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# Divalent Ytterbium Iodide Supported by β-Diketiminato Based Tridentate Ligand: Synthesis, Structure and Small Molecule Activation

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**Summary of main observation and conclusion** Divalent ytterbium iodide [LYb($\mu$-I)(THF)]$_2$ (**1**; L = [MeC(NDIPP)CHC(Me)NCH$_2$CH$_2$NMe$_2$]$^-$, DIPP = 2,6-($^i$Pr)$_2$C$_6$H$_3$) was synthesized and its reactivity was studied. Complex **1** was synthesized by salt metathesis of YbI$_2$(THF)$_2$ with the potassium salt of ligand (KL) in high yield. In the reactions with trimethylsilyl azide, azobenzene, sulfur and diphenyl disulfide, complex **1** acts as a 2e reductant. In the reaction with CO$_2$, the central carbon atom of β-diketiminato backbone in **1** nucleophilically attacks the CO$_2$ molecule to give a divalent ytterbium carboxylate.

## Background and Originality Content

The chemistry of divalent rare-earth metal complexes is currently one of the most rapidly developing areas in organometallic chemistry, and their use as reducing agents in small molecule activation receives increasing attention.[1,2] A vast array of divalent rare-earth metal complexes have been found to possess high or versatile reactivity toward a series of small molecules, even including the unreactive molecule N$_2$.[3-10] The ancillary ligands of these complexes were dominated by cyclopentadienyl ligand (Cp) or its substituted analogues at the beginning,[4] ligands other than Cp and its derivatives were introduced in the last two decades. Some bulky N-containing ligands, such as amidinates,[7] guanidinates,[8] and tris(pyrazoly)borates,[9] have received attention, due to their strong donating ability and easily adjustable electronic and steric properties. The β-diketiminato ligands as one kind of monoanionic N-containing ligands, have been widely used in the stabilization of metal complexes across the periodic table.[10] The chemistry of β-diketiminato ligands supported trivalent rare-earth metal complexes is well known, in comparison, divalent rare-earth metal complexes have been much less studied.[11] Heteroleptic β-diketiminato ytterbium(II) halides remained unknown until 2009 (Figure 1, (a) and (b)), owing to the strong tendency to undergo ligand redistribution reactions.[11c] In 2011, another bulky β-diketiminato ytterbium(II) iodide (Figure 1, (c)) was reported.[11d] The reductivity of these β-diketiminato ytterbium(II) iodides was not reported. Recently, we have developed a type of β-diketiminato based multidentate ligands, which stabilize a series of highly reactive rare-earth metal complexes.[12] By employing a β-diketiminato based tetradentate ligand, we successfully synthesized a ytterbium(II) iodido complex (Figure 1, (d)).[13] Despite this iodide can be used as the precursor for the synthesis of ytterbium(II) alkyl complex, its reductivity to small molecules is rather sluggish. Recently, we synthesized a ytterbium(II) iodide supported by β-diketiminato based tridentate ligand. This new ytterbium(II) complex is able to undergo redox reactions with trimethylsilyl azide, azobenzene, sulfur and diphenyl disulfide as well as nucleophilic reaction with CO$_2$. Herein, we report these results.

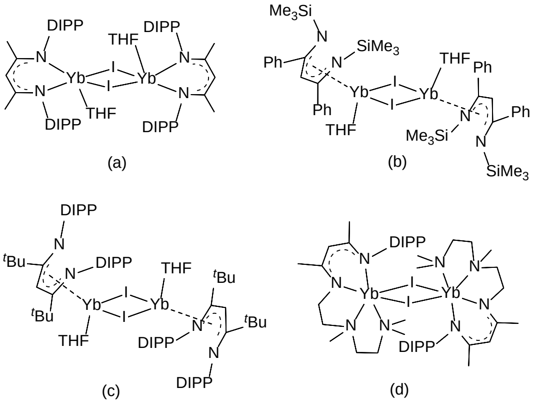


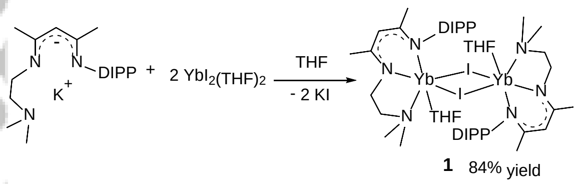
**Figure 1** Reported divalent ytterbium iodido complexes supported by β-diketiminato type ligands

## Results and Discussion

The reaction of YbI$_2$(THF)$_2$ with a potassium salt of ligand KL (L = [MeC(NDIPP)CHC(Me)NCH$_2$CH$_2$NMe$_2$]$^-$, DIPP = 2,6-($^i$Pr)$_2$C$_6$H$_3$) in

THF at room temperature provided a divalent ytterbium iodide [LYb($\mu$-I)(THF)]$_2$ (**1**) as a deep brown solid in 84% yield (Scheme 1). The complex was characterized by NMR spectroscopy ($^1$H, $^{13}$C{$^1$H}), IR spectroscopy, elemental analysis, and single-crystal X-ray crystallography (Figure 2). The single-crystal X-ray crystallography indicated that complex **1** exits a dimmer, in which each ytterbium ion is coordinated by three nitrogen atoms of L, two bridging iodides and one oxygen of THF in a distorted octahedral geometry. The structure of **1** is similar to that of [L'Yb($\mu$-I)]$_2$ (L' = [MeC(NDIPP)CHC(Me)NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$]$^-$),[13] where the THF in **1** is replaced by the terminal amino group of L'. Two Yb–I bond lengths in **1** are not equal, one is 3.184(1) Å while the other is 3.229(1) Å.

