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含六磷杂并环[3.1.0]己烷四负离子的三核稀土镥配合物的分离与结构表征

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摘要 白磷直接合成有机膦化合物具有重要的科学意义, 因为其不仅避免了磷化工生产过程中产生的大量污染, 而且可以用于合成许多结构新颖的含磷化合物. 从镥杂环戊二烯与白磷的反应中分离并表征了一例新颖的三核稀土金属配合物[{(η^5-C_5Me_5)LuCl}$_3$(THF)P_6][Li(THF)$_4$]. 该配合物具有一个六磷杂并环[3.1.0]己烷四负离子配体, 相比于其他已知的六磷杂己烷类配体, 该配体目前仍未被报道. X 射线单晶衍射实验表明, 该六磷杂并环[3.1.0]己烷四负离子配体采取的船式构象, 与三个稀土金属分别以 η^1, η^3, η^3 的方式配位, 形成一个结构新颖的[P_6Lu_3]笼状结构. 密度泛函理论(DFT)计算表明, 该化合物在其两侧分别有一个三中心两电子键.
关键词 多膦配体; 白磷活化; 稀土金属配合物

Isolation and Characterization of a Trinuclear Rare-Earth Metal Complex Containing a Bicyclo[3.1.0]-P_6^{4-} Ligand

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Abstract Direct synthesis of organophosphorus compounds from white phosphorus (P_4) is of great significance because this process avoids the industry pollution synthetic methods and provides the possibilities for many novel phosphorus-containing compounds. A trinuclear rare-earth metal complex [{(η^5-C_5Me_5)LuCl}$_3$(THF)P_6][Li(THF)$_4$] from lutetacyclopentadiene mediated P_4 functionalization was isolated and characterized. This novel complex contains a bicyclo[3.1.0]-P_6^{4-} ligand which is an unreported type. X-ray diffraction analysis shows that the bicyclo[3.1.0]-P_6^{4-} ligand adopts a boat-like conformation. Three lutetium atoms coordinate to this ligand in η^1, η^3, η^3 mode, respectively, and a novel [P_6Lu_3] cage has been formed. Density functional theory (DFT) calculations indicate that there are two three-center two-electron bonds.
Keywords polyphosphorus ligand; white phosphorus activation; rare-earth-metal complex

1 Introduction

Metal mediated functionalization of white phosphorus to phosphorus-based chemicals has been a hot area in recent years.[1~5] One major interest in this field is searching for different types of polyphosphorus ligands, which is of fundamental theoretical significance despite that sometimes the yield is low. Among various polyphosphorus ligands, the search of different types of P_6 ligands derived from P_4 has been exploring. Since Scherer *et al* reported the first triple-decker sandwich molybdenum complex bearing a *cyclo*-P_6 ligand,[6] the P_6 ligands of structural diversity have received continuous attention in both experimental characterization and theoretical calculations.[7,8] In 1980s, Scherer *et al*. characterized a series of transition metal *cyclo*-P_6 complexes in which the *cyclo*-P_6 ligands could be viewed as *cyclo*-P_6^{6-}, *cyclo*-P_6^{4-}, *cyclo*-P_6^{2-} and *cyclo*-P_6, respectively (Scheme 1a).[9~11] Then, a binuclear thulium complex bearing a bicyclic P_6^{4-} ligand via thulium-mediated P_4 reductive functionalization was ob-

