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Salt metathesis reactions of $LnCl_3$ (Sc, Y *vs.* Sm, Yb) with potassium diphenylmethanide $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]K(THF)\}_2$

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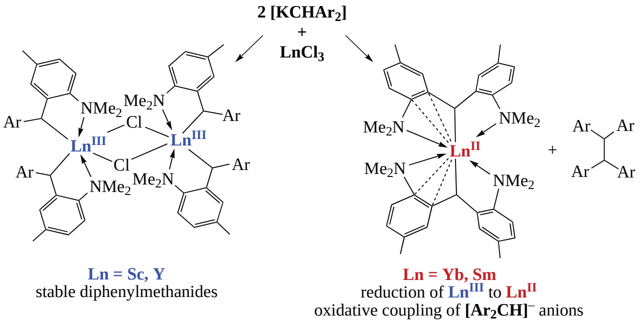
The outcome of salt metathesis reactions between the equimolar amounts of $LnCl_3$ and dimeric potassium diphenylmethanide $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]K(THF)\}_2$ depends on the rare-earth metal ion. In the case of Sc^{III} and Y^{III}, the reactions afford chlorido-bis(diphenylmethanido) complexes $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ln^{III}(\mu\text{-}Cl)\}_2$, in which the diphenylmethanido ligands perform bidentate κ^2-CN coordination according to the X-ray data. For Yb^{III} and Sm^{III}, these reactions result in the spontaneous reduction of Ln^{III} to Ln^{II} and the formation of known bis(diphenylmethanido) complexes $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ln^{II}$ and the product of oxidative coupling of diphenylmethanido anions.



Keywords: rare-earth metals, diphenylmethanides, synthesis, structure, oxidative coupling.

Highly reactive rare-earth metal alkyl complexes have attracted attention due to their unique reactivity.[1] However, the development of this area of organometallic chemistry was slowed down by difficulties in the stabilization of coordination spheres of large[2] and electropositive[3] rare-earth ions whose σ-bonded alkyl derivatives are prone to the intramolecular reactions of β-hydrogen elimination or β-hydrogen abstraction of hydrocarbyl ligands.[4] The kinetic stabilization and synthesis of isolable and thermally stable rare-earth alkyl species can be reached due to the coordination and steric saturation of the coordination sphere of a metal ion and the selection of appropriate alkyl ligands. This problem can be solved by the application of bulky hydrocarbyl ligands with no β-hydrogen atoms [CH_2SiMe_3,[5] $CH(SiMe_3)_2$,[6] and CH_2Ph][7] or with pendant Lewis base groups capable of coordinating to the metal center [$C(SiMe_3)_2(SiMe_2OMe)$,[6(*a*)] *o*-$Me_2NC_6H_4CH_2$,[8] bis(phosphinimino)methanide,[9] and bis(pyrazolyl)methanide[10]].

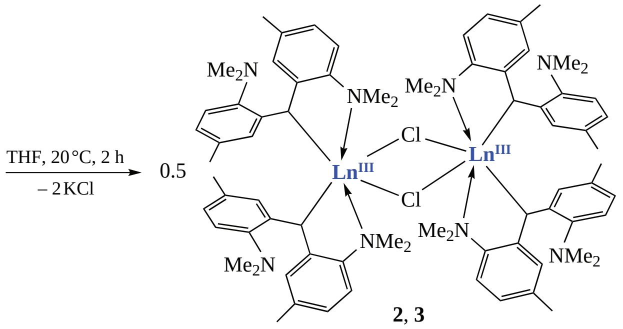
The diphenylmethanido anion is a suitable coordination environment, which can provide the synthesis of isolable rare-earth hydrocarbyl complexes due to the absence of β-H atoms along with negative charge delocalization within the conjugated π-system and the accessibility of non-covalent metal–arene interactions. Until recently, only one example of Ln^{III} diphenylmethanides, $Lu^{III}(CH_2SiMe_3)_2(CHPh_2)(THF)_2$, was known.[11] Then, it was demonstrated that the modification of a diphenylmethanido skeleton by the introduction of Bu^t substituents into the *para*-positions of phenyl rings[12] or by the addition of NMe_2 groups in the *ortho*-positions[13] resulted in the synthesis of thermally robust Ln^{II} (Yb, Sm) diphenylmethanides. The $[NC_{sp^3}N]$-pincer type diphenylmethanido ligand with pendant imidazolyl substituents in the *ortho*-positions of the diphenylmethane skeleton was also suitable for the preparation of heteroleptic Ln^{III} (Sc, Y) alkyl-diphenylmethanido derivatives.[14]