**Scheme 1** Synthesis of [LYb($\mu$-I)(THF)]$_2$ (**1**)



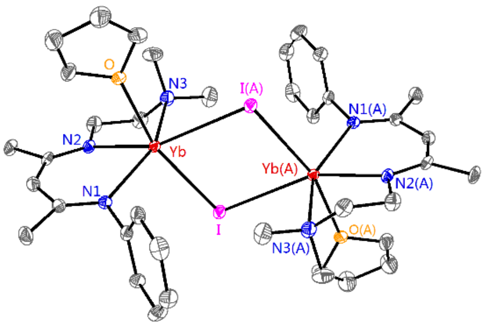
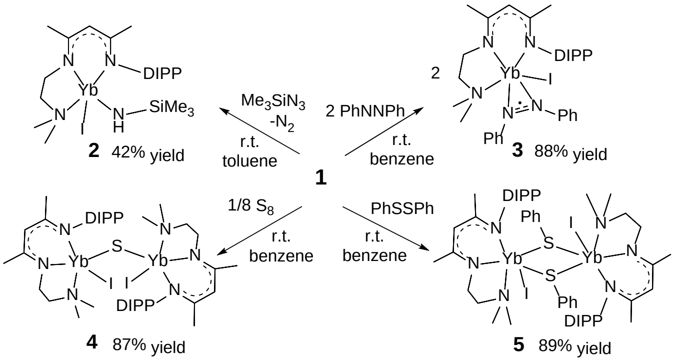


**Figure 2** Molecular structure of complex **1** with ellipsoids at 30% probability level. DIPP isopropyl groups and hydrogen atoms were omitted for clarity. Selected bond distances [Å] and angles [°]: Yb–N1 2.463(4), Yb–N2 2.410(4), Yb–N3 2.608(4), Yb–O 2.492(3), Yb–I 3.184-(1), Yb–I(A) 3.229(1), Yb–I–Yb(A) 97.78(1), I–Yb–I(A) 82.22(1).

Complex **1** was treated with one equivalent of trimethylsilyl azide (Me$_3$SiN$_3$) in toluene at room temperature. The color of the reaction mixture changed immediately from deep brown to orange accompanied by an evolution of dinitrogen. After 30 minutes, the solvent was removed under vacuum, and the residue was extracted with hexane. From the hexane extraction, a trivalent ytterbium amido iodide LYbI(NHSiMe$_3$) (**2**) was obtained in 42% yield (based on Yb) as an orange solid. The $^1$H NMR spectrum of the product which is not soluble in hexane was recorded in $d_8$-THF, showing the complex is paramagnetic (the Yb(III) species). Due to the paramagnetic property of the complex, the $^1$H NMR signals are broad and not informative for the structure of the complex. The complex **2** was fully characterized by $^1$H NMR spectroscopy, IR spectroscopy, elemental analysis, and single-crystal X-ray crystallography. The $^1$H NMR spectroscopy of **2** exhibited the signals ranged from 35 to -38 ppm, in line with the paramagnetic property of the Yb(III) complex. Different from **1**, complex **2** is a monomer (Figure 3). The ytterbium ion is coordinated by three nitrogen atoms of L, one nitrogen atom of the amido ligand, and one iodide in a distorted square pyramidal geometry. The Yb–N1 and Yb–N2 bond lengths in **2** are significantly shorter than those in **1**, (2.278(5) and 2.297(5) Å vs 2.463(4) and 2.410(4) Å), in consistent with an oxidation state change from Yb(II) of **1** to Yb(III) of **2**.[14] Organic azides usually act as two-electron oxidants in the reactions with low valent metal complexes by denitrogenative reaction, providing high valent metal imido complexes.[15] Pan and Wang reported the formation of a tetranuclear Sm(III) bridging imido complex [{Me$_2$Si[NC(Ph)N(DIPP)]$_2$}$_2$Sm$_4$($\mu_3$-NSiMe$_3$)$_4$] via a reaction of a Sm(II) complex [{Me$_2$Si[NC(Ph)N(DIPP)]$_2$}SmI$_2$Li$_2$(THF)(Et$_2$O)$_2$] with Me$_3$SiN$_3$.[7b] We propose that the reaction of **1** with Me$_3$SiN$_3$ generates a trivalent ytterbium imido intermediate **A** (Scheme 3), which is unstable and subsequently undergoes a hydrogen abstraction reaction to provide the final product **2**. To find out where the hydrogen comes from and identify the byproduct(s) of this reaction, the residue of the extraction which is not soluble in hexane was treated with D$_2$O, and then characterized by the $^1$H and $^2$D NMR spectroscopy. The deuteration products, [MeC(N(D)DIPP)CHC(CH$_2$D)NCH$_2$CH$_2$NMe$_2$], [MeC(N(D)DIPP)CHC(CH$_2$D)=O] and [MeC(N(H)DIPP)CDC(CH$_2$ D)=O], were detected. Apparently, [MeC(N(D)DIPP)CHC(CH$_2$D)NCH$_2$CH$_2$NMe$_2$] is from the deuteration reaction of dianonic ligand [MeC(NDIPP)CHC(=CH$_2$)NCH$_2$CH$_2$NMe$_2$]$^{2-}$, while [MeC(N(D)DIPP)CHC(CH$_2$D)=O] and [MeC(N(H)DIPP)CDC(CH$_2$D)=O] are caused by the further hydrolysis reaction of [MeC(N(D)DIPP)CHC(CH$_2$D)NCH$_2$CH$_2$NMe$_2$] with D$_2$O. This result clearly indicated that the hydrogen comes from the other ligand in **A**, and the byproduct is reasonably formulated as [{MeC(NDIPP)CHC(=CH$_2$)NCH$_2$CH$_2$NMe$_2$}YbI(THF)] (Scheme 3).