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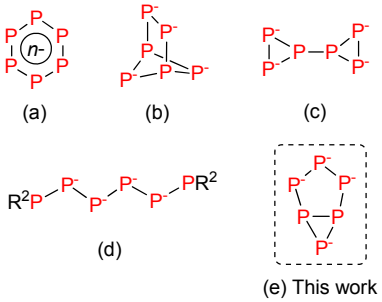
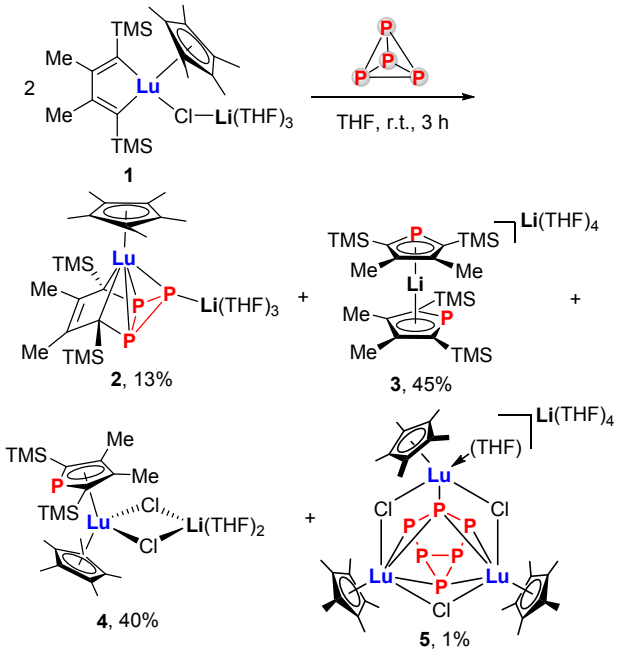


Scheme 1 Representative examples of P_6 ligands

tained (Scheme 1b).[12] Later, a binuclear niobium complex bearing $^{c}P_3$-$^{c}P_3$; ligand was documented (Scheme 1c).[13] Besides P_6 ligands derived from P_4, a 3d/4f complex having $^{c}P_3$-$^{c}P_3$ ligand[14] (Scheme 1c) and these complexes bearing linear P_6^{6-} or P_6^{4-} ligands[15,16] (Scheme 1d) could also be obtained by other methods. Although four types of P_6 ligands have been reported, the new type of bicyclo[3.1.0]- P_6^{4-} ligand is unexplored (Scheme 1e).

Rare-earth metals mediated functionalization of P_4 is rare due to the mismatch of the soft-hard properties between phosphorus and rare-earth metals.[17] Recently, we have reported the reaction of Ph, TMS-substituted lutetacyclopentadienes with P_4 which affords the corresponding lutetium *cyclo*-P_3 complexes and phospholyl lithium.[18,19] Then, to investigate the substituent effect of lutetacyclopentadienes, the reaction of Me,TMS-substituted lutetacyclopentadienes with P_4 was carried out. In this reaction, a trinuclear rare-earth metal complex $[\{(\eta^5\text{-}C_5Me_5)LuCl\}_3(THF)P_6][Li(THF)_4]$ was isolated which contains the bicyclo[3.1.0]-P_6 ligand mentioned above. It also represents the first P_6 complex directly derived from P_4 involved rare-earth metals.



Scheme 2 Reaction of **1** and P_4

2 Results and discussion

Reaction of two equivalents of Me, TMS-substituted lutetacyclopentadiene (**1**) with P_4 was carried out in THF at room temperature (Scheme 2). After 3 h, the expected *cyclo*-P_3 lutetium complex (**2**) and the aggregated phospholyl lithium (**3**) were obtained.[19b,9c] Besides, the sandwich lutetium complex (**4**) was isolated as a new complex. Interestingly, an unexpected trinuclear rare-earth metal complex $[\{(\eta^5\text{-}C_5Me_5)LuCl\}_3(THF)P_6][Li(THF)_4]$ (**5**) having a bicyclo[3.1.0]- P_6^{4-} ligand was also observed in this reaction.

The structure of **4** was determined by X-ray diffraction analysis which reveals that **4** crystallizes in the $P2_1/c$ space group. There are two independent molecules of **4** in a unit cell which have the similar structural features so that Figure 1 shows one of them. The lutetium is supported by a Cp* ligand, a phospholyl ligand and two chlorine atoms. The lithium bridges the two chlorine atoms and also coordinates to two THF molecules. Both the bond lengths and the bond angles are located in the normal range compared to the known examples.[20] In this reaction, **4** was formed directly from P_4 while the previous methods always need an additional step to prepare the phospholyl lithium, sodium or potassium first.[21]

