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A first oxalamidino complex of samarium *via* reduction-coupling of carbodiimine: synthesis and molecular structure of [η^4-$C_2(NR)_4$][$(MeC_5H_4)_2Sm(HMPA)$]$_2$·2THF (R = Pr^i, Cy)

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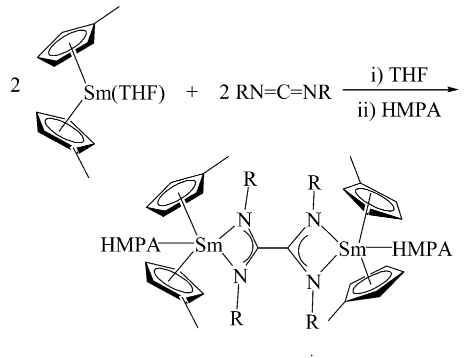
Treatment of the THF solution of $(MeC_5H_4)_2Sm(THF)$ with an equivalent of carbodiimine [RN=C=NR] (R = Pr^i or Cy; Cy = cyclohexyl) in the presence of an equivalent of hexamethylphosphoric triamide (HMPA) at room temperature gives, *via* a reduction-coupling reaction of carbodiimine, the corresponding bimetallic oxalamidino complex of samarium [η^4-$C_2(NR)_4$][$(MeC_5H_4)_2Sm(HMPA)$]$_2$·2THF.

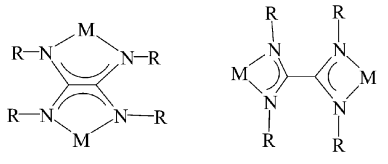
Since the late transition metal diimine complexes have been found to display efficient activity for olefin polymerization,[1] the chemistry of non-metallocene complexes has attracted considerable attention. Oxalic amidines can act as diamide or diamidinate ligands after deprotonation and these ligands can be easily modified in their electronic and steric effects by variation of the substitutes on the nitrogen atoms. Moreover, they can adopt several possible coordination modes in their metal complexes. Therefore, oxalamidino ligands have recently attracted increasing interest. To date, a few of oxalamidino complexes of transition and main metals have been developed.[2–7] Most of these published complexes were synthesized by the deprotonation reaction of oxalic amidines with corresponding metal complexes[2–7] or by transmetallation reaction.[6] Only one example in the literature has been synthesized through reductive coupling of carbodiimine by dicarbonylbis-(cyclopentadienyl)titanium(II).[8] Surprisingly, no such kind of complex for a lanthanide element has been reported yet. Organosamarium(II) complexes are strong reducing agents. They are known to be able to react with a variety of unsaturated substrates, such as aromatic ketones,[9] CO,[10] CO_2,[11] ^tBuCP,[12] butadiene,[13] PhNCO[14] *etc.*, to give the corresponding bimetallic complexes *via* reduction-coupling reaction of these reactants. Carbodiimine can be considered as the isoelectronic analogue of PhNCO and CO_2, accordingly, we attempted to synthesize an oxalamidino complex of samarium by the reaction of organosamarium(II) complex directly with carbodiimine. In this communication we now report the first oxalamidino complex of samarium formed directly *via* reduction-coupling reaction of carbodiimine mediated by Sm(II) complex, and this oxalamide complex exhibits a hitherto unobserved binding mode.

When one equivalent of carbodiimine was added into the THF suspension of $(MeC_5H_4)_2Sm(THF)$, the dark brown color of the suspension changed immediately into homogeneous bright yellow solution. The color change indicated that Sm(II) was oxidized to corresponding Sm(III). By addition of one equivalent of HMPA, after workup, yellow crystals of the corresponding oxalamidino complexes **1** and **2** were obtained in good yields (Scheme 1).† **1** and **2** were characterized by full spectroscopy data and **1** was also characterized by single crystal X-ray diffraction.‡ The oxalamidino metal complexes normally have their molecular structures of types **A** and **B** (Scheme 2), according to the coordinated mode of bridging ligand to the metals. However, almost all the structurally characterized complexes reported so far have the structure of type **A**,[5,6,8] no example having the type **B** structure has been structurally characterized by X-ray analysis. In order to understand the structure of the title complex in the solid-state, the molecular structure of **1** was determined and is shown in Fig. 1.



