6}Sc\textsubscript{5}P\textsubscript{5} (Sc\textsubscript{5}P\textsubscript{5})].[16] The exclusive formation of M\textsubscript{P} in the case of lanthanum and lutetium was expected since La\textsubscript{naph} and Lu\textsubscript{naph} are structurally similar to Y\textsubscript{naph} but different from Sc\textsubscript{naph} because of the extra THF molecule coordinated to scandium. With the exact stoichiometry (Eq 2), the reaction went to complete conversion and naphthalene was the only by-product. 3\textsuperscript{1}P NMR spectra of the crude reaction mixture showed peaks only for M\textsubscript{P}. Crystalline La\textsubscript{P} and Lu\textsubscript{P} were isolated in good yield after crystallization from various organic solvents. It was found that La\textsubscript{P} was more soluble than Lu\textsubscript{P} in common organic solvents: La\textsubscript{P} was soluble in hexanes and in aromatic solvents, while Lu\textsubscript{P} was almost insoluble in hexanes and only slightly soluble in aromatic solvents. While the solubility of Lu\textsubscript{P} was similar to that of previously reported Y\textsubscript{P}, the solubility of La\textsubscript{P} was different but similar to that of the THF free compound Sc\textsubscript{3}P\textsubscript{5}. The unexpected solubility properties of M\textsubscript{P} (M = Sc, Y, La, Lu) echo the different solubilities of M\textsubscript{naph} described above.

The molecular structures of La\textsubscript{P} (Figure 2) and Lu\textsubscript{P} (Figure 3) were determined by single-crystal X-ray diffraction. While Lu\textsubscript{P} is isostructural to Y\textsubscript{P}, and shows each lutetium with one coordinating THF molecule, La\textsubscript{P} crystallized in the P\textbar 1 space group and two out of the three lanthanum atoms coordinate a diethyl ether ligand instead of THF. Different batches of La\textsubscript{P} showed different ratios between THF and diethyl ether as coordinating solvent molecules. Similar to La\textsubscript{P}, some batches of La\textsubscript{naph} also had diethyl ether replacing THF based on 1\textsuperscript{H} NMR spectroscopy. We attribute this lack of selectivity between THF and diethyl ether to the weaker Lewis acidity of La(III) when compared to that of Y(III) and Lu(III).[22]

Both La\textsubscript{P} and Lu\textsubscript{P} structures feature a central Zintl-type polyphosphide P\textsubscript{3}\textsuperscript{4-} anion surrounded by three (NN\textsuperscript{6}M(solv)) fragments. Except for Sc\textsubscript{3}P\textsubscript{5}, which does not coordinate any THF, all the other M\textsubscript{P} adopt the same coordination environment. The small ionic size of scandium may explain this difference. The lack of THF coordination in Sc\textsubscript{3}P\textsubscript{5} is compensated by a close contact between scandium and the ferrocene backbone, as shown by the extremely short Sc-Fe distance of 2.80 Å, about 0.22 Å shorter than the sum of the covalent radii of scandium and iron.[15] Despite this difference in coordination environment, P-P distances (Table 1) show a clear trend: the larger the rare-earth metal ionic radius, the shorter the P\textsuperscript{edge}-P\textsuperscript{bottom} distance, which is accompanied by a slight lengthening of the other two types of P-P bonds. In alkali earth metal stabilized P\textsubscript{3}\textsuperscript{4-} compounds, the three distinguishable P-P bonds also have different distances, with the shortest being P\textsuperscript{edge}, P\textsuperscript{bottom}, and the longest the P\textsuperscript{bottom}/P\textsuperscript{bottom} distance within the bottom
Hydrogen atoms were omitted for clarity. Lutetium and silicon in light blue, and carbon in grey.

Selected distances [Å] and angles [°]:

- Lu1-N1 2.184(5), Lu1-N2 2.178(5), Lu2-N3 2.187(5), Lu2-P6 2.807(2), Lu3-P6 2.876(2), Lu3-P3 2.910(2), P1-P2 2.178(2), P2-P3 2.183(2), P2-P6 2.180(2), P3-P4 2.180(3), P6-P5 2.180(2), P1-P7 2.183(2), P4-P5 2.246(2), P5-P7 2.242(2), P7-P4 2.228(2), N1-Lu-N2 127.43(19), N3-Lu2-N4 129.08(19), N5-Lu3-N6 125.10(20), P1-Lu1-P3 69.95(4), P1-Lu2-P6 70.37(4), P6-Lu3-P3 71.39(4), P1-P2-P3 99.56(8), P3-P2-P6 101.13(9), P1-P2-P6 99.02(8), P2-P3-P4 100.56(9), P3-P4-P5 105.34(9), P4-P5-P7 105.60(9), P5-P6-P7 105.34(9), P4-P5-P7 105.60(9), P5-P6-P7 59.79(7), P5-P7-P4 60.60(7), P4-P5-P7 61.71(7).