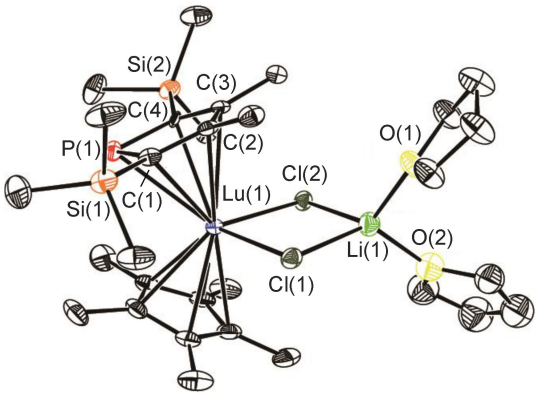


Figure 1 ORTEP drawing of **4**

Ellipsoids are set at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu(1)—P(1) 2.8651 (18), Lu(1)—C(1) 2.704(6), Lu(1)—C(2) 2.734(6), Lu(1)—C(3) 2.728(6), Lu(1)—C(4) 2.695(6), P(1)—C(1) 1.771(7), P(1)—C(4) 1.742(6), C(1)—C(2) 1.418(9), C(2)—C(3) 1.412(9), C(3)—C(4) 1.423(9); C(1)—P(1)—C(4) 91.5(3), P(1)—C(1)—C(2) 111.0(5), C(1)—C(2)—C(3) 112.5(6), C(2)—C(3)—C(4) 113.2(6), P(1)—C(4)—C(3) 111.3(5).

The structure of **5** was determined by X-ray diffraction analysis (Figure 2). The analysis reveals that **5** crystallizes in the *P*-1 space group. **5** is a separated ion pair consisting of a negative charged $[P_6Lu_3]$ moiety and a lithium counter cation. The $[P_6Lu_3]$ moiety has a pseudo mirror plane along the P(1)—P(4)—Lu(3) plane. Each lutetium is supported by a Cp* ligand and every two lutetiums have a bridging chlorine atom. Lu(1) and Lu(2) coordinate to the P_6 ligand in a η^3 mode while Lu(3) coordinates in a η^1 mode. All of the Lu—P bond lengths are in the normal range of those found in the known lutetium phosphine or