R = Cy (**1**), Pr^i (**2**)

Scheme 1



A (diamide) **B** (diamidinate)

Scheme 2

It is interesting that the complex has the molecular structure of type **B**. This result undoubtedly demonstrated that the structure mode **B** really exists and can be structurally characterized. The new result should be of interest in understanding the numerous coordination modes of oxalamidino ligands to metals.

The complex consists of symmetric dimeric units, [$(MeC_5H_4)_2SmCN_2Cy_2(HMPA)$]$_2$. Methylcyclopentadienyl rings are bonded to the samarium atoms in η^5 fashion. The bridging ligand, which formed from the dimerization of two *N,N′*-dicyclohexylcarbodiimine, acts as a tetradentate ligand chelating two Sm through the four nitrogen atoms. One oxygen atom from HMPA coordinates to Sm forming the coordinate number of nine for each Sm atom. The oxygen atom occupies a position roughly in the plane defined by the Sm, the two ligand nitrogen atoms and one C atom of the ligand $C_2(NCy)_4$ formed. The methylcyclopentadienyls are located above and below that plane, oriented in such a way to minimize interaction with the cyclohexyl groups and HMPA group. The two planes formed by the atoms Sm1, N4, N5, C19 and Sm1A, N4A, N5A, C19A respectively, are nearly perpendicular (the angle between the two planes is 86.5°). Such

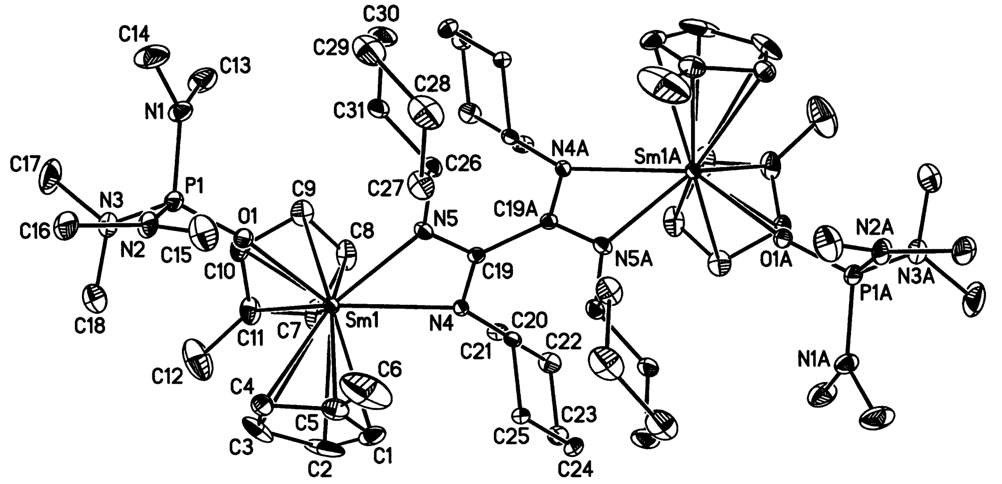


Fig. 1 ORTEP diagram of complex **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sm1–Cent1 2.578(12), Sm1–Cent2 2.582(12), Sm1–O1 2.431(4), Sm1–N4 2.560(5), Sm1–N5 2.447(5), C19–N4 1.319(7), C19–N5 1.336(7), C19–C19A 1.536(11); Cent1–Sm1–Cent2 125.9(4), N4–Sm1–N5 53.35(15).

an arrangement will lead to minimizing the interaction between these neighbouring cyclohexyl groups. The bond distances of N5–C19, N4–C19 and C19–C19A are 1.336(7), 1.319(7) and 1.536(11) Å, respectively, which indicate that the C–N bonds are intermediate in length between a single and a double bond, while the C–C bond is single. The bond character indicates electronic delocalization all over the two $\mathrm{CN_2}$ units. This result obviously demonstrates that the method to prepare an oxalamidino complex through the reduction-coupling reaction of carbodiimine with the metal complex is not a special case for the Ti(II) complex,[8] but a convenient and direct way for metals in low oxidation state.

