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ARTICLE

Reactivity of Ytterbium(II) Silylamide Supported by a Pyrrolyl-Cyclopentadienyl Ligand†

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Reactivity of a divalent ytterbium amide $LYbN(SiMe_3)_2$ (**1**, L = Me_4C_5-$SiMe_2$-NC_4H_4) supported by a pyrrolyl functionalized cyclopentadienyl ligand has been investigated. Reactions of **1** with element sulfur led to the oxidation of the ytterbium to yield the disulfide bridged ytterbium complex $[LYbN(SiMe_3)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**2**) while that with $AgBPh_4$ resulted in the oxidation of the amide ligand to give the divalent ytterbium complex $LYb(BPh_4)$ (**3**) along with the formation of silver and N-N coupling product $[N(SiMe_3)_2]_2$. Reaction of **1** with phenol, phenylacetylene and aniline led to the formation of the corresponding ytterbium aryloxide $[LYb(\mu\text{-}OAr^1)]_2$ (**4**, Ar^1 = 2,6-tBu$_2$-4-MeC_6H_2), ytterbium alkynyl complex $[LYb(\mu\text{-}C{\equiv}CAr^2)]_2$ (**5**, Ar^2 = 4-tBuC_6H_4) and ytterbium amide $[(Me_4C_5\text{-}SiMe_2\text{-}NHAr^3)Yb(\mu\text{-}NHAr^3)]_2$ (**6**, Ar^3 = 2,6-iPr$_2C_6H_3$), respectively. The structural analysis of the reaction products revealed that the silyl bridged pyrrolyl arm is not coordinated to the ytterbium center in compounds **2**, **4** and **5**. The formation of **6** involved the cleavage of the Si–$N_{pyrrole}$ bond, the same bond cleavage was also observed in the reaction of **1** with red phosphorus, leading to the pyrrolide bridged complex $[LYb(\mu\text{-}\eta^1{:}\eta^5\text{-}NC_4H_4)]_2$ (**7**).

Introduction

Divalent lanthanide complexes bearing one functionalized cyclopendienyl (Cp) ligand and one reactive group such as amide and alkyl groups could undergo electron transfer and/or σ-bond metathesis reactions, and thus have been applied to the synthesis of diverse lanthanide complexes and some catalytic transformations.[1] Consequently, the design of functionalized Cp ligands is crucible to tune the reactivity of this class of divalent lanthanide species. In this line, several Cp ligands with neutral σ-donor arms have been reported to stabilized this type of complexes, albeit existing as a dimmer or with associated solvents in most of the cases.[2]

Recently, we have communicated the synthesis of the first *ansa*-sandwich divalent lanthanide amide (**1**, $LYbN(SiMe_3)_2$, L = Me_4C_5-$SiMe_2$-NC_4H_4) featuring a neutral pyrrolyl-functionalized Cp ligand.[3] The pyrrolyl arm in this case acts as a neutral π ligand, thus forming *ansa*-metallocene like molecule. It is anticipated that the relatively weak π interaction between the pyrrolyl ring and the ytterbium center in the molecule may lead to high reactivity.[4] The primary reactivity toward dioxygen indicated that the pyrrolyl arm is labile in the molecule. This result prompted us to extend this chemistry with other substrates. Herein, we present detailed studies on reactivity of **1** toward a range of typical reagents, including sulfur, $AgBPh_4$, phenol, phenylacetylene, aniline and red phosphorus.

Results and discussion

Reaction of 1 with sulfur and AgBPh₄. In order to explore the reactivity of **1** with oxidation reagents, we have studied the reaction of **1** with O_2, which afforded a dinuclear trivalent ytterbium species *via* intramolecular C−H and Si−N bond oxygenation. For further understanding this unique oxidation process, the reaction of **1** with sulfur was studied (Scheme 1). Reaction of **1** with element sulfur at room temperature is quite slow compared to that with O_2 and proceeded 2 d to yield the disulfide-bridged dimer $[LYbN(SiMe_3)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**2**) in moderate yield (43%). The paramagnetic complex **2** was characterized by elemental analysis and X-ray crystallographic analysis.
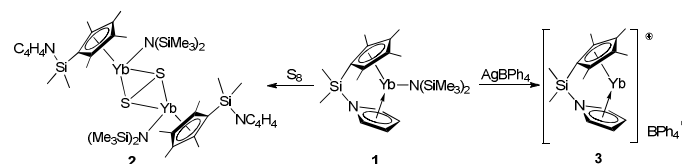
Scheme 1 Reactions of **1** with sulfur and AgBPh₄.