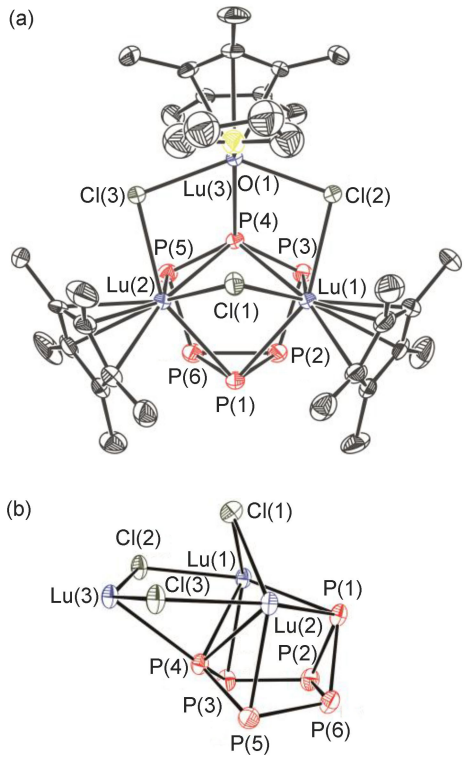


Figure 2 ORTEP drawing of **5** (a) and its [$P_6Lu_3Cl_3$] core (b) Ellipsoids are set at 30% probability level. Hydrogen atoms, lithium counter cation and its coordinating THF molecules are omitted for clarity. Cp* ligands and THF are also omitted in the structure of the [$P_6Lu_3Cl_3$] core. Selected bond lengths [Å] and angles [°]: Lu(1)—P(1) 2.828(3), Lu(1)—P(3) 2.729(3), Lu(1)—P(4) 2.883(4), Lu(2)—P(1) 2.822(3), Lu(2)—P(4), 2.753(4), Lu(2)—P(5) 2.721(3), Lu(3)—P(4) 2.753(4), P(1)—P(2) 2.236(5), P(1)—P(6) 2.236(5), P(2)—P(3) 2.188(4), P(2)—P(6) 2.205(5), P(3)—P(4) 2.182(4), P(4)—P(5) 2.179(4), P(5)—P(6) 2.179(4); P(2)—P(1)—P(6) 59.10(15), P(1)—P(2)—P(3) 112.44(17), P(1)—P(2)—P(6) 60.46(15), P(3)—P(2)—P(6) 107.58(17), P(2)—P(3)—P(4) 97.79(16), P(3)—P(4)—P(5) 107.82(18), P(4)—P(5)—P(6) 97.96(17), P(1)—P(6)—P(2) 60.45(15), P(1)—P(6)—P(5) 112.80(18), P(2)—P(6)—P(5) 107.59(18)

phosphide compounds (2.785～2.977 and 2.782～2.947 Å, respectively).[22] The lutetium-phosphide bond lengths [Lu(1)—P(3), 2.729(3) Å; Lu(2)—P(5), 2.721(3) Å] are significantly shorter than the lutetium-phosphine bond lengths [Lu(1)—P(1), 2.828(3) Å; Lu(1)—P(4), 2.883(4) Å; Lu(2)—P(1), 2.822(3) Å; Lu(2)—P(4), 2.879(3) Å]. The bicyclo[3.1.0]-P_6 ligand takes a boat-like conformation composing of an envelope shaped five-membered ring and a three-membered ring. The P(2)—P(3)—P(5)—P(6) plane has an acute dihedral angle with the P(1)—P(2)—P(6) plane as 106.488°, while it has an obtuse dihedral angle with the P(3)—P(4)—P(5) plane as 132.771°. All the P—P bond lengths are in the typical range of P—P single bond length.[1] The P—P bonds of the three- membered ring [P(1)—P(2), 2.236(5) Å; P(1)—P(6), 2.236(5) Å] are slightly longer than those of the five-membered ring [P(2)—P(3), 2.188(4) Å; P(3)—P(4), 2.182(4) Å; P(4)—P(5), 2.179(4) Å; P(5)—P(6), 2.179(4) Å], since the three-membered ring has a larger ring strain. In addition, upon Lu(1) and Lu(2) capping the puckered bicyclo-[3.1.0]-P_6 moiety, a [P_6Lu_2] cage is formed which could be viewed as an analogue of the known Zintl-P_7 cage[23] by replacement of one edge P atom by two Lu atoms.

To the best of our knowledge, it is the first time that the bicyclo[3.1.0]-P_6 ligand is incorporated into metal complexes, despite the fact that two neutral polyphosphane compounds with this P_6 motif linked with four ^{t}Bu or Cp* substituents have been reported.[24,25] Complex **5** is also the first example that rare-earth metal fragments activate P_4 affording a P_6 ligand.

The $^{31}P\{^1H\}$ NMR spectrum of **5** shows four sets of peaks corresponding to the four types of phosphorus atoms. The P(1) atom shows a triplet of triplet locating at δ −188.18 with $^1J_{PP}$ and $^2J_{PP}$ values at about 198 and 48 Hz, respectively. The P(2)/P(6) atoms show a triplet of doublet locating at δ 9.63 with $^1J_{PP}$ and $^1J_{PP}$ values at about 208 and 90 Hz, respectively. The P(3)/P(5) atoms show a multiplet locating between δ −76.43 and −74.46. The P(4) atom shows a pseudo triplet locating at δ −31.91 with $^1J_{PP}$ value at about 372 Hz.