**Scheme 2** Reactions of complex **1** with trimethylsilyl azide, azobenzene, elemental sulfur, and diphenyl disulfide



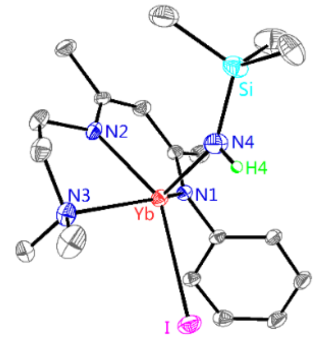
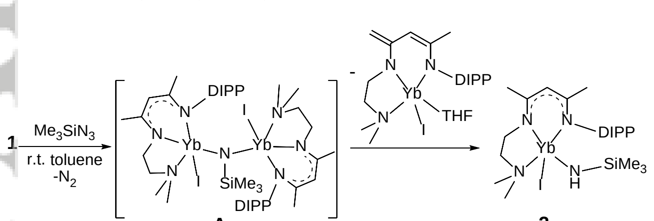


**Figure 3** Molecular structure of complex **2** with ellipsoids at 30% probability level. DIPP isopropyl groups and hydrogen atoms (except H4) were omitted for clarity. There are four crystallographically independent molecules in the unit cell. The bond lengths and angles listed are the average of four molecules. Selected bond distances [Å] and angles [°]: Yb–N1 2.278(5), Yb–N2 2.297(5), Yb–N3 2.421(5), Yb–N4 2.118(5), Yb–I 2.943(1), Yb–N4–Si 139.6(3).

**Scheme 3** Proposed pathway for the formation of **2**



**A** **2**

In the reactions with low valent metal complexes, azobenzene (PhN=NPh) can be reduced to anionic $Ph_2N_2^-$, dianionic $Ph_2N_2^{2-}$, or $PhN^{2-}$ species, and these processes are regarded to be relevant to the studies of $N_2$ fixation.[16] Reaction of complex **1** with azobenzene in a 1 : 2 molar ratio in benzene at room temperature led to a dark blue solution, from which trivalent ytterbium complex LYbI(PhNNPh) (**3**) was obtained in 88% yield (Scheme 2). On the other hand, the reaction of complex **1** with azobenzene in a 1 : 1 molar ratio gave an unidentified mixture. The $^1$H NMR spectroscopy of **3** showed a paramagnetic property. Single-crystal X-ray crystallography showed that a radical anion ($PhNNPh^{-}$) coordinates to the ytterbium ion in a $\eta^2$-*N,N'* fashion (Figure 4), the Yb–N4 bond length (2.237(4) Å) is slightly shorter than the Yb–N5 bond length (2.287(4) Å). The Yb–N$^{azobenzene}$ bond length difference of 0.05 Å (Yb–N4 *vs* Yb–N5) is comparable with that found in a related samarium complex $[(C_5Me_5)_2Sm(N_2Ph_2)(THF)]$ (0.04 Å),[16a] on the other hand, is significant shorter than that reported in $[(C_5Me_5)\{Ph_3B(\mu\text{-}\eta^1{:}\eta^6\text{-}Ph)\}Sm(\eta^2\text{-}N_2Ph_2)]$ (0.28 Å).[16d] The N4–N5 bond length of 1.347(5) Å is close to that of 1.331(17) Å found in the KPhNNPh radical,[5c] which is intermediate between the N=N bond length (1.25 Å in azobenzene) and the N–N single bond length (1.45 Å in hydrazine). Although a number of samarium(III) and thulium(III) complexes containing monoanionic reduced azobenzene have been reported, the structurally characterized ytterbium (III) analogues are very scarce.[17]

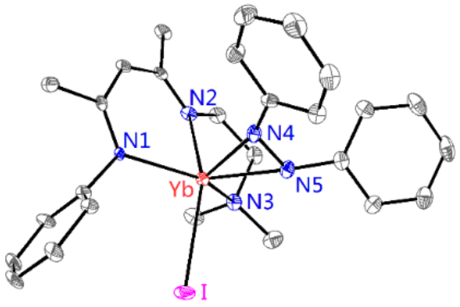


**Figure 4** Molecular structure of complex **3** with ellipsoids at 30% probability level. DIPP isopropyl groups and hydrogen atoms were omitted for clarity. Selected bond distances [Å] and angles [°]: Yb–N1 2.289(4), Yb–N2 2.284(4), Yb–N3 2.447(4), Yb–N4 2.237(4), Yb–N5 2.287(4), Yb–I 2.923(1), N4–N5 1.347(5).

Dc magnetic measurements for **3** were performed in the temperature range from 2 to 300 K under 1 kOe of dc field (Figure 5), featuring typical paramagnetic behaviours for lanthanide ions. At 300 K, the $\chi_mT$ value of **3** is 2.46 emu K mol$^{-1}$, in good agreement with the non-interacting theoretical values of 2.57 emu K mol$^{-1}$ for $Yb^{3+}$ ions ($^2F_{7/2}$, $S$ = 1/2, $L$ =3, $J$ = 7/2, $g_J$ = 8/7). On decreasing the temperature, a general decrease of the $\chi_mT$ product was observed because of the depopulation of sublevels of the ground $J$ multiplet split by the crystal field and/or weak antiferromagnetic dipolar interactions. The field dependence of magnetization of **3** (Figure 6) shows a linear increase at 2 K and fails to reach saturation at 5 T. This result is associated with the possible contribution of $Yb^{3+}$ magnetic anisotropy. In addition, the $M$ versus $H/T$ plots are non-superposition, implying the presence of low-lying excited levels.

