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**Rare-Earth-Metal Complexes**

# Well-Defined Soluble $P^{3-}$-Containing Rare-Earth-Metal Compounds**

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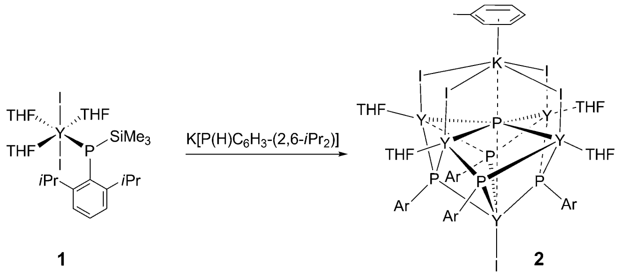
Transition-metal–phosphorus coordination compounds have attracted intense attention and been extensively studied in the past half century.[1–6] Such coordination compounds not only have a fundamental bearing on the theory of coordination chemistry, but also are known to have important applications, especially in the area of synthetic chemistry. A great number of transition-metal–phosphorus coordination compounds, including $PR_nH_{3-n}$ ($n=1$–3),[2] $[PR_nH_{2-n}]^-$ ($n=1$–2),[2] $[PR]^{2-}$,[5] and $P^{3-}$ containing species,[6] have been synthesized. One exception is those with rare-earth-metal ions. Rare-earth-metal ions are among the hardest Lewis acids, whereas phosphines and phosphides are soft Lewis bases; thus, according to Pearson's hard and soft acids and bases (HSAB) principle, rare-earth-metal–phosphorus coordination is a mismatch.[7,8] Up to now, only a handful of examples of Ln–$PR_3$[9] and Ln–$PR_2$[10] (Ln = rare-earth metal) coordination compounds have been reported, and examples of Ln=PR coordination compounds are even more sparse and have been reported just recently.[11,12] The synthesis of soluble rare-earth-metal coordination compounds containing a $P^{3-}$ ligand remains a challenging task primarily because the substituent-free phosphido has a strong tendency to assemble into an oligo-phosphorous one. Reduction of white phosphorus ($P_4$) with the low-valent rare-earth-metal compound $[(\eta^5\text{-}C_5Me_5)_2Sm]$ produces the polyphosphido compound $[\{(\eta^5\text{-}C_5Me_5)_2Sm\}_4P_8]$.[13] $P^{3-}$ containing rare-earth-metal compounds are only precedent in solid-state chemistry, where the LnP compounds possess rock salt (NaCl) type structures,[2] which provides high lattice energy for the stabilization of $P^{3-}$. Herein, we report the synthesis and characterization of well-defined soluble $P^{3-}$ containing rare-earth-metal coordination compounds.

Reaction of $YI_3(THF)_{3.5}$ with 1 equivalent of $K[P(SiMe_3)C_6H_3\text{-}(2,6\text{-}iPr_2)]$ in toluene gave the desired yttrium phosphido diiodide $[Y\{P(SiMe_3)C_6H_3\text{-}(2,6\text{-}iPr_2)\}I_2(thf)_3]$ (**1**) in 71 % yield. Compound **1** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (see the Supporting Information). Reaction of **1** with 1 equivalent of $K[P(H)C_6H_3\text{-}(2,6\text{-}iPr_2)]$ in toluene resulted in a new compound (**2**; Scheme 1). The NMR spectral data for **2** in $C_6D_6$ are intriguing and disagree with what was expected for yttrium diphosphido iodide $[Y\{P(SiMe_3)C_6H_3\text{-}(2,6\text{-}iPr_2)\}\{P(H)C_6H_3\text{-}(2,6\text{-}iPr_2)\}I(thf)_n]$. For example, the $^{31}P$ NMR spectrum of **2** reveals two signals at $\delta = 347.4$ and 154.7 ppm, which are dramatically downfield from that observed for **1** ($\delta = -62.5$ ppm) and other reported yttrium phosphido compounds: $[Y\{P(SiMe_3)_2\}_3]_2$ ($\delta = -107.8$ ppm),[14] $[Cp^*{}_2Y\{P(H)Ph\}]_2$ ($\delta = -107$ ppm)[15] and $[Y\{P(H)C_6H_2\text{-}2,4,6\text{-}Me_3\}Cl_2(thf)_3]_2$ ($\delta = -18.9$ ppm).[16] The signal at $\delta = 154.7$ ppm is comparable to that reported for the bridging phosphinidene unit in a lutetium phosphinidene $[\{2\text{-}(R_2P)C_6H_4\}_2NLu(\mu\text{-}PMes)]_2$ ($\delta = 186.7$ ppm).[11] Moreover, in the $^1H$ NMR spectrum, the signals for the -Si$Me_3$ group of the $[P(SiMe_3)C_6H_3\text{-}(2,6\text{-}iPr_2)]^-$ ligand and for the -P$H$ group of the $[P(H)C_6H_3\text{-}(2,6\text{-}iPr_2)]^-$ ligand were not observed.