To better understand the bonding between the three lutetium metals and the bicyclo[3.1.0]-P_6 ligand as well as the charge distribution of the negative charged P_6 ligand, density functional theory (DFT) calculations were performed to check canonical molecular orbitals (CMOs, Figure 3). HOMO shows that the lone electron pair of P(4) has an interaction with the *d* orbitals of both Lu(1) and Lu(2) simultaneously, which could be viewed as a P(4) centered three-center two-electron bond. Analogously, HOMO-2 show another three-center two-electron bond among P(1), Lu(1) and Lu(2) centered at P(1). HOMO−1 shows the interaction between P(3)/P(5) and Lu(1)/Lu(2), while HOMO-7 shows the interaction between P(4) and Lu(3). According to the NBO analysis, all of the P—P bonds are formed by overlap of their corresponding *p* orbitals, and all of the Lu—P bonds are formed by overlap of the *p* orbitals

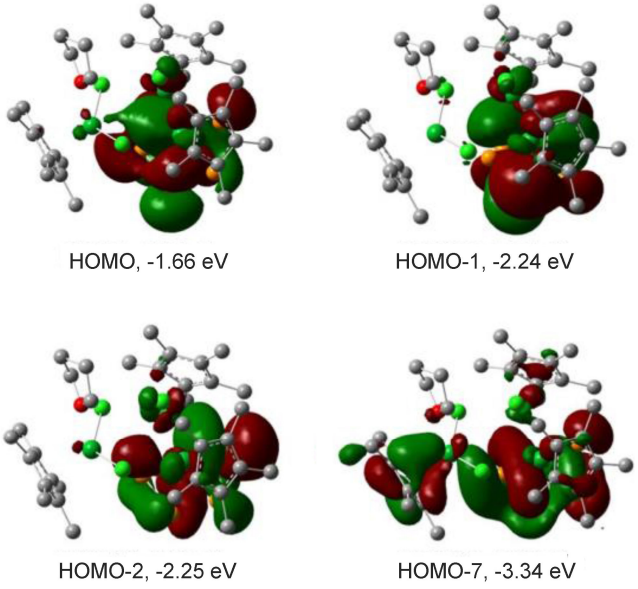


Figure 3 Selected canonical molecular orbitals of **5**

of the phosphorus atoms and the *d* orbitals of the lutetium metals.

3 Conclusions

In summary, we have isolated a trinuclear rare-earth metal complex **5** containing a bicyclo[3.1.0]-P_6 ligand, which is an unreported type and represents the first example that rare-earth metal fragments activate P_4 affording a P_6 ligand. The bonding situations of this novel complex **5** were discussed based on X-ray diffraction analysis and DFT calculations.

4 Experimental section

4.1 Instruments and reagents

All operations were performed under an atmosphere of dry nitrogen in a Vigor (SG 1200/750TS-F) glovebox. Anhydrous THF, hexane and toluene were purified using an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. THF-d_8 was purchased from Cambridge Isotope Laboratory (CIL), degassed, and vacuum transferred to 4 Å molecular sieves. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes (Wilmad 528-JY). NMR spectra were recorded on a Bruker Avance 400 MHz and a Bruker Avance 500 MHz spectrometers. ^{1}H NMR chemical shifts were reported with reference to solvent resonances of THF-d_8 at δ 3.58. ^{31}P{^{1}H} NMR chemical shifts were reported with respect to 85% H_3PO_4 (aq.) (δ 0.0) standard. **1** was prepared according to the literature procedure.[26] Other reagents were commercially available and used without further purification. Caution! P_4 is light-sensitive and highly flammable upon exposure to air. It should be handled with care.[3c]

4.2 Generation of the crystals of 2～5

P_4 (123.9 mg, 1.0 mmol) was added to a THF solution (20 mL) of **1** (1298.4 mg, 2.0 mmol) in one portion. The reaction mixture was stirred at room temperature for 3 h and **1** was consumed completely monitored by ^{1}H NMR. After removal of the solvent under reduced pressure, the reddish yellow solid was extracted by 6 mL of hexane. The extract was concentrated to 4 mL at room temperature by volatilization and then stored at −25 ℃ for three days affording **3** as colorless crystals along with few yellowish red crystals referred to **5**. After crystallization, the remaining supernatant liquid of the extract mainly contains **2** monitored by ^{31}P{^{1}H} NMR. The residue was dissolved in 5 mL of THF. Then hexane (about 20 mL) was added till the first precipitation appears and the solution was stored at −25 ℃ affording the crystals of **4** along with that of **3**.

