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Rare-earth metal complexes having an unusual indolyl-1,2-dianion through C–H activation with a novel η^1:(μ_2–η^1:η^1) bonding with metals†

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Studies on the reactions of 3-(*tert*-butyliminomethine)indole or 3-(*tert*-butylaminomethylene)indole with rare-earth metal amides [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ (RE = Y, Yb) led to the discovery of different reactivity patterns with isolation of novel rare-earth metal complexes having a unique indolyl-1,2-dianion in a novel η^1:(μ_2–η^1:η^1) bonding mode through C–H activation.

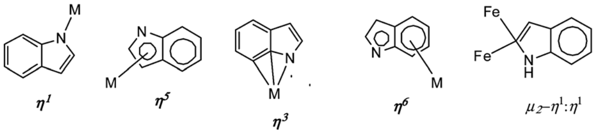

Fig. 1 The reported bonding mode of an indolyl ligand with transition metals.

Functionalization of heterocyclic compounds through C–H bond cleavage is a concerted research effort not only for the reasons that the heterocyclic frameworks have been widely accepted as a pivotal structure in numerous natural products and pharmaceutical agents, but also for the reasons that the C–H and C–N bond activation may be important processes in the removal of heterocyclic compounds-containing impurities from fuels.[1] The C–H bond activation initiated by rare-earth metal complexes can be classified as the following. (1) Rare-earth metal aluminum mixed metal complexes initiated C–H activation leading to isolation of the novel methylene or methine bridged lanthanide–aluminum metal clusters or aluminum-free rare-earth metal clusters.[2] (2) Reactions of rare-earth metal alkyls (for example [RE(CH$_2$SiMe$_3$)$_3$(thf)$_x$] or hydrides with suitable ligands afforded new kinds of the C–H bond activation rare-earth metal complexes.[3] (3) Reactions of structurally well-defined cyclopentadienyl or cyclopentadienyl-free ligands supported rare-earth metal alkyl complexes with aromatic compounds produced the sp^2 or sp^3 C–H bond activation complexes, of these, reactions of chelating ferrocene–diamido rare-earth metal complexes with *N*-heterocyclic compounds are noticeable, that led to not only C–H bond activation, but also to the C–C coupling and ring-opening which may be potentially applicable in decomposition of nitrogen-containing impurities from fuels.[4] (4) C–H bond activation initiated by well-defined rare-earth metal amido complexes that is relatively less documented.[5] (5) Very recently, rare-earth metal imido complexes that initiated C–H activation were reported to display a new kind of reactivity of rare-earth metal complexes.[6]

To the best of our knowledge, the only reported mono-anion indolyl ligands have been found to bind with transition metal in an η^1-mode through the nitrogen atom,[7a] an η^3-fashion *via* the nitrogen atom and the fused carbons of the indolyl ring,[7a] an η^5-manner through the five-membered heterocyclic ring,[7b] an η^6-mode through the benzo ring,[7c] and a μ_2–η^1:η^1 bonding mode with iron[7d] (see Fig. 1). Rare-earth metal complexes supported by functionalized indolyl ligands displayed activities in olefin polymerization in the presence of aluminum alkyl cocatalyst.[8] All of the reported indolyl complexes to date incorporated indolyl mono-anions, the indolyl-1,2-dianion and its bonding mode with transition metals remain to be reported (Fig. 3).

Herein, we will report the first example of novel tetranuclear rare-earth metal complexes incorporating a unique indolyl-1,2-dianion ligand having an unusual η^1:(μ_2–η^1:η^1) bonding mode with metals through imino-directed C–H bond activation initiated by rare-earth metal amido complexes (Fig. 2 and 3).

Reactions of [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ (RE = Y, Yb) with 1.5 equivalents of 3-(*tert*-butyliminomethine)indole (3-(*t*-Bu–N=CH)C$_8$H$_5$NH) in toluene at 110 °C produced the tetranuclear complexes {[η^1:(μ_2–η^1:η^1):η^1-3-(*t*-BuN=CH)-C$_8$H$_4$N]RE$^{III}{}_2$(μ_2-Cl)$_2$(THF)[N(SiMe$_3$)$_2$](η^1:η^1-[μ–η^5:η^2-3-(*t*-Bu-N=CH)C$_8$H$_5$N]$_2$Li)}$_2$ (RE = Y(**1**), Yb (**2**)) (Scheme 1, route 1, Fig. 2 and 3) having a rare indolyl-1,2-dianion ligand in an unusual η^1:(μ_2–η^1:η^1) bonding mode with rare-earth metals in good yields. The complexes were characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy as well as X-ray analyses. They are air and moisture sensitive, but stable in an inert atmosphere for months. They are soluble in polar solvents and toluene.