Table 1. P-P distances of M₃P₇ (unit: Å, error in brackets, all are averaged values).

<table>
<thead>
<tr>
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<th>P₃ respectful</th>
<th>P₃ respectful</th>
<th>P₃ respectful</th>
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</thead>
<tbody>
<tr>
<td>Sc₃P₇[+]</td>
<td>2.201(2)</td>
<td>2.197(2)</td>
<td>2.229(2)</td>
</tr>
<tr>
<td>Lu₃P₇</td>
<td>2.183(2)</td>
<td>2.181(2)</td>
<td>2.232(2)</td>
</tr>
<tr>
<td>Y₃P₇</td>
<td>2.188(2)</td>
<td>2.176(3)</td>
<td>2.238(2)</td>
</tr>
<tr>
<td>La₃P₇</td>
<td>2.191(2)</td>
<td>2.161(2)</td>
<td>2.258(2)</td>
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[a] Unlike the other M₃P₇, Sc₃P₇, has no THF molecule coordinating to scandium.

In the case of lanthanum, the difference between the P-P distances is comparable to the case of alkali earth P₇⁺ binary complexes, while for Sc₃P₇, the difference between P-P distances is minimized and actually close to that observed for silyl substituted P₃R₃ organic compounds. For instance, in P₃(SiMe₃)₃, P₃ respectful, P₃ respectful, P₃ respectful, distances are 2.180(4), 2.192(4), and 2.214(4) Å. The trend observed by us shows that M₃P₇ (M = Y, La, Lu) compare well to ionic compounds, while Sc₃P₇ is akin to covalent, organic compounds.

Variable temperature NMR spectroscopic studies. P₇⁺ is the major product of P₇ activation by strong reductants or nucleophiles as well as the “dead-end” of other polyphosphide species decompositions.[16, 23] Intense experimental and theoretical studies have been performed on its alkali and alkali earth metal complexes. For example, Li₃P₇ was studied by variable temperature and 2D ³¹P NMR spectroscopy.[26-28] and it was found that the ³¹P NMR spectrum of Li₃P₇ in THF-d₈ is temperature dependent: at low temperature (-60 °C), three distinguishable signals were observed for the three different types of phosphorus atoms in P₇⁺; however, upon warming, coalescence took place and, eventually, at high temperature (50 °C) only one peak was observed. This phenomenon was attributed to a fluxional behaviour of P₇⁺.[28] The free P₇⁺ anion can tautomerize to essentially the same tautomer (there are 1680 of them)[28] by simultaneously breaking one P₃ respectful-P₃ respectful bond and forming a new P-P bond between two P₃ respectful atoms right next to the two P₃ respectful atoms of the P-P bond that breaks. This tautomerization mechanism, which is analogous to bullvalene tautomerization,[28] was calculated to have a low energy barrier,[30] and was further supported by a topology study.[31] Apparently, this tautomerization only takes place in highly ionic compounds like Li₃P₇ and Cs₃P₇,[32] no tautomerization was observed for silyl substituted P₃R₃ compounds.[28, 32] Since the bonding character of rare-earth metals is in between ionic and covalent, and because of our observations of different P-P distances between the four solid state molecular structures, we became interested in studying the solution behaviour of M₃P₇ (M = Sc, Y, La, and Lu).

The ³¹P NMR spectra of Sc₃P₇, Y₃P₇, and La₃P₇, at 25 °C in benzene-d₆ or toluene-d₈ were similar and showed three well resolved peaks that integrated to a 3:1:3 ratio, indicating that the tautomerization of the P₇⁺ anion was frozen. However, the ³¹P NMR spectrum (25 °C, benzene-d₆) of La₃P₇ showed only one, broad signal centred at -75 ppm, similarly to Li₃P₇ in THF-d₈.
Therefore, $^{31}P$ NMR spectra (Figure 4) were collected from -75 °C to 107 °C ($La_3P_7$ was stable throughout the variable temperature measurement and even at 85 °C for at least 24 h without any noticeable decomposition).

![Figure 4](image-url)

Figure 4. Overlay of $^{31}P$ NMR spectra (toluene-$d_8$) of $La_3P_7$ at different temperatures. Chemical shifts were referenced to an external standard (85% H3PO4) at 25 °C.

