Facile construction of the guanidine substituent or guanidinate anionic ligand through addition of the adjacent amino group to carbodiimide†

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The reaction of *N*,*N*′-dicyclohexylcarbodiimide (DCCI) with $[Cp_2Yb(o\text{-}H_2NC_6H_4S)]_2$ (Cp = C_5H_5) (**1**) forms the monomer product $Cp_2Yb[SC_6H_4N{=}C(NHCy)_2]$ (**2**), indicating that the adjacent NH_2 group can add to the C=N double bonds of carbodiimide to construct a neutral guanidine group. When DCCI reacts with $[Cp_2Y(o\text{-}H_2NC_6H_4S)]_2{\cdot}2THF$ (**4**), a dimer product $[CpY(\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)(THF)]_2$ (**5**) was isolated, through the amino group addition and cyclopentadienyl elimination. Interestingly, on treatment of **4** with one or two equivalent of ^{i}PrN=C=N^{i}Pr at the same conditions gave an amino group partial addition product $CpY(THF)[\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C\text{-}(NH^iPr)N^iPr)](\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4NH_2)YCp_2{\cdot}THF$ (**6**), where only one NH_2 group can add to the C=N double bonds of carbodiimide molecule, another one is remained. However, when we extended this reaction to the gadolinium complex, a novel co-crystalline compound $\{Cp_2Gd[SC_6H_4N{=}C(NHCy)_2]\}{\cdot}\{CpGd(THF)[\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)][\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4NH_2]GdCp_2{\cdot}THF\}$ (**8**) was obtained from the reaction of $[Cp_2Gd(o\text{-}H_2NC_6H_4S)]_2$ (**7**) with DCCI. In order to investigate the sequence of addition and the elimination of the cyclopentadienyl group, a deprotonation reaction of the addition product has also been studied. Reaction of $CpYb[SC_6H_4NC(NH^iPr)_2]_2(THF)$ (**9**), formed by reaction of Cp_3Yb with two equivalent of *o*-aminothiophenol, and subsequently with 2 equiv. of ^{i}PrN=C=N^{i}Pr, with one equiv. of Cp_3Yb gave a cyclopentadienyl elimination product $[CpYb(\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NH^iPr)N^iPr)(THF)]_2$ (**3**). This result reveals that addition of the NH_2 group to carbodiimide is prior to the elimination of cyclopentadienyl group. All of new compounds have been characterized by elemental analysis and spectroscopic properties. The solid-state structures of complexes **2**, and **5–9** were determined by single-crystal X-ray diffraction.

Introduction

The search for new ligands to support metal complexes receives a continual interest in inorganic chemistry and organometallic chemistry.[1] Some efforts focus on the amidinate and guanidinate ligand systems. The amidinates are known to be versatile ligands in organometallic chemistry.[2] The relative guanidinate anion can impart a similar coordination environment while offering increased stability due to the possibility of the additional zwitterionic resonance structure. Moreover, guanidinate ligands provide tunability in terms of steric and electronic properties by variation of the organic substituents on the nitrogen atoms.[3] These organometallic guanidinates were usually prepared by metathesis and insertion.[4–7] However, there are some disadvantages about the two synthetic protocols: it is very difficult to completely remove the salt MCl (alkali metal chlorides) in most cases; another is the low reactivity of the metal–ligand bonds toward carbodiimide molecules. In fact, a more alluring strategy for preparation of these organometallic guanidinates is through the addition of amino group to carbodiimide.[8–11]

Our recent interest is in the investigation of the ligand-based substituent effects on activity of organolanthanides toward unsaturated organic small molecules. We found the adjacent amino group of the *o*-aminothiophenolate ligand readily adds into the C=N bond of carbodiimide or isocyanate to construct a novel guanidinate or thiazolate skeleton.[9,10] In order to extend the scope of these additions and obtain more information about their mechanisms, the reactions of organolanthanide *o*-aminothiophenolate complexes with DCCI and ^{i}PrN=CN^{i}Pr have been investigated. Herein, we would like to report these results. Three aspects are mainly included in this contribution: (i) the steric hindrance effects of the substituted group R of RN=C=NR (R = cyclohexyl, isopropyl); (ii) the radii effects of the rare earth metal ions and (iii) the reaction sequence of the amino group addition and cyclopentadienyl elimination.

Results and discussion

Reactions of lanthanocene derivatives containing the *o*-aminothiophenolate ligand with carbodiimides

We first investigated the reaction of $[Cp_2Yb(o\text{-}H_2NC_6H_4S)]_2$ (**1**)[10a] with *N*,*N*′-dicyclohexylcarbodiimide (DCCI). The addition of two molar equiv. of DCCI to a THF solution of **1** at ambient temperature results in a N–H bond addition product

