ORGANOMETALLICS

Insertion of Isocyanate and Isothiocyanate into the Ln–P σ -Bond of Organolanthanide Phosphides

Weiyin Yi,[†] Jie Zhang,^{*,†} Longcheng Hong,[†] Zhenxia Chen,[†] and Xigeng Zhou^{*,†,‡}

[†]Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai 200032, People's Republic of China

S Supporting Information

ABSTRACT: The synthesis, structure, and reactivity of organoyttrium phosphides toward phenyl isocyanate (PhNCO) and phenyl isothiocyanate (PhNCS) are described. Reaction of $(Tp^{Me2})CpYCH_2Ph(THF)$ $(Tp^{Me2} = tris(3,5-dimethylpyrazolyl)$ borate; $Cp = C_5H_5$) with 1 equiv of HPPh₂ in THF at ambient temperature gives an organoyttrium phosphide $(Tp^{Me2})CpYPPh_2$ -(THF) (1). Treatment of 1 with 1 equiv of PhNCO in THF at ambient temperature results in monoinsertion of PhNCO into the $Y-P \sigma$ -bond to yield complex $(Tp^{Me2})CpY[OC(PPh_2)NPh]$ -(THF) (2), whereas reaction of 1 with 2 equiv of PhNCO affords the PhNCO diinsertion product $(Tp^{Me2})CpY[OC(PPh_2)-$ N(Ph)C(O)NPh] (4). However, reaction of 1 with PhNCS under the same conditions is independent of the stoichiometric



ratio and gives only the monoinsertion product $(Tp^{Me2})CpY[SC(PPh_2)NPh]$ (3). Moreover, 1 can effectively catalyze the cyclotrimerization of PhNCO under mild conditions, but does not catalyze the cyclotrimerization of PhNCO. In addition, the reaction of Cp₂LnPPh₂(THF) with PhNCS affords the insertion products Cp₂Ln[SC(PPh₂)NPh](THF) (Ln = Y (6), Er (7), Dy (8)). All new complexes were characterized by elemental analysis, IR, and/or ¹H, ¹³C and ³¹P NMR, and their solid-state structures, except 4, were determined through single-crystal X-ray diffraction analysis. These reactions represent the first example of isocyanate and isothiocyanate insertions into the Ln-P σ -bond and provide an efficient method for the construction of phosphaureido, phosphadiureido, and phosphathioureido ligands.

■ INTRODUCTION

There is fundamental interest in the reactivity of organolanthanide complexes with unsaturated organic small molecules, because this is the source for developing new catalytic reactions and catalysts.^{1,2} Many efforts have focused on a detailed understanding of insertions of such substrates into the Ln-H,³ Ln-C, Ln-N, or Ln-S bonds of organolanthanide complexes over the last decades. The accumulated information in this field indicates that the occurrence of the insertion strongly depends on the degree of steric saturation around the central metal ion and the nature of the ligand. In contrast, studies on the basic chemistry of organolanthanide phosphides have been very limited,^{7–9} despite recent significant advances in catalytic hydrophosphinylation.^{9b,c} This is mainly due to the weak bonding interaction between a rare-earth ion and a organic phosphorus ligand, which renders these complexes difficult to synthesize and characterize.⁷ Well-defined organolanthanide complexes containing organic phosphorus anion ligands are mainly limited to the divalent lanthanide metals.8 The first structurally characterized trivalent lanthanocene complexes bearing the Ln–P σ -bond was reported in 1986.^{7c} Recently,

organolanthanide phosphides stabilized by a half-sandwich ligand, such as $[Me_2Si(C_5Me_4)(NC_6H_2Me_3-2,4,6)]$, have been reported.^{9a} However, stoichiometric transformation of the Ln–P bond remains little explored.

