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Graphical Abstract



Four kinds of heterobimetallic organo rare earth complexes bearing aryloxide-NHC ligands were prepared, and their structures were fully analyzed by single-crystal X-ray diffraction and DFT calculations.

Synthesis and Characterization of Heterobimetallic Organo Rare Earth Complexes Bearing Aryloxide-N-Heterocyclic Carbene Ligands

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MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, PR China. **Abstract:** Two aryloxide-substituted N-heterocyclic carbene (NHC) proligands 3-[(2-hydroxynaphthalenyl) methyl]-1-mesityl-3,4,5,6tetrahydropyrimidinium chloride (H₂L1) and 3-(2-hydroxybenzyl)-1-mesityl-3,4,5,6-tetrahydropyrimidinium chloride (H₂L2) were designed and easily synthesized via three step-synthetic processes in high yield. Four heterobimetallic potassium-NHC rare earth complexes L1KLnN"₃ and L2KLnN"₃ (L1, Ln=Y (1a), Nd (1b); L2, Ln=Y (2a), Nd (2b), N"=N(SiMe₃)₂) were obtained by *in-situ* reaction of N-heterocyclic carbene proligands H₂L1 and H₂L2 with Ln[N(SiMe₃)₂]₃ and KN(SiMe₃)₂ in toluene. The K-NHC rare earth complexes were characterized by single-crystal X-ray crystallography and Y complexes were characterized by ¹H and ¹³C NMR spectroscopy. DFT calculations were employed to further investigate charge distributions and interactions within these compounds.

Keywords: N-heterocyclic carbene, rare earth complexes, potassium-NHC, DFT calculation, X-ray diffraction

1. Introduction

N-heterocyclic carbene ligands (NHCs) have been highly valued in organometallic chemistry [1-7] since the first thermally stable NHC generated by Arduengo in 1991 [8]. In coordination compounds, the NHCs mainly play a role as versatile ligands to stabilize the metal center, modifying the steric and electronic properties around the metal by combining with neutral or anionic donors [9-10]. The pendent groups of NHCs have contributed great importance to regulating the steric and electronic properties. For instance, the pincer systems of amido-fuctionalized NHCs were used to stabilize the complexes of Ti, Zr and Hf [11]; phenoxy-modified NHC ligand allowed the preparation of Ni bromide compound [12]. Rare earth metal complexes bearing indenyl- and fluorenyl- functionalized NHC ligands were synthesized successfully [13-14] and exhibited high catalytic activities toward polymerization and copolymerization reactions [15-17]. Organo lanthanide complexes containing bis(phenolate) NHCs with saturated or unsaturated backbone had given rise to controlled polymerization of cyclic or vinyl monomers [18-20].

NHCs with saturated backbone have effect of increasing donor ability, and their transition metal complexes with 6-membered expanded ring have been prepared [21-23], and these ligands were barely applied in rare earth metal chemistry. The strongly basic properties of NHCs also allow their use as ligands for the synthesis of alkali-metal complexes. The first diamino carbene-type alkali-metal complex was reported by Alder [24], and then Arnold et al. presented the first crystal structure of a potassium NHC complex [25]. Li, Na complexes with NHC ligands [26-27] were synthesized and characterized in the meantime. The resulting NHCs were anticipated to stabilize the alkali metal ions in tuning the coordination sphere or rigidity of the complexes. Density functional theory calculations were utilized to design Li complexes [28] as well. Comparatively, rare earth metal complexes containing functionalized alkali-NHC structures have been less explored. Breakthroughs were achieved by Arnold group, they discovered the lithium carbene

'ate' complex containing rare earth tri(alkyl), and these abnormal complexes allowed a new way in the formation of carbon-carbon bonds [29]. Herein, we designed and synthesized backbone saturated aryloxide-N-heterocyclic carbene proligands in an easy and effective method and prepared the corresponding heterobimetallic organo rare earth complexes were prepared and characterized. The structures of the complexes were further studied by DFT calculations.