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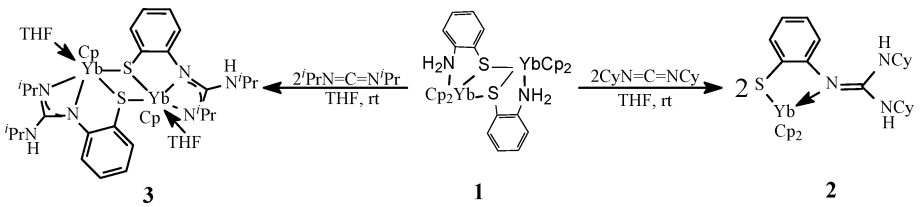
$Cp_2Yb[SC_6H_4N{=}C(NHCy)_2]$ (**2**), as shown in Scheme 1. X-Ray diffraction analysis indicates that the neutral guanidine substituent is coordinated to the central metal with η^1-bonding mode, no elimination of cyclopentadienyl group takes place, which is significantly different from the observation in the reaction of **1** with *N*,*N*′-diisopropylcarbodiimide (^{i}PrN=C=N^{i}Pr) ([CpYb(μ-η^2:η^1-$SC_6H_4N{=}C(NH^iPr)N^iPr$)(THF)]$_2$ (**3**)).[10a] The reactive discrimination in the two reactions maybe attribute to the difference of the nucleophilic ability of the formed neutral guanidine group due to the effect of steric hindrances in the R groups (R = cyclohexyl, isopropyl). Furthermore, both of two hydrogen atoms of the *ortho*-position amino group shift on the nitrogen atoms of carbodiimide moiety in this reaction.

To further investigate the scope of the addition, we also synthesized the complex $[Cp_2Y(o\text{-}H_2NC_6H_4S)]_2{\cdot}2THF$ (**4**) by the reaction of Cp_3Y with *o*-aminothiophenol in THF at room temperature, and examined its reactivity toward DCCI and ^{i}PrN=C=N^{i}Pr. Treatment of two equiv. of DCCI with **4** in THF at ambient temperature gave a centrosymmetric dimer product [CpY(μ-η^2:η^1-$SC_6H_4N{=}C(NHCy)NCy$)(THF)]$_2$ (**5**) (Scheme 2). Herein, accompanied with the amino group addition to carbodiimide, the elimination of the cyclopentadienyl group takes place. This is different from the observation in the reaction of **1** and DCCI, but similar to that of reaction of **1** with ^{i}PrN=C=N^{i}Pr. Interestingly, **4** reacts with two equiv. of *N*,*N*′-diisopropylcarbodiimide, only the amino group partial addition product CpY(THF)[μ-η^2:η^1-$SC_6H_4N{=}C(NH^iPr)N^iPr$)](μ-$\eta^2$:$\eta^1$-$SC_6H_4NH_2$)$YCp_2{\cdot}$THF (**6**) can be isolated, of which only one amino group add into the C=N double bonds of carbodiimide molecules. An increase of the reaction temperature cannot obtain the amino group completed addition product, similar to **5**. Reaction of complex **4** with two equivalent of ^{i}PrN=C=N^{i}Pr under the reflux temperature for 24 h also give **6**, the residue NH_2 group cannot further add into the C=N bonds of the other carbodiimide molecules.

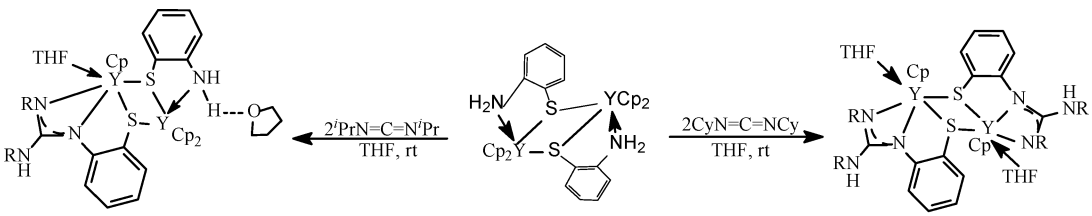
When we extend this addition to other lanthanides with larger ionic radii, their reactions seem to be more complicated. For example, the reaction of DCCI with $[Cp_2Gd(o\text{-}H_2NC_6H_4S)]_2$ (**7**) in a 1 : 1 ratio gave an interesting co-crystalline compound {$Cp_2Gd[SC_6H_4N{=}C(NHCy)_2]$}·{$CpGd(THF)[\mu\text{-}\eta^3{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)][\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4NH_2]GdCp_2{\cdot}THF$} (**8**), which is in fact an equimolar mixture of two complexes: one is $Cp_2Gd[SC_6H_4N{=}C(NHCy)_2]$ (**8a**), which is a NH_2 addition product and similar to **2**, another is a NH_2 partial addition and Cp-abstraction product {$CpGd(THF)[\mu\text{-}\eta^3{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)][\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4NH_2]GdCp_2{\cdot}THF$}(**8b**), and similar to **6**, as shown in Scheme 3. We try to isolate a single component through increase of the quantities of carbodiimide or **7**, but not obtain the success. The formation of the co-crystalline compound **8** should be the balance of two components of **8a** and **8b** in the crystallizing process. The results indicate that the NH_2 group addition and/or cyclopentadienyl elimination are strongly effected by the factors of the rare earth metal ion character and the steric hindrance of the R group of carbodiimide.