The scorpionate-supported tris(pyrazolyl)borate ligands $(Tp^{R,R'})$ have been widely applied in organolanthanide chemistry, because their steric profiles can be modified by variation of the substituents in the 3-positions of the pyrazolyl rings.¹⁰ Recently, we have been investigating the synthesis and reactivity of rare-earth organometallic derivatives with the scorpionate-supported Tp^{Me2} ligand^{10c,d} and demonstrated that mixed Tp^{Me2}/Cp lanthanide chlorides $(Tp^{Me2})CpLnCl(THF)$ that are prepared by the cyclopentadienyl-exchange of Cp_2LnCl reacts with KTp^{Me210c} are a suitable precursor for preparation of a variety of mixed Tp^{Me2}/Cp rare-earth derivatives. For example, transformation of $(Tp^{Me2})CpYCl(THF)$ to $(Tp^{Me2})CpYCH_2Ph(THF)$ is easily realized via its salt metathesis with KCH₂Ph.¹¹ However, similar reaction of $(Tp^{Me2})_2LnCl$ with

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KCH₂SiMe₃ does not afford the corresponding alkyl complex $(Tp^{Me2})_2LnCH_2SiMe_3$ due to ligand degradation of Tp^{Me2} .¹² To further explore the reactivity of $(Tp^{Me2})CpYCH_2Ph(THF)$, we investigated its reaction with HPPh₂ and thus synthesized the mixed Tp^{Me2}/Cp yttrium phosphide $(Tp^{Me2})CpYPPh_2(THF)$. It has been found that $(Tp^{Me2})CpYPPh_2(THF)$ not only undergoes the Y–P bond insertions with phenyl isocyanate and phenyl isothiocyanate under mild conditions but also catalyzes the cyclotrimerization of phenyl isothiocyanate through the Y–P bond insertion process. Phenyl isothiocyanate insertion into the Ln–P *σ*-bond of $Cp_2LnPPh_2(THF)$ is also observed. In this contribution, we would like to report these results.

EXPERIMENTAL SECTION

General Procedure. All operations involving air- and moisturesensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques. The solvents of THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. $(Tp^{Me2})CpYCH_2Ph(THF)^{11}$ and $Cp_2LnPPh_2(THF)^{7c}$ were prepared according to the procedures described in the literature. Phenyl isocyanate, phenyl isothiocyanate, and HPPh₂ were purchased from Aldrich and were used without purification. Elemental analyses for C, H, and N were carried out on a Rapid CHN-O analyzer. The ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were recorded by means of a Bruker DMX-400 NMR spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C; 160 MHz for ³¹P).

Synthesis of (Tp^{Me2})CpYPPh₂(THF) (1). HPPh₂ (0.590 g, 3.00 mmol) was added to a 40 mL THF solution of (Tp^{Me2})CpYCH₂Ph-(THF) (1.84 g, 3.00 mmol) at room temperature. After stirring for overnight, the solvent was removed under vacuum and the solid residue was washed with 10 mL of n-hexane for two times. This solid material was collected by filtration and dried for 5 h on a vacuum line. Yield: 1.78 g (84%). The yellow powder was recrystallized from the mixed solvent of toluene and *n*-hexane to give 1 as yellow crystals. Anal. Calcd for C36H45N6BOPY: C, 61.03; H, 6.40; N, 11.86. Found: C, 60.78; H, 6.33; N, 12.07. IR (Nujol, cm⁻¹): 1573 m, 1543 s, 1261 s, 1202 m, 1071 s, 1033 s, 983 w, 930 m, 860 m, 838 m, 782 m, 695 s, 647 s. ¹H NMR (400 MHz, C_6D_6): δ 7.06–7.47 (m, 10H, C_6H_5), 6.42 (s, 5H, C_5H_5), 5.63 (s, 3H, H-4(Tp^{Me2})), 3.52 (m, 4H, O(CH₂CH₂)₂), 2.41 (s, 9H, CH₃-Tp^{Me2}), 2.18 (s, 9H, CH₃-Tp^{Me2}), 1.28 (m, 4H, O(CH₂CH₂)₂). ¹³C NMR (100 MHz, C_6D_6): δ 150.28, 144.57, 140.37 (d, J_{PC} = 14.8 Hz), 134.33 (d, J_{PC} = 17.2 Hz), 133.22 (d, J_{PC} = 18.1 Hz), 128.60, 110.12, 106.22, 70.05, 25.44, 14.61, 13.29. ³¹P {¹H} (160 MHz, C_6D_6): δ -19.07.