Here, we report on the synthesis and structures of chlorido-bis(diphenylmethanido) complexes of Sc^{III} and Y^{III} containing bidentate κ^2-CN $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^-$ ligands and on the spontaneous reduction of Ln^{III} to Ln^{II} in the course of the salt metathesis reactions of potassium diphenylmethanide with $LnCl_3$ (Ln = Yb, Sm).

To synthesize diphenylmethanido derivatives of Ln^{III}, we carried out salt metathesis reactions of anhydrous $LnCl_3$

$\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]K(THF)\}_2 + LnCl_3$

1 Ln = Sc, Y



2, 3

2 Ln = Sc, 75%
3 Ln = Y, 88%

Scheme 1

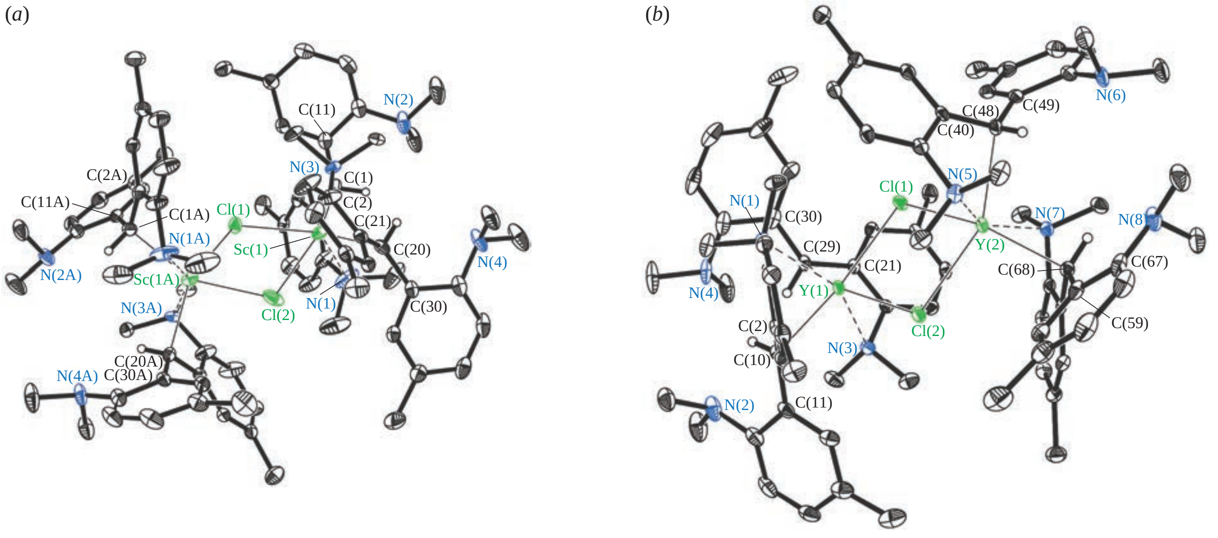


Figure 1 (*a*) Molecular structure of $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Sc(\mu\text{-}Cl)\}_2$ **2**. Selected bond distances (Å): Sc(1)−C(20) 2.304(3), Sc(1)−C(1) 2.316(4), Sc(1)−N(1) 2.395(3), Sc(1)−N(3) 2.481(8), Sc(1)−Cl(2) 2.585(2), Sc(1)−Cl(1) 2.674(2), and Sc(1)−Sc(1A) 4.090(2). (*b*) Molecular structure of $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Y(\mu\text{-}Cl)\}_2$ **3**. Selected bond distances (Å): Y(1)−C(10) 2.446(6), Y(1)−C(29) 2.457(6), Y(2)−C(48) 2.435(6), Y(2)−C(67) 2.463(6), Y(1)−N(3) 2.506(5), Y(1)−N(1) 2.527(4), Y(1)−Cl(1) 2.696(2), Y(1)−Cl(2) 2.736(2), Y(2)−N(7) 2.501(5), Y(2)−N(5) 2.519(5), Y(2)−Cl(1) 2.714(2), Y(2)−Cl(2) 2.715(2).Thermal ellipsoids are given with a 30% probability. Hydrogen atoms (except for diphenylmethanido CH) are omitted for clarity.

