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Diamidophosphine as a Precursor of the Iminophosphonamidinate Ligand in the Yttrium Complex

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Abstract—Diamidophosphine ^{t}BuP(NHMes)$_2$(H_2L) is synthesized by the treatment of ^{t}BuPCl$_2$ with two equivalents of KNHMes (Mes is 2,4,6-$Me_3C_6H_2$). The reaction of H_2L with potassium hydride in THF (THF is tetrahydrofuran) affords the anionic form HL^- with the hydrogen atom migrating from nitrogen to phosphorus, which is confirmed by the ^{1}H and ^{31}P NMR data. The structure of the formed iminophosphonamidinate anion HL^- is determined by X-ray diffraction (XRD) in the crystalline phase of K[K(THF)$_2$](^{t}BuPH(NMes)$_2$)$_2$·C_7H_8 (KHL). The reaction of KHL with yttrium chloride gives complex [Y(^{t}BuPH(NMes)$_2$)$_2$Cl] ([Y(HL)$_2$Cl]) in which, according to the XRD data, ligands HL^- are in the iminophosphonamidinate PH form. The ^{1}H and ^{31}P NMR spectra confirm that this structure of the complex exists in the solution.

Keywords: rare-earth metals, yttrium, diamidophosphines, iminophosphonamidinates, crystal structure, coordination compounds

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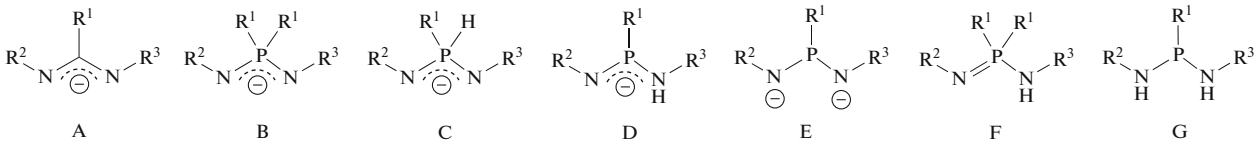
INTRODUCTION

In the coordination chemistry of rare-earth metals (Ln = Sc, Y, La, Ce...Lu), amidinates $[R^1C(NR^2)(NR^3)]^-$ (A, Scheme 1) are among the most popular *N*,*N*′-chelating anionic ligands considered as a successful alternative to cyclopentadienides that makes it possible to fulfill more completely the practical application potential of the Ln complexes [1–3].



Scheme 1. Anionic ligands and their protonated forms (proligands) considered in this work. In all cases, R^i are different or the same aliphatic, aromatic, or heterocyclic radicals.

Iminophosphonamidinates of two types, $[R^1_2P(NR^2)(NR^3)]^-$ (B) and $[R^1HP(NR^2)(NR^3)]^-$ (C), are similar to amidinates (A) and become more popular in the recent time as functional ligands. According to the Cambridge Crystallographic Data Centre (CCDC), about 200 structurally characterized metal complexes bearing ligands B and C are presently known [4]. These are mainly the complexes of metals of subgroups 1, 2, and 4–12. The fraction of coordination compounds of Ln is yet low: ~15%. The coordination compounds of Ln with ligands B have first been synthesized in the 1990s [5, 6], but their chemistry started to develop only 20 years after the discovery when the alkyl complexes [{$Ph_2P(NDipp)_2$}-Ln$(R)_2$(THF)] (Dipp = 2,6-^{i}Pr$_2C_6H_3$; Ln = La, Nd, Sc, Lu, Y, Er) were found to efficiently catalyze isoprene polymerization, and the microstructure of the polymers depends on the alkyl substituent R and Ln [7, 8]. Owing to these results, the problem of developing synthesis methods and extending the library of the known coordination compounds of Ln with ligands B and with their PH analogs (anions C) became topical.

The classical approach to the generation of anions B is the deprotonation of iminophosphonamides $[R^1R^2P(=NR^3)(NHR^4)]$ (F) by strong bases (tertiary amines, amides, or metal hydrides, butyllithium, etc.) [9–11]. However, the synthetic approach to PH anions $[R^1HP(NR^2)(NR^3)]^-$ (C) is

the single deprotonation of phosphinediamides [$R^1P(NHR^2)(NHR^3)$] (G) leading to the formation of an equilibrium mixture of tautomers C (PH form) and D (NH form) (Scheme 1) [12–15].

