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[(2,6-²Pr)-C₆H₃PSi(CH₃)₃] was prepared from (2,6-²Pr)-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 (2,6-²Pr₂)-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, CMe₂), 1.26 (d, \(^3J_{HH} = 6.6\) Hz, 12H, CHMe₂) and 0.29 (d, \(^3J_{PH} = 6.2\) Hz, 18H, SiMe₃). 

\(^{31}\)P NMR (120 MHz, C₆D₆, 25°C): \(\delta -168\) ppm. This product was further proved by compared to that prepared from the reaction of K[(2,6-\(\text{o-Pr}2\))-C₆H₃P(SiMe₃)] with Me₃SiI.

**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 (Ph₂C=)P(C₆H₂-2,6-\(\text{o-Pr}2\)) in high purity (19.5 mg, 90% yield). 

\(^1\)H NMR (300 MHz, CDCl₃, 25°C) \(\delta 7.73-7.71\) (m, 2H, m-Ardip-H), 7.52-7.50 (m, 3H, o-Ar-H), 7.39 (t, \(^3J_{HH} = 7.65\) Hz, 1H, p-Ardip-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, CMe₂), 1.35 (d, \(^5J_{PH} = 6.9\) Hz, 6H, CHMe₂), 1.17 (d, \(^5J_{PH} = 6.6\) Hz, 6H, CHMe₂). 

\(^{13}\)C NMR (75 MHz, CDCl₃, 25°C) \(\delta 191.5\) (d, \(^1J_{PC} = 43.2\) Hz, P=C), 151.1 (d, \(^2J_{PC} = 5.4\) Hz, o-Ardip), 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-Ardip), 129.4 (s, Ardip 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, Ardip or Ar), 33.1 (d, \(^3J_{CP} = 8.6\) Hz, CHMe₂), 25.1 (s, CHMe₂),
22.5 (s, CH\textsubscript{Me2}). \textsuperscript{31}P NMR (120 MHz, CDCl\textsubscript{3}, 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\textalpha\ radiation (\(\lambda = 0.71073 \text{ Å}\)). 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:**

5. *SMART* Version 5.628, Bruker Asx Inc.