Synthesis of (Tp^{Me2})CpY[OC(PPh₂)NPh](THF) (2). PhNCO (0.083 g, 0.70 mmol) was added to a solution of 1 (0.497 g, 0.70 mmol) in 15 mL of THF at room temperature. After being stirred for overnight, the reaction mixture was worked up by the method described above. Colorless crystals of 2 were obtained in 76% yield, 0.440 g. Anal. Calcd for C43H50N7BO2PY: C, 62.41; H, 6.09; N, 11.85. Found: C, 62.29; H, 6.05; N, 11.95. IR (Nujol, cm⁻¹): 1583 m, 1543 s, 1495 w, 1414 w, 1343 w, 1261 s, 1203 s, 1071 s, 1035 s, 1022 s, 921 m, 869 w, 801 s, 785 s, 695 s, 643 s. ¹H NMR (400 MHz, C_6D_6): δ 7.92–7.96 (m, 4H, C_6H_5), 7.43–7.48 (m, 2H, C_6H_5), 7.35–7.40 (m, 1H, C_6H_5), 7.07–7.20 (m, 8H, C_6H_5), 6.53 (s, 5H, C_5H_5), 5.46 (s, 3H, H-4(Tp^{Me2})), 3.54–3.57 (m, 4H, $O(CH_2CH_2)_2$), 2.14 (s, 9H, CH_3 - Tp^{Me2}), 2.11(s, 9H, CH₃-Tp^{Me2}), 1.37–1.43 (m, 4H, O(CH₂CH₂)₂). ¹³C NMR (100 MHz, C_6D_6): δ 149.70, 139.71, 138.44 (d, J_{PC} = 10 Hz), 136.52, 134.31 (d, J_{PC} = 18 Hz), 133.18 (d, J_{PC} = 18 Hz), 130.03, 128.82, 128.64, 125.07, 122.09, 111.05, 106.82, 67.87, 25.79, 13.44, 13.32. $^{31}\mathrm{P}$ $\{^{1}\mathrm{H}\}$ (160 MHz, C_6D_6): δ -20.13.

Synthesis of (Tp^{Me2})**CpY**[**SC**(**PPh**₂)**NPh**] (3). Following the procedure described for 2, reaction of 1 (0.496 g, 0.70 mmol) with PhNCS (0.096 g, 0.70 mmol) gave $3 \cdot C_7H_8$ as colorless crystals. Yield: 0.447 g (74%). Anal. Calcd for $C_{46}H_{50}N_7BSPY$: C, 63.97; H, 5.84; N, 11.35. Found: C, 64.12; H, 5.88; N, 11.12. IR (Nujol, cm⁻¹): 1726 w, 1591 s, 1542 s, 1415 w, 1309 w, 1261 s, 1199 s, 1072 s, 1038 s, 982 s, 903 w, 835 w, 794 s, 695 s, 645 m. ¹H NMR (400 MHz, C₆D₆): δ 8.21–8.25 (m, 2H, C₆H₅), 7.61–7.65 (m, 2H, C₆H₅), 7.28–7.31 (m, 2H, C₆H₅), 7.12–7.20 (m, 2H, C₆H₅), 7.01–7.03 (m, 4H, C₆H₅), 6.86–6.92 (m, 3H, C₆H₅), 6.26 (s, 5H, C₅H₅), 5.52 (s, 1H, H-4(Tp^{Me2})), 5.47 (s, 1H, H-4(Tp^{Me2})), 2.70 (s, 3H, CH₃- Tp^{Me2}), 2.18 (s, 3H, CH₃- Tp^{Me2}), 2.15 (s, 3H, CH₃- Tp^{Me2}), 2.11 (s, 3H, CH₃- Tp^{Me2}), 1.96 (s, 3H, CH₃- Tp^{Me2}). ¹³C NMR (100 MHz, C₆D₆): δ 150.31, 143.90, 137.15, 136.55, 134.31 (d, J_{PC} = 14 Hz), 133.26 (d, J_{PC} = 11 Hz), 129.01, 125.45, 124.08, 124.06, 111.69, 111.85, 106.70, 14.29, 13.04. ³¹P {¹H} (160 MHz, C₆D₆): δ 7.39.