Depending on the solvent and electron-donor and steric parameters of organic substituents R^i, the equilibrium between the NH and PH forms in the solution can strongly be shifted to the direct or back side. However, the earlier obtained data on the structures of the magnesium and yttrium complexes [12, 15] and thermal transformation of the NH form of the magnesium complex into the PH form on heating in the solid phase [11] suggest that the complexes with the ligand in the form of tautomer C in the crystal are thermodynamically preferable.

The consecutive synthetic chain of new diamidophosphine ^{t}BuP(NHMes)$_2$ (H_2L), its potassium salt isolated as the solid phase K[K(THF)$_2$]-(^{t}BuPH(NMes)$_2$)$_2$·C_7H_8 (KHL), and yttrium complex [Y(^{t}BuPH(NMes)$_2$)$_2$Cl] ([Y(HL)$_2$Cl]) was accomplished in this work. The HL^- anion was found to exist as the PH form (C) in the crystalline phases of KHL and [Y(HL)$_2$Cl] and in the THF solution.

EXPERIMENTAL

The reactions were carried out in evacuated Schlenk flasks with J. Young Teflon valves or in two-section tubes. Substances were loaded for syntheses and samples were prepared for studies by physical methods in an argon glove box. Solvents were distilled over the K/Na alloy (in the case of THF, with benzophenone addition), degassed, and stored prior to use over a drying agent in evacuated vessels connected with a vacuum condensation apparatus. ^{1}H (500.13 MHz) and ^{31}P (202.45 MHz) NMR spectra were detected on a Bruker Avance III-500 spectrometer. Analyses to C, H, and N were conducted at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences) on a Euro EA 3000 instrument. IR spectra were recorded on a FT-801 spectrometer (Simex) in KBr pellets. The initial reagents were synthesized as follows: ^{t}BuPCl$_2$ was prepared using a known procedure [16], and KNHMes was synthesized by the deprotonation of NH_2Mes with an equivalent amount of KH in diethyl ether followed by the evaporation of the solvent. Compound YCl_3 was used in the commercially available form (DAlKHIM) without additional purification.

XRD of single crystals of compounds KHL and [Y(HL)$_2$Cl] was performed at the Center for Collective Use at the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences) by L.V. Zargarova and T.S. Sukhikh on a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector and an IμS 3.0 microfocus source (MoK_α radiation, λ = 0.71073 Å, Montel focusing mirrors). The crystal structures were solved using the SHELXT software [17] and refined using the SHELXL software [18] with the OLEX2 graphical interface [19]. The atomic shift parameters for non-hydrogen atoms were refined anisotropically. Hydrogen atoms are arranged geometrically, except those at the P atoms in the structure of ([Y(HL)$_2$Cl], which were localized by the residual electron density map. Restraints were imposed on the bond lengths (DFIX) and atomic displacement parameters (RIGU, ISOR) for the disordered THF molecules in the structure of KHL. The crystallographic characteristics of the compounds are given in Table 1.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2291231 (KHL) and 2291232 ([Y(HL)$_2$Cl]); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of H_2L. Two Schlenk flasks were loaded with KNHMes (0.605 g, 3.5 mmol) and ^{t}BuPCl$_2$ (0.277 g, 1.7 mmol). Toluene (~20 and 10 mL) were condensed into the flasks with KNHMes and ^{t}BuPCl$_2$, respectively, using a vacuum condensation apparatus. Then the Schlenk flasks were connected with an evacuated bent adapter through which a suspension of KNHMes was added by portions to a solution of ^{t}BuPCl$_2$ cooled to 0°C. The color of the mixture changed to crimson in a short time, and the mixture turned beige-colored in 30 min. The reaction mixture was heated to 110°C and stirred at this temperature for 12 h. After cooling to room temperature, the mixture was centrifuged. The solid precipitate was washed with toluene (10 mL) and again separated by centrifugation. The combined solution was transferred to a Schlenk vessel and evaporated to dryness in vacuo. The formed solid residue (H_2L) was washed with hexane (~5 mL) and dried in vacuo. The yield was 0.337 g (54%).