2. Results and discussion

2.1 Synthesis of aryloxide-N-heterocyclic carbene proligands

Roche et al. presented a valuable access to prepare unsymmetrical and symmetrical 1,2-diamide and they expanded their application to obtain the unsymmetrical imidazolidinium proligand by reaction N-monoarylate of 1.2-diamine dihydrobromide salt and 1-pyrenecarboxaldehyde [30]. Herein we synthesized aryloxide-substituted NHC salts using similar strategy. The reactions were carried out in three steps depicted in scheme 1. The N-monoarylate diamine dihydrobromide salts (A-2HBr) were prepared according to the literature [30]. Simple neutralization reaction was processed, using N-monoarylate diamine dihydrobromide salts (A-2HBr) and KOH to generate the N-monoarylate diamine (A), which was condensed with aldehyde Ar-CHO in the first step. NaBH₄ was added to the mixture to yield the unsymmetrical disubstituted diamine (M), and further cyclization used underwent a classic procedure with HCI and CH(OEt)₃ [31], providing the desired unsymmetrical substituted NHC proligands H₂L1-H₂L2. Finally, phenyl and naphthyl functional groups were incorporated into the NHC proligands. Synthetic routes were shown in scheme 1. Proligands H₂L1-H₂L2 were characterized by ¹H, ¹³C NMR spectroscopy and elemental analysis. The ¹H NMR spectra showed typical singlet resonances at δ 8.87 (H₂L1), 8.68 (H₂L2) ppm for the pyrimidinium proton (NCHN), and carbon signals (NCHN) at δ 165.69 (H₂L1), 156.73 (H₂L2) ppm showed up in ¹³C NMR spectra, commensurating with that reported for similar NHC structures [19, 21-22].

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Scheme 1. Syntheses of aryloxide-N-heterocyclic carbene proligands H₂L1-H₂L2.

2.2 Synthesis and characterization of heterobimetallic organo rare earth complexes

The aryloxide N-heterocyclic carbene proligand H₂L1 could be applied to synthesize the rare earth metal complexes in two pathways. H₂L1 and equivalent Ln[N(SiMe₃)₂]₃ were firstly reacted to form phenolate rare earth complex, then 2 equiv. of KN(SiMe₃)₂ were added to deprotonate the proton on the C₂-H on the ring the pyrimidinium proton (NCHN) to form carbene-K structure. In the other approach, proligand H₂L1 was first treated with 2 equiv. of KN(SiMe₃)₂ at -20°C for deprotonation to obtain anionic functionalized NHC and sequently adding Ln[N(SiMe₃)₂]₃ to obtain rare earth complex. These procedures were speculated through in-situ NMR analysis, and the proposed reaction mechanism was depicted in scheme S1 (supporting information, page 2). The complexes 1a and 1b were stable in dry nitrogen atmosphere, but they were very sensitive to moisture. The complexes were soluble in benzene, toluene and THF, and partially soluble in n-hexane.





Sterically less bulky proligand H_2L2 was also studied as a reactant. The proligand H_2L2 was reacted with $Ln[N(SiMe_3)_2]_3$ (Ln=Y, Nd) and 2 equiv. of KN(SiMe_3)_2 in the same method as to complex 1a, obtaining similar potassium-NHC rare earth metal complexes 2a and 2b.



Scheme 3. Syntheses of heterobimetallic organo rare earth complexes 2a and 2b.

Complexes **1a** and **2a** were characterized by ¹H and ¹³C NMR, and the structures of four complexes were fully confirmed by the single-crystal X-ray diffraction analysis. In the ¹H NMR spectra, the characteristic resonance of ylidene proton was disappeared completely and signals of methyl protons in the bis(trimethylsilyl) amido groups showed at δ 0.64/0.10 ppm for **1a**, 0.58/0.10 ppm for **2a** respectively. The carbene carbon signal of complex **1a** appeared at δ 231.7 ppm, **2a** at δ 227.2 ppm in ¹³C NMR spectra, comparable to δ 226.7 ppm found in complex 1,3-diisopropyl-3,4,5,6-tetrahydropyrimid-2-ylidene-K [32], indicating the coordination interaction of carbene carbon to potassium in solution.