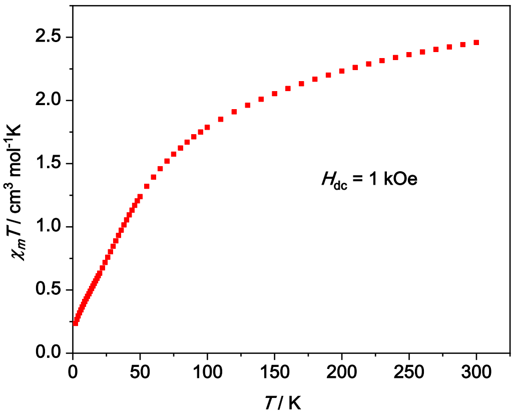


**Figure 5** Plot of $\chi_mT$ *versus* $T$ of **3** from 2 to 300 K.

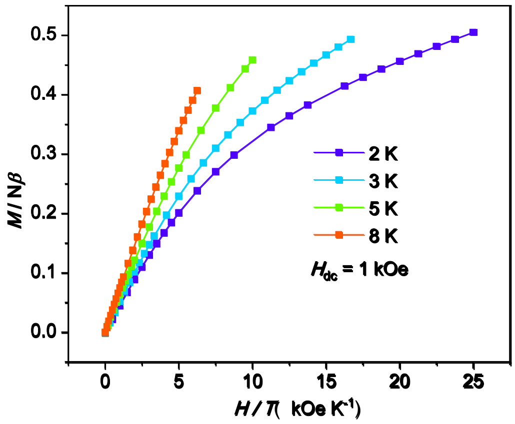


**Figure 6** Plot of *M versus H/T* at the indicated temperatures.

Reactions of **1** with elemental sulfur and diphenyl disulfide were also studied (Scheme 2). Treatment of **1** with elemental sulfur ($S_8$) in a 8 : 1 molar ratio in benzene provided a sulfide bridged dinuclear Yb(III) complex [LYbI]$_2$($\mu$-S) (**4**) in 87% yield. In **4**, the Yb–S distance and Yb–S–Yb angle are 2.479(1) Å and 140.29(7)°, respectively (Figure 7). It has been reported that the reactions of divalent rare-earth metal complexes, such as $(C_5Me_5)_2Sm(THF)_2$,[18a] [{$Me_2Si(C_5Me_4)(NC_4H_4)$}YbN($SiMe_3$)$_2$],[18b] (Tp$^{iPr2}$)$_2$Ln (Ln = Yb, Sm; Tp$^{iPr2}$ = hydro-tris(3,5-diisopropylpyrzolyl)borate),[9c] and [{HC(NDIPP)$_2$}$_2$Ln(THF)$_2$] (Ln = Yb, Sm),[7f] with excess $S_8$ give disulfide or polysulfide complexes. But complex **1** reacts with excess $S_8$ to yield a complicated mixture. The reaction of **1** with an equivalent diphenyl disulfide (PhSSPh) in benzene resulted in a phenyl sulfide bridged Yb(III) dimer [LYbI($\mu$-SPh)]$_2$ (**5**) in 89% yield. This product is different from the reactions of PhSSPh with [$(C_5Me_5)_2Yb(OEt_2)$] or [{HC(NDIPP)$_2$}$_2$Yb(THF)$_2$], which give the monomers [$(C_5Me_5)_2Yb(SPh)(OEt_2)$][19] or [{HC(NDIPP)$_2$}$_2$Yb(SPh)(THF)][7h]. Complex **5** was also characterized by single-crystal X-ray crystallography (Figure 7). The Yb–S distance in **5** (2.755(1) Å) is much longer than that in **4** (2.479(1) Å), this is reasonable as PhS$^-$ is monoanionic while S$^{2-}$ is dianionic. The Yb–S–Yb in **5** is much smaller than that in **4**, 115.88(4)° *vs* 140.29(7)°.

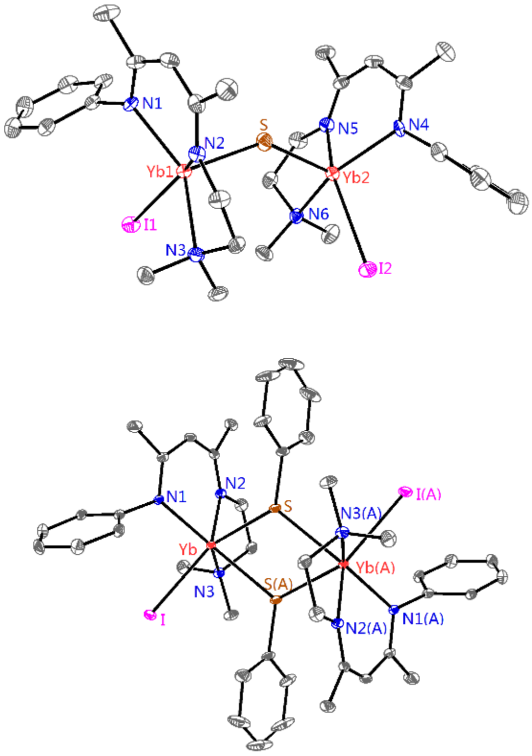
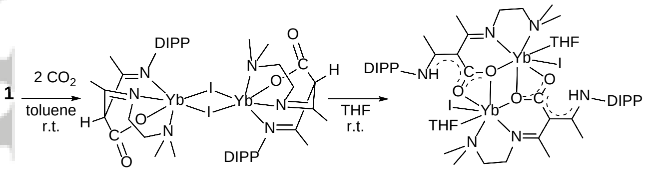


**Figure 7** Molecular structure of complexes **4** (top) and **5** (bottom) with ellipsoids at 30% probability level. DIPP isopropyl groups and hydrogen atoms were omitted for clarity. Selected bond distances [Å] and angles [°]: **4**: Yb1–N1 2.250(4), Yb1–N2 2.278(4), Yb1–N3 2.407(4), Yb1–I1 2.956(1), Yb1–S 2.479(1), Yb2–N4 2.259(4), Yb2–N5 2.281(4), Yb2–N6 2.429(4), Yb2–I2 2.953(1), Yb1–S–Yb2 140.29(7), S–Yb1–I1 109.51(4), S–Yb2–I2 110.96(4). **5**: Yb–N1 2.296(3), Yb–N2 2.275(3), Yb–N3 2.458(3), Yb–I 2.949(1), Yb–S 2.755(1), Yb–S–Yb(A) 115.88(4), S–Yb–S(A) 64.12(4).