For $C_{22}H_{33}N_2P$			
Anal. calcd., %	C, 74.1	H, 9.3	N, 7.8
Found, %	C, 73.6	H, 9.5	N, 7.4

^{1}H NMR (THF-d_8; δ, ppm): 1.27 d (9H, CH_3, $^3J_{P^tBu}$ = 12.3 Hz), 2.16 s (6H, CH_3), 2.22 s (12H, CH_3), 4.26 d (2H, NH), 6.70 d (4H, CH). ^{31}P NMR (THF-d_8): δ_p 69.01 ppm.

IR (ν, cm^{-1}): 3372 m, 3351 m, 2930 s, 2727 m, 1772 w, 1741 m, 1724 m, 1608 m, 1481 vs, 1369 s, 1342 s, 1299 s, 1268 s, 1243 vs, 1221 vs, 1154 s, 1030 s, 1011 s, 958 m, 935 m, 855 vs, 750 s, 703 s, 605 s, 566 s.

Synthesis of KHL. Solid H_2L (800 mg, 2.2 mmol) and KH (90 mg, 2.2 mmol) were loaded in a Schlenk flask. THF (~20 mL) was condensed on a mixture of

Table 1. Crystallographic characteristics and structure refinement details for compounds KHL and $[Y(HL)_2Cl]$

Parameter	Value	
	KHL	$[Y(HL)_2Cl]$
Empirical formula	$C_{29.5}H_{44}N_2OPK$	$C_{44}H_{64}N_4P_2ClY$
FW	512.73	835.29
Temperature, K	150(2)	150(2)
Space group	$P\bar{1}$	$P2_1/n$
a, Å	12.6376(5)	12.4063(3)
b, Å	12.6479(5)	26.1922(7)
c, Å	19.0132(7)	14.1352(3)
α, deg	84.9310(10)	90
β, deg	85.1650(10)	99.8370(10)
γ, deg	75.9020(10)	90
V, Å^3	2929.8(2)	4525.68(19)
Z	4	4
ρ_{calc}, g/cm^3	1.162	1.226
μ, mm^{-1}	0.259	1.451
F(000)	1108.0	1768.0
Crystal size	0.2 × 0.17 × 0.15	0.39 × 0.15 × 0.11
Range of data collection over 2θ, deg	3.33–48.81	3.11–58.256
Ranges of *h, k, l*	$-14 \le h \le 14$, $-14 \le k \le 14$, $-22 \le l \le 21$	$-14 \le h \le 16$, $-35 \le k \le 35$, $-19 \le l \le 19$
Number of measured reflections	28465	63184
Number of independent reflections (R_{int}, R_σ)	9600 (0.0412, 0.0467)	12046 (0.0530, 0.0410)
Number of data/restraints/refined parameters	9600/151/663	12046/0/493
GOOF for F^2	1.047	1.036
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0738$, $wR_2 = 0.1894$	$R_1 = 0.0336$, $wR_2 = 0.0828$
R factor (all data)	$R_1 = 0.1026$, $wR_2 = 0.2109$	$R_1 = 0.0495$, $wR_2 = 0.0883$
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.94/–0.54	0.73/–0.32

the solid reagents. The reaction mixture was stirred at room temperature for 1 h, and then the gas phase was removed by short-term opening of the flask valve to the vacuum line. After this, the mixture was stirred for 12 h and evaporated in vacuo. Toluene (~10 mL) was condensed on the formed solid residue, and the resulting suspension was stirred at room temperature for 1 h. The white powdered precipitate corresponding to the formula of KHL was separated by centrifugation and dried in vacuo. The yield was 0.536 g (62%).

For $C_{29.5}H_{44}N_2OPK$

Anal. calcd., %	C, 69.1	H, 8.6	N, 5.5
Found, %	C, 68.7	H, 8.2	N, 5.1

^{1}H NMR (THF-d_8; δ, ppm): 0.82 d (9H, CH_3, $^3J_{P^tBu}$ = 15.7 Hz), 2.13 s (6H, CH_3), 2.35 s (12H, CH_3), 6.62 s (4H, CH), 7.66 d (1H, PH, $^1J_{PH}$ = 383 Hz). ^{31}P NMR (THF-d_8), δ, ppm: 0.73 d ($^1J_{PH}$ = 383 Hz).

IR (ν, cm^{-1}): 2933 s, 2727 m, 2172 s, 2027 m, 1726 m, 1608 m, 1471 vs, 1424 s, 1307 vs, 1268 s, 1213 m, 1165 s, 1048 s, 993 s, 920 s, 891 m, 863 s, 853 s, 815 s, 769 s, 748 m, 715 m, 685 m, 614 m.