(Ln = Sc, Y) with dimeric potassium diphenylmethanide $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]K(THF)\}_2$[15] **1** in THF at ambient temperature for 2 h (Scheme 1). The reactions afforded chlorido-bis(diphenylmethanido) complexes $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ln^{III}(\mu\text{-}Cl)\}_2$ [Ln = Sc (**2**), Y (**3**)]. After the separation of KCl and recrystallization of reaction products from a THF/hexane mixture, complexes **2** and **3** were isolated as bright yellow crystals in 75 and 88% yields, respectively. Note that the use of excess **1** (1.5 equiv.) in the reactions with $ScCl_3$ and YCl_3 did not allow us to substitute the third chlorido ligand most likely due to steric factors.

The molecular structures of complexes **2** and **3** (Figure 1) were determined by X-ray diffraction analysis† (Table S1, Online Supplementary Materials). Complexes **2** and **3** have dimeric structures where two rare-earth metal ions are bonded by two μ^2-bridging chlorido ligands [Ln−Cl: 2.585(2)–2.674(2) Å, **2**; 2.696(2)–2.736(2) Å, **3**; Ln···Ln: 4.090(2) Å, **2**; and 4.267(2) Å, **3**]. Unlike recently synthesized Ln^{II} bis(diphenylmethanides) $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ln^{II}$ [Ln = Yb (**4**), Sm (**5**)],[13] in which diphenylmethanido ligands $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]$ have a tridentate $[NC_{sp^3}N]$-pincer coordination, only one NMe_2 group of each ligand in Ln^{III} complexes **2** and **3** coordinates to the rare-earth metal ion, while the second one is drifted away from the metal center. The bidentate coordination of the $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^-$ carbanion to rare-earth metal ions in **2** and **3** occurs due to covalent Ln−C and coordination Ln−N bonds similarly to the $[o\text{-}Me_2NC_6H_4CH_2]^-$ ligand. Note that, unlike complexes **4** and **5**, no short contacts between the *ipso*- and *ortho*-carbon atoms of phenyl rings within five-membered LnCCCN metallacycles were detected in **2** and **3**. Thus, the coordination mode of the diphenylmethanido ligands $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^-$ in Ln^{III} complexes **2** and **3** can be classified as κ^2-CN.

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† *Crystal data for* **2**. $C_{76}H_{100}Cl_2N_8Sc_2$, *M* = 1286.48, monoclinic, space group *C*2/*c*, 100 K, *a* = 13.8079(6), *b* = 24.4696(12) and *c* = 21.6657(9) Å, β = 92.397(4)°, *Z* = 4, *V* = 7155.0(6) Å^3, d_{calc} = 1.194 g cm^{-3}, F_{000} = 2752. A yellow prism-shaped single crystal with dimensions of 0.26 × 0.21 × 0.14 mm was selected, and the intensities of 49325 reflections were measured using a Rigaku OD Xcalibur diffractometer (ω-scans technique, $\lambda[\mathrm{Mo}K_\alpha]$ = 0.71073 Å, μ = 0.311 mm^{-1}, $2\theta_{max}$ = 50.06°). After merging of equivalents and absorption corrections, 6318 independent reflections (R_{int} = 0.0818) were used for the structure solution and refinement. Final *R* factors: R_1 = 0.0620 [4335 reflections with $I > 2\sigma(I)$], wR_2 = 0.1593 (all reflections), GOF = 1.022.