The single-crystal X-ray diffraction analyses revealed monomeric structures with the Ln[N(SiMe₃)₂]₃ bonding to the aryloxide oxygen, generating a K-NHC structure with a toluene molecule coordinated to K (figure 1-2). The selected bond lengths and angles were shown in table 1. The coordination sphere of rare earth metal center adapted a distorted tetrahedral geometry, with the Ln-Namino average bond length being 2.279 Å for 1a, 2.369 Å for 1b, 2.279 Å for 2a, 2.375 Å for 2b. These structure data are longer than the corresponding distances of 2.223 Å for Y-Namino and 2.29 Å for Nd-Namino found in the starting materials Y[N(SiMe₃)₂]₃ [33] and Nd[N(SiMe₃)₂]₃ [34] . The Y-O1 bond length in complex 1a (2.115(2) Å) is marginally elongated in comparison with the Y-O1 linkage observed in 2a (2.107(2) Å), and the Nd-O1 bond length in complex 1b is longer than 2b as well. The Ln-O (Ln=Y, Nd) bond lengths in organometallic complexes previously reported are in wide range, for Y-O bond lengths (2.031-2.147 Å) [35-36] and Nd-O distances (2.206-2.280 Å) [37-39]. We believe that it is the steric effect of ligand to be the most important factor to influence the bond distance. So the bond length will be elongated by addition of ligands with more bulkier pendants.

The potassium cation, however, features potassium-NHC structure in which it connected to the carbene center. The $K-C_{carbene}$ -centroid_{NHC} angles are approaching linearity (range 178.3-179.9°), so there is no severe distortion. The bond length of potassium-C_(carbene), K1-C2 = 2.863(7) Å for 1a, 2.832(5) Å for 1b, 2.853(3) Å for 2a and 2.852(3) Å for 2b, which are shorter than the reported potassium NHC complex (K-C_{carbene}=3.048) [40] the Ln(III)-K(I) heterobimetallic and complexes [N"2Ln(L-)K(DME)]2 (K-Ccarbene=2.954) [41], but much longer than the average bond length of normal Ln-C_{carbene} [18-19, 42-43]. It is worth noting that the potassium cation is coordinated augmented by significant n-interaction with the π -system provided by the N-substituent groups in NHC ligand and the toluene molecule, which can be easily understood by the small shorter distance of



Figure 1. X-ray structure of complex 1a, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Complex 1b is isomorphous with 1a.



Figure 2. X-ray structure of complex 2a, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Complex 2b is isomorphous with 2a.

potassium to the aromatic groups, for K-Plane_{Mes} distances range from 3.259 to 3.319 Å, K-Plane_{Ar} distances range 2.908-2.920 Å and K-Plane_{toluene} distances range 2.961-3.146 Å. As a result, the potassium cation was wrapped tightly by the aryloxide-N-heterocyclic carbene ligands, avoiding the affection of other metals in the reaction system, rare earth metal, for example.

2.3 Theoretical calculations

In order to provide an assessment of the binding of the aryloxide-N-heterocyclic carbene ligands to the alkali metal and the rare earth metals within these unusual heterobimetallic compounds, we have undertaken density functional theory (DFT) calculations upon the single-crystal structures **1a** and **2a** [44]. The DFT-optimized structures of complexes **1a** and **2a** are showed in figure 3 and 4, and the comparison of selected parameters between X-ray structures and DFT calculations were depicted in table 1.