The structure of **2** is shown in Fig. 1 with selected structural parameters. **2** features a dinuclear structure with a

crystallographic central symmetry in which the two sulfur atoms acts as $\eta^2:\eta^2$-bridging ligands. Each ytterbium atom is coordinated to one η^5-cyclopentadiene group, two bridging sulfur atoms and one nitrogen atom of the amido ligand. Yb1–N2 bond distance of 2.165(4) Å in **2** is remarkably shorter than that (2.300(2) Å) in **1** and those of other divalent ytterbium species with Yb-N(SiMe$_3$)$_2$ group.[4c,5] The distance of Yb1 to the Cp center (2.289 Å) is also shorter than that (2.412(2) Å) in **1**. The decreases in the bond distances is accordance with the formation of the Yb(III) species (difference of ionic radii between Yb^{2+} and Yb^{3+} is 0.15 Å).[6] The Yb–S distance of 2.6660(12) Å is in the typical range for an Yb^{3+}–S single bond and shorter than an Yb^{3+}←:S dative bond.[7] The S–S bond distance of 2.146(2) Å is comparable with 2.115(4) Å found in [Cp$_2$Yb(THF)]$_2$(μ-η^2:η^2-S$_2$) and the average value 2.10 Å in (THF)$_6$Yb$_4$I$_2$(μ-η^2:η^2-S$_2$)(μ_4-S).[8] Evans and co-workers have reported that the reactions of divalent lanthanide complex [(C$_5$Me$_5$)$_2$Sm]$_2$(THF)$_2$ with S$_8$ and Ph$_3$P=S yielded trisulfide [(C$_5$Me$_5$)$_2$Sm]$_2$(S$_3$)(THF) and monosulfide [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-S)(THF) *via* oxidation of the low-valent lanthanide center, respectively.[9] The present result represents the first example of lanthanide disulfide complex obtained by the direct oxidation of a divalent lanthanide complex with sulfur.
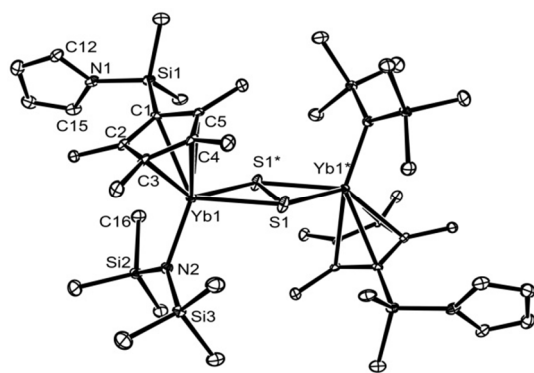

Fig. 1 ORTEP representation of the X-ray structure of **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Yb1–N2 2.165(4), Yb1–S1 2.6660(12), S1–S1* 2.146(2), Si1–N1 1.763(4), Si1–C1 1.862(4), Si2–N2 1.706(4), Si3–N2 1.718(4), N1–C15 1.387(5), N1–C12 1.390(5), N2–Yb1–S1* 114.82(10), N2–Yb1–S1 105.21(10), S1–Yb1–S1* 47.46(4), S1*–S1–Yb1 66.27(5), Yb1–S1–Yb1* 132.54(4).