*Scheme 1.* Synthesis of **2** from **1**.

Single crystals of **2** suitable for X-ray diffraction analysis were obtained from a solution in toluene. Compound **2** (Figure 1) is a polymetallic yttrium phosphinidene phosphide (33 % yield). The signals at $\delta = 347.4$ and 154.7 ppm in the

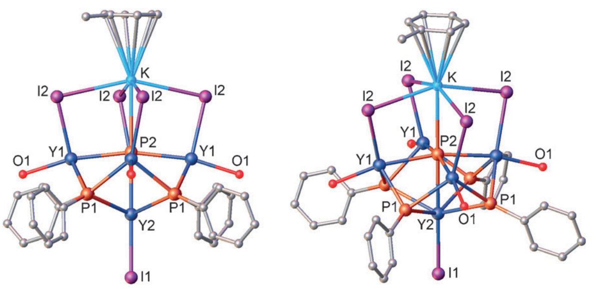


*Figure 1.* Two views of molecular structure of **2**. Isopropyl groups on the Ar rings, hydrocarbon fragments of thf molecules, all hydrogen atoms, and solvents in the lattice are omitted for clarity.

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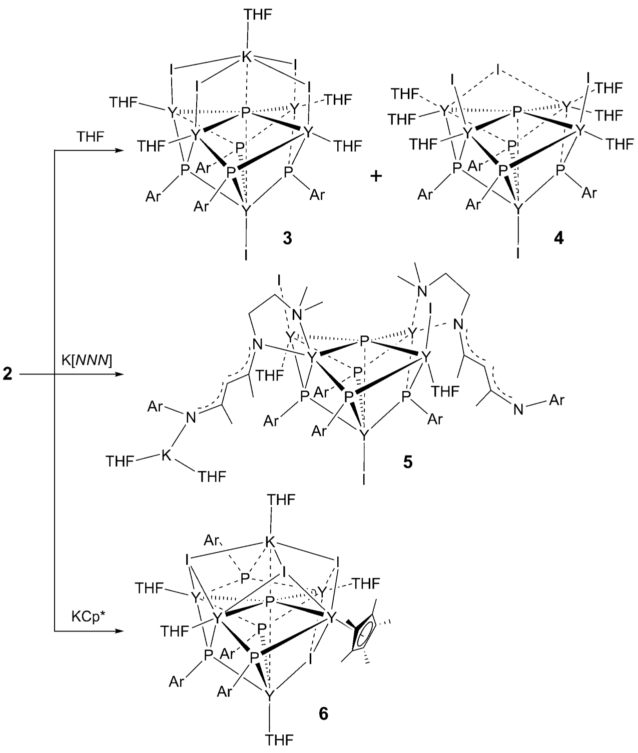
$^{31}$P NMR spectrum of **2** are, thus, assigned to $P^{3-}$ and $[PR]^{2-}$ ligands, respectively. Compound **2** has some rather remarkable structural features. In general, the total structure adopts a pseudo-$C_{4v}$ point group symmetry. Five $Y^{3+}$ centers occupy the vertices of a square pyramid while the four $\mu_3$-$[PR]^{2-}$ ligands cap the side faces of this pyramid. The basal and apical $Y^{3+}$ centers are in strikingly different environments; each of the four basal centers form bonds to the unique $\mu_6$-$P^{3-}$ ligand (2.7770(4) Å), two $\mu_3$-$[PR]^{2-}$ ligands, one $\mu$-$I^-$ ligand, and a thf ligand, while the apical center is coordinated by the $\mu_6$-$P^{3-}$ ligand (2.8850(19) Å), four $\mu_3$-$[PR]^{2-}$ ligands, and a terminal $I^-$ ligand. The distances from the P atoms of $[PR]^{2-}$ ligands to the basal Y1 atoms are 2.6720(11) and 2.7100(11) Å, while those to the apical Y2 atom are significantly longer (2.9801(10) Å). A $K^+$ center closes the open face of the heavy atom core, forming four bonds to four $\mu$-$I^-$ ligands and a contact with the $\mu_6$-$P^{3-}$ ligand. A disordered toluene molecule complements the coordination sphere of the $K^+$ center to a pseudooctahedron and K–C distances range from 3.18 to 3.25 Å. It is noteworthy that the $P^{3-}$ ligand in this soluble coordination compound has an octahedral coordination environment, which is similar to those observed in solid-state LnP compounds.[2]