It can be seen that the DFT-optimized models are similar to X-ray structures, but the calculated bond lengths are slightly longer than the corresponding distances learned from X-ray analysis. Natural bond orbital (NBO) analysis shows that the positive charge is mainly distributed on the electropositive potassium and rare earth metals (NBO charges, K +0.917, Y +1.914 for **1a**; K +0.920, Y +1.903 for **2a**.), and only marginally spreads to the carbene carbon of the NHC ligand. The negative



Figure 3. DFT-optimized structure of complex 1a and calculated NBO charges.



Figure 4. DFT-optimized structure of complex 2a and calculated NBO charges.

charge is mainly occupied on nitrogen atoms on the three bis(trimethylsilyl)amid groups and aryloxide oxygen on the ligand. Moreover, the second-order perturbation theory analysis of the donor-acceptor linkage in the NBOs is employed to indicate that the C-K interactions are contributed by donation of the carbon-based and sp-hybridized lone pair into the potassium metal 4s orbitals with a very weak interaction (K-C 8.6 kcal/mol, **1a**; 9.9 kcal/mol, **2a**). These interactions are evidently weaker than the bond Li-C (23 kcal/mol), Na-C (15 kcal/mol) [45], probably because the increasing size and atomic weight of the alkali metal center. The functionalized anion anchor enhances the interactions between NHC ligands and yttrium cation, with much higher second-order perturbation energy in Y-O bond (75.84 kcal/mol for **1a**, 73.38 kcal/mol for **2a**.).

3. Conclusion

In summary, two aryloxide-substituted NHC proligands H_2L1-H_2L2 were synthesized in an easy and effective strategy. Reactions of proligands H_2L1 and H_2L2 with $Ln[N(SiMe_3)_2]_3$ (Ln=Y, Nd) and KN(SiMe_3)_2 in toluene obtained the heterobimetallic organo rare earth complexes 1a-b, 2a-b,- For the first time, We were able to determine and the molecular structures of heterobimetallic organo rare earth complexes 1a-b, 2a-b, 2a-b were determined in the solid state by single-crystal X-ray diffractometry. These complexes showed a K-NHC structure with rare earth $Ln[N(SiMe_3)_2]_3$ bonding to the aryloxide oxygen. The charge distributions and metal-ligand interactions were investigated within 1a and 2a by density functional theoretical (DFT) methods. Natural bond orbital (NBO) analysis showed that the positive charge was mainly distributed on the electropositive potassium and rare earth metals.

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	1a (Ln=Y)	1a (DFT)	1b (Ln=Nd)	2a (Ln=Y)	2a (DFT)	2b (Ln=Nd)
K1-C2	2.863(7)	2.924	2.832(5)	2.853(3)	2.939	2.852(3)
Ln-O1	2.115(2)	2.195	2.245(3)	2.107(2)	2.194	2.205(2)
Ln-N1	2.279(3)	2.309	2.403(4)	2.269(3)	2.295	2.357(2)
Ln-N2	2.290(3)	2.321	2.367(4)	2.284(6)	2.301	2.379(2)
Ln-N3	2.270(3)	2.297	2.339(4)	2.285(3)	2.334	2.388(2)
N4-C2-N5	115.8(3)	116.34	115.6(4)	115.7(3)	116.32	115.9(3)
Ln-01-C7	149.7(2)	148.65	155.1(3)	152.3(2)	149.95	152.9(3)
O1-Ln-N1	107.95(9)	107.23	98.58(13)	107.11(9)	107.62	105.59(8)
O1-Ln-N2	107.96(9)	108.63	106.17(13)	106.17(9)	106.46	104.60(8)
O1-Ln-N3	97.76(9)	96.95	110.02(13)	97.98(9)	99.04	96.08(8)

Table 1. Selected bond lengths(Å) and angles(°) for complexes 1a-2b.