In order to study the sequence of the NH_2 addition and Cp elimination, an extension experiment has also been designed. As shown in Scheme 4, the amino group bis-addition product



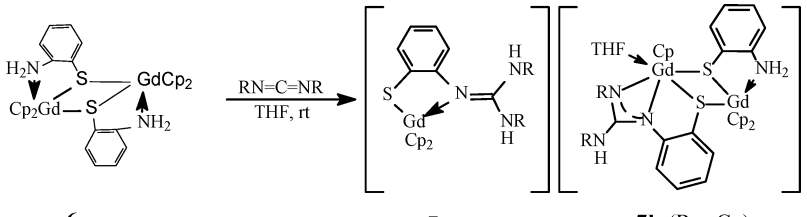
3 **1** **2**

Scheme 1



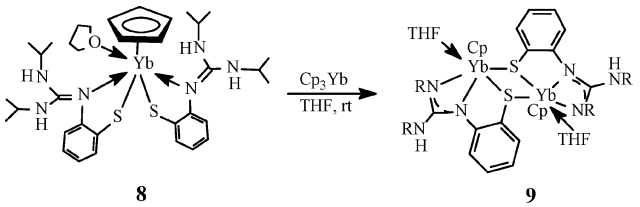
6 (R = ^{i}Pr) **4** **5** (R = Cy)

Scheme 2



6 **7a** **7b** (R = Cy)

Scheme 3



Scheme 4

$CpYb[SC_6H_4NC(NH^iPr)_2]_2(THF)$ (**9**), prepared by reaction of Cp_3Yb with two equivalent of *o*-aminothiophenol, and subsequently with two equiv. of $^iPrN{=}C{=}N^iPr$, readily reacts with one equiv. of Cp_3Yb to give a Cp elimination product $[CpYb(\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NH^iPr)N^iPr)(THF)]_2$ (**3**). This product was previously obtained by reaction of $^iPrN{=}C{=}N^iPr$ with **1**.[10a] This result indicates that the new formed guanidine groups can further provide one proton to eliminate the cyclopentadienyl group of Cp_3Yb. In other words, the N–H bond addition to the C=N bond of carbodiimide molecules should be prior to the elimination of cyclopentadienyl group in our observations.

All of the new complexes are air- and moisture-sensitive. They are high or moderately soluble in THF and slightly soluble in *n*-hexane, and were characterized by elemental analysis and spectroscopy properties, which were in good agreement with the proposed structures. The mass spectra display that all of them are characterized by the molecule ion peaks. In the IR spectra, the characterized absorption at *ca.* 2100 cm^{-1} for the ν_{as}(N=C=N) stretch of free carbodiimides is absent, but the new strong band at *ca.* 1530 cm^{-1} attributable to the guanidinate anionic and/or at *ca.* 1570 cm^{-1} attributable to the neutral guanidine group is present.[10a] Their structures of **2**, and **5–9** have also been identified by X-ray single-crystal diffraction analysis.

Crystal structures

The molecular structure of **2** is shown in Fig. 1. Selected bond lengths and angles of **2** are listed in Table 1. The X-ray crystal

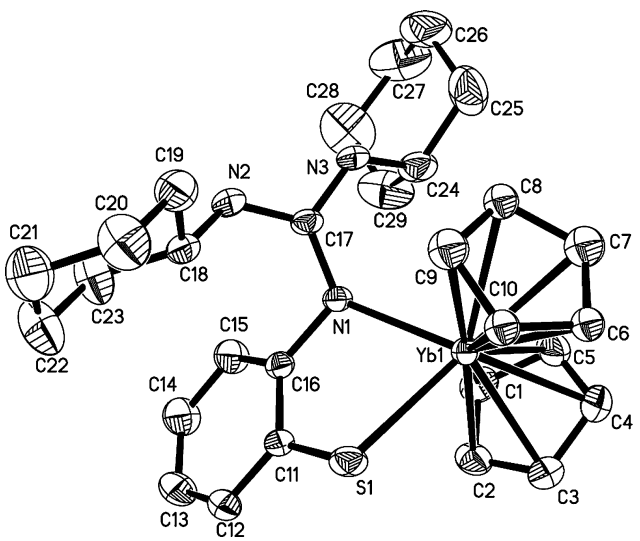


Fig. 1 Thermal ellipsoid plot of $Cp_2Yb[SC_6H_4N(H)C(NHCy){=}NCy]$, **2**, with ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **2**