In conclusion, we have shown that the bimetallic oxalamidino complex is easily available *via* reduction-coupling of the corresponding carbodiimine in the presence of Sm(II) complex. We reason that it might be possible to synthesize this complex with other lanthanide elements and transition metals in low oxidation state by this method. This work is proceeding in our laboratory.

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Notes and references

† *Complex 1*: To THF solution of $\mathrm{(MeC_5H_4)_2Sm}$ (3.6 mmol), which was synthesized by the reaction of $\mathrm{SmI_2}$ with $\mathrm{Na(MeC_5H_4)}$ in 1 : 2 mole ratio at room temperature, was added a THF solution of N,N′-dicyclohexylcarbodiimide (0.78 g, 3.6 mmol), the color of the solution changed immediately from dark brown to bright yellow. Then HMPA (3.6 mmol) was added to the reaction system by syringe, the mixture was stirred for 3 h. 1.01 g of yellow crystals were obtained from the concentrated THF solution at 0 °C (56% based on Sm), m.p.: 135–137 °C (dec.) (Found: C, 54.69; H, 8.11; N, 9.25; Sm, 20.02%. $\mathrm{C_{70}H_{124}N_{10}O_4P_2Sm_2}$ requires C, 54.81; H, 8.09; N, 9.14; Sm, 19.62%); ^{1}H NMR ($\mathrm{C_6D_6}$, ppm): 12.07 (s, 2H), 11.56 (s, 2H), 9.34 (s, 4H), 8.84–7.56 (m, 8H), 3.50 (s, 8H), 2.85 (s, 36H), 1.65 (s, 8H), 1.50–1.36 (m, 20H), 1.30 (m, 4H), 1.25–0.91 (m, 20H), 0.67 (s, 12H); IR (KBr): 2927 (s), 2851 (s), 1638 (s), 1458 (m), 1298 (s), 1198 (s), 987 (s). Complex **2**: The synthesis of complex **2** was carried out as described that for complex **1**, but *N,N′*-diisopropylcarbodiimide (3.0 mmol) was used instead of *N,N*-dicyclohexylcarbodiimine. 0.67 g of yellow microcrystals were obtained from concentrated THF solution (33% based on Sm), m.p.: 160–162 °C (dec.) (Found: C, 50.61; H, 7.64; N, 10.23; Sm, 22.27%. $\mathrm{C_{68}H_{108}N_{10}O_4P_2Sm_2}$ requires C, 50.71; H, 7.87; N, 10.20; Sm, 21.91%); ^{1}H NMR ($\mathrm{C_6D_6}$, ppm): 8.60–8.39 (m, 4H), 7.56–7.01 (m, 12H), 3.62 (s, 8H), 3.10 (m, 4H), 2.20 (s, 36H), 1.85 (s, 8H), 1.45–1.35 (m, 24H), 1.11 (brs, 12H); IR (KBr): 2925 (s), 2854 (s), 1645 (s), 1489 (s), 1463 (s), 1298 (s), 1197 (s), 1173 (s), 987 (s).

‡ *Crystallographic data for* $\mathrm{[(MeC_5H_4)_2Sm(HMPA)(RN)C(NR)–]_2{\cdot}2THF}$, (**1·2THF**): $\mathrm{C_{70}H_{124}N_{10}O_4P_2Sm_2}$. M = 1532.43, monoclinic, space group *C*2/*c* (#15), a = 26.679(5), b = 15.220(2), c = 21.545(4) Å, β = 114.29(2), V = 7974(3) Å^3, Z = 4, D_c = 1.276 g·cm^{-3}, (Mo–Kα) = 0.71070 Å, F(000) = 3200, T = 193 K, μ = 1.546 mm^{-1}, 31467 collected reflections, 8903 independent reflections, R indices R = 0.0637, wR = 0.1522. CCDC 244736. See http://www.rsc.org/suppdata/cc/b4/b410599k/ for crystallographic data in .cif or other electronic format.

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