Synthesis of (Tp^{Me2})CpY[OC(PPh₂)N(Ph)CONPh] (4) and (PhNCO)₃ (5). To the 10 mL THF solution of 2 (0.414 g, 0.5 mmol) was added slowly phenyl isocyanate (0.060 g, 0.5 mmol) at -35 °C, and then the reaction mixture was slowly warmed to room temperature. After stirring overnight at room temperature, all volatile substances were removed under reduced pressure. The residue was then washed using hexane and recrystallized in toluene/hexane to give 4 as a yellow powder. Yield: 0.197 g (45%). Anal. Calcd for C46H47N8BO2PY: C, 63.17; H, 5.42; N, 12.81. Found: C, 62.95; H, 5.27; N, 12.45. IR (Nujol, cm⁻ 1): 1607 m, 1586 m, 1540 s, 1199 s, 1070 s, 1034 s, 982 s, 909 m, 842 w, 811 s, 689 s, 665 w, 646 s. ¹H NMR (400 MHz, C_6D_6): δ 6.99–7.73 (m, 10H, C₆H₅), 6.72-6.79 (m, 10H, C₆H₅), 6.22 (s, 5H, C₅H₅), 5.68 (s, 2H, H-4(Tp^{Me2})), 5.49 (s, 1H, H-4(Tp^{Me2})), 2.41 (s, 3H, CH₃-Tp^{Me2}), 2.24 (s, 6H, CH₃-Tp^{Me2}), 1.97 (s, 6H, CH₃-Tp^{Me2}), 1.92 (s, 3H, CH₃-Tp^{Me2}). ¹³C NMR (100 MHz, C₆D₆): δ 169.17, 151.78, 150.38, 145.64, 143.46, 138.85, 135.54 (d, J_{PC} = 19 Hz), 133.14 (d, J_{PC} = 21 Hz), 128.76 (d, *J*_{PC} = 19 Hz), 128.65, 125.47, 124.22, 125.55, 121.96, 116.01, 113.17, 115.51, 106.48, 14.69, 13.36, 13.26, 13.02. ³¹P {¹H} (160 MHz, C₆D₆): $\delta - 20.05$

PhNCO (10 equiv, 0.830 g, 7.0 mmol) was added slowly to a solution of 1 (0.497 g, 0.70 mmol) in 30 mL of THF at -35 °C. The reaction mixture was warmed slowly to room temperature and then continued to stir overnight at room temperature. The reaction mixture was concentrated to dry. To the residue was added 10 mL of water, and it was extracted with toluene. The organic portions were dried by Na₂SO₄. The solvent was removed in vacuo. Yellow crystals of **5** were obtained by recrystallization in the mixed solvent of toluene and hexane. Yield: 0.692 g (83%). This product was identified as (PhNCO)₃ by MS and unit cell measurement.^{4k}

Synthesis of Cp₂Y[SC(PPh₂)NPh](THF) (6). PhNCS (0.140 g, 1.03 mmol) was added to a solution of Cp₂YPPh₂(THF) (0.490 g, 1.03 mmol) in 20 mL of THF at room temperature. After being stirred for overnight, the solvent was removed under vacuum and the solid residue was washed with 5 mL of n-hexane. This solid material was collected by filtration and was recrystallized from the solvent mixture of THF and hexane to give 6 as colorless crystals. Yield: 0.485 g (77%). Anal. Calcd for C₃₃H₃₃NOSPY: C, 64.81; H, 5.44; N, 2.29. Found: C, 64.60; H, 5.32; N, 2.45. IR (Nujol, cm⁻¹): 1648 m, 1589 s, 1578 w, 1525 w, 1450 s, 1342 m, 1201 m, 1168 m, 1099 m, 1077 s, 1013 s, 975 s, 864 m, 777 s, 696 s, 665 w. ¹H NMR (400 MHz, C_6D_6): δ 7.35–6.75 (m, 15H, C_6H_5), 6.36 (s, 10H, C₅H₅), 3.57 (m, 4H, O(CH₂CH₂)₂), 1.40 (m, 4H, O- $(CH_2CH_2)_2$). ¹³C NMR (100 MHz, C₆D₆): δ 135.61 (d, J_{PC} = 21 Hz), 135.54 (d, J_{PC} = 19 Hz), 133.20, 132.60, 129.22, 129.12, 128.64, 124.61, 124.34, 111.75, 110.24, 67.95, 25.84. ³¹P {¹H} (160 MHz, $C_6 D_6$): δ 12.63.