Bond lengths/Å			
Yb(1)–N(1)	2.307(6)	Yb(1)–C(10)	2.619(14)
Yb(1)–C(3)	2.577(9)	Yb(1)–C(4)	2.621(9)
Yb(1)–C(8)	2.581(17)	Yb(1)–C(5)	2.622(10)
Yb(1)–C(2)	2.582(9)	Yb(1)–S(1)	2.645(2)
Yb(1)–C(7)	2.584(16)	S(1)–C(11)	1.770(8)
Yb(1)–C(1)	2.603(9)	N(1)–C(17)	1.318(9)
Yb(1)–C(9)	2.603(16)	N(2)–C(17)	1.351(10)
Yb(1)–C(6′)	2.607(15)	N(3)–C(17)	1.354(10)
Bond angles/°			
N(1)–Yb(1)–S(1)	75.66(16)	N(1)–C(17)–N(3)	120.1(7)
C(17)–N(1)–Yb(1)	128.7(5)	N(2)–C(17)–N(3)	116.6(7)
N(1)–C(17)–N(2)	123.3(7)		

analysis results reveal **2** is a solvent-free monomer with ytterbium atom bonded to two η^5-cyclopentadienyl rings and one chelating ligand $[SC_6H_4N{=}C(NHCy)_2]^-$. The coordination number of Yb^{3+} is eight. The neutral guanidine moiety is only coordinated to the center metal by one nitrogen atom, and is significantly different from the observations in others guanidinate compounds, in which the guanidinate anionic ligand is usually coordinated to the metal by two nitrogen atoms.[3,7] Two N–H bonds of the amino group additions to the two C=N double bonds of the carbodiimide molecule has been confirmed from their structure parameters. The bond angles around C17 are consistent with sp^2 hybridization, and the three C–N distances of the guanidine moiety are partial averaged (C17–N1 1.318(9) Å, C17–N2 1.351(10) Å, and C17–N3 1.354(10) Å). The distance of C17–N1 is slightly longer than the C=N double distance (1.28 Å),[12] the distances of C17–N2 and C17–N3 are significantly shorter than the $C(sp^2)$–$N(sp^3)$ single bond distances (1.416 Å),[13] indicating that the π-electrons of the C=N double bond in the present structure are delocalized over the N_3C core. Consistent with this observation, the distance of Yb1–N1 is 2.307(6) Å, significantly shorter than the corresponding distance in the original compound $[Cp_2Yb(\mu\text{-}\eta^1{:}\eta^2\text{-}H_2NC_6H_4S)]_2{\cdot}2THF$ (**1**) (Yb1–N1 2.459(2) Å),[9] indicating a contribution from the increase of the nucleophilicity of the guanidine moiety.

The crystal structure of complex **5** (Fig. 2 and Table 2) show that the adjacent amino group in **5** has combined with *N*,*N*′-diisopropylcarbodiimide, forming a novel guanidinate dianionic ligand $[SC_6H_4N{=}C(NHCy)NCy]^{2-}$, which connected the central metal with the $\mu\text{-}\eta^2{:}\eta^1$-bonding mode. One hydrogen atom of the adjacent amino group shifts to the uncoordinated nitrogen atom. The guanidinate ligand also exhibits delocalized bonding throughout the N_3C guanidinate core. The planarity of YN_2C ring and nearly equivalent C12–N1 and C12–N2 (1.337(4) and 1.320(4) Å, respectively), Y1–N1 and Y1–N2 (2.320(3) Å and 2.382(3) Å, respectively) bond lengths suggest the existence of a resonance stabilization in the YbN_2C ring and no hydrogen atom at coordinated nitrogen atom. The distance between the central carbon and uncoordinated nitrogen (C12–N3 1.378(4) Å) is significantly shorter than the expected for $C(sp^2)$–$N(sp^3)$ single bonds ($C–N_{av}$, 1.416),[13] and indicate a stronger p–π conjugation between the lone-pair electron on non-coordinated nitrogen and the N–C–N unit.

Table 2 Selected bond lengths (Å) and angles (°) for **5**

Bond lengths/Å			
Y(1)–N(1)	2.320(3)	Y(1)–C(1)	2.699(4)
Y(1)–N(2)	2.382(3)	Y(1)–S(1)	2.7899(11)
Y(1)–O(1)	2.435(3)	Y(1)–C(12)	2.806(4)
Y(1)–C(3)	2.652(4)	S(1)–Y(1A)	2.8376(13)
Y(1)–C(4)	2.672(4)	N(1)–C(12)	1.337(4)
Y(1)–C(2)	2.680(4)	N(2)–C(12)	1.320(4)
Y(1)–C(5)	2.685(4)	N(3)–C(12)	1.378(4)
Bond angles/°			
N(1)–Y(1)–N(2)	56.23(10)	N(2)–C(12)–N(1)	113.1(3)
N(1)–Y(1)–S(1)	69.73(7)	N(2)–C(12)–N(3)	124.1(3)
N(2)–Y(1)–S(1)	125.92(8)	N(1)–C(12)–N(3)	122.9(3)
S(1)–Y(1)–S(1A)	82.99(3)	N(2)–C(12)–Y(1)	57.84(18)
C(12)–N(1)–Y(1)	96.5(2)	N(1)–C(12)–Y(1)	55.24(17)
C(12)–N(2)–Y(1)	94.2(2)	N(3)–C(12)–Y(1)	177.6(3)

Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 2, -z + 1$.

