An unprecedented lanthanide phosphinidene halide: synthesis, structure and reactivity†

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The synthesis and structural characterization of an unprecedented lanthanide phosphinidene species [(THF)$_3$(I)Nd(μ-PC$_6$H$_3$-2,6-^{i}Pr$_2$)]$_2$ are described; the phosphinidene moiety in this complex reacts as a carbene.

Lanthanide complexes have very rich and diversified coordinating properties and reactivities,[1–2] and have been widely used in organic[3] and polymer synthesis.[4] However, the chemistry of lanthanide alkylidene and phosphinidene complexes remains underdeveloped because of a scarcity of these complexes. This is not due to the lack of interest in preparing these complexes, but due to the relative mismatch between the acidic and hard Ln^{3+} (d^0) ions and the soft alkylidene (or phosphinidene) groups, and the shortage of synthetic strategies to access these complexes. To date, only very few examples of the lanthanide alkylidene complexes have been reported,[5–9] and the lanthanide phosphinidene complexes are even more sparse. This year, Kiplinger *et al.* reported the first lanthanide phosphinidene complex, a late-lanthanide Lu phosphinidene complex [{2-(R$_2$P)C$_6$H$_4$}$_2$NLu(μ-PMes)]$_2$ (R = ^{i}Pr), which was prepared by a α-hydrogen abstraction reaction of {2-(R$_2$P)C$_6$H$_4$}$_2$NLu(CH$_2$SiMe$_3$)$_2$ with MesPH$_2$ at 80 °C.[10] On the other hand, transition metal phosphinidene complexes have demonstrated rich structural features and reactivities,[11–15] including phosphinidene transfer reactions with ketones, imines, epoxides and halides,[13a,16] cycloaddition of alkynes,[17] catalytic hydrophosphination and carboamination of alkynes,[18] insertion reactions with nitriles and isonitriles,[16a,12e] and intramolecular C–H bond activation.[19] The trivalent lanthanide ions are highly oxo-, nitro- and halophilic, and usually of high coordination number, therefore, high reactivities of the lanthanide phosphinidene complexes are expected. Herein, we report an unprecedented lanthanide phosphinidene halide [(THF)$_3$(I)Nd(μ-PC$_6$H$_3$-2,6-^{i}Pr$_2$)]$_2$, which is formed *via* a silyl redistribution reaction. This complex can be an excellent candidate for the facile synthesis of other Nd phosphinidene complexes simply *via* a salt elimination.

The reaction of NdI$_3$(THF)$_{3.5}$ with 2 equivalents of K[(2,6-^{i}Pr$_2$)-C$_6$H$_3$PSiMe$_3$] in THF gave a dark red solution, from which we obtained dark red crystals of **1** by layering with hexane.‡ This product is readily soluble in THF, toluene and benzene, but insoluble in hexane. In agreement with Nd(III) complexes' paramagnetic properties, the solution NMR spectra of **1** showed very broad and featureless signals. The mother liquor was analyzed and a silyl redistribution product (2,6-^{i}Pr$_2$)-C$_6$H$_3$P(SiMe$_3$)$_2$[20] (^{1}H NMR (C$_6$D$_6$): δ = 0.29 (d, $^3J_{P–H}$ = 6.2 Hz, 18 H, SiMe$_3$), 1.26 (d, $^3J_{H–H}$ = 6.6 Hz, 12H, ^{i}Pr$_2$); ^{31}P NMR (C$_6$D$_6$): δ = −168 ppm) was detected.