Synthesis of Cp₂Er[SC(PPh₂)NPh](THF) (7). PhNCS (0.154 g, 1.14 mmol) was added to a solution of Cp₂ErPPh₂(THF) (0.630 g, 1.14 mmol) in 20 mL of THF at room temperature. After being stirred for



overnight, the reaction mixture was worked up by the method described above. Pink crystals of 7 were obtained in 69% yield, 0.543 g. Anal. Calcd for $C_{33}H_{33}NOSPEr$: C, 57.45; H, 4.82; N, 2.03. Found: C, 57.28; H, 4.70; N, 2.15. IR (Nujol, cm⁻¹): 1649 m, 1588 s, 1578 w, 1521 w, 1450 s, 1342 m, 1262 m, 1168 m, 1075 s, 1013 s, 973 s, 865 m, 740 s, 699 s, 664 w.

Synthesis of Cp₂Dy[SC(PPh₂)NPh](THF) (8). Following the procedure described for 6, reaction of Cp₂DyPPh₂(THF) (0.540 g, 0.98 mmol) with PhNCS (0.132 g, 0.98 mmol) gave 8 as yellow crystals. Yield: 0.483 g (72%). Anal. Calcd for $C_{33}H_{33}NOSPDy: C, 57.85; H, 4.86; N, 2.04.$ Found: C, 57.70; H, 4.93; N, 2.10. IR (Nujol, cm⁻¹): 1649 m, 1587 s, 1578 w, 1522 w, 1440 s, 1342 m, 1262 m, 1169 m, 1099 m, 1075 s, 1020 s, 974 s, 865 m, 776 s, 695 s, 664 w.

X-ray Data Collection, Structure Determination and Refinement. Suitable single crystals of complexes 1–3 and 6–8 were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program.¹³ The structures were solved by the direct method using the SHELXL-97 program.¹⁴ All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. All calculations were performed using the Bruker Smart program.

RESULTS AND DISCUSSION

Synthesis and Characterization of Mixed Tp^{Me2}/Cp Yttrium Phosphide (Tp^{Me2})CpYPPh₂(THF) (1). Treatment of (Tp^{Me2})CpYCH₂Ph(THF) with 1 equiv of HPPh₂ in THF at room temperature gave the expected complex (Tp^{Me2})CpYPPh₂-(THF) (1) in 84% isolated yield, companying with release of a toluene molecule (Scheme 1).

Complex 1 is air- and moisture-sensitive and is readily dissolved in THF and toluene and is sparingly soluble in *n*-hexane. It was characterized by elemental analysis, IR, and ¹H NMR spectra, which were in good agreement with the proposed structure. In ¹H NMR spectra, four single peaks at 6.42, 5.63, 2.41, and 2.18 ppm are attributed to *H*-Cp, 4-*H*-Tp^{Me2}, 3-*Me*-Tp^{Me2}, and 5-*Me*-Tp^{Me2}, respectively. The chemical shifts of the coordinated THF molecule are shown at 3.52 and 1.28 ppm as two multiplet peaks. The Ph/Cp molar ratio of **2** indicates the occurrence of the displacement of the CH₂Ph group by a PPh₂ unit.

Recrystallization of 1 in toluene/*n*-hexane afforded paleyellow crystals suitable for single-crystal X-ray diffraction analysis. The molecular structure and important bond lengths/angles of 1 are displayed in Figure 1. Compound 1 is a solvated



Figure 1. ORTEP diagram of $(Tp^{Me2})CpYPPh_2(THF)$ (1) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–O1 2.411(3), Y1–N1 2.463(4), Y1–N5 2.480(4), Y1–N3 2.507(4), Y1–C16 2.677(5), Y1–C18 2.684(5), Y1–C19 2.684(5), Y1–C17 2.686(5), Y1–C20 2.688(5), Y1–P1 2.845(2); O1–Y1–P1 100.0(1), N1–Y1–P1 86.6(1), N5–Y1–P1 86.4(1), N3–Y1–P1 161.0(1).