Table 3 Selected bond lengths (Å) and angles (°) for **6**

Bond lengths/Å			
Y(1)–N(2)	2.296(4)	Y(2)–C(33)	2.636(6)
Y(1)–N(4)	2.389(4)	Y(2)–C(34)	2.650(6)
Y(1)–O(1)	2.422(3)	Y(2)–C(29)	2.653(7)
Y(1)–C(2)	2.654(5)	Y(2)–C(31)	2.655(6)
Y(1)–C(1)	2.659(5)	Y(2)–C(30)	2.663(6)
Y(1)–C(4)	2.665(5)	Y(2)–C(25)	2.676(7)
Y(1)–C(5)	2.667(5)	Y(2)–C(26)	2.696(6)
Y(1)–C(3)	2.670(5)	Y(2)–S(1)	2.8142(14)
Y(1)–S(2)	2.7774(14)	S(1)–C(6)	1.770(5)
Y(1)–C(18)	2.789(5)	S(2)–C(12)	1.783(5)
Y(1)–S(1)	2.8372(14)	N(1)–C(11)	1.441(5)
Y(2)–N(1)	2.557(4)	N(2)–C(18)	1.348(6)
Y(2)–C(28)	2.612(7)	N(3)–C(18)	1.382(6)
Y(2)–C(27)	2.629(6)	N(4)–C(18)	1.322(6)
Y(2)–C(32)	2.634(7)		
Bond angles/°			
N(2)–Y(1)–N(4)	56.80(13)	N(4)–C(18)–N(3)	124.2(5)
N(2)–Y(1)–S(2)	69.99(10)	N(2)–C(18)–N(3)	122.6(5)
S(2)–Y(1)–S(1)	79.78(4)	N(3)–C(18)–Y(1)	171.7(3)
N(4)–C(18)–N(2)	113.2(4)		

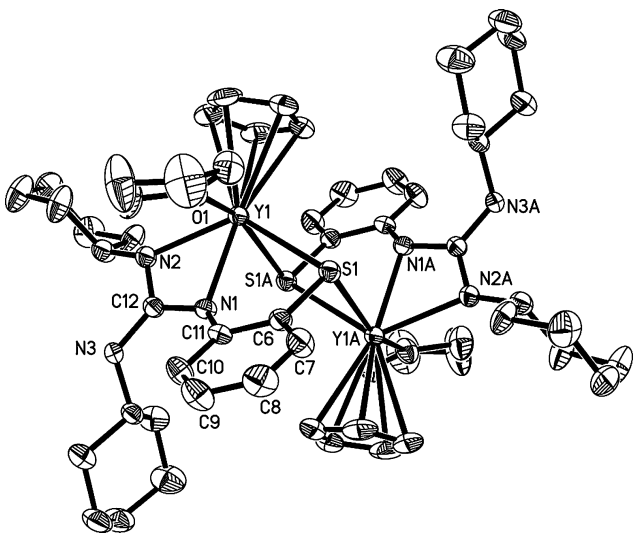


Fig. 2 Thermal ellipsoid plot of $[CpY(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)\text{-}NCy)(THF)]_2$, **5**, with ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

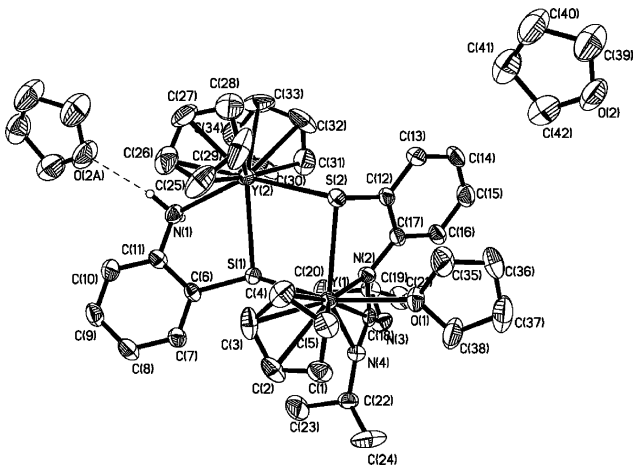


Fig. 3 Thermal ellipsoid plot of $CpY(THF)[\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4N{=}C(NH^iPr)N^iPr)]$ $(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4NH_2)YCp_2{\cdot}THF$, **6**, with ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

Fig. 3 and Table 3 shows complex **6** has a unique unsymmetrical dinuclear structure, in which the CpY and Cp_2Y fragments connect with the $[SC_6H_4N{=}C(NH^iPr)N^iPr]^{2-}$ and $[SC_6H_4NH_2]^-$ units. The dianionic ligand $[SC_6H_4N{=}C(NH^iPr)N^iPr]^{2-}$ also connects with two yttrium ions with the $\mu\text{-}\eta^2\text{:}\eta^1$-mode, similar to the observation in **5**. The residual NH_2 group also connects with one uncoordinated THF molecule through the intermolecular N–H···O hydrogen bond interaction.