A two-section tube with sections (a) and (b) arranged at an angle of 90° was used to prepare single crystals [20]. The powder was loaded in section (a), and THF (5 mL) was condensed on the powder result-

ing in the formation of a transparent solution. Then the tube was sealed, and empty section (b) was placed in a vessel with cold water, whereas the solution in section (a) was at room temperature. In ~3 days, a slow decrease in the solution volume in section (a) resulted in the formation of colorless crystals due to the condensation of the solvent into section (b). Residues of the mother liquor were decanted to section (a), and the crystals were washed with a minor amount of THF by the back condensation of a portion of the solvent into section (a) and repeated decantation. Finally, section (a) was sealed off and placed in an argon box, where section (a) was opened and crystals of KHL suitable for XRD were taken.

Synthesis of $[Y(HL)_2Cl]$. Solid YCl_3 (0.078 g, 0.4 mmol) and KHL (0.410 g, 0.8 mmol) were loaded into a Schlenk flask. THF (~10 mL) was condensed on a mixture of the solid reagents. The reaction mixture was stirred at room temperature for 24 h. The resulting solution was evaporated in vacuo, and toluene (~10 mL) was condensed on the formed solid residue. The resulting mixture was filtered directly into a two-section tube, which was then sealed. The crystallization of $[Y(HL)_2Cl]$ was carried out by the method similar to that used in the case of KHL. The yield of crystalline $[Y(HL)_2Cl]$ was 0.214 g (64%).

For $C_{44}H_{64}N_4P_2ClY$

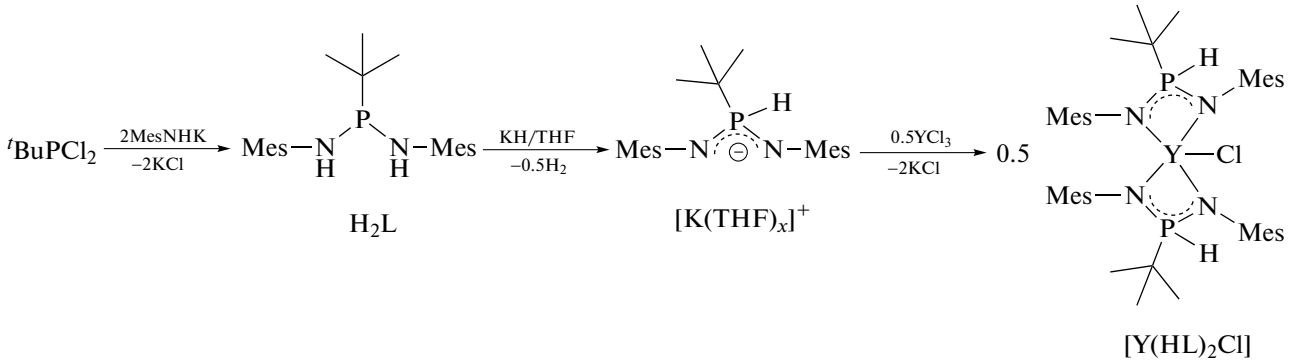
Anal. calcd., %	C, 63.3	H, 7.7	N, 6.7
Found, %	C, 62.9	H, 7.5	N, 6.3

^{1}H NMR (THF-d_8; δ, ppm): 0.74 d (9H, CH_3, $^3J_{P^tBu}$ = 15.7 Hz), 2.18 s (6H, CH_3), 2.45 br.s (12H, CH_3), 6.71 s (4H, CH), 7.67 d (1H, PH, $^1J_{PH}$ = 432 Hz). ^{31}P NMR (THF-d_8; δ, ppm): 27.75 d ($^1J_{PH}$ = 432 Hz).

IR (ν, cm^{-1}): 2941 s, 2859 s, 2728 w, 2306 m, 1956 w, 1726 w, 1609 w, 1476 vs, 1371 m, 1303 s, 1230 vs, 1159 s, 1061 m, 1023 s, 996 s, 944 m, 853 m, 810 m, 786 m, 723 m, 613 m, 564 w.

RESULTS AND DISCUSSION

New diamidophosphine ^{t}BuP(NHMes)$_2$ (H_2L) was synthesized by the reaction of ^{t}BuPCl$_2$ with KNHMes (2 equiv) in THF (Scheme 2).