Scheme 2



monomer with the yttrium atom bonded to one κ^3 -Tp^{Me2} ligand, one η^5 -Cp ring, one PPh₂ ligand, and one THF molecule. The coordination number of the center metal ion is 8. The Y–P distance of 2.845(2) Å is in the normal range of Ln–P σ -bonds.^{9a,15} The Y–O(THF) distance is 2.411(3) Å, a normal donor Y–O bond length. The Y–C(Cp) and Y–N(Tp^{Me2}) distances are also in the normal ranges.^{10a}

Reactions of 1 with PhNCO and PhNCS. With mixed Tp^{Me2}/Cp yttrium phosphide 1 in hand, we next explored its reactivity toward PhNCO and PhNCS. As shown in Scheme 2, 1 was allowed to react with 1 equiv of PhNCO in THF at ambient temperature, affording an organoyttrium phosphaureido complex (Tp^{Me2})CpY[OC(PPh₂)NPh](THF) (2), indicating that one isocyanate molecule is inserted into the Y–P σ -bond of 1. PhNCS reacts with 1 under the same conditions to yield the corresponding Y–P bond insertion product (Tp^{Me2})CpY[SC(PPh₂)NPh](3). These reactions represent the first example of isocyanate and isothiocyanate insertion into the lanthanide–phosphorus bond of organolanthanide complexes and provide a

C(20)

C(2

C(19)

C(6)



Figure 2. ORTEP diagram of $(Tp^{Me2})CpY[OC(PPh_2)NPh](THF)$ (2) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1-O1 2.352(3), Y1-N1 2.518(3), Y1-O2 2.526(3), Y1-N3 2.530(3), Y1-N5 2.555(3), Y1-N7 2.564(3), P1-C22 1.894(4), O1-C22 1.271(4), N7-C22 1.304(5); O1-C22-N7 117.7(4), O1-C22-P1 117.2(3), N7-C22-P1 124.9(3), O1-C22-Y1 54.1(2), N7-C22-Y1 63.6(2), P1-C22-Y1 169.4(2).

practical strategy for the in situ construction of phosphaureido and phosphathioureido ligands.

Further investigation results indicated that 1 is an efficient catalyst for cyclotrimerization of phenyl isocyanate.^{4k,1} Treatment of 1 with 10 equiv of PhNCO in THF at room temperature gave the cyclotrimerization product (PhNCO)₃ (5) in 83% isolated yield. To explore the mechanism of the cyclotrimerization,¹⁶ the subsequent reaction of 2 with another equivalent of PhNCO under the same conditions was examined, and the diinsertion product (Tp^{Me2})CpY[OC(PPh₂)N(Ph)C-(O)NPh] (4) was obtained in 45% isolated yield. Treatment of 4 with the third equivalent or excess of PhNCO did not afford the triinsertion product; instead, the cyclotrimer 5 was isolated (Scheme 2). We also carried out the reaction of 3 with an excess of PhNCS under the similar conditions, but only the starting materials PhNCS and 3 were recovered.

Complexes 2–4 were characterized by standard spectroscopic and analytical techniques. In the IR spectra data of 2 and 3, in addition to the characteristic absorptions assigned to Tp^{Me2} and Cp groups, a new band is observed at ca. 1583 cm⁻¹ for 2 (1591 cm⁻¹ for 3), which may be assigned to the absorption of the delocalized mode of the O–C–N (S–C–N) unit of the resulting phosphaureido (phosphathioureido) ligand.^{4k,5s} The bonding mode was further proven by single-crystal X-ray diffraction on complexes 2 and 3. The ¹H NMR spectra of 2 and 3 display two different splitting behaviors of the Tp^{Me2} ligand, viz a single peak at 5.54 ppm assigned to 4-H-Tp^{Me2} and two single peaks at 2.14 and 2.11 ppm assigned to 3-*Me*-Tp^{Me2} and 5-*Me*-Tp^{Me2} in 2, three single peaks at 5.52, 5.49, and 5.47 ppm assigned to 4-*H*-Tp^{Me2} and six single peaks at 2.70, 2.18, 2.15, 2.13, 2.11, and 1.96 ppm assigned to 3-*Me*-Tp^{Me2} and 5-*Me*-Tp^{Me2} in 3. The ¹H NMR spectrum of 4 shows the Cp/Ph molar ratio of 1/4, suggesting that two PhNCO units contact with a PPh₂ group.