The silver reagent AgBPh$_4$ has been widely used for the generation of cationic complexes in organometallic chemistry. Reaction of **1** with one equivalent of AgBPh$_4$ at room temperature for 2 d furnished a red solution, from which red crystals of LYb(BPh$_4$) (**3**) was isolated in 52% yield (Scheme 1). **3** is NMR active and its ^{1}H NMR resonances for the supporting ligand L in the ^{1}H NMR spectrum of **3** was found in normal regions. It is noted that the two singlets at δ 5.92 and 6.09 ppm can be assigned to the protons on pyrrolyl ring, which are high-field shifted compared to those observed in free ligand LH (δ 6.33 and 6.81 ppm), suggesting that the pyrrolyl ring is coordinated to the ytterbium ion. The resonance around δ 0 ppm, typical for the N(SiMe$_3$)$_2$ hydrogen atoms, was vanished

in the ^{1}H NMR spectrum, indicating that this group fell off during the reaction. The singlet at δ −6.00 ppm in the ^{11}B NMR spectrum of **3** indicated the separated borate anion [BPh$_4$]$^-$.[10] The reactions of lanthanocenes with AgBPh$_4$ have been previously investigated by several groups.[11] In contrast, the non-ion paired complex (C$_5$Me$_5$)YbBPh$_4$ was found in the reaction of (C$_5$Me$_5$)$_2$Yb with AgBPh$_4$. The formation of the N-N coupling product (Me$_3$Si)$_2$NN(SiMe$_3$)$_2$ was very likely due to the decomposition of the formed AgN(SiMe$_3$)$_2$, similar to the fate of AgC$_5$Me$_5$. The existence of the pyrrolyl arm apparently plays a key role in the formation of the separated ion pair **3**.

Reaction of 1 with phenol, phenylacetylene and aniline. The reactions of **1** with phenol, phenylacetylene and aniline were studied (Scheme 2). When Ar^{1}OH (Ar^1 = 2,6-*t*Bu$_2$-4-MeC$_6$H$_2$) was added to a dark green solution of **1** in toluene, the color of the solution immediately changed to red, from which the compound [LYb(μ-OAr^1)]$_2$ (**4**) was isolated in high yield (71%) after standard workup. **4** have been characterized by elemental analysis, ^{1}H NMR, and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectrum of **4**, the pyrrolyl ring showed similar resonances (δ 6.44 and 6.50 ppm) with those observed in the free ligand LH (δ 6.33 and 6.81 ppm) but significantly low-field shifted in comparison with those in **1** (δ 6.09 and 6.48 ppm), indicating the absence of the interaction between metal center and pyrrolyl ring.
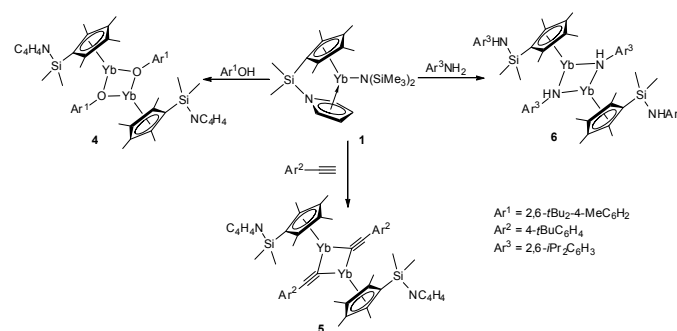
Scheme 2 Reactions of 1 with σ-bond metathesis reagents.