In contrast to the redox reactions with trimethylsilyl azide, azobenzene, sulfur and diphenyl disulfide, complex **1** undergoes a nucleophilic reaction with $CO_2$ to give a new divalent ytterbium complex **6** (Scheme 4). When a $C_6D_6$ solution of **1** was exposed to $CO_2$ (1 atm) at room temperature, the colour of the solution changed from deep brown to deep red immediately. Monitoring of the reaction by $^1$H NMR spectroscopy revealed that complex **1** was completely converted into complex **6**. The reaction was scaled up in toluene, which afforded **6** in 91% isolated yield. A Similar nucleophilic addition was demonstrated by Piers when a trivalent scandium cation [{$^t$BuC(NDIPP)CHC($^t$Bu)NDIPP]ScMe]$^+$ was treated with excess $CO_2$,[20] however such reaction was not reported for the related divalent rare-earth metal complexes. It should be noted that some divalent ytterbium complexes undergo reduction reaction with $CO_2$.[5c,5g] Complex **6** was characterized by elemental analysis, IR spectroscopy, $^1$H and $^{13}$C{$^1$H} NMR spectroscopy. The $^1$H NMR spectrum of **6** in $C_6D_6$ displays four multiplets at $\delta$ = 3.24, 2.93, 2.39, and 1.72 ppm, attributable to the four hydrogen atoms of the –$NCH_2CH_2N$– fragment of the ligand, which reveals that the amino sidearm is coordinated to the ytterbium ion. In addition, the *C*H(C=N)$_2$CO$_2$ protons give rise to a singlet at $\delta$ = 5.05 ppm in the $^1$H

NMR spectrum, whilst the carboxylate carbon $CH(C=N)_2CO_2$ shows a signal at $\delta$ = 178 ppm in the $^{13}C\{^1H\}$ NMR spectrum, which are comparable to those observed in the related scandium complex.[20] Interestingly, recrystallization of **6** in THF provided a divalent ytterbium complex **7**. Different from **6**, complex **7** is insoluble in toluene and benzene, and even in THF, the solubility of **7** is very low. The molecular structure of **7** was determined by single-crystal X-ray diffraction. Complex **7** is a dimer, in which each ytterbium ion is coordinated by one oxygen atom and two nitrogen atoms of the newly formed ligand $[MeC(N(H)DIPP)C(CO_2)C(Me)NCH_2CH_2NMe_2]^-$, two oxygen atoms of the second ligand, one oxygen atom of THF, and one iodide in a distorted pentagonal bipyramidal geometry. The trigonal-planar geometry around the C3 atom ($\Sigma$ = 360°) clearly indicates that the hydrogen on the C3 atom in **6** shifts to the N1 atom in **7**. The $Yb–O^{carboxylate}$ bond lengths (Yb–O1 2.413(2), Yb–O1(A) 2.482(2), and Yb–O2(A) 2.478(2) Å) are comparable with those observed in $(NHC^{Dipp}\text{-}CO_2)_3Yb(THF)_2$ ($NHC^{Dipp}$ =1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene).[21]

**Scheme 4** Reaction of **1** with $CO_2$



6 7

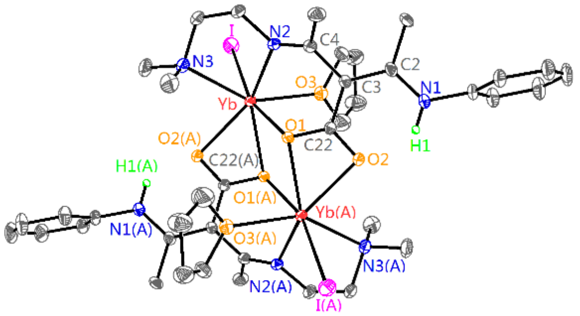


**Figure 8** Molecular structure of complex **7** with ellipsoids at 30% probability level. DIPP isopropyl groups and hydrogen atoms (except H1 and H1A) were omitted for clarity. Selected bond distances [Å] and angles [°]: Yb–N2 2.543(3), Yb–N3 2.586(4), Yb–I1 3.174(3), Yb–O1 2.413(2), Yb–O1(A) 2.482(2), Yb–O2 2.478(2), Yb–O3 2.448(3), C22–O1 1.289(4), C22–O2 1.268(4), C22–C3 1.463(5), N1–C2 1.347(5), C2–C3 1.394(5), C3–C4 1.483(4), C4–N2 1.289(5), O1–Yb–O1(A) 70.68(9), Yb–O1–Yb(A) 109.32(9), C2–C3–C4 119.6(3), C2–C3–C22 121.3(3), C4–C3–C22 119.1(3).

## Conclusions

Salt metathesis of $YbI_2(THF)_2$ with potassium salt (KL) (L = $[MeC(NDIPP)CHC(Me)NCH_2CH_2NMe_2]^-$, DIPP = 2,6-$(^iPr)_2C_6H_3$)) in THF at room temperature provides a divalent ytterbium iodide $[LYb(\mu\text{-}I)(THF)]_2$ (**1**) in high yield. Complex **1** easily undergoes redox reaction with trimethylsilyl azide to generate a trivalent ytterbium imido complex, which is instable and the imido ligand in it subsequently abstracts a hydrogen from the ligand L to give a trivalent ytterbium amido complex. In the reactions with azobenzene, sulfur and diphenyl disulfide, complex **1** also shows its reductivity and the reactions produce ytterbium(III) azobenzene, ytterbium (III) sulfide, and ytterbium(III) phenylsulfide, respectively. Complex **1** also reacts with $CO_2$, in this case the central carbon atom of β-diketiminato backbone in **1** nucleophilically attacks the $CO_2$ molecule to give a divalent ytterbium carboxylate.