Figure 3. ORTEP diagram of $(Tp^{Me2})CpY[SC(PPh_2)NPh]$ (3) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–N1 2.410(4), Y1–N5 2.420(5), Y1–N2 2.456(5), Y1–N7 2.579(5), Y1–S1 2.823(2), S1–C1 1.723(6), P1–C1 1.877(6), N1–C1 1.310(7); N1–C1–S1 117.9(4), N1–C1–P1 120.4(4), S1–C1–P1 121.3(4), N1–C1–Y1 51.0(3), S1–C1–Y1 67.0(2), P1–C1–Y1 170.9(3).

The X-ray structural analysis results show that 2 is a solvated monomer with the yttrium atom bonded to one κ^3 -Tp^{Me2} ligand, one η^5 -cyclopentadienyl ring, one chelating phosphaureido ligand [OC(PPh₂)NPh], and one THF (Figure 2). The coordination number of the central Y³⁺ ion is 9. The coordinated phosphaureido group forms essentially a planar four-membered ring with the Y atom within experimental errors. The bond angles around C22 are consistent with sp² hybridization. The N7-C22 and O1-C22 bond lengths, 1.304(5) and 1.271(4) Å, are in intermediate values between the corresponding C-N and C-O single- and double-bond distances and are similar to the values observed in $(C_5H_4Me)_2Y[OC(N^iPr_2)NPh](THF)$ (N1-C1 1.323(5) Å; O1-C1 1.297 (4) Å). These bond parameters indicate substantial electronic delocalization over the O-C-N unit.^{4k,17} Consistent with this, the Y-N7 and Y-O1 distances, 2.564(3) and 2.352(3) Å, are intermediate between the values observed for a Y-N and Y-O single bond distance and a Y-N and Y-O donor bond distance and are comparable to the corresponding values found in $(C_5H_4Me)_2Y[OC(N'Pr_2)NPh]$ (THF) (Y–N1 2.401(2) Å; Y–O1 2.285(2) Å).^{5s} The P1–C22 distance is 1.894(4) Å, a typical P-C single bond, and is comparable with that found in $[Me_2Si(C_5Me_4)(NC_6H_2Me_3-2,4,6)]$ $La[(iPrN)_2C(PPh_2)](THF)$ (P1-C1 1.915(3) Å).^{9a} The bond lengths and angles of $(Tp^{Me2})CpY$ unit are in the normal ranges.

Positive structural verification of **3** was also provided by a single-crystal X-ray analysis (Figure 3). The structural determination results show that **3** is a solvent-free monomer, and the Ph₂P group has combined with PhNCS, forming a four-membered heterometallacycle. The C1–N1 and C1–S1 bond distances (1.310(7) and 1.732(6) Å) are in agreement with those found in $\{(C_5H_4Me)_2Y[SC(N^iPr_2)NPh]\}_2$ (C13–N1 1.304(3) Å; C13–S1 1.727(3) Å).^{5p} The Y–S bond distance of 2.823(2) Å is comparable with that found in $(C_5H_4Me)_2Nd[\eta^2-SC-(SPh)NPh]$ (THF) (2.881 Å), if the difference in metallic radii

Scheme 3



Figure 4. ORTEP diagram of $Cp_2Ln[SC(PPh_2)NPh](THF)$ (Ln = Y (6), Er (7), Dy (8)) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 1.	Selected	Bond	Lengths	(Å)	and Angles	(°) for 6–8
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	Ln = Y(6)	Ln = Er(7)	Ln = Dy (8)
Ln1-O1	2.435(6)	2.429(5)	2.464(3)
Ln1-N1	2.485(8)	2.462(5)	2.484(3)
Ln1-S1	2.773(6)	2.760(5)	2.775(5)
N1-C1	1.229(10)	1.281(8)	1.297(5)
S1-C1	1.750(9)	1.761(6)	1.718(5)
P1-C1	1.878(10)	1.865(7)	1.877(5)
N1-Ln1-S1	59.5(5)	59.1(5)	58.7(5)
Ln1-N1-C1	102.0(6)	104.1(4)	102.1(3)
Ln1-S1-C1	80.8(4)	81.2(2)	81.3(2)
N1-C1-S1	117.7(8)	115.6(5)	117.9(4)
N1-C1-P1	124.0(7)	125.8(5)	122.7(3)
S1-C1-P1	118.3(6)	118.5(4)	119.3(2)

is considered.¹⁵ The P1–C1 (1.877(6) Å) distance is in agreement with that found in 2 (1.894(4) Å).