Complex **7** (Fig. 4, Table 4) is a centrosymmetric dimeric structure, with the *o*-aminothiophenolate ligand as both a bridging and side-on donating group. Each gadolinium atom is coordinated by two cyclopentadienyl rings, two bridging sulfur atoms and one chelating nitrogen atom to form an edge-bridged tetrahedral geometry. No intermolecular N–H···O hydrogen bond interaction has been found due to the lack of THF molecules in the crystal lattice of **7**, which is different from the observed result of **1**.[9]

The quality of the crystallographic data for **8** is poor with the value of R on the high side ($R_1 = 0.0731$, $wR_2 = 0.1835$) thus the bond distances and bond angles for **8** will not be discussed. However, the overall structure of **8** was clearly determined as shown in Fig. 5. The structure of **8** is consistent of two independent units of $Cp_2Gd[SC_6H_4N{=}C(NHCy)_2]$ (**8a**) and $\{CpGd(THF)[\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)][\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4NH_2]GdCp_2\}$(**8b**). In **8a**, the gadolinium atom is coordinated to two η^5-cyclopentadienyl groups and one chelated ligand $[SC_6H_4N{=}C(NHCy)_2]$, similar to **2**. In **8b**, the Cp_2Gd and CpGd moieties are connected by one $\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy$ guanidinate ligand and one $\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_6H_4NH_2$ aminothiophenolate ligand. The gadolinium atom is also coordinated to one oxygen atom from the solvent THF molecule in CpGd moiety. The overall structure of **8b** is similar to **6**.

Table 4 Selected bond lengths (Å) and angles (°) for **7**

Bond lengths/Å			
Gd(1)–N(1)	2.545(5)	Gd(2)–C(22)	2.671(6)
Gd(1)–C(1)	2.645(7)	Gd(2)–C(19)	2.670(8)
Gd(1)–C(2)	2.666(7)	Gd(2)–C(18)	2.680(8)
Gd(1)–C(8)	2.669(6)	Gd(2)–C(24)	2.677(8)
Gd(1)–C(5)	2.679(7)	Gd(2)–C(20)	2.692(7)
Gd(1)–C(9)	2.682(6)	Gd(2)–C(26)	2.706(6)
Gd(1)–C(3)	2.687(6)	Gd(2)–C(21)	2.706(7)
Gd(1)–C(4)	2.697(7)	Gd(2)–C(17)	2.711(7)
Gd(1)–C(7)	2.701(6)	Gd(2)–C(25)	2.715(6)
Gd(1)–C(10)	2.708(6)	Gd(2)–S(2)	2.826(2)
Gd(1)–C(6)	2.708(6)	S(1)–C(16)	1.764(6)
Gd(1)–S(1)	2.8307(18)	S(2)–C(32)	1.758(7)
Gd(2)–N(2)	2.541(5)	N(1)–C(11)	1.424(7)
Gd(2)–C(23)	2.653(6)	N(2)–C(27)	1.431(8)
Bond angles/°			
N(1)–Gd(1)–S(1)	65.25(11)	C(16)–S(1)–Gd(1)	94.7(2)
N(2)–Gd(2)–S(2)	65.06(12)	C(16)–S(1)–Gd(2)	126.9(2)
Gd(1)–S(1)–Gd(2)	103.12(6)	Gd(2)–S(2)–Gd(1)	103.66(6)
C(32)–S(2)–Gd(2)	96.8(2)	C(11)–N(1)–Gd(1)	110.8(3)
C(32)–S(2)–Gd(1)	128.2(2)	C(27)–N(2)–Gd(2)	112.9(4)

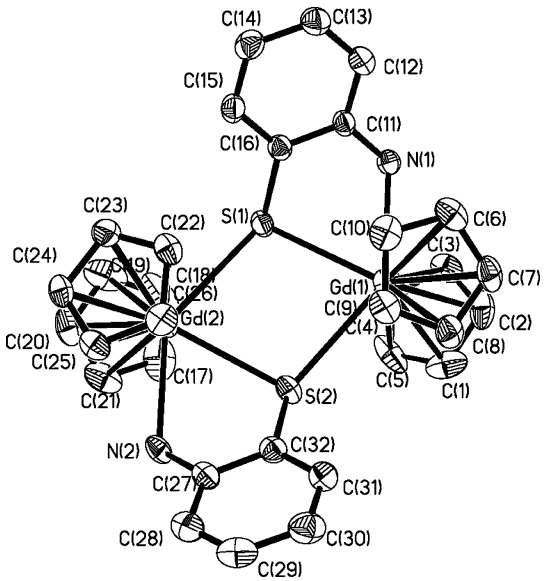


Fig. 4 Thermal ellipsoid plot of $[Cp_2Gd(o\text{-}H_2NC_6H_4S)]_2$, **7**, with ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

The X-ray analysis (Fig. 6 and Table 5) shows **9** is a solvated monomer, and the neutral guanidine group of the $[SC_6H_4NC(NH^iPr)_2]^-$ ligands is coordinated to the central metal with the η^1-bonding mode. The ytterbium atom carries with one η^5-cyclopentadienyl group and one THF molecule and is chelated by two $[SC_6H_4NC(NH^iPr)_2]^-$ ligands. The coordination number of the central metal ion is eight. The overall structure of **9** is similar to that of the complex $CpEr[SC_6H_4NC(NH^iPr)_2]_2(THF)$.[10a]