## Experimental

### General Procedures

All manipulations were performed under an atmosphere of nitrogen using Schlenk techniques or in a nitrogen-filled glovebox. Toluene, THF, hexane, $C_6D_6$, and $d_8$-THF were dried over Na/K alloy, transferred under vacuum, and stored in the glovebox. Azobenzene, trimethylsilyl azide, and diphenyl disulphide were used as received. Elemental sulfur was purified by sublimation before use. $CO_2$ (99.9%) was further dried by passing through the activated 4 Å molecular sieves. $YbI_2(THF)_2$[22] was synthesized following a literature procedure. KL (L = $[MeC(NDipp)CHC(Me)NCH_2CH_2NMe_2]^-$) was synthesized similar to that of LiL but using KH instead of $^nBuLi$.[23] $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian 400 MHz, a Bruker 400 MHz or an Agilent 400 MHz spectrometer. Chemical shifts $\delta$ were reported in ppm with references to the residual resonance of the deuterated solvents for proton and carbon spectroscopies. IR spectra were recorded in KBr pellets on an ALPHA II FT-IR spectrometer. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

**$[LYb(\mu\text{-}I)(THF)]_2$ (1).** To a THF solution (2 mL) of $YbI_2(THF)_2$ (311 mg, 0.54 mmol) was added a THF solution (2 mL) of KL (200 mg, 0.54 mmol) at room temperature. The reaction was stirred for 1 hour, resulting in a deep brown solution with gray precipitates. After filtration, the solvent was removed under vacuum, and the residue was extracted with a mixture solution of toluene (18 mL) and THF (2 mL). The solvent of the extraction was removed under vacuum, and the residue was washed with hexane (2 mL × 3) and dried under vacuum to give **1** as a deep brown solid. Yield: 320 mg (84%). $^1H$ NMR (400 MHz, $d_8$-THF, 25 °C): $\delta$ 7.03 (d, $^3J_{H-H}$ = 6.8 Hz, 4H, *m*-Ar*H* of DIPP), 6.94 (t, $^3J_{H-H}$ = 6.8 Hz, 2H, *p*-Ar*H* of DIPP), 4.48 (s, 2H, MeC(N)C*H*), 3.62 (br, 8H, THF-*H*, overlapped with the residual solvent resonance of the deuterated solvent), 3.42 (br, 4H, $NCH_2$), 3.15 (m, 4H, $CHMe_2$), 2.65 (br, 4H, $NCH_2$), 2.36 (br, 12H, $NMe_2$), 1.84 (s, 6H, C*Me*), 1.77 (br, 8H, THF-*H*), 1.48 (s, 6H, C*Me*), 1.24 (d, $^3J_{H-H}$ = 6.0 Hz, 12H, $CHMe_2$), 1.09 (d, $^3J_{H-H}$ = 6.0 Hz, 12H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $d_8$-THF, 25 °C): $\delta$ (ppm) 165.7, 163.4 (imine *C*), 148.7 (*i*-Ar*C* of DIPP), 142.2 (*o*-Ar*C* of DIPP), 123.6 (*m*-Ar*C* of DIPP), 123.5 (*p*-Ar*C* of DIPP), 95.2 (MeC(N)*C*H), 68.0 (THF-*C*), 60.5, 48.3 ($NCH_2$), 45.7 ($NMe_2$), 28.1 ($CHMe_2$), 26.0, 25.1, 24.7, 22.8 ($CHMe_2$, C*Me* and THF-*C*). IR (KBr, $cm^{-1}$): *v* 3051 (m), 2956 (s), 2928 (s), 2864 (s), 2825 (s), 1624 (m), 1541 (s), 1517 (s), 1460 (s), 1414 (s), 1379 (s), 1364 (s), 1344 (s), 1312 (s), 1265 (s), 1248 (s), 1228 (s), 1174 (s), 1094 (s), 1027 (s), 933 (s), 876 (s), 786 (s), 758 (s). Anal. Calcd for $C_{50}H_{84}I_2N_6O_2Yb_2$ (**1**): C, 42.86; H, 6.04; N, 6.00. Found: C, 42.54; H, 5.87; N, 6.07.

**$LYbI(NHSiMe_3)$ (2).** To a toluene solution (10 mL) of **1** (1150 mg, 0.82 mmol) was added a toluene solution (1 mL) of trimethylsilyl azide (98 mg, 0.85 mmol) at room temperature. After stirring for 30 minutes, the solvent was removed under vacuum, and the residue was extracted with hexane (4 mL × 3). The solvent of the extraction was removed under vacuum affording product **2** as an orange solid. Yield: 488 mg (42% yield based on Yb). $^1$H NMR (400 MHz, $C_6D_6$, 25 $^oC$): $\delta$ 34.46, 22.15, 18.22, 17.16, 11.67, 4.82, 3.24, 2.49, 2.00, -0.84, -4.78, -18.63, -19.81, -27.52, -28.06, -32.95, -37.93. The paramagnetism of complex **2** prevents meaningful NMR signal assignment. IR (KBr, cm$^{-1}$): $v$ 2955 (s), 2891 (m), 1532 (s), 1460 (s), 1437 (s), 1395 (s), 1343 (s), 1314 (s), 1254 (s), 1239 (s), 1178 (m), 1096 (m), 1019 (s), 939 (m), 892 (s), 825 (m). Anal. Calcd for $C_{24}H_{44}IN_4SiYb$ (**2**): C, 40.22; H, 6.19; N, 7.82. Found: C, 40.62; H, 6.16; N, 7.66.