Reactions of Cp₂LnPPh₂(THF) with PhNCS. Examples of insertions into the Ln-P bond are rare.^{9a} To explore the effect of the ancillary ligands on the Ln-P bond insertion, we further investigated the reactions of Cp₂LnYPPh₂(THF)^{7c} with PhNCS and PhNCO. As shown in Scheme 3, reaction of PhNCS with a solution of Cp₂LnPPh₂(THF) in THF at room temperature gave the corresponding insertion products Cp₂Ln[SC(PPh₂)NPh]-(THF) (Ln = Y (6), Er (7), Dy (8)). Complexes 6–8 exhibit the

 ν (S \div C \doteq N) stretching band in the 1587–1589 cm⁻¹ region.^{5p} The ¹H NMR spectra of **6** contain resonances at δ 7.35–6.75 assignable to the phenyl ring, and at 6.36 assignable to the Cp ring. **6**–**8** are solvated monomers, different from that of **3**. It might be attributed to the more steric hindrance of the Tp^{Me2} ligand compared to that of the Cp group. Consistent with this observation, two characteristic multiplet peaks at 3.58 and 1.32 ppm assigned to a coordinated THF in the ¹H NMR spectra of **6** are present. It should be noted that the reaction of Cp₂YPPh₂(THF) with PhNCO under the same conditions gave a complicated mixture.

As shown in Figure 4, complexes 6-8 possess similar solvated mononuclear structures. Selected bond distances and angles are given in Table 1. The yttrium metal is coordinated to two η^{5} cyclopentadienyl rings, one chelating phosphathioureido ligand $[SC(PPh_2)NPh]$, and one THF molecule to form a distorted bipyramidal geometry. The coordination number of the central Ln^{3+} is 9. The Y1–N1 and Y1–S1 distances (2.485(8) and 2.773(5) Å) in 6 are slightly different from the corresponding values in 3 (2.410(4) and 2.823(2) Å) due to the steric effect of the coordinated THF unit. The N1–C1, S1–C1, and P1–C1 distances (1.30(1), 1.75(1), and 1.88(1) Å) of the $[SC(PPh_2)NPh]$ unit in 6 are comparable to the corresponding values found in 3 (1.31(1), 1.72(1), and 1.88(1) Å).

The structural parameters of 7 and 8 are very similar to those found in 6 (Figure 4, Table 1); they have no unusual distances and angles in the Cp₂Ln and [SC(PPh₂)NPh] units. The Ln–N and Ln–S distances (2.462(5) and 2.760(5) Å in 7, 2.484(3) Å and 2.775(5) Å in 8) are similar to the corresponding values found in 6 (2.485(8) and 2.773(5) Å), if the difference in ionic radii is considered.¹⁵

CONCLUSIONS

The first organoyttrium phosphide with the Tp^{Me2} ligand, $(Tp^{Me2})CpYPPh_2(THF)$ (1), has been synthesized by the protolysis reaction of the corresponding alkyl complex with HPPh₂. 1 can undergo controllable Y–P bond mono- or diinsertion with PhNCO, depending on the stoichiometric ratio, to form the corresponding phosphaureido or phosphadiureido complex, whereas reaction of 1 with PhNCS gives only the Ln–P bond monoinsertion product. Furthermore, 1 can catalyze the cyclotrimerization of PhNCO under mild conditions, through stepwise insertions of isocyanates into the Y–P or N bond. It is found that PhNCS can also insert into the Ln–P σ -bond of Cp₂LnPPh₂(THF). These insertions provide an efficient route to organolanthanide complexes incorporating phosphaureido or phosphathioureido ligands.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangjie@fudan.edu.cn (J.Z.), xgzhou@fudan.edu.cn (X.Z.).

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