The solid-state structure of **4** was established by X-ray single-crystal analysis, which is depicted in Fig. 2 with the relevant bond parameters. The OAr^1 bridged dimer **4** features a crystallographic central symmetry. Each ytterbium atom in **4** is coordinated by a η^5-coordinated cyclopentadienyl ligand and two bridging OAr^1 ligands. The pyrrolyl ring is away from the ytterbium atom probably caused by the dimeric structure of **4** and the steric effect around the central metal atom from the bulky OAr^1 groups. The average bond distance of the Yb–O bond (2.329(2) Å) is comparable with the those (range from 2.253 to 2.365 Å) in dimeric divalent ytterbium aryloxide complexes [(Ar^{1}O)Yb(μ-OAr^1)]$_2$.[12]
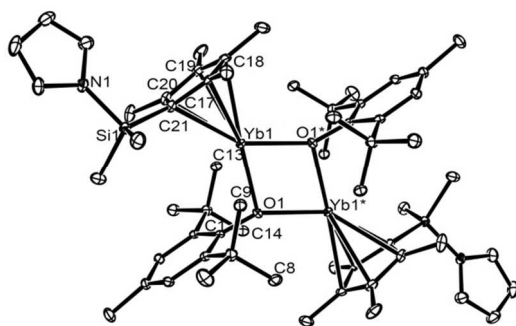
Fig. 2 ORTEP representation of the X-ray structure of **4**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Yb1–O1* 2.302(2), Yb1–O1 2.356(2), Yb1–C17 2.684(3), Yb1–C18 2.698(3), Yb1–C21 2.702(3), Yb1–C19 2.729(3), Yb1–C20 2.738(3), Yb1–C13 2.981(3), Yb1–C9 2.999(3), Yb1–C1 3.009(3), Si1–N1 1.781(3), Si1–C21 1.842(3), Si1–C26 1.865(4), Si1–C25 1.866(4), O1–C1 1.372(4), O1–Yb1–O1* 74.78(8), O1–Yb1–C13 95.35(8), O1–Yb1–C13 66.34(8), O1–Yb1–C9 99.05(8), O1–Yb1–C9 66.36(8), C13–Yb1–C9 124.31(9), C13–Yb1–C1 62.44(9), C9–Yb1–C1 62.07(9), C1–O1–Yb1 150.21(18), C1–O1–Yb1 104.52(17), N1–Si1–C21 105.44(15).

Reaction of **1** with one equivalent of $Ar^2C\equiv CH$ in toluene at room temperature (Scheme 2) yielded the alkynyl complex $[LYb(\mu\text{-}C\equiv CAr^2)]_2$ (**5**, Ar^2 = 4-tBuC$_6$H$_4$) as black crystals in moderate yield (42%). The structure of **5** was characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy, and elemental analysis. In the ^{1}H NMR spectrum, the pyrrolyl ring shows resonances at δ 6.34, 6.95 and 7.09 ppm, which is low-field shifted compared to complex **1** due to the absence of the pyrrolyl ring coordination to the ytterbium atom as observed in **4**. The absorption centered at $\tilde{v}$ 2155 cm^{-1} in the IR spectrum is the typical value for a C≡C triple bond stretching vibration in the lanthanide compounds with a bridging -C≡CR group.[1i,13] Based on the data, the structure of **4** is likely dimeric as shown in Scheme 2.[1i]

In contrast to the reactions with phenol and phenylacetylene, the reaction of **1** with Ar^3NH_2 (Ar^3 = 2,6-iPr$_2$C$_6$H$_3$) led to the cleavage of the Si–N$_{pyrrole}$ and Yb–N bonds with the formation of the new Si–N and Yb–N bonds, yielding the ytterbium complex $[(Me_4C_5\text{-}SiMe_2\text{-}NHAr^3)Yb(\mu\text{-}NHAr^3)]_2$ (**6**) (Scheme 2). This reaction requires two equivalents of Ar^3NH_2 and a high yield (78%) of **6** was obtained. The structure of **6** was characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis. The typical resonances for N(SiM$_3$)$_2$ ligand and pyrrolyl ring disappeared in the NMR spectra of **6** and two Ar^{3}NH moieties appeared in the ^{1}H NMR based on the integration. It is obviously that Ar^{3}NH$_2$ cleaved the Si–N and Yb–N bonds in **1**. It is proposed that the initially formed $[LYb(\mu\text{-}NHAr^3)]_2$ may occur a intramolecular nucleophilic attack. The Si atom was attacked by the nucleophilic NHAr^3 group to generate the intermediate $[(Me_4C_5\text{-}SiMe_2\text{-}NAr^3)Yb]_2$. The labile Yb–N bond in intermediate $[(Me_4C_5\text{-}SiMe_2\text{-}NAr^3)Yb]_2$ was cleavage by Ar^{3}NH$_2$ to form **6**.