The residue of the extraction was also dried under vacuum to give an orange solid (529 mg). Its $^1$H NMR spectrum was recorded in $d_8$-THF, but the signals are too broad to provide useful information. The toluene (1 mL) suspension of the residue (91 mg) was treated with 0.05 mL of $D_2O$, resulting in a color changing of the suspension to pale yellow. The solvent was removed under vacuum, and the residue was divided into two parts. One was extracted with 1 mL of $C_6D_6$ and recorded by $^1$H NMR spectroscopy, the other part was extracted with 1 mL of $C_6H_6$ and recorded by $^2$H NMR spectroscopy. The $^1$H and $^2$H NMR spectroscopy study indicated the C–H activation of methyl group in monoanionic ligand L to form a dianionic ligand $[MeC(NDIPP)CHC(=CH_2)NCH_2CH_2NMe_2]^{2-}$.

**LYbI(PhNNPh) (3).** To a benzene solution (2 mL) of **1** (141 mg, 0.10 mmol) was added a benzene solution (1 mL) of azobenzene (36 mg, 0.20 mmol) at room temperature. After stirring for 30 minutes, the solvent was removed under vacuum. The residue was washed with hexane (2 mL) and dried under vacuum to give **3**·$C_6H_6$ as a blue solid. Yield: 156 mg (88%). The complex is paramagnetic. $^1$H NMR (400 MHz, $C_6D_6$, 25 $^oC$): $\delta$ 67.47, 60.41, 54.96, 47.12, 28.14, 27.20, 18.84, 16.22, 12.92, 11.24, 8.02, 6.11, 4.15, 2.49, -1.53, -1.94, -5.07, -9.99, -12.77, -13.40, -15.46, -162.34, -170.56. IR (KBr, cm$^{-1}$): $v$ 3052 (w), 2960 (s), 2925 (m), 2864 (m), 1521 (s), 1475 (s), 1458 (s), 1439 (s), 1395 (s), 1341 (s), 1314 (s), 1254 (m), 1177 (m), 1097 (m), 1019 (s), 936 (m), 792 (m), 758 (s), 675 (s). Anal. Calcd for $C_{39}H_{50}IN_5Yb$ (**3**·$C_6H_6$): C, 52.70; H, 5.67; N, 7.88. Found: C, 53.01; H, 5.98; N, 7.80.

**[LYbI]$_2$($\mu$-S) (4).** To a benzene solution (2 mL) of **1** (140 mg, 0.10 mmol) was added a benzene solution (1 mL) of sulfur (3.2 mg, 0.013 mmol) at room temperature. After 40 minutes, the volatiles of the reaction solution were removed under vacuum, and complex **4**·$C_6H_6$ was obtained as a red solid. Yield: 119 mg (87%). The complex is paramagnetic. $^1$H NMR (400 MHz, $C_6D_6$, 25 $^oC$): $\delta$ 93.65, 73.95, 69.11, 52.60, 33.44, 28.67, 23.68, 21.42, 21.39, 11.80, 11.52, 10.35, 8.84, 7.85, 3.51, 2.45, 1.65, 1.22, -2.38, -8.06, -11.78, -12.45, -18.81, -21.76, -23.79, -24.34, -25.04, -29.05, -29.68, -30.89, -35.85, -40.24, -43.46, -55.52. IR (KBr, cm$^{-1}$): $v$ 3057 (w), 2960 (s), 2924 (m), 2867 (m), 1626 (m), 1525 (s), 1459 (s), 1437 (s), 1391 (s), 1340 (s), 1317 (m), 1253 (m), 1177 (m), 1098 (m), 1017 (m), 936 (m), 843 (w), 783 (m), 760 (m). Anal. Calcd for $C_{48}H_{74}I_2N_6SYb_2$ (**4**·$C_6H_6$): C, 42.17; H, 5.46; N, 6.15. Found: C, 42.63; H, 5.43; N, 6.03.

**[LYbI($\mu$-SPh)]$_2$ (5).** To a benzene solution (2 mL) of **1** (140 mg, 0.10 mmol) was added a benzene solution (1 mL) of diphenyl disulphide (22 mg, 0.10 mmol) at room temperature. After 30 minutes, the precipitate was collected, washed with benzene (2 mL), and dried under vacuum to afford **5**·$C_6H_6$ as a red solid. Yield: 138 mg (89%). The complex is paramagnetic. $^1$H NMR (400 MHz, $C_6D_6$, 25 $^oC$): $\delta$ 32.62, 19.09, 17.36, 13.83, 11.98, 11.32, 8.58, 7.35, 6.82, 6.81, 5.83, 5.03, 4.67, 3.44, 1.61, 0.58, -0.09, -0.56, -4.03, -5.60, -9.01, -9.82, -12.69, -13.83, -17.96, -50.24, -63.78. IR (KBr, cm$^{-1}$): $v$ 3056 (w), 2957 (s), 2923 (m), 2865 (m), 1580 (w), 1525 (s), 1436 (s), 1390 (s), 1340 (s), 1314 (m), 1250 (m), 1177 (m), 1098 (m), 1020 (m), 934 (m), 790 (m), 762 (m), 739 (m), 692 (m). Anal. Calcd for $C_{60}H_{84}I_2N_6S_2Yb_2$ (**5**·$C_6H_6$): C, 46.39; H, 5.45; N, 5.41. Found: C, 45.92; H, 5.48; N, 5.02.