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† Electronic supplementary information (ESI) available: Experimental details, characterization data for new compounds, scheme for preparation of **4** and **5**, figures for structures of complexes **1–7**. CCDC 842358–842362 (**1–5**), 896822 (**6**), and 896821 (**7**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc36045d

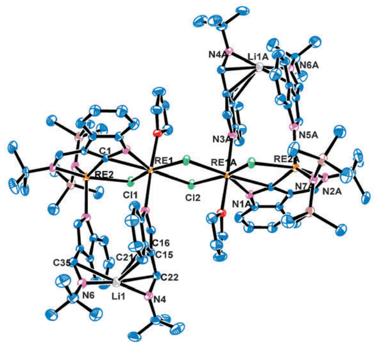


Fig. 2 Representative molecular structure of complexes **1** and **2**.

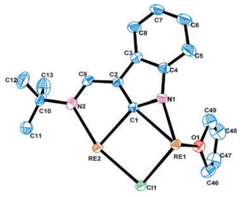
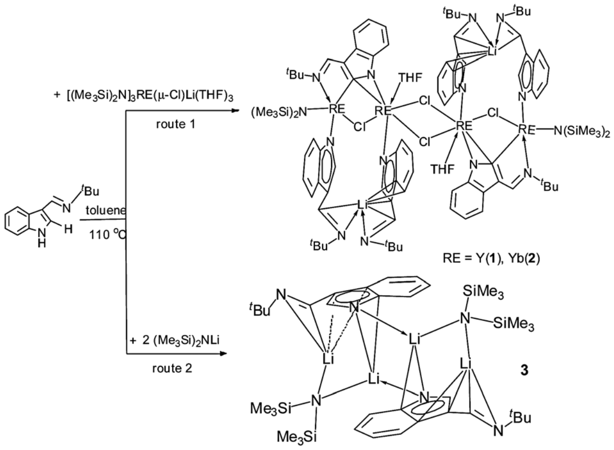


Fig. 3 The bonding of the unique indolyl 1,2-dianion with metals in complexes **1** and **2**.



Scheme 1 Reactions of 3-(*tert*-butyliminomethine)indole with rare-earth metal amides and lithium amide.

Solid state structural analyses revealed that complexes **1** and **2** are centrosymmetric dimeric clusters consisted of four rare-earth metal ions and two lithium ions supported by four imino-substituted indolyl monoanions coordinated to rare-earth metals in an η^1 mode through an indolyl nitrogen atom, two amido ligands $N(SiMe_3)_2$, and two unique imino-substituted indolyl-1,2-dianions having a novel η^1:(μ_2-η^1:η^1) bonding with metals as indicated in Fig. 3. The formation of the unique indolyl 1,2-dianion clearly indicates that an sp^2 C–H activation occurred.

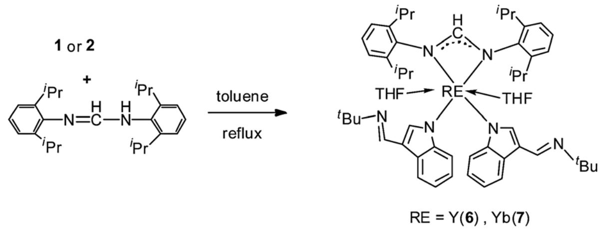
The Y–C(1) bond lengths of 2.551(8) Å and 2.665(8) Å in complex **1** are comparable to the Yb–C(1) bond lengths of 2.506(12) Å and 2.654(10) Å found in complex **2** taking into account the ionic radii difference between the yttrium and ytterbium ions.[9] Although Ln–C(1) distances in complexes **1** and **2** are significantly longer than the values reported for related compounds $[Y(CH_2SiMe_3)_3(THF)_2]$ (2.427(19) Å),[10] $[Ap'_2YCH_2SiMe_3(thf)]$ (Ap'_2 = 2, 6 − (diisopropylphenyl)[6-(2,6-dimethylphenyl)pyridin-2-yl]amido (2.342(5) Å),[11] [[*t*-BuC$_6$H$_3$-(CH═N)C$_6$H$_3$-*i*-Pr$_2$]$_2$YCH$_2$SiMe$_2$Ph] (2.384(2) Å),[11] [O{(CH$_2$)$_2$-C$_9$H$_6$}$_2$YCH$_2$SiMe$_3$] (2.376(8), 2.35 (1) Å),[11] [Ln(CH$_2$SiMe$_3$)$_3$-(NHC)] (2.363(2), 2.355(2), 2.345(2) Å, NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[11] and those found in σ-boryl ligand supported rare-earth metal alkyls,[12] the RE–C(1) distances found in **1** and **2** can still be comparable to those of Ln–C(1) (carbene carbon) distances,[13] and the Y–C distances (av. 2.61 Å) in bridging methyl ligands in eight-coordinate [(1,3-Me$_2$C$_5$H$_3$)$_2$Y-(μ-Me)]$_2$.[14] Comparing bond distances of Li(1)–N(4) (2.010(2) Å), Li(1)–C(22) (2.530(2) Å), Li(1)–C(15) (2.550(2) Å), Li(1)–C(16) 2.560(2) Å), Li(1)–C(21) (2.600(2) Å), and Li(1)–N(6) (1.990(2) Å), Li(1)–C(35) (2.610(2) Å), Li(1)–C(28) (2.760(2) Å), Li(1)–C(29) (2.740(2) Å), Li(1)–C(34) (2.670(2) Å) with those of Li to C$_5$ ring distances found in CpLi(solvent)$_x$ and IndLi(solvent)$_x$ (here ind = indenyl),[15] the bonding between lithium and indolyl ligands can be best described as η^5:η^2 mode.