Consistent with the formation of **2**, two by-products $HP(Si(CH_3)_3)C_6H_3$-(2,6-*i*Pr$_2$) [$^1$H NMR ($C_6D_6$): $\delta = 0.12$ ppm (d, $^3J_{PH} = 4.4$ Hz, 9H, $Si(CH_3)_3$), 3.62 ppm (d, $^1J_{PH} = 206.0$ Hz, P*H*); $^{31}$P NMR ($C_6D_6$): $\delta = -164.2$ ppm] and (1,3-*i*Pr$_2$)-$C_6H_4$ [$^1$H NMR ($C_6D_6$): $\delta = 2.76$ ppm (sept, $^3J_{HH} = 6.8$ Hz, C*H*-$(CH_3)_2$)] were observed in the mother liquor. The formation of **2** apparently involves P–Si(or H) and P–C bonds cleavage.[12,17] Monitoring of the reaction by $^{31}$P NMR spectroscopy in $C_6D_6$ revealed a reaction intermediate formed after the first 10 min of the run. This intermediate exhibited one dd type signal at $\delta = -62.2$ ppm ($^1J_{YP} = 142.9$ Hz, $^2J_{PP} = 10.7$ Hz) and one ddt type signal at $\delta = -95.5$ ppm ($^1J_{PH} = 181.8$ Hz, $^1J_{YP} = 65.9$ Hz, $^2J_{PP} = 10.7$ Hz), and was suggestively assigned a structure of [Y{P(Si(CH$_3$)$_3$)C$_6$H$_3$-(2,6-*i*Pr$_2$)}$_2${P(H)C$_6$H$_3$-(2,6-*i*Pr$_2$)}]. The assignment was further supported by monitoring of a reaction of [Y{P(Si(CH$_3$)$_3$)C$_6$H$_3$-(2,6-*i*Pr$_2$)}$_2$I(thf)$_3$] with K[P(H)C$_6$H$_3$-(2,6-*i*Pr$_2$)]. Along with the reaction progress of **1** with K[P(H)C$_6$H$_3$-(2,6-*i*Pr$_2$)], the intensities of the signals related to the intermediate decreased, while those related to **2** and HP(Si(CH$_3$)$_3$)C$_6$H$_3$-(2,6-*i*Pr$_2$) increased. Mechanistic details of how [Y{P(Si(CH$_3$)$_3$)C$_6$H$_3$-(2,6-*i*Pr$_2$)}$_2${P(H)C$_6$H$_3$-(2,6-*i*Pr$_2$)}] reacts with other species in the reaction mixture to give the final product **2** are presently unclear.

Treatment of **2** with THF provided two other polymetallic yttrium phosphinidene phophides **3** and **4** (Scheme 2). The structure of **3** resembles that of **2**, with the coordinated toluene replaced by a THF molecule (Figure 2). Unlike pseudo-$C_{4v}$-symmetrical **2** and **3**, **4** possesses only a pseudo-$C_s$ point group symmetry as a result of the loss of KI; one of the $I^-$ ligands links two $Y^{3+}$ centers in $\mu$-mode (Figure 2). In **4**, the $P^{3-}$ ligand adopts an unusual rectangular pyramid coordination mode, and is positioned 0.30 Å below the base of a rectangular pyramid defined by five $Y^{3+}$ centers.



***Scheme 2.*** Syntheses of **3**–**6**.

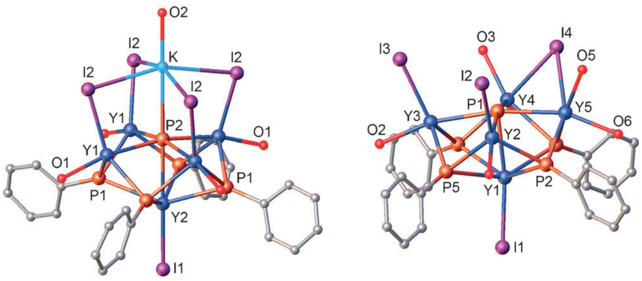


***Figure 2.*** Molecular structures of **3** (left) and **4** (right). Isopropyl groups on the Ar rings, hydrocarbon fragments of thf molecules, all hydrogen atoms, and solvents in the lattice are omitted for clarity.