Single crystals of **1** suitable for X-ray analysis were obtained by slow diffusion of hexane into the THF solution; the molecular structure is shown in Fig. 1. Complex **1** crystallizes in the orthorhombic space group *Pbca*. The structure reveals a lanthanide phosphinidene halide from a silyl redistribution reaction (Scheme 1). **1** represents the first example of an early lanthanide phosphinidene complex. The complex exists as a centrosymmetric dimer featuring bridging phosphinidene units; an iodide and three THF molecules complete the pseudo-octahedral coordination sphere of each Nd(III). The two Nd–P distances in **1** are unequal (2.73 *vs.* 2.78 Å), and atoms Nd, P1, NdA and P1A form a rhombus. The oxygen atoms of four THF molecules lie approximately in the plane defined by the Nd$_2$P$_2$ moiety, while two other THF molecules and the two iodides sit above and below this plane in an *anti* arrangement (Fig. 1b). The Nd–I distance of 3.1205(8) Å falls in the range of 3.06 to 3.17 Å observed for Nd–I bonds in other reported trivalent Nd complexes.[21] The Nd–Nd distance (4.0733(13) Å) indicates there is no bonding interaction between two metal centers. Similar to that observed in [{2-(R$_2$P)C$_6$H$_4$}$_2$NLu(μ-PMes)]$_2$,[10] the phosphorus atom in **1** adopts a trigonal planar structure (C(1)–P(1)–Nd = 136.45(17)°, Nd–P(1)–Nd = 95.37(5)°, C(1)–P(1)–NdA = 127.29(17)°, $\sum$ = 359°). On the other hand, the positions of the Ar substituents of the phophinidene moieties in these two complexes are opposite, the Ar substituents in **1** are nearly perpendicular to the Nd–P1–NdA–P1A plane with a dihedral angle of 81.29°, while those in [{2-(R$_2$P)C$_6$H$_4$}$_2$NLu(μ-PMes)]$_2$ are nearly planar with the Nd–P1–NdA–P1A plane.

A preliminary reactivity study established that the phosphinidene moiety in **1** can react as a carbene, similar to those in {(Me$_3$SiNCH$_2$CH$_2$)$_3$N}Ta=PR,[13a] Cp$_2$Zr(=PC$_6$H$_2$-2,4,6-^{t}Bu$_3$)-(PMe)$_3$[16a] and [{2-(R$_2$P)C$_6$H$_4$}$_2$NLu(μ-PMes)]$_2$.[10] The reaction of **1** with benzophenone gave Ph$_2$C=PC$_6$H$_3$-2,6-^{i}Pr$_2$ nearly quantitatively (90% yield, ^{13}C NMR (CDCl$_3$): δ = 191.5 ppm (d, $J_{C–P}$ = 43.2 Hz); ^{31}P NMR (CDCl$_3$): δ = 234.9 ppm) along with some toluene and THF-insoluble products, presumably the resulting Nd oxo complex (Scheme 2). In this case, **1** has the advantage of no waste of the ancillary ligands, such as [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$, Cp$^-$ and {2-(R$_2$P)C$_6$H$_4$}$_2$N$^-$.

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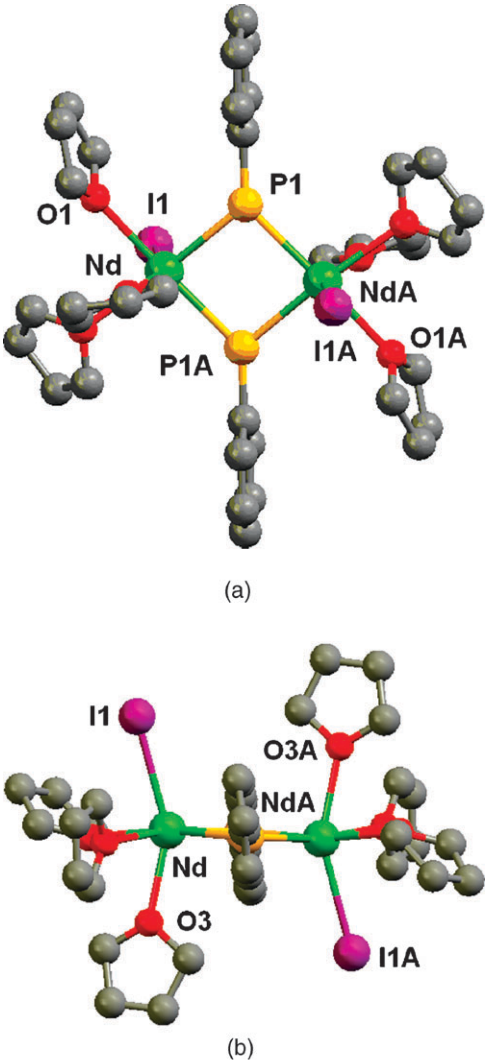
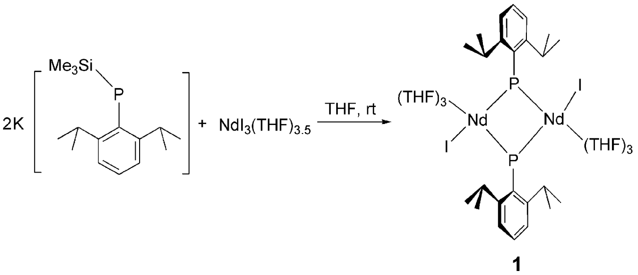
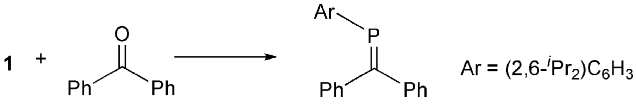