The variable temperature $^{31}P$ NMR spectra clearly showed the fluxional behaviour of $P_7^{3-}$ in $La_3P_7$ and a coalescence temperature comparable to that of Li$_2P_3$. However, surprisingly, this behaviour took place in non-polar solvents (benzene or toluene) for $La_3P_7$, while for Li$_2P_3$, it was only observed in polar and strongly coordinating solvents such as THF, DME (1,2-dimethoxethane), and TMEDA (tetramethylethenediamine); without a strongly coordinating solvent, Li$_2P_3$ decomposes. This difference suggests two possibilities that account for the fluxional behaviour: (1) $La_3P_7$ can dissociate to separate ion pairs in non-polar solvents, a behavior that would mimic that of Li$_2P_3$, and (2) the (NN)$_2$La(THF) fragment can migrate rather easily from one phosphorous atom to another, allowing the valence tautomerization to occur. In the first case, a cationic (NN)$_2$La(THF) species would have to be generated in a non-polar solvent. Although the ferrocene backbone of the NN$_2$diamide ligand can provide some electronic stabilization and steric shielding, a coordination number of three (two nitrogen and one ferrocene donors) for lanthanum is not reasonable especially in non-polar and weakly coordinating aromatic solvents for $La_3P_7$. Therefore, we dismissed the idea of a separate ion pair in solution. The second possible mechanism for $P_7^{3-}$ tautomerization in $La_3P_7$ requires the simultaneous breaking and formation of four La-P bonds (Figure 5). The tautomerization involves one of the five-member rings of $P_7^{3-}$: a $P_{n=5}$-$P_{n=5}$ bond breaks while a $P_{n=6}$-$P_{n=6}$ bond forms; at the same time, the lanthanum fragment coordinated to that face migrates from two $P_{n=5}$ atoms to two $P_{n=6}$ atoms. The other two lanthanum centres only break and form one La-P bond each. Such a process, together with the necessary breaking and formation of P-P bonds, is made possible by the coordination of lanthanum to two neighbouring $P_{n=6}$ atoms and two neighbouring $P_{n=5}$ atoms. To support this hypothesis, the average La-$P_{n=6}$ distance is 3.10 Å, while the average La-$P_{n=5}$ distance is 3.54 Å. The 0.44 Å difference is smaller than the corresponding distance difference in the other $M_3P_7$ (M = Sc: 0.67 Å, Lu: 0.57 Å, Y: 0.53 Å). If it is assumed that the metal-P distances vary linearly with the strength of the metal-P interaction, then it will be easier to form new metal-P bonds for $La_3P_7$ than for $Y_3P_7 > Lu_3P_7 > Sc_3P_7$. Consequently, we found that the tautomerization also took place in $Y_3P_7$ but at a high temperature (coalescence temperature higher than 75 °C). Unfortunately, the low solubility of $Y_3P_7$ in aromatic solvents and the high coalescence temperature prevented a detailed variable temperature $^{31}P$ NMR spectroscopy study for this complex.

Figure 5. Proposed mechanism for valence tautomerization of $P_7^{3-}$ in $La_3P_7$ (NN$_2$ ligand and THF molecule were omitted for clarity). The red solid line represents the La-P bond to break. The red dashed line represents the La-P bond to form. The blue solid line represents the P-P bond to break. The blue dashed line represents the P-P bond to form. The black solid line represents the La-P and P-P bonds not affected by this particular tautomerization process.

Conclusions

In summary, we successfully synthesized and characterized the inverse sandwich naphthalene complexes $La$-$naph$ and $Lu$-$naph$ and utilized them in direct $P_7^{3-}$ activation. $La_3P_7$ and $Lu_3P_7$ were formed exclusively in those reactions. In the two series, $M_3-naph$ and $M_3P_7$, $La$-$naph$ and $La_3P_7$ showed counterintuitive physical properties compared to the other three metal (scandium, yttrium, lutetium) complexes. However, structural data for $M_3P_7$ complexes confirm the general trend predicted by the ionic size of rare-earth metals. The tautomerization of the $P_7^{3-}$ anion in $La_3P_7$ took place at a similar temperature as in the ionic Li$_2P_3$ compound, but in non-polar and non-coordinating aromatic solvents. Instead of a separated ion pair mechanism, a lanthanum assisted mechanism was proposed for the valence tautomerization of $P_7^{3-}$ in $La_3P_7$. The ability of rare-earth metals to effect P-P activation in a controllable fashion as well as their capacity to support the resulting polyphosphide was demonstrated by the exclusive formation of the robust $M_3P_7$ family. The Lewis basic ferrocene backbone likely plays an important role to stabilize $M_3$-$naph$ and $M_3P_7$ complexes.