Crystal data for **3**. $C_{76}H_{100}Cl_2N_8Y_2 \cdot C_4H_8O$, *M* = 1446.46, monoclinic, space group *Pn*, 100 K, *a* = 16.5565(8), *b* = 12.9744(6) and *c* = 17.9722(8) Å, β = 100.3570(10)°, *Z* = 2, *V* = 3797.7(3) Å^3, d_{calc} = 1.265 g cm^{-3}, F_{000} = 1528. A yellow prism-shaped single crystal with dimensions of 0.40 × 0.20 × 0.15 mm was selected, and the intensities of 39798 reflections were measured using a Bruker Smart Apex diffractometer (ω-scans technique, $\lambda[\mathrm{Mo}K_\alpha]$ = 0.71073 Å, μ = 1.640 mm^{-1}, $2\theta_{max}$ = 57.40°). After merging of equivalents and absorption corrections, 19206 independent reflections (R_{int} = 0.0397) were used for the structure solution and refinement. Final *R* factors: R_1 = 0.0527 [15618 reflections with $I > 2\sigma(I)$], wR_2 = 0.1224 (all reflections), GOF = 1.027.

Crystal data for **6**. $C_{38}H_{50}N_4$, *M* = 562.82, triclinic, space group $P\bar{1}$, 298 K, *a* = 9.7599(5), *b* = 9.8086(5) and *c* = 19.7235(10) Å, α = 99.649(2)°, β = 96.827(2)°, γ = 107.339(2)°, *Z* = 2, *V* = 1748.02(16) Å^3, d_{calc} = 1.069 g cm^{-3}, F_{000} = 612. A yellow prism-shaped single crystal with dimensions of 0.16 × 0.14 × 0.05 mm was selected, and the intensities of 20099 reflections were measured using a Bruker D8 Quest diffractometer (ω-scans technique, $\lambda[\mathrm{Mo}K_\alpha]$ = 0.71073 Å, μ = 0.063 mm^{-1}, $2\theta_{max}$ = 50.22°). After merging of equivalents and absorption corrections, 5871 independent reflections (R_{int} = 0.0533) were used for the structure solution and refinement. Final *R* factors: R_1 = 0.0846 [3422 reflections with $I > 2\sigma(I)$], wR_2 = 0.1617 (all reflections), GOF = 1.084.

The X-ray diffraction data for **2**, **3** and **6** were collected using the CrysAlis^{Pro} (ref. 22) and APEX3[23] software packages. The structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELX[24] and SADABS[25] and scaling algorithms implemented in CrysAlis^{Pro} were used to perform area-detector scaling and absorption corrections. Structure of **3** was refined as two-component inversion twin with a domain ratio of 0.47/0.53. All non-hydrogen atoms and diphenylmethanido hydrogen atoms in **2** and **3** were found from the Fourier syntheses of electron density (all non-hydrogen atoms were refined anisotropically). Other hydrogen atoms in **2**, **3** and **6** were placed in calculated positions and refined in the 'riding' model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms [$U(H)_{iso} = 1.5U_{eq}$ for methyl groups].

For more detail, see Online Supplementary Materials.

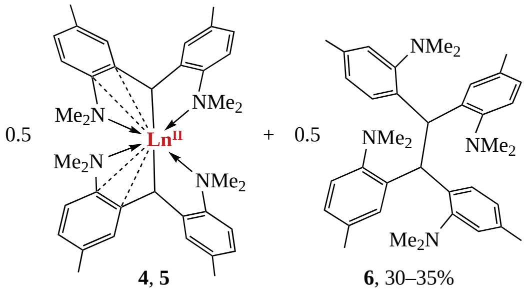
CCDC 2024644–2024646 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

The Sc–C bond lengths in **2** [2.304(3) and 2.316(4) Å] are greater than analogous lengths in six-coordinated Sc complexes with *o*-dimethylaminobenzyl ligands [2.261(3)–2.287(3) Å].[16] However, no Sc−N bond elongation in **2** [2.395(3) and 2.481(8) Å] was observed, as compared to previously reported Sc compounds [2.384(3)–2.492(4) Å].[16] In Y complex **3,** both Y−C [2.435(6)–2.463(6) Å] and Y−N [2.501(5)–2.527(5) Å] bond lengths fall within a range common for six-coordinated yttrium *o*-dimethyaminobenzyl derivatives [Y−C, 2.413(4)–2.487(3) Å; Y−N, 2.497(2)–2.610(4) Å].[16(*a*),17]

In the ^{1}H NMR spectra of **2** and **3** (C_6D_6, 293 K), the CH group protons of the diphenylmethanido ligands appeared as broad singlets at 3.60 and 3.35 ppm, respectively, while the related carbons gave broad signals at 70.4 and 63.8 ppm. Complexes **2** and **3** were stable in C_6D_6 solutions at ambient temperature for several weeks without decomposition or symmetrization.

