

Supporting information

An unprecedented lanthanide phosphinidene halide: synthesis, structure and reactivity

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Experimental Section

General Procedures. All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a glovebox. THF was distilled from Na-benzophenone ketyl and degassed prior to use, toluene and hexane were dried over Na/K alloy. C₆D₆ and THF-d₈ were dried over Na-K alloy, distilled under vacuum and stored in the glovebox. NdI₃(THF)_{3.5} was prepared from metal Nd and iodine in THF according to the standard procedure.¹ K[(2,6-*i*Pr)-C₆H₃PSi(CH₃)₃] was prepared from (2,6-*i*Pr)-C₆H₃PHSi(CH₃)₃ and KH following the literature.² ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer at 300 MHz, 75 MHz and 120MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external H₃PO₄ (85%) for phosphorus chemical shifts. Elemental analysis was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Analysis of the mother liquor. The dark red mother liquor was transferred to a Schlenk tube, and the solvent was removed in vacuo. The dark red residue was dissolved in 1.5 mL of C₆D₆, and the solution was filtered through a short silica gel column. ¹H NMR and ³¹P NMR spectra of the solution were recorded, and (2,6-*i*Pr₂)-C₆H₃P(SiMe₃)₂ was detected. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 7.06-7.14 (m, 3H, Ph-*H*), 4.29 (m,

2H, $CHMe_2$), 1.26 (d, $^3J_{H-H} = 6.6$ Hz, 12H, $CHMe_2$) and 0.29 (d, $^3J_{P-H} = 6.2$ Hz, 18H, $SiMe_3$). ^{31}P NMR (120 MHz, C_6D_6 , 25 °C): δ -168 ppm. This product was further proved by compared to that prepared from the reaction of $K[(2,6-^iPr_2)-C_6H_3P(SiMe_3)]$ with Me_3SiI .

Reaction of (1) with benzophenone. Benzophenone (11.1 mg, 0.06 mmol) and **1** (41.5 mg, 0.03 mmol) were mixed in 6 mL of toluene, the reaction solution became pale yellow immediately. The reaction mixture was stirred for 2 h at room temperature, and some precipitates formed. The reaction mixture was filtered, and evaporation of the solution in vacuo afforded a solid residue. The solid residue was extracted with hexane. Evaporation of the hexane solution gave a pale yellow solid. NMR study showed it was $(Ph_2C=)P(C_6H_2-2,6-^iPr_2)$ in high purity (19.5 mg, 90% yield). 1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.73-7.71 (m, 2H, m- $Ar_{dip}-H$), 7.52-7.50 (m, 3H, o- $Ar-H$), 7.39 (t, $^3J_{HH} = 7.65$ Hz, 1H, p- $Ar_{dip}-H$), 7.23-7.15 (m, 4H, m- $Ar-H$; 1H, o- $Ar-H$), 7.06-7.03 (m, 2H, p- $Ar-H$), 3.61 (m, 2H, $CHMe_2$), 1.35 (d, $^5J_{PH} = 6.9$ Hz, 6H, $CHMe_2$), 1.17 (d, $^5J_{PH} = 6.6$ Hz, 6H, $CHMe_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 191.5 (d, $^1J_{PC} = 43.2$ Hz, $P=C$), 151.1 (d, $^2J_{PC} = 5.4$ Hz, o- Ar_{dip}), 144.6 (d, $^2J_{PC} = 25.5$ Hz, ipso- Ar), 142.6 (d, $^2J_{PC} = 14.6$ Hz, ipso- Ar), 137.4 (d, $^1J_{PC} = 44.3$ Hz, ipso- Ar_{dip}), 129.4 (s, Ar_{dip} or Ar), 129.0 (d, $^3J_{PC} = 6.9$ Hz, o- Ar), 128.7 (d, $^3J_{PC} = 4.2$ Hz, o- Ar), 128.2, 127.9, 127.6, 127.3 and 122.7 (s, Ar_{dip} or Ar), 33.1 (d, $^3J_{CP} = 8.6$ Hz, $CHMe_2$), 25.1 (s, $CHMe_2$),

22.5 (s, CHMe₂). ³¹P NMR (120 MHz, CDCl₃, 25 °C) δ 234.9.

X-ray Crystallography. Suitable single crystals of **1** were sealed in thin-walled glass capillaries, and data collection was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. The software used is listed in the references 3-7.

References:

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