Reaction of 1 with red phosphorus. Activation of P$_4$ can afford not only diverse structures but also useful synthons.[14] Roesky et al. recently reported the first molecular polyphosphide lanthanide complex $[(C_5Me_5)_2Sm]_4P_8$.[15]

Compound **1** reacted with red phosphorus but not with P$_4$. From the mixture of two equivalents of red phosphorus with **1** in hot toluene, the red crystals of $[LYb(\mu\text{-}\eta^1:\eta^5\text{-}NC_4H_4)]_2$ (**7**) were obtained in 31% yield after 2 d (Scheme 3). In the ^{1}H NMR spectrum, although the related resonances for the ligand can be found, the six signals observed in the range of δ 6.34–7.36 ppm with the integration ratio of 1:2:2:1:1:1 could be assigned to the hydrogen atoms for the pyrrolyl rings, inferring that there are two types of the pyrroles in **7**. No resonance was observed in the ^{31}P NMR spectrum.
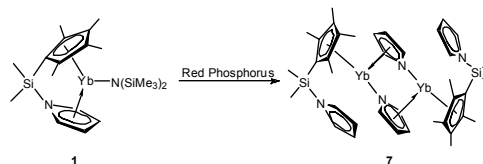
Scheme 3 Reaction of **1** with red phosphorus.

The structure of **7** was finally established by X-ray crystallographic analysis (Fig. 3). Compound **7** is a dimer with a crystallographic central symmetry. Each ytterbium atom is coordinated to one cyclopentadiene group and one pyrrolide group in η^5 fashion, one nitrogen atom of the other pyrrolyl ring in η^1 fashion. The bond distance of Yb1–N2* of 2.446(6) Å is comparable with those (2.456 Å) found in dinuclear trivalent ytterbium species $\{(\eta^5\text{-}C_9H_6)CH_2[\mu\text{-}\eta^1:\eta^5\text{-}(\alpha\text{-}NC_4H_3)]Yb(DME)\}_2$ (DME = 1,2-dimethoxyethane).[4j] The distance of central ytterbium atom to the centroid of bridging pyrrolyl ring is 2.491 Å, which is slightly shorter than that (2.562 Å) in $\{(\eta^5\text{-}C_9H_6)\text{-}CH_2\text{-}[\mu\text{-}\eta^1:\eta^5\text{-}(\alpha\text{-}NC_4H_3)]Yb(DME)\}_2$. Whereas the distance of Yb1 to centroid of pyrrolyl ring of N1-C1-C2-C3-C4 is 2.899 Å, which is remarkable longer than that of 2.589(2) Å in **1**. Although the formation of **7** is not mechanistically understandable at this stage, the reaction is reproducible under the experimental conditions.
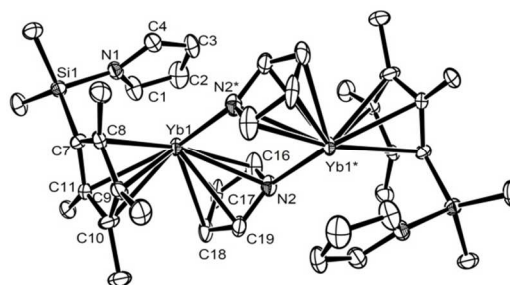
Fig. 3 ORTEP representation of the X-ray structure of **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Yb1–N2* 2.446(6), Yb1–C19 2.737(8), Yb1–C16 2.747(9), Yb1–N2 2.751(6), Yb1–C18 2.763(8), Yb1–C17 2.778(8), Yb1–N1 2.991(7), N2*–Yb1–C19 90.7(3), N2–Yb1–C16 89.7(3), C19–Yb1–C16 46.6(3), N2–Yb1–N2 72.9(2), N2*–Yb1–N1 107.8(2), C1–N1–Yb1 87.4(5), C4–N1–Yb1 77.3(5), Si1–N1–Yb1 92.7(2), Yb1–N2–Yb1 107.1(2).

Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon

by using modified Schlenk line and glovebox techniques. Elemental analyses were carried out on an Elementar Vario EL analyzer. The ^{1}H, ^{11}B and ^{13}C NMR spectroscopic data were recorded on a Bruker AV400 spectrometer. Chemical shifts were referenced to residual solvent peaks (^{1}H and ^{13}C NMR) or external BF$_3$·Et$_2$O (^{11}B NMR). Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrophotometer. EI-MS were recorded on VG ZAB-HS. The solvents (toluene and *n*-hexane) were freshly distilled from sodium and degassed prior to use. **1** was synthesized according to the published procedures.[3] Other chemicals were of analytical grade and were used as received.

Synthesis of [LYbN(SiMe$_3$)$_2$]$_2$(μ-η^2:η^2-S$_2$) (2). To a mixture of **1** (0.29 g, 0.5 mmol) and S$_8$ (0.016 g, 0.5 mmol) was added by toluene (25 mL). The mixture was then stirred for 2 d and concentrated to 5 mL to give yellow crystals of **2** at –20 °C for two d (0.13 g, 43%). M.p.: 273 °C (dec.). Anal. Calcd for C$_{42}$H$_{80}$N$_4$S$_2$Si$_6$Yb$_2$ (1219.83): C 41.35, H 6.61, N 4.59. Found: C 40.62, H 6.68, N 3.96.

Synthesis of LYb(BPh$_4$) (3). To a mixture of **1** (0.29 g, 0.5 mmol) and AgBPh$_4$ (0.22 g, 0.5 mmol) was added by toluene (50 mL) at room temperature. After stirring for additional 2 d, the mixture was concentrated to 10 mL. Storage at 0 °C for several d affords red solid of **3** (0.2 g, 52%). M.p.: 276 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 23 °C): δ 0.37 (s, 6H, SiMe$_2$), 1.62 (s, 6H, C$_5$Me$_4$), 1.77 (s, 6H, C$_5$Me$_4$), 5.92 (s, 2H, NC$_4$H$_4$), 6.09 (s, 2H, NC$_4$H$_4$), 6.93−7.77 (m, 20H, Ar-*H*). ^{13}C NMR (C$_6$D$_6$, 101 MHz, 23 °C): δ 1.13 (SiMe$_2$), 11.68 (C$_5$Me$_4$), 15.04(C$_5$Me$_4$), 111.51 (NC$_4$H$_4$), 116.30 (NC$_4$H$_4$), 121.30 (*C$_5$*Me$_4$), 123.39 (*C$_5$*Me$_4$), 123.80, 128.15, 128.69, 134.75 (Ar-*C*). ^{11}B NMR (C$_6$D$_6$, 128MHz, 23 °C): δ −6.00. Anal. Calcd for C$_{39}$H$_{41}$BNSiYb (736.25): C 63.67, H 5.62, N 1.90. Found: C 62.58, H 5.60, N 1.65.

Synthesis of [LYb(μ-OAr^1)]$_2$ (4). A solution of Ar^{1}OH (0.11 g, 0.50 mmol) in 10 mL toluene was added dropwise to a solution of **1** (0.29 g, 0.50 mmol) in toluene (20 mL) at room temperature, and then the green solution turned to red immediately. After the mixture was stirred for additional 4 hours, the mixture was heated to 60 °C to dissolve the red precipitation and give red crystals of **4** at –40 °C (0.23 g, 71%). M.p.: 158 °C (dec.). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 23 °C): δ 0.35 (s, 12H, SiMe$_2$), 1.43 (s, 36H, CMe$_3$), 1.60 (s, 12H, C$_5$Me$_4$), 1.83 (s, 12H, C$_5$Me$_4$), 2.29 (s, 6H, Ar-*Me*), 6.44 (s, 4H, NC$_4$H$_4$), 6.50 (s, 4H, NC$_4$H$_4$), 7.00−7.13 (m, 4H, Ar-*H*). ^{13}C NMR (C$_6$D$_6$, 101 MHz, 23 °C): 2.69 (SiMe$_2$), 11.53 (C$_5$Me$_4$), 14.36 (C$_5$Me$_4$), 30.42 (*p-Me*), 31.64 (CMe$_3$), 35.11 (*C*Me$_3$), 110.92 (NC$_4$H$_4$), 111.52 (NC$_4$H$_4$), 121.46 (*C$_5$*Me$_4$), 123.47 (*C$_5$*Me$_4$), 125.85, 126.44, 126.91, 127.42, 155.85 (Ar-*C*). EI-MS: m/z 637.1. Anal. Calcd for C$_{60}$H$_{90}$N$_2$O$_2$Si$_2$Yb$_2$ (1273.62): C 56.58, H 7.12, N 2.20. Found: C 56.14, H 7.33, N 1.98.