Scheme 2. Synthesis of diamidophosphine H_2L, its deprotonation with potassium hydride, and the synthesis of complex $[Y(HL)_2Cl]$.

The structure of the isolated compound was confirmed by the ^{1}H and ^{31}P NMR and IR spectral and elemental analysis (C, H, N) data. The ^{1}H NMR spectrum exhibits a doublet with a chemical shift of 1.27 ppm and the splitting constant on the phosphorus atom $^3J_{PH}$ = 12.3 Hz, a group of singlet signals characteristic of mesityl groups (2.16, 2.22, 6.70 ppm), and a doublet with a chemical shift of 4.26 ppm ($^2J_{PNH}$ = 7.1 Hz) corresponding to the protons of the amino groups. The ^{31}P NMR spectrum contains one broadened signal δ_p = 69.01 ppm, whose position is characteristic of diamidophosphines [21, 22]. The IR spectrum contains no absorption bands in a range of 2400–2100 cm^{-1} characteristic of stretching vibrations of the P–H bond. All these data along with a satisfactory coincidence of the elemental analysis results assert that the composition and structure of the synthesized compound correspond to the diamide form of H_2L.

The treatment of H_2L with potassium hydride in THF results in the formation of potassium salt $[K(THF)_x][HL]$ in the solution and hydrogen evolution (Scheme 2). The use of even two equivalents of KH did not result in the elimination of the second proton, which indirectly indicates the migration of the remained proton to the phosphorus atom, since a lower acidity of the PH form (C) seems reasonable to be expected. The migration of the proton to phosphorus is indicated by the fact that the ^{31}P NMR spectrum contains the doublet with a chemical shift of 0.73 ppm and the splitting constant $^1J_{PH}$ = 383 Hz, and the ^{1}H NMR spectrum exhibits the doublet with the same splitting constant at 7.66 ppm. No signal correspond-

ing to the NH form (D) was observed. In addition, the ^{1}H NMR spectrum contains a set of signals corresponding to two equivalent mesityl fragments. Thus, the equilibrium C ↔ D in the solution is shifted to the left almost completely.

The salt of anion HL^- was isolated as a finely crystalline solid phase of KHL containing solvate toluene by the evaporation of the reaction solution in THF followed by the treatment with toluene. Like in the solution, the HL^- anion in the KHL phase also exists in form C, which is indicated by the presence in the IR spectrum of the band at 2172 cm^{-1} corresponding to stretching vibrations of the P–H bond and the absence of bands in a range of 3600–3000 cm^{-1} characteristic of N–H stretching vibrations.

The recrystallization of KHL from THF gave the crystals suitable for XRD. A single crystal chosen randomly from the overall crystalline mass was used for the XRD experiment, which showed the chain structure of potassium iminophosphonamidinate KHL (Fig. 1a). The infinite chains arranged along the *b* axis are formed by the $(^t$BuPH(NMes)$_2)^-$ anions (HL^-) and potassium cations. The crystal contains two structurally independent HL^- anions in each of which the phosphorus atoms are disordered over two positions: at different sides from the K(2)N(1)N(2) and K(2)N(3)N(4) planes. The positions of the phosphorus atoms are populated in a ratio of ~80 : 20. The positions with a higher population are shown in Fig. 1 (they will be discussed further). The geometry of both HL^- anions corresponds to the *E*,*Z* configuration, which provides a possibility of the *ansa* coordination of HL^- to the K(2) ion by the N(2) and N(4) nitrogen atoms and π systems of two mesityl substituents (Fig. 1b). In each case, two sets of distances from K(2) to the carbon atoms of the aromatic ring are observed: three distances within 3.07–3.26 Å and three distances in a range of 3.43–3.60 Å, which allows the π-coordination mode to be interpreted as η^3. The P–N bonds are of different lengths: the P(1A)–N(1) (1.618(4) Å) and P(2A)–N(3) (1.629(4) Å) distances are slightly longer than P(1A)–N(2) (1.569(3) Å) and P(2A)–N(4) (1.581(3) Å), which can be due to different directions of the mesityl groups and a slightly different multiplicity of the P–N bond. The NPN angles are close to tetrahedral angles (N(2)P(1A)N(1) 111.7(2)° and N(4)P(2A)N(3) 110.33(19)°). The coordination ensembles of two HL^- anions and K(2) are linked to each other into chains through the K(1) cations, whose coordination sphere additionally contains two THF molecules. The N(1) and N(3) nitrogen atoms are closest to the K(1) ions. The K(1)–N(1) and K(1)–N(3) bond lengths are 2.755(3) and 2.758(3) Å, which are slightly shorter than K(2)–N(2) and K(2)–N(4): 2.893(3) and 2.825(3) Å, respectively. In addition, the distances from K(1) to the *ipso*-carbon atoms C(6) and C(7) are short (3.289(4) and 3.219(4) Å), which are close to the distance from K(2) to the nearest carbon atoms of the aromatic rings.