When the 3-(*tert*-butyliminomethine)indole 3-(*t*-BuN═CH)-C$_8$H$_5$NH was reacted with excess lithium amide LiN(SiMe$_3$)$_2$ (2 equivalents), the dimeric lithium product {η^4:η^2:η^1-3-(*t*-BuN═CH)C$_8$H$_5$NLi$_2$[N(SiMe$_3$)$_2$]}$_2$ (**3**) (Scheme 1, route 2, Fig. S3 (ESI†)) was isolated and characterized, no C–H bond activation product was observed. This result suggested that the formation of the unique indolyl 1,2-dianion is not due to the decomposition of the [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ to LiN(SiMe$_3$)$_2$, which is then responsible for the C–H bond cleavage, but the rare-earth metal amides [(Me$_3$Si)$_2$N]$_3$RE^{III}-(μ-Cl)Li(THF)$_3$ would be responsible for the C–H bond activation. The bonding of the ligand 3-(*t*-Bu–N═CH)C$_8$H$_5$N with metal found in **3** also represents the first example of (η^4:η^2:η^1) bonding mode of indolyl ligands to be reported by comparing the lithium to indolyl ring distances with those of Li to C$_5$ ring distances found in CpLi(solvent)$_x$ and IndLi(solvent)$_x$.[15]

On the basis of these results, the formation of the unique indolyl-1,2-dianion may first go through silylamine elimination to give the indole deprotonated intermediate, which then coordinated to [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ with subsequent C–H activation/cyclometallation affording the intermediate with the unique indolyl-1,2-dianion having unusual η^1:(μ_2–η^1:η^1) bonding with metals, further reactions with rare-earth metal amides followed by reassembly produced the final products (see Scheme S1, ESI†).

Further experiments reveal that reactions of rare-earth metal amides [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ with 3-(*tert*-butylaminomethylene)indole 3-(*t*-BuNHCH$_2$)C$_8$H$_5$NH produced, after workup, the only indole deprotonated complexes [μ-{[η^1:η^1:η^1:η^1-3-(*t*-BuNHCH$_2$)Ind]$_2$Li}RE[N(SiMe$_3$)$_2$]$_2$] (RE = Y(**4**), Yb(**5**)), even the protons on the amino groups have not been removed. No C–H bond activation was observed (see Scheme S2 and Fig. S4 and S5 for the structures of complexes **4** and **5** in ESI†), and the indolyl ligand bonded with the rare-earth metal through nitrogen in an η^1 mode. These results are completely different to those results indicated in Scheme 1 (route 1), the results suggested that substituents on the indolyl ring have a great influence on the reactivity of the indoles with the rare-earth metal amides and the bonding of the indolyl ligands with the rare-earth metals.

Experiments for study on the reactivity of the complexes **1** and **2** with amidine (2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH–NH(2,6-^{i}Pr$_2$C$_6$H$_3$)



Scheme 2 Reactivity of complexes having indolyl-1,2-dianion.

afforded the complexes having an *N*-coordinated indolyl ligand and the corresponding amidinate ligand $[(2,6\text{-}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N})_2\mathrm{CH}]^-$ (Scheme 2, Fig. S6 and S7 (ESI†)). The results indicated that a carbon anion in the indolyl-1,2-dianion abstracted the proton from the pro-ligand amidine, as a result, the indolyl-1,2-dianion was transferred to a normal indolyl anion and the amidine was transferred to an amidinate ligand to form the final complexes **6** and **7**, indicating that the carbon anion is more reactive than the indolyl nitrogen anion.

In summary, reactivity studies between 3-(*tert*-butyliminomethine)indole or 3-(*tert*-butylaminomethylene)indole and rare-earth metal amides have led to the discovery of different reaction patterns with isolation of novel rare-earth metal complexes $\{[\eta^1{:}(\mu_2\text{–}\eta^1{:}\eta^1){:}\eta^1\text{-}3\text{-}(t\text{-BuN{=}CH})\mathrm{C_8H_4N}]\mathrm{RE}^{\mathrm{III}}{}_2(\mu_2\text{-Cl})_2(\mathrm{THF})\text{-}[\mathrm{N(SiMe_3)_2}](\eta^1{:}\eta^1\text{-}[\mu\text{–}\eta^5{:}\eta^2\text{-}3\text{-}(t\text{-BuN{=}CH})\mathrm{C_8H_5N}]_2\mathrm{Li}\}_2$ incorporating an unusual indolyl 1,2-dianion in a novel $\eta^1{:}(\mu_2\text{-}\eta^1{:}\eta^1)$ bonding mode through C–H activation. The results suggested that substituents on the indole ring have a great influence on the reactivity patterns of indoles with rare-earth metal amides. Further study on the reactivity of substituted indole with rare-earth metal amides is now in progress.

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