Conclusion

The present results demonstrate that the nucleophilic addition of the adjacent amino group with carbodiimide takes readily place to construct the guanidine substituents or guanidinate anionic ligands. The N–H bonds of the amino group can selectively add to the C=N bond of carbodiimide molecule, and provide some new methods for the construction of novel $[SC_6H_4N{=}C(NHR)NR]^{2-}$ or $[SC_6H_4N{=}C(NHR)_2]^-$ ligands. Further study indicate that the

Table 5 Selected bond lengths (Å) and angles (°) for **9**

Bond lengths/Å			
Yb(1)–O(1)	2.354(6)	Yb(1)–S(2)	2.703(3)
Yb(1)–N(1)	2.356(7)	Yb(1)–S(1)	2.709(3)
Yb(1)–N(4)	2.480(8)	N(1)–C(7)	1.318(11)
Yb(1)–C(28)	2.634(11)	N(2)–C(7)	1.340(10)
Yb(1)–C(30)	2.661(12)	N(3)–C(7)	1.321(11)
Yb(1)–C(31)	2.663(11)	N(4)–C(20)	1.321(12)
Yb(1)–C(27)	2.663(12)	N(5)–C(20)	1.374(12)
Yb(1)–C(29)	2.672(11)	N(6)–C(20)	1.333(12)
Bond angles/°			
N(3)–C(7)–N(2)	118.4(8)	N(4)–C(20)–N(5)	125.4(9)
N(3)–C(7)–N(1)	116.7(8)	N(4)–C(20)–N(6)	119.0(9)
N(2)–C(7)–N(1)	124.9(8)	N(5)–C(20)–N(6)	115.6(9)

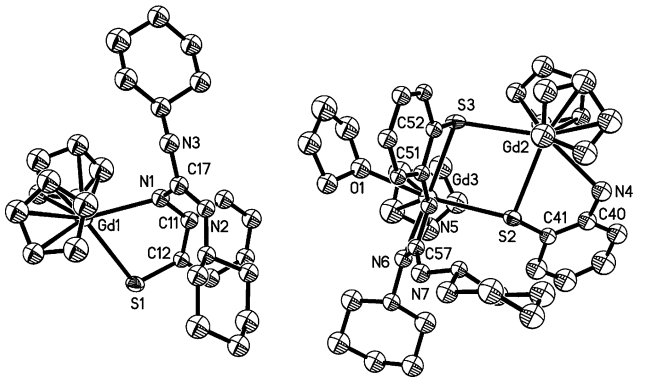


Fig. 5 Thermal ellipsoid plot of $\{Cp_2Gd[SC_6H_4N(H)C(NHCy){=}NCy]\}\cdot\{CpGd(THF)[\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)][\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4NH_2]\text{-}GdCp_2\cdot THF\}$, **8**, with ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules in the lattices omitted for clarity.

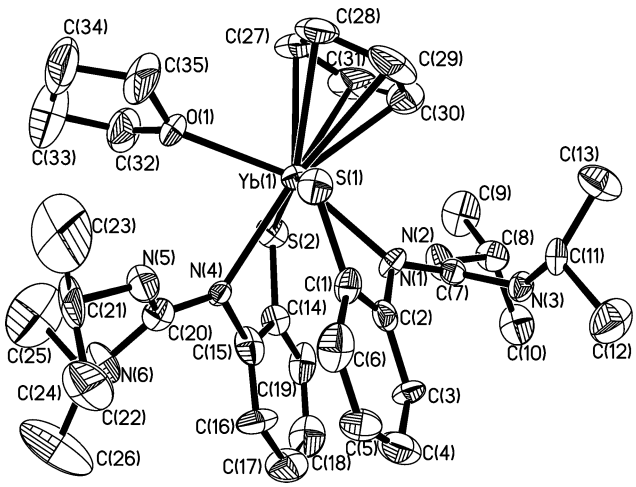


Fig. 6 Thermal ellipsoid plot of $CpYb[SC_6H_4NC(NH^iPr)_2]_2(THF)$, **9**, with ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

selectivity of the amino group addition to C=N bonds of carbodiimide and/or elimination of cyclopentadienyl group can be strongly affected by the factors of metal ionic characters/radii and the steric hindrance of the substituted groups of carbodiimide, and reveals the N–H bonds addition to the C=N bond of carbodiimide molecules is prior to the elimination of the cyclopentadienyl group.

Experimental

General procedures

All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques. The solvents of THF, toluene, *n*-hexane were refluxed and distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Cp_3Ln[14] and $[Cp_2Yb(o\text{-}H_2NC_6H_4S)]_2{\cdot}2THF$ (**1**).[10a] were prepared by the literature methods, respectively. *N*,*N*′-Dicyclohexylcarbodiimide (DCCI), *N*,*N*′-diisopropylcarbodiimide and *o*-aminothiophenol were purchased from Aldrich and were used without purification. Elemental analyses for C, H and N were carried out on a Rapid CHN-O analyzer. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a Philips HP5989A instrument operating in EI mode. Crystalline samples of the respective complexes were rapidly introduced by the direct inlet techniques with a source temperature of 200 °C. The values of *m*/*z* refer to the isotopes ^{12}C, ^{1}H, ^{14}N, ^{16}O, ^{32}S, ^{158}Gd, ^{89}Y and ^{174}Yb. ^{1}H NMR data were obtained on a Bruker DMX-500 NMR spectrometer and were referenced to residual aryl protons in C_6H_6 ($\delta = 7.16$ ppm).