Solvate toluene molecules are located in cavities between the zigzag chains of the HL^- anions and potassium cations, which is surprising because the substance was recrystallized from THF. This selectivity of toluene inclusion attracts attention, but we cannot assert that the solvate composition of the whole crystalline mass corresponds to the composition of this crystal. That is why, the non-recrystallized finely crystalline phase of KHL was introduced into the reaction with YCl_3. This phase was characterized by elemental analysis, the knowledge of which makes it possible to specify the metal/ligand ratio more precisely.

To evaluate what complexes can be formed in the reaction of YCl_3 with KHL, we considered the data on the known Ln compounds with the iminophosphonamidinate ligands (Scheme 1). The family of these complexes is scanty, and the first examples of the compounds containing ligands C have been synthesized recently: [Y(PhHP(NBtd)$_2$)(PhP(NBtd)$_2$)] and [{Y(PhHP(NBtd)$_2$)(PhP(NBtd)$_2$)}$_2$(μ-$C_4H_8O_2$}] (Btd is 2,1,3-benzodithiazol-4-yl, $C_4H_8O_2$ is 1,4-dioxane) [15]. These complexes simultaneously contain monoanion C and doubly deprotonated form of diamidophosphine: dianion E (Scheme 1, R^1 = Ph, $R^2 = R^3$ = Btd), and both anionic ligands are coordinated to yttrium by both nitrogen atoms of the NPN fragment and also by the nitrogen atoms of the Btd heterocycles.

All other known examples of the iminophosphonamidinate complexes of rare-earth metals contain ligands of the type B in which $R^1 = R^2$ = Ph. The majority of them represents compounds of small Ln(III) ions [Ln{R^1R^2P(NR^3)(NR^4)}(CH_2SiMe_3)$_2$(THF)] (Ln = Sc, Y, Lu, Er) bearing only one ligand of the type B in which R^3 and R^4 are the same or different substituted aryls (*o*-tolyl, Mes, Dipp, etc.) [7, 8, 23, 24]. Complexes of larger Ln(III) ions with one ligand of the type B are presented by only three examples: [Nd{Ph_2P($NSiMe_3$)$_2$}(η^8-COT)(THF)] (COT is cyclooctatetraenide) [25], [Nd{Ph_2P(NAr)(NPy)}-(BH_4)$_2$(BH_3)(THF)$_2$] (Ar is 2,6-di(ethyl)phenyl, Py is 2-pyridyl) [26], and [La{Ph_2P(NDipp)}(*p*-Tol)$_2$(THF)] (*p*-Tol is *p*-tolyl) [8]. Only seven structurally characterized complexes containing two iminophosphonamidinate ligands are known: "ate" heterometallic complexes [{Ph_2P($NSiMe_3$)$_2$}$_2$Ce(μ-Cl)$_2$Li(THF)$_2$] [27] and [{Ph_2P($NSiMe_3$)$_2$}$_2$Sm(μ-I)$_2$Li(THF)$_2$] [6], neutral halide complexes [M(Ph_2P-(N^tBu)$_2$)$_2$Cl] (M = Y, Lu), and alkyl complexes [M(Ph_2P(N^tBu)$_2$)$_2$(CH_2SiMe_3)] (M = Y, Sm, Nd) [28].