Experimental Section

Experimental Details

**General considerations.** All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glove box unless otherwise specified. Solvents, toluene, hexanes, diethyl ether (Et$_2$O), and tetrahydrofuran (THF) were purified using a two-column solid-state purification system by the method of Grubbs and transferred to the glove box without exposure to air. n-Pentane was distilled over calcium hydride under a dinitrogen atmosphere. Methanol was distilled over calcium oxide under a dinitrogen atmosphere. All solvents were stored on activated molecular sieves and/or sodium for at least a day prior to use. NMR solvents, benzene-$d_6$ (C$_6$D$_6$) and toluene-$d_8$ (C$_8$D$_8$), were obtained from Cambridge Isotope Laboratories, degassed or brought.
THF (6 mL), P<sub>2</sub>O<sub>5</sub> was added to the solution. The reaction mixture was allowed to warm up to 25 °C and stirred for 3 h. The resulting dark red solution was filtered through Celite and dried under reduced pressure. The remaining red solid was dispersed in EtO and stored in a -35 °C freezer for 5 days. A black crystalline solid was obtained on a medium frit after filtration. Yield: 0.289 g, 59.0%.<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ, ppm: 4.28 and 2.73 (br s, 4H each, C<sub>6</sub>H<sub>5</sub> each, CH on naphthalene fragment), 4.20 and 3.85 (br s, 8H each, CH on Cp rings), 4.09 (br s, 2H, CH<sub>2</sub>O on THF), 3.61 (br s, 8H, CH<sub>2</sub>O on EtO), 1.52 (br s, 2H, CH<sub>2</sub>O on THF), 1.26 (m, 12H, CH<sub>2</sub>H on EtO), 1.01 (s, 3H, (CH<sub>3</sub>)<sub>3</sub>C), and 0.30 (s, 24H, Si(CH<sub>3</sub>)<sub>3</sub>).<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ, ppm: 156.8, 122.0, 99.5, and 71.0 (C or CH on naphthalene fragment), 109.4 (CN on Cp rings), broad peaks around 66.8 (CH on Cp rings), 27.7 ((CH<sub>3</sub>)<sub>3</sub>C), 20.7 (CH<sub>3</sub>C), and -24.5 (Si(CH<sub>3</sub>)<sub>3</sub>). An analytical pure sample was obtained by recrystallization from a concentrated hexanes solution in a -35 °C freezer for two days. Anal. (%): Calcd. for C<sub>67</sub>H<sub>47</sub>N<sub>2</sub>O<sub>3</sub>Fe<sub>2</sub>La<sub>2</sub>Si<sub>2</sub>, Mw = 1435.354: C, 51.88; H, 7.02; N, 3.90. Found: C, 51.28; H, 7.05; N, 3.46.

**Synthesis of La<sub>2</sub>P<sub>n</sub>.** To a solution of La<sub>n</sub>-naph (0.200 g, 0.133 mmol) in THF (12 mL), P<sub>2</sub>O<sub>5</sub> (0.0227 g, 0.183 mmol) was added. The color changed gradually from dark red to orange in 10 min. The reaction mixture was allowed to stir at 25 °C for 1 h. The volatiles were removed under reduced pressure. The resulting yellow-orange solid was dissolved in toluene and washed with cold n-pentane. Yield: 0.109 g, 53.9%.<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ, ppm: 4.13, 4.07, 3.89, and 3.49 (4H each, CH on Cp rings), 4.03 (br s, 12H, CH<sub>2</sub>O on THF), 1.53 (br s, 12H, CH<sub>2</sub>H on THF), 1.12 (s, 54H, (CH<sub>3</sub>)<sub>3</sub>C), and 0.56 and 0.25 (12H each, Si(CH<sub>3</sub>)<sub>3</sub>).<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ, ppm: 103.8 (CN on Cp rings), 71.0, 67.6, and 65.3 (CH on Cp rings), 28.4 ((CH<sub>3</sub>)<sub>3</sub>C), 25.5 (CH<sub>3</sub>C), and -0.4 and -0.5 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. (%): Calcd. for C<sub>67</sub>H<sub>47</sub>N<sub>2</sub>O<sub>3</sub>Fe<sub>2</sub>La<sub>2</sub>Si<sub>2</sub>, with one molecule of n-pentane (C<sub>5</sub>H<sub>12</sub>), Mw = 2357.922: C, 42.82; H, 6.41; N, 3.56. Found: C, 41.93; H, 6.40; N, 3.52.

**Supporting Information** (see footnote on the first page of this article): Experimental details, NMR spectra, and X-ray data.

**Acknowledgments**

This work was supported by UCLA, Sloan Foundation, and NSF CAREER. The authors thank the Kaner group (UCLA) for generous gifts of K<sub>2</sub>C<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>.

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Zintl-type $P_7^{3-}$ complexes were synthesized from direct activation of $P_4$ by lanthanum and lutetium naphthalene complexes. The $P_7^{3-}$ complexes showed fluxional behaviour dependent on the rare-earth metal.

**Key Topic**

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$P_4$ Activation by Lanthanum and Lutetium Naphthalene Complexes Supported by a Ferrocene Diamide Ligand

**Keywords:** $P_4$ activation / naphthalene complexes / ferrocene diamide ligand / Zintl-type polyphosphide