Synthesis of [LYb(μ-C≡CAr^2)]$_2$ (5). To a solution of **1** (0.29 g, 0.50 mmol) in toluene (20 mL) was added dropwise (0.09 g, 0.55 mmol) of Ar^{2}C≡CH at ambient temperature. After stirred for additional 4 hours, the mixture was concentrated to 5 mL and heated to 50 °C for 10 mins to redissolve resulting precipitate, then cooled to 0 °C for 1 d to give black crystals of **5** (0.12 g, 42%). M.p.:175 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 23 °C): δ 0.18 (s, 12H, SiMe$_2$), 1.09 (s, 18H, CMe$_3$), 1.83 (s, 12H, C$_5$Me$_4$), 2.13 (s, 12H, C$_5$Me$_4$), 6.34 (m, 2H, NC$_4$H$_4$), 6.95 (m, 2H, NC$_4$H$_4$), 7.09 (m, 4H, NC$_4$H$_4$), 7.15−7.53 (m, 8H, Ar-*H*). ^{13}C NMR (C$_6$D$_6$, 101 MHz, 23 °C): δ 1.37 (SiMe$_2$), 11.37 (C$_5$Me$_4$), 14.56 (C$_5$Me$_4$), 31.06 (CMe$_3$), 53.62 (*C*≡CAr), 54.47 (C≡*C*Ar), 125.67, 132.01, 136.48, 147.54 (Ar-*C*). IR (cm^{-1}): $\tilde{v}$ 2155 (s, C≡CAr). Anal. Calcd for C$_{54}$H$_{70}$N$_2$Si$_2$Yb$_2$ (1149.40): C 56.43, H 6.14, N 2.44. Found: C 55.69, H 5.98, N 2.11.

Synthesis of [(Me$_4$C$_5$-SiMe$_2$-NHAr^3)Yb(μ-NHAr^3)]$_2$ (6). To a solution of **1** (0.29 g, 0.50 mmol) in toluene (20 mL) was added dropwise 190 μL(0.20 g, 1 mmol) of Ar^{3}NH$_2$ at room temperature and stirred for additional 2 hours. Concentrating the solution to 2 mL, and 5 mL *n*-hexane was carefully added to give red crystals of **6** (0.26 g, 78%). M.p.: 127 °C (dec.). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 23 °C): δ 0.14 (s, 6H, SiMe$_2$), 1.15 (br, 24H, CHMe$_2$), 1.81 (s, 6H, C$_5$Me$_4$), 1.98 (s, 6H, C$_5$Me$_4$), 2.33 (s, 1H, N*H*), 2.62 (s, 1H, N*H*), 2.86 (br, 1H, C*H*Me$_2$), 3.16 (br, 1H, C*H*Me$_2$), 3.43 (br, 2H, C*H*Me$_2$), 6.90–7.35 (m, 11H, Ar-*H*). ^{13}C NMR (C$_6$D$_6$, 101 MHz, 23 °C): δ −0.25 (SiMe$_2$), 11.46 (C$_5$Me$_4$), 14.67 (C$_5$Me$_4$), 22.55 (CHMe$_2$), 23.98 (CHMe$_2$), 28.06 (*C*HMe$_2$), 28.12 (*C*HMe$_2$), 56.71 (*C$_5$*Me$_4$), 118.91 (*C$_5$*Me$_4$), 123.09 (*C$_5$*Me$_4$), 123.37, 123.95, 127.35, 132.25, 133.10, 136.55, 139.48, 144.07 (Ar-*C*). Anal. Calcd for C$_{64}$H$_{96}$N$_4$Si$_2$Yb$_2$ (1323.72): C 58.07, H 7.31, N 4.23. Found: C 57.18, H 7.43, N 4.20.