4. Experimental

4.1 General procedures.

All operations except ligands synthesis were carried out under dry argon using Schlenk techniques. Hexane and toluene were distilled from sodium benzophenone ketyl prior to use. Lanthanide chloride was prepared from lanthanide oxide according to the literature [46]. All other reagents and solvents were commercially available and used without further purification. Metal analyses were performed by complexometric titration. NMR spectra were recorded on a Bruker Avance 400 DMX (¹H NMR at 400 MHz, ¹³C NMR at 101 MHz) spectrometer or Agilent Direct Drive 2 (¹H NMR at 600 MHz, ¹³C NMR at 151 MHz). Elemental analyses were performed by direct combustion with a Flash EA-1112 instrument. Ln[N(SiMe₃)₂]₃ (Ln=Y, Nd) were prepared according to literature procedures [47].

4.2 Synthesis of H₂L1.

The proligand H₂L1 was synthesized in three steps. Firstly, N-mono-(2,4,6-trimethylphenyl)-1,3-diaminedihydro bromide salt (A-2HBr 5 g, 14 mmol) was reacted with KOH (1.38 g, 28 mmol) in water to afford N-mono-(2,4,6-trimethylphenyl)-1,3-diamine (A) in 98% yield. Then A (2.6 g, 13.7 mmol) and 2-Hydroxy-1-naphthaldehyde (2.3 g, 13.7 mmol) were suspended in MeOH (50 mL), the reaction mixture was heated to 40°C and stirred for another 1h resulting in the formation of an orange suspension. Secondly, NaBH₄ (1 g, 26 mmol) was added slowly to the mixture until the solution turned yellow. This reaction solution was stirred overnight before solvent was evaporated to dryness with brown oil appeared. The resulting oil was triturated with water, and filtrated to yield a yellow powder (M1). In the last step, the obtained yellow powder M1 was dissolved in EtOH, and then concentrated HCI (1 mL) was added dropwise to the solution and stirred for about 1 hour. After the solvent was evaporated to dryness, a yellow solid was obtained. The preceding solid (3 g) was suspended in 20 mL of triethylorthoformate, formic acid was added (one drop) and the suspension was heated to 110 °C overnight. The white powder H₂L1 obtained was filtrated, washed with ethyl ether and dried in vacuum. Yield: 67%. ¹H NMR (400MHz, d₆-DMSO, 25°C): δ 8.87(s, 1H, NCHN), 8.11(d, 1H, $C_{10}H_6$), 7.83(m, 2H, $C_{10}H_6$), 7.54(m, 2H, C₁₀H₆), 7.34(t, 1H, C₁₀H₆), 7.06(s, 2H, C₆H₂Me₃), 5.20(s, 2H, CH₂), 3.35-3.48 (m, 4H, NCH₂CH₂CH₂N), 2.22-2.28 (d, 9H, C₆H₂Me₃), 2.11(m, 2H, NCH₂CH₂CH₂N). ¹³C NMR (101 MHz, d₆-DMSO, 25°C) 165.69(NCHN), 156.21, 154.16, 138.97, 137.13, 135.03, 133.36, 130.69, 129.40, 128.78, 127.85, 127.03, 122.59, 121.74, 118.54, 109.43(Ar-C), 48.61(CH₂), 44.92(CH₂), 41.58(CH₂), 20.55(CH₃), 18.77(CH₃), 17.09(CH₂). Anal. Calcd. for $C_{24}H_{27}CIN_2O$: C, 72.99; H, 6.89; N, 7.09. Found: C, 72.65; H, 6.95, N, 6.99.