Compound **2** reacted with a potassium salt of β-diketiminato based tridentate ligand K[MeC(NAr)CHC(Me)(NCH$_2$CH$_2$NMe$_2$)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (KL) to give yttrium phosphinidene phophide **5** in a 76 % yield (Scheme 2). During the reaction, the two $I^-$ ligands coordinate to the $Y^{3+}$ centers of **2** at the pyramid base plane are replaced with two L ligands. Compound **5** crystallizes in a rare trigonal space group *R*3*c* (a racemic twin). The core of **5** is a positively charged pentanuclear yttrium phosphinidene phosphide composed of five $Y^{3+}$ centers, one $\mu_5$-$P^{3-}$ ligand, four $\mu_3$-$[PR]^{2-}$ ligands, three terminal $I^-$ ligands, and two thf ligands (Figure 3). The β-diketiminato backbone of L displays a delocalized electronic structure and adopts a rare W-conjugated conformation.[18] Ligand L coordinates to a $Y^{3+}$ center through a ketiminato nitrogen donor and an amine nitrogen donor at one end, and to a $K^+$ ion through the remaining ketiminato nitrogen atom at the other end. With $K^+$ ions as linkages, the compound is concatenated into helical chains as shown in Figure 3.

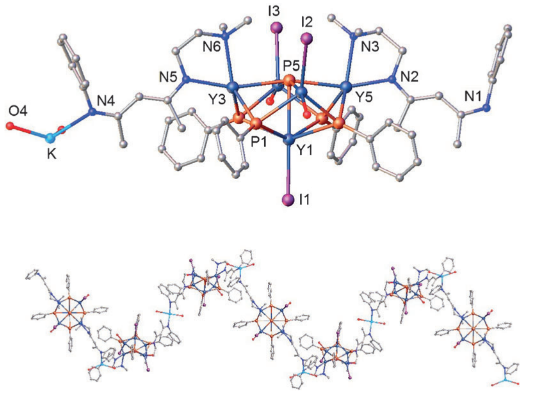


*Figure 3.* Molecular structure of **5**. Isopropyl groups on the Ar rings, hydrocarbon fragments of thf molecules, all hydrogen atoms, and solvents in the lattice are omitted for clarity.

Reaction of **2** with KCp* (Cp* = $[C_5Me_5]^-$) provided a cyclopentadienyl yttrium phosphinidene phosphide **6** in a 52% yield (Scheme 2), which shows remarkable structural differences relative to the compounds **2**–**5**. In **6**, five $Y^{3+}$ centers occupy the vertices of a pyramid as observed in **2**–**5**; however, the side faces of the pyramid are occupied by one $\mu_3$-$I^-$ ligand and three $\mu_3$-phosphinidene ligands instead of four $\mu_3$-phosphinidene ligands in **2**–**5** (Figure 4).[19] The apical Y1 center is coordinated by one $\mu_6$-$P^{3-}$ ligand, three $\mu_3$-$[PR]^{2-}$ ligands, one $\mu_3$-$I^-$ ligand, and one thf ligand. Four base $Y^{3+}$ centers exhibit three types of coordination environment. The Y2 and Y4 centers are coordinated by one $\mu_6$-$P^{3-}$ ligand, two $\mu_3$-$[PR]^{2-}$ ligands, two $\mu_3$-$I^-$ ligands, and one thf ligand; the Y3 center is coordinated by one $\mu_6$-$P^{3-}$ ligand, three $\mu_3$-$[PR]^{2-}$ ligands, one $\mu_3$-$I^-$ ligand, and one thf ligand; the Y5 center is coordinated by one $\mu_6$-$P^{3-}$ ligand, one $\mu_3$-$[PR]^{2-}$ ligand, three $\mu_3$-$I^-$ ligands, and one $\eta^5$-$[Cp^*]^-$ ligand. A $K^+$ center coordinates to one $\mu_6$-$P^{3-}$ ligand, one $\mu_3$-$[PR]^{2-}$ ligand, three $\mu_3$-$I^-$ ligands, and one thf ligand, and adopts a pseudooctahedral coordination environment.

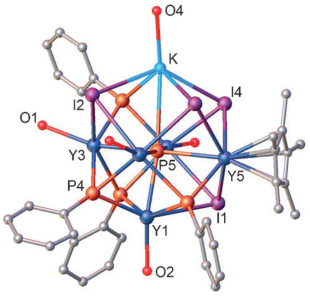


*Figure 4.* Molecular structure of **6**. Isopropyl groups on the Ar rings, hydrocarbon fragments of thf molecules, and all hydrogen atoms are omitted for clarity.

In summary, the first soluble $P^{3-}$ containing rare-earth-metal coordination compounds were synthesized and structurally characterized. The $P^{3-}$ ligands in these coordination compounds display two kinds of coordination modes: octahedral and rectangular pyramidal. The results reported herein extend the $P^{3-}$ coordination chemistry to the rare-earth-metal series and fill in the gap between coordination compounds and solid-state inorganic compounds of the rare-earth metal containing $P^{3-}$ ligand.

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[19] CCDC 837250, 837251, 837252, 837253, 837254, and 837255 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.