Fig. 1 Two views of the molecular structure of **1**. Isopropyl groups on the Ar substituents and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd–P1 = 2.7314(15), Nd–P1A = 2.7769(16), Nd···NdA = 4.0733(13), Nd–O1 = 2.536(4), Nd–O2 = 2.557(4), Nd–O3 = 2.499(4), Nd–I1 = 3.1205(8), ∠P1–Nd–P1A = 84.63(5), ∠Nd–P1–NdA = 95.37(5), ∠C1–P1–Nd = 136.45(17), ∠C1–P1–NdA = 127.29(17). The 'A' denoted atoms are at the symmetrically equivalent positions ($-x + 2$, $-y$, $-z + 1$).



Scheme 1 Synthesis of complex **1**.

In summary, a reaction of $NdI_3(THF)_{3.5}$ with K[(2,6-$^iPr_2$)-$C_6H_3PSiMe_3$] produced a dinuclear lanthanide phosphinidene halide [$(THF)_3(I)Nd(\mu\text{-}PC_6H_3\text{-}2,6\text{-}^iPr_2)]_2$ (**1**) *via* a silyl redistribution reaction. The isolation of the above complex is significant, because it demonstrates that neither sterically demanding nor strong π-electronic donating ancillary ligands are necessary for the stabilization of the lanthanide phosphinidene species, even those with early lanthanide ions. The new lanthanide phosphinidene exhibits properties similar to a carbene. It is noteworthy that **1** has the Nd–I bond, and therefore it is capable of acting as a precursor for the facile synthesis of other Nd phosphinidene complexes simply *via* a salt elimination. Further studies are planned to prepare new Nd phosphinidene complexes, especially the terminal ones, from **1**, and probe the reactivities of **1** with CO_x, NO_x, imines and other substrates.



Scheme 2 Reaction of **1** with benzophenone.

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Notes and references

‡ Synthesis of the complex **1**: A solution of K[(2,6-$^iPr_2$)-$C_6H_3P(SiMe_3)$] (158 mg, 0.52 mmol) in 3 mL of THF was added to a suspension of $NdI_3(THF)_{3.5}$ (200 mg, 0.26 mmol) in 5 mL of THF; the color of the reaction solution turned dark red in several minutes. The reaction mixture was stirred for 5 d at room temperature. The precipitate was removed by centrifugation, and the clear dark red solution was concentrated to about 2 mL under vacuum. 12 mL of hexane was layered to give dark red crystals (68 mg, 39% yield). Single crystals suitable for X-ray analysis were obtained by diffusion of hexane into a THF solution. The NMR signals are very broad and not informative as the trivalent Nd complex is paramagnetic. Anal. calcd for $C_{48}H_{82}I_2Nd_2O_6P_2$: C, 42.41; H, 6.08%. Found: C, 41.59; H, 5.80%.
Crystallographic data for **1**: $C_{48}H_{82}I_2Nd_2O_6P_2$, M = 1359.36, orthorhombic, a = 16.594(5) Å, b = 17.531(5) Å, c = 19.604(6) Å, U = 5703(3) Å^3, T = 293 K, space group *Pbca*, Z = 4, 31 839 reflections collected, 6224 unique (R_{int} = 0.0981). Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0473, wR_2 = 0.1096.

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