4.3 Synthesis of H₂L2.

Proligand H₂L2 was prepared similarly to H₂L1, except 2-Hydroxybenzaldehyde (1.7 g, 13.7 mmol) was used in the second step to produce M2. Finally, white powder of H₂L2 was obtained by cyclization of M2. Yield: 70%. ¹H NMR(400MHz, CDCl₃, 25°C): δ 8.68(s, 1H, NCHN), 7.84(d, 1H, C₁₀H₆), 7.75(t, 2H, C₁₀H₆), 7.70(d, 1H, C₁₀H₆), 7.48(t, 1H, C₁₀H₆), 7.29(t, 1H, C₁₀H₆), 6.75(s, 2H, C₆H₂Me₃), 5.37(s, 2H, CH₂), 3.99-4.09(m, 4H, NCH₂CH₂N), 2.20(s, 6H, C₆H₂Me₃), 2.12(s, 3H, C₆H₂Me₃).¹³C NMR (101 MHz, d₆-DMSO, 25°C) δ 156.73(NCHN), 154.63, 138.94, 137.07, 135.02, 130.87, 130.02, 129.35, 119.53, 118.86, 115.79(Ar-C), 54.24(CH₂), 44.95(CH₂), 41.80(CH₂), 20.53(CH₃), 18.78(CH₃), 17.14(CH₂). Anal. Calcd for C₂₀H₂₅ClN₂O: C, 69.65; H, 7.31; N, 8.12. Found: C, 69.57; H, 7.31, N, 7.97.

4.4 Synthesis of complex 1a.

A suspension of H₂L1(0.05 g, 0.13 mmol) in toluene (10 mL) was treated with Y[N(SiMe₃)₂]₃ (0.07 g, 0.13 mmol) at room temperature and stirred for about 30min. Then the toluene solution of KN(SiMe₃)₂ (0.05g, 0.26 mmol) was added to the stirring reactant. The mixture was stirred overnight at room temperature, and then the solvent was removed under vacuum. A hexane/toluene solvent mixture was added to extract complex 1a. Colorless block crystals were obtained at -20°C in a week. Yield: 35%. ¹H NMR (600MHz, C₆D₆, 25°C):δ 7.63(d, 1H, C₁₀H₆), 7.50(d, 1H, C₁₀H₆), 7.42(d, 1H,C₁₀H₆), 7.37(d, 1H,C₁₀H₆), 7.21(tri, 1H, C₁₀H₆), 6.44(s, 2H, C₆H₂Me₃), 5.00(s, 2H, CH₂), 2.86, 2.34(t, t, 2H, 2H, NCH₂CH₂CH₂N), 1.65,1.52(s, s, 3H, 6H, C₆H₂Me₃), 1.23(m, 2H,NCH₂CH₂CH₂N), 0.64 (s, 36H, N[Si(CH₃)₃]₂), 0.10 (s, 18H, N[Si(CH₃)₃]₂). ¹³C NMR (151 MHz, C₆D₆, 25°C) δ 231.71(C_{carbene}-K), 161.50, 144.58, 135.75, 135.02, 134.75, 129.61, 129.50, 129.34, 128.74, 128.35, 127.65, 125.61, 124.42, 123.57, 121.29, 117.22(Ar-C), 52.90(CH₂), 42.68(CH₂), 42.01(CH₂), 21.63(CH₃), 20.70(CH₃), 17.65(CH₂), 5.94(N[Si(CH₃)₃]₂), 2.67 (N[Si(CH₃)₃]₂).

4.5 Synthesis of complex 1b.

A suspension of H_2L1 (0.05 g, 0.13 mmol) in toluene (10 mL) was treated with KN(SiMe_3)_2 (0.05 g, 0.26 mmol) at -20°C and

References

another Nd[N(SiMe₃)₂]₃(0.08 g, 0.13 mmol) was added to the stirring reactant. The solution was warmed to room temperature slowly, and stirred for another 10h. The solvent was removed under vacuum and a hexane/toluene solvent mixture was added to extract complex 1b. Little blue block crystals were obtained at -20°C in 2-3 days. Yield: 40%.