Analogous reactions of dimeric **1** with $LnCl_3$ (Ln = Yb, Sm) are accompanied by the spontaneous reduction of Ln^{III} to Ln^{II}. Homoleptic complexes $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ln^{II}$ [Ln = Yb (**4**), Sm (**5**); Scheme 2] were isolated from the reaction mixtures in 28 and 25% yields, respectively. Compounds **4** and **5** were synthesized by salt metathesis reactions between equimolar amounts of divalent $LnI_2(THF)_2$ and dimeric **1** and fully characterized.[13] In these reactions, $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2$ **6** was a by-product. It is most likely that the reactions of $LnCl_3$ (Ln = Yb, Sm) with **1**, similarly to the case of Sc and Y, afford transient chlorido-bis(diphenylmethanido) derivatives, which spontaneously undergo intramolecular oxidation of the diphenylmethanidocarbanion to the $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^{\bullet}$ radical and the reduction of Ln^{III} to Ln^{II}. The recombination of these two radicals affords **6**, while the symmetrization of chloridodiphenylmethanido complexes $\{[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]Ln^{II}Cl\}$ can lead to the formation of **4**, **5** and $LnCl_2(THF)_n$. Compound **6** was isolated as colorless crystals in 30–35% yields after the extraction of reaction products with hexane and characterized by NMR spectroscopy and GC–MS and X-ray diffraction analysis† (see Online Supplementary Materials). Unfortunately, our attempts to isolate $LnCl_2(THF)_n$ from their mixtures with KCl were unsuccessful.

The spontaneous reduction of Yb^{III} ions accompanied by the oxidative dimerization of covalently bound ligands (Yb^{3+}/Yb^{2+}, $E_{½} = -1.15$ V)[18] was reported previously. Methyl,[19] benzyl,[7(*b*)] hydrido,[20] and silylamido $[N(SiMe_3)_2]^-$ ligands[21] promote the reduction of Yb^{III} affording Yb^{II} species and the products of oxidative coupling of ligands. For Sm^{III} complexes, such reactions are less common (Sm^{3+}/Sm^{2+}, $E_{½} = -1.55$ V)[18] and only one example of the Sm^{III}/Sm^{II} reduction in a reaction of $Sm^{III}[CH_2C_6H_4NMe_2\text{-}o]_3$ with the penta(aryl)cyclopentadiene $[C_5(C_6H_4\text{-}Bu\text{-}4)_5]H$ giving samarocene $[C_5(C_6H_4\text{-}Bu\text{-}4)_5]_2Sm^{II}$ was described.[8(*b*)]



4, **5**

6, 30–35%

4 Ln = Yb, 28%
5 Ln = Sm, 25%

Scheme 2

In conclusion, the application of the diphenylmethanido ligand $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^-$ allowed us to synthesize Sc^{III} and Y^{III} chlorido-bis(diphenylmethanides), while the spontaneous reduction of Ln^{III} to Ln^{II} accompanied by the oxidation of the diphenylmethanido carbanion occurred with Sm^{III} and Yb^{III}. Smaller ionic radii of Ln^{III} ions (Sc^{3+}, 0.75 Å; Y^{3+}, 0.87 Å; CN = 6)[2(*a*)] compared to those of Ln^{II} (Yb^{2+}, 1.02 Å; Sm^{2+}, 1.15 Å; CN = 6)[2] resulted in a change of the coordination mode of diphenylmethanido ligands from $[NC_{sp^3}N]$ pincer in Ln^{II} complexes[13] to bidentate κ^2-CN in Ln^{III} derivatives.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.016.

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