**[{MeC(NDIPP)CH(CO$_2$)C(Me)NCH$_2$CH$_2$NMe$_2$}Yb($\mu$-I)]$_2$ (6) and [{MeC(NHDIPP)C(CO$_2$)C(Me)NCH$_2$CH$_2$NMe$_2$}YbI(THF)]$_2$ (7).** A toluene solution (5 mL) of **1** (370 mg, 0.53 mmol) was placed in a tube with a Teflon stopcock. The tube was taken out of the glovebox and connected to a Schlenk line. The solution of **1** was degassed at low temperature, and then exposed to 1.0 atm of $CO_2$ at room temperature. After stirring for 1 hour, the volatiles were removed under vacuum, and the residue was washed with hexane (2 mL × 3), dried under vacuum to afford **6** as a dark red solid. Yield: 322 mg (91%). $^1$H NMR (400 MHz, $C_6D_6$, 25 $^oC$): $\delta$ 7.16 (m, 6H, Ar*H* of DIPP, overlapped with the residual solvent resonance of the deuterated solvent), 5.05 (s, 2H, MeC(N)C*H*), 3.24 (m, 6H, C*H*Me$_2$ and NC*H*$_2$), 2.93 (m, 2H, NC*H*$_2$), 2.68 (s, 6H, N*Me*$_2$), 2.39 (m, 8H, N*Me*$_2$ and NC*H*$_2$), 2.15 (s, 6H, C*Me*), 1.96 (s, 6H, C*Me*), 1.72 (m, 2H, NC*H*$_2$), 1.43 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH*Me*$_2$), 1.22 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$, 25 $^oC$): $\delta$ (ppm) 179.1 (imine *C*), 178.4 (O*C*O), 167.9 (imine *C*), 146.6 (*i*-Ar*C* of DIPP), 136.74, 136.66 (*o*-Ar*C* of DIPP), 124.1 (*p*-Ar*C* of DIPP), 123.4, 123.2 (*m*-Ar*C* of DIPP), 70.4 (MeC(N)*C*H), 59.3 (N*C*H$_2$), 49.2 (N*Me*$_2$), 48.9 (N*C*H$_2$), 44.7 (N*Me*$_2$), 28.2, 28.0 (*C*HMe$_2$), 23.9, 23.4, 22.5 (CH*Me*$_2$), 22.3, 21.0 (C*Me*). IR (KBr, cm$^{-1}$): $v$ 3061 (w), 2963 (s), 2868 (m), 2834 (m), 2790 (m), 1665 (m), 1630 (s), 1580 (s), 1466 (s), 1397 (s), 1364 (m), 1232 (m), 1170 (m), 1019 (m), 934 (m), 780 (m), 760 (m). Anal. Calcd for $C_{22}H_{34}IN_3O_2Yb$ (**6**): C, 39.29; H, 5.10; N, 6.25. Found: C, 39.28; H, 5.22; N, 6.04. Complex **7** was isolated as dark red crystals, when complex **6** (103 mg, 0.15 mmol) was dissolved in 1 mL of THF and stood at -35 $^oC$. Yield: 78 mg (69%). The NMR spectra of complex **7** were not obtained due to its poor solubility in the deuterated organic solvents, even in the $d_8$-THF, the solubility of **7** is very low. IR (KBr, cm$^{-1}$): $v$ 3064 (w), 2963 (s), 2869 (m), 2831 (m), 2721 (w), 1593 (s), 1571 (s), 1522 (s), 1459 (s), 1421 (s), 1361 (s), 1301 (s), 1258 (s), 1183 (m), 1101 (m), 1043 (m), 930 (m), 808 (m), 770 (m). Anal. Calcd for $C_{52}H_{84}I_2N_6O_6Yb_2$ (**7**): C, 41.94; H, 5.69; N, 5.64. Found: C, 42.06; H, 5.95; N, 5.64.

### Magnetic Characterization.

The polycrystalline sample was stuffed in capsules with parafilm covered to protect them from air and water. Direct current (dc) magnetism of poly crystals were performed on a Quantum Design MPMS3 magnetometer (VSM module). Capsule, parafilm and molecule formula (Pascal constant)[24] were considered when the diamagnetic correction was carried on the data.

### X-ray Crystallography

Single crystals of **1** suitable for single-crystal X-ray diffraction were grown from a mixture solution of toluene and THF, those of **2** were from a hexane solution, those of **3** were from a mixture solution of benzene and hexane, those of **4** were from a mixture solution of toluene and benzene, those of **5** were from toluene, and those of **7** were from a mixture solution of THF and hexamethyl disiloxane.[25] The crystals were mounted under a nitrogen atmosphere on a glass fiber. Data collection of **1** and **2** were performed on a Bruker APEX-II CCD with Ga K$\alpha$ radiation ($\lambda$ = 1.34139 Å), those of **3**, **4**, **5**, and **7** were performed on a Bruker D8 Venture with Ga K$\alpha$ radiation ($\lambda$ = 1.34139 Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS program.[26] All 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. Calculations were carried out using the SHELXL-97, SHELXL-2014 or Olex2 program.[27] Crystallographic data and refinement parameters are listed in Table S1.

## Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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# Entry for the Table of Contents

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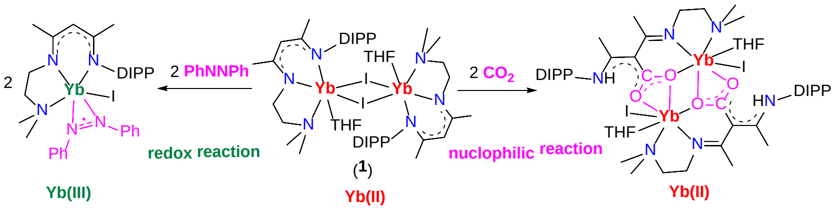
**Divalent Ytterbium Iodide Supported by β-Diketiminato Based Tridentate Ligand: Synthesis, Structure and Small Molecule Activation**



Divalent ytterbium iodide $[LYb(\mu\text{-}I)(THF)]_2$ (**1**; L = $[MeC(NDIPP)CHC(Me)NCH_2CH_2NMe_2]^-$, DIPP = 2,6-$(^iPr)_2C_6H_3$) was synthesized. This complex easily undergoes redox reactions with trimethylsilyl azide, azobenzene, sulfur and diphenyl disulfide and nucleophilic reaction with $CO_2$.

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