4.6 Synthesis of complex 2a.

A suspension of H₂L2 (0.05 g, 0.14 mmol) in toluene (10 mL) was treated with Y[N(SiMe₃)₂]₃ (0.08 g, 0.14 mmol) at room temperature and stirred for about 30min. Then KN(SiMe₃)₂ (0.06 g, 0.26 mmol) toluene solution was added to the stirring reactant. The mixture was stirred overnight at room temperature, and then the solvent was removed under vacuum. A hexane/toluene solvent mixture was added to extract complex 2a. Colorless block crystals were obtained at -20°C in a week. Yield: 38%. ¹H NMR (600 MHz, C₆D₆, 25°C) δ 7.13 (t, 1H, C₆H₄), 7.08 (d, 1H, C₆H₄), 7.05 (dd, 1H, C₆H₄), 7.03 – 6.99 (m, 1H, C₆H₄), 6.57 (s, 2H, C₆H₂Me₃), 4.55 (s, 2H, CH₂), 2.77 (s, 2H, NCH₂CH₂CH₂N), 2.39 (s, 2H, NCH₂CH₂CH₂N), 2.08 (s, 3H, C₆H₂Me₃), 1.81 (s, 6H, C₆H₂Me₃), 1.49 (d, 2H, NCH₂CH₂CH₂N), 0.58 (s, 36H, N[Si(CH₃)₃]₂), 0.10 (s, 18H, N[Si(CH₃)₃]₂). ¹³C NMR (151 MHz, C₆D₆, 25°C) δ 227.16(C_{carbene}-K), 164.45, 144.41, 137.90, 136.46, 135.18, 132.43, 129.62, 129.34, 128.56, 126.85, 125.67, 123.63, 114.28(Ar-C), 55.63(CH₂), 43.35(CH₂), 42.15(CH₂), 32.00(CH₂), 20.85(CH₃), 21.45(CH₃), 21.21(tol), 17.58(CH₂), 6.90(N[Si(CH₃)₃]₂), 2.67(N[Si(CH₃)₃]₂).

4.7 Synthesis of complex 2b.

A suspension of H₂L2 (0.05 g, 0.14 mmol) in toluene (10 mL) was treated with Nd[N(SiMe₃)₂]₃ (0.09 g, 0.14 mmol) at room temperature and stirred for about 30min. Then another KN(SiMe₃)₂ (0.06 g, 0.26 mmol) toluene solution was added to the stirring reactant. The mixture was stirred overnight at room temperature, and then the solvent was removed under vacuum. A hexane/toluene solvent mixture was added to extract complex 2b. Blue block crystals were obtained at -20°C in a week. Yield: 36%

4.8 X-ray crystallographic study

Single crystals of complexes 1a-2b were sealed in liquid paraffin oil for determination of the single-crystal structures. Data were collected at 170 K on a CrysAlisPro, Oxford DiffractionLtd. using graphite-monochromatic Mo Ka radiation (I ¼0.71073 A). The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3ABSPACK scaling algorithm. All structures were solved by direct methods, and refined by full-matrix least-square methods based on $|F|^2$. The structures were solved and refined using SHELX-97 programs. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically.

Appendix A. Supplementary material

CCDC 1519631-1519634 contain the supplementary crystallographic data for complexes 1a-2b.

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- [44] All geometries of intermediates and transition states (TSs) were optimized using B3LY91 method. Hydrogen, oxygen, nitrogen and silicon atoms were optimized under all electron 6-31g(d,p) basis. Potassium atom was described under 6-31+g(d,p) basis. Yttrium atom was represented using Stuttgart-Drensden pseudopotential with adapted basis. Frequency calculations confirmed that the intermediate had zero imaginary frequency. Natural bonding orbital (NBO) analysis was employed to calculate atom charges and coordinate energies. All calculations were performed using Gaussian 09 program.

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Highlights:

- > Two aryloxide-substituted N-heterocyclic carbene proligands were designed and synthesized.
- Four heterobimetallic potassium-NHC rare earth complexes were prepared, and they have been characterized by single-crystal X-ray diffraction.
- DFT calculations were employed to further investigate charge distributions and interactions within these compounds.