Synthesis of [LYb(μ-η^1:η^5-NC$_4$H$_4$)]$_2$ (7). To a mixture of **1** (0.29 g, 0.5 mmol) and red phosphorus (0.016 g, 0.5 mmol) was condensed ca. 30 mL of toluene. After stirring for additional 2 d, the mixture was heated to 60 °C and then filtrated. The red crystals of **7** at room temperature was afforded after 2 d (0.08 g, 31%). M.p.: 290 °C (dec.). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 23 °C): δ 0.05 (s, 12H, SiMe$_2$), 1.61 (s, 12H, C$_5$Me$_4$), 1.72 (s, 12H, C$_5$Me$_4$), 6.34 (m, br, 2H, NC$_4$H$_4$), 6.52 (s, br, 4H, NC$_4$H$_4$), 6.72 (s, br, 4H, NC$_4$H$_4$), 6.95 (m, br, 2H, NC$_4$H$_4$), 7.14 (m, br, 2H, NC$_4$H$_4$), 7.34 (m, br, 2H, NC$_4$H$_4$). Anal. Calcd for C$_{38}$H$_{52}$N$_4$Si$_2$Yb$_2$ (967.10): C 47.19, H 5.42, N 5.79. Found: C 46.20, H 5.22, N 5.58.

X-ray Structural Determination. All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were resolved by direct methods and refined by full matrix least squares on F^2.[16] Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. The ORTEP-3 program was utilized to draw the molecules.[17] Crystals of **2**, **4** and **7** suitable for X-ray analysis were obtained from toluene at −35 °C. The crystallographic data and the refinement of complexes **2**, **4** and **7** are summarized in Table 1.

Table 1 Crystallographic detail for **2**, **4** and **7**

	2	0.54·C$_7$H$_8$	**7**
formula	C$_{42}$H$_{80}$N$_4$S$_2$Si$_6$Yb$_2$	C$_{37}$H$_{51}$NOSiYb	C$_{38}$H$_{52}$N$_4$Si$_2$Yb$_2$
fw	1219.84	726.92	967.10
T (K)	113(2)	113(2)	113(2)
Space group	$P2_1$/c	$P2_1$/n	$P2_1$/c
a (Å)	9.2449(18)	12.621(3)	13.088(3)
b (Å)	23.135(5)	13.590(3)	15.696(3)
c (Å)	13.238(3)	19.916(4)	8.9682(18)
α (deg)	90.00	90.00	90.00
β (deg)	106.95(3)	95.21(3)	91.92(3)
γ (deg)	90.00	90.00	90.00
V (Å^3)	2708.5(9)	3402.0(12)	1841.2(6)
Z	2	4	2
d_{calcd} (g/cm^3)	1.496	1.419	1.744
F(000)	1232	1488	952
GOF	1.107	1.058	0.962
R_1, wR_2 ($I > 2\sigma(I)$)	0.0310, 0.0584	0.0254, 0.0576	0.0491, 0.1320
R_1, wR_2 (all data)	0.0369, 0.0610	0.0294, 0.0593	0.0638, 0.1472
CCDC	1025673	1025674	1025675

Conclusions

Reactions of **1** with different substrates yielded new types of ytterbium complexes. This study demonstrated that **1** with the labile pyrrolyl π arm featured high and diverse reactivity compared to other cyclopentadienyl ytterbium amides.[1f,1h,12] The labile pyrrolyl ligand may either participate in chemical reactions or stabilize reactive species as observed in the formation of cationic **3**. The lability of the ligand may facilitate catalytic processes, which will be waiting for the further investigations.

Acknowledgements

Notes and references

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†Electronic Supplementary Information (ESI) available: CIF files for compounds **2**, **4** and **7**. CCDC 1025673-1025675. See DOI: 10.1039/b000000x/

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Journal Name

ARTICLE

Reactivity of Ytterbium(II) Silylamide Supported by a Pyrrolyl-Cyclopentadienyl Ligand

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Diverse and high reactivity of a divalent ytterbium amide with the labile pyrrolyl π arm has been demonstrated.