Of course, the available sampling of the iminophosphonamidinate complexes is not representative

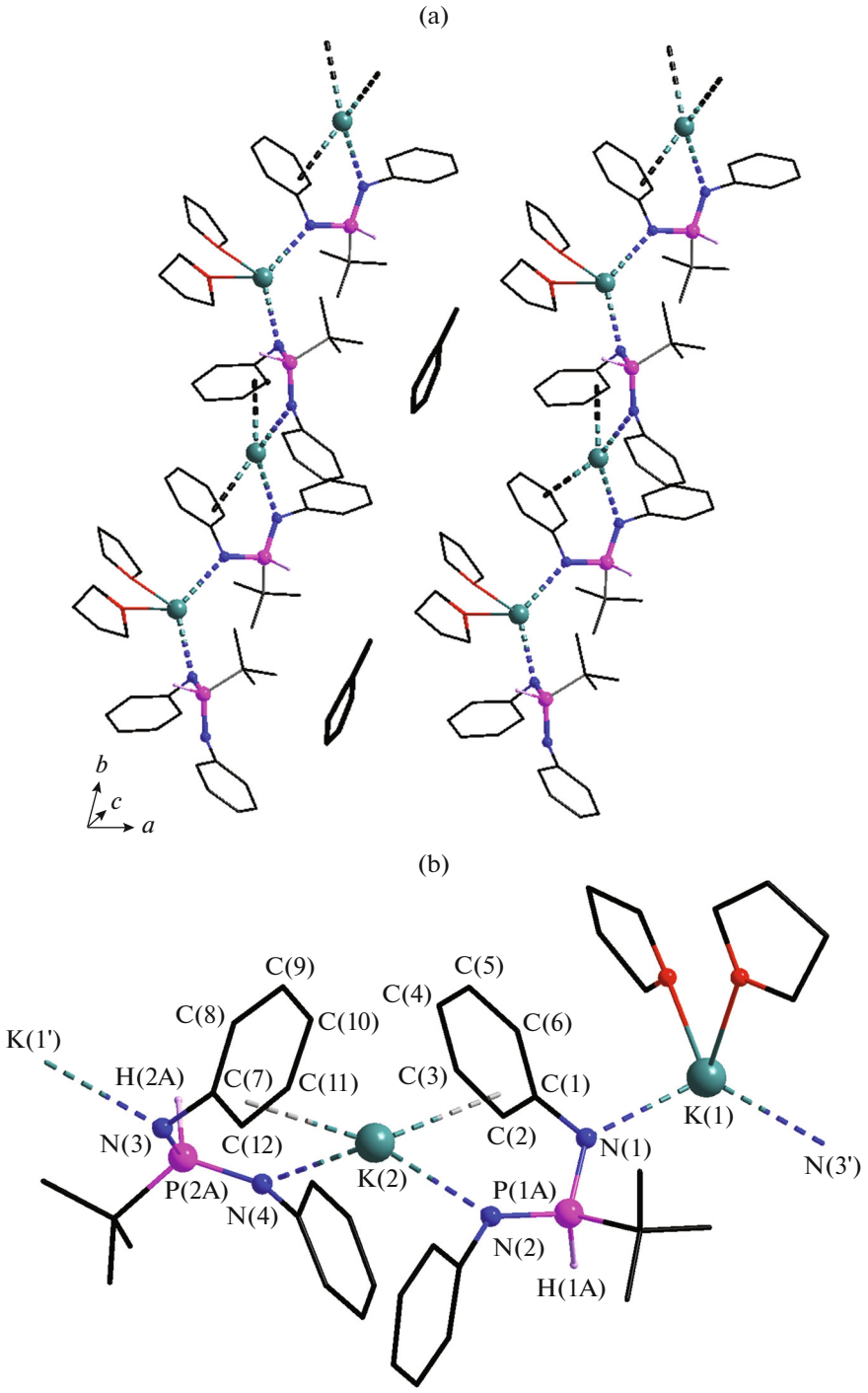


Fig. 1. Structure of $K[K(THF)_2]({}^tBuPH(NMes)_2)_2 \cdot C_7H_8$ (KHL): (a) the packing of chains of alternating HL^- anions and potassium cations and (b) the structure of the building block $K[K(THF)_2]({}^tBuPH(NMes)_2)_2$. The CH_3 groups of the mesityl fragments and hydrogen atoms at the carbon atoms are omitted. Contacts of the potassium ions with the nitrogen atoms and the π system of the aromatic cycles are shown by dash.

and rather dissimilar to make generalizing conclusions. However, when evaluating the volume of the $(Ph_2P(N^tBu)_2)^-$ ligands as the closest to that of HL^-, we can expect the substitution of only two chloride ions in the coordination sphere of yttrium as well.

Indeed, the reaction of YCl_3 with KHL (2 equiv) gave complex $[Y(HL)_2Cl]$. Moreover, the same compound was found to be formed when the $YCl_3 : HL^-$ ratio changes to 1 : 3; i.e., the third chloride ion is not substituted under the same synthesis conditions.