4.3 Generating the NMR spectra of 5

The *in situ* ^{1}H NMR and ^{31}P NMR showed no signal of **5** due to its low yield. **5** crystalized as several red crystals from the large proportion of yellowish colorless crystals **3**. By isolating the red crystals one by one under microscope, about 3 mg of **5** was obtained although impurities still remain concomitant. The ^{31}P NMR experiment was conducted at room temperature for about 1 h (scan number 1600). The ^{31}P{^{1}H} COSY NMR experiment was conducted at room temperature for about 1 d.

4.4 Determination of the yields of 2～5

The NMR yields of **2**～**4** (13%, 45% and 40%, respectively) could be determined by ^{1}H NMR with hexamethylbenzene as internal standard. **5** couldn't be detected by the *in situ* ^{1}H NMR or ^{31}P NMR because the yield of **5** is very low as about 1% (*ca*. 3 mg **5** was isolated).

(η^5-C_5Me_5)Lu{$Me_2(SiMe_3)_2Li(THF)_3C_4P_3$}] (**2**): ^{1}H NMR (400 MHz, THF-d_8) δ: 0.34 (s, 18H, $SiMe_3$), 1.76～1.79 (m, 12H, β-CH_2, THF), 1.93 (s, 15H, C_5Me_5), 2.22 (s, 6H, Me), 3.60～3.63 (m, 12H, α-CH_2, THF); ^{31}P NMR (162 MHz, THF-d_8) δ: −85.15 (t, 1P, $^1J_{PP}$=211.9 Hz, PLi), −199.46 (t, 2P, $^1J_{PP}$=211.9 Hz, PC).

{η^5-$C_4PMe_2(SiMe_3)_2$}(η^5-C_5Me_5)Lu{$Cl_2Li(THF)_2$} (**4**): ^{1}H NMR (400 MHz, THF-d_8) δ: 0.25 (s, 18H, $SiMe_3$), 1.76～1.79 (m, 8H, β-CH_2, THF), 1.99 (s, 15H, C_5Me_5), 2.19 (s, 6H, Me), 3.60～3.63 (m, 8H, α-CH_2, THF); ^{31}P NMR (162 MHz, THF-d_8) δ: 159.49 (s).

[{(η^5-C_5Me_5)LuCl}$_3$(THF)P_6][Li(THF)$_4$] (**5**): ^{1}H NMR (500 MHz, THF-d_8) δ: 1.76～1.79 (m, 16H, β-CH_2, THF), 1.90 (s, 45H, C_5Me_5), 3.61～3.63 (m, 16H, α-CH_2, THF); ^{31}P NMR (202 MHz, THF-d_8) δ: 9.63 (td, $^1J_{PP}$=ca. 208 Hz, $^1J_{PP}$=ca. 90 Hz, 2P, LuPP*P*PLi), −31.91 (t, $^1J_{PP}$=ca. 372 Hz, 1P, Lu*P*PPPLi), − 74.46 ～ 76.43 (m, 2P, LuP*P*PPLi), −188.18 (tt, $^1J_{PP}$=ca. 198 Hz, $^2J_{PP}$=ca. 48 Hz, 1P, LuPPP*P*Li).

4.5 X-ray crystallographic studies

Single crystals of **4** and **5** suitable for X-ray analysis were grown as shown in experimental section. The crystals were wrapped in mineral oil and then were frozen at 180 or 100 K. Data collections were performed at 180 or 100 K on a SuperNova diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Using Olex2,[27] the structure were solved with the ShelXS or Superflip structure solution program using Charge Flipping[28] and refined with the ShelXL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all of the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of their parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication numbers: CCDC 1869142 (**4**), 1869143 (**5**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Supporting Information X-ray data of **4** and **5**, Computational details of **5**, and NMR spectra of new products. The Supporting Information is available free of charge via

the Internet at http://sioc-journal.cn/.

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(Li, L.; Fan, Y.)