The structure of $[Y(HL)_2Cl]$ was determined by single crystal XRD (Fig. 2). In this compound, two anions of the type C are coordinated to yttrium by the nitrogen atoms. Unlike KHL, the ligands adopt a more symmetric *Z*,*Z* configuration close to C_s. In both cases, yttrium, phosphorus, hydrogen (PH), and central carbon atom of the *tert*-butyl group lie in the same plane, and the nitrogen and *ipso*-carbon atoms of the mesityl substituents are equally remote from this plane. The deviation from the C_s symmetry appears due to the asymmetric arrangement of the peripheral organic groups: the mesityl substituents and methyl groups of the *tert*-butyl radicals.

The NPN angles in $[Y(HL)_2Cl]$ (100.26(7)° N(1)P(1)N(2) and 100.42(7)° N(3)P(2)N(4)) are smaller than the corresponding values for KHL. The Y–N bond lengths are nearly the same and fall onto a range of 2.33–2.34 Å, which is typical of the yttrium complexes with other ligands B and C, whose Y–N bond lengths lie in a range of 2.29–2.38 Å [15, 28, 29]. The P–N bond lengths in $[Y(HL)_2Cl]$ are also almost equivalent: 1.61–1.62 Å, and their lengths are characteristic of other ligands of this type in the coordination sphere of Ln(III) (1.59–1.62 Å). The aromatic rings of two ligands are brought together in pairs, and the distance between the planes is 3.6–3.9 Å, which can be interpreted as the π-stacking interaction.

As in the case of KHL, the IR spectrum of $[Y(HL)_2Cl]$ exhibits the characteristic band with a maximum at 2306 cm^{-1} corresponding to the P–H stretching vibrations. No bands characteristic of N–H stretching vibrations are observed. The ^1H NMR spectrum indicates that the mesityl substituents, *tert*-butyl groups, and protons bound to phosphorus are equivalent. The doublet with the splitting constant $^1J_{PH}$ = 432 Hz corresponds to the latter. The ^{31}P NMR spectrum also contains one doublet with the same splitting constant. No signals corresponding to the protons of the NH groups were observed.

Thus, new diamidophosphine ^{t}BuP(NHMes)$_2$ (H_2L) was synthesized and characterized. Its deprotonation with potassium hydride was found to give the HL^- anion that exists in the form of the PH tautomer. The structure of HL^- in the $K[K(THF)_2]$-(^{t}BuPH(NMes)$_2$)$_2$·C_7H_8 (KHL) salt in the solid phase was determined by XRD. The reaction of KHL with yttrium chloride afforded complex $[Y(^t$BuPH(NMes)$_2)_2Cl][Y(HL)_2Cl]$ in which ligand HL^- also exists in the iminophosphonamidinate PH form, which was determined for the crystalline phase and solution by XRD and ^1H and ^{31}P NMR spectra, respectively.

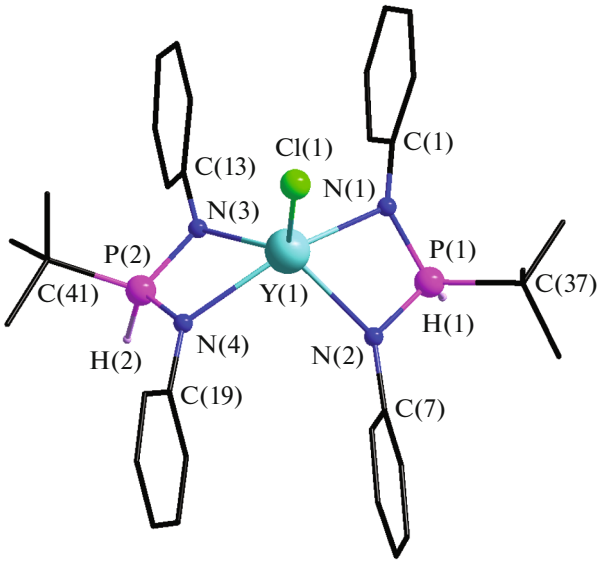


Fig. 2. Structure of the molecule $[Y(^t$BuPH-(NMes)$_2)_2Cl][Y(HL)_2Cl]$. The CH_3 groups of the mesityl fragments and hydrogen atoms at the carbon atoms are omitted.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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