Synthesis of $Cp_2Yb[SC_6H_4N{=}C(NHCy)_2]$ (2). A THF solution of DCCI (0.239 g, 1.16 mmol in 10 mL THF) was slowly added to a 30 mL THF solution of **1** (0.579 g, 0.58 mmol) at room temperature and stirred for 24 h. The reaction solution was concentrated to *ca.* 5 mL under reduced pressure. Yellow crystals of **2** were obtained at –20 °C after several days. Yield: 0.493 g (67%). C, H, N analysis (%): calcd for $C_{29}H_{38}N_3SYb$: C 54.96, H 6.04, N 6.63; found: C 54.73, H 6.44, N 5.96. ^{1}H NMR δ/ppm: 6.94–7.20 (4H, C_6H_4), 6.46 (10H, C_5H_5), 4.20 (2H, N*H*), 3.55–3.60 (2H, unique C*H*), 0.90–1.43 (20H, C_6H_{10}). IR (Nujol) ν/cm^{-1}: 3382 m, 1591 w, 1570 m, 1534 s, 1424 s, 1064 m, 1033 s, 920 m, 774 s, 742 s, 598 w. MS (70 eV): *m*/*z* (%): 634 (7) [M].

Synthesis of $[Cp_2Y(o\text{-}H_2NC_6H_4S)]_2{\cdot}2THF$ (4). Cp_3Y (0.748 g, 2.63 mmol) and *o*-aminothiophenol (0.330 g, 2.63 mmol) were mixed in 50 mL of THF. After stirring for 24 h at room temperature, all volatile substances were removed under vacuum to give yellow powder. Colourless crystals of **4** were obtained by recrystallization from THF at –20 °C during several days. Yield: 0.829 g (76%). C, H, N analysis (%): calcd for $C_{40}H_{48}N_2O_2S_2Y_2$: C 57.83, H 5.82, N 3.37; found: C 57.49, H 5.63, N 3.56. ^{1}H NMR δ/ppm: 7.00–7.24 (m, 8H, C_6H_4), 6.01 (s, 20H, C_5H_5), 4.01 (4H, N*H*), 3.57 (m, 8H, $O(CH_2)_2(CH_2)_2$), 1.41 (m, 8H, $O(CH_2)_2(CH_2)_2$). IR (Nujol) ν/cm^{-1}: 3572 s, 3300 w, 3220 m, 1590 s, 1556 m, 1306 m, 1267 s, 1153 m, 1061 s, 1010 s, 906 m, 784 s, 700 m, 642 w. MS (70 eV): *m*/*z* (%): 686 (27) [M – 2THF].

Synthesis of $[CpY(\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)(THF)]_2$ (5). Following the procedure described for **2**, the reaction of DCCI (0.248 g, 1.20 mmol) with **4** (0.496 g, 0.60 mmol) gave **5** as colourless crystals. Yield: 0.433 g (65%). C, H, N analysis (%): calcd for $C_{56}H_{80}N_6O_2S_2Y_2$: C 60.53, H 7.26, N 7.56; found: C 60.74, H 7.22, N 7.69. ^{1}H NMR δ/ppm: 7.00–7.18 (m, 8H, C_6H_4), 6.03 (s, 10H, C_5H_5), 3.55–3.59 (m, 12H, $O(CH_2)_2(CH_2)_2$, unique C*H*), 2.69 (m, 20H, C_6H_{10}), 2.22 (2H, N*H*), 0.87–1.42 (br, 28H, $O(CH_2)_2(CH_2)_2$, C_6H_{10}). IR (Nujol) ν/cm^{-1}: 3380 s, 3040 s, 1530 s, 1423 s, 1400 s, 1345 m, 1300 s, 1238 s, 1146 m, 1068 s, 1030 s, 881 s, 772 s, 741 s. MS (70 eV): *m*/*z* (%): 483 (24) [1/2M – THF].

Synthesis of $CpY(THF)[\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NH^iPr)N^iPr)](\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4\text{-}NH_2)YCp_2{\cdot}THF$ (6). Complex **6** was prepared similarly to **5** from the reaction of *N*,*N*′-diisopropylcarbodiimide (0.156 g, 1.24 mmol) with **4** (0.516 g, 0.62 mmol) to give colourless crystals **6**. Yield: 0.376 g (68%). C, H, N analysis (%): calcd for $C_{42}H_{56}N_4O_2S_2Y_2$: C 56.63, H 6.34, N 6.29; found: C 56.42, H 6.45, N 6.29. ^{1}H NMR δ/ppm: 6.94–7.22 (8H, C_6H_4), 6.05 (15H, C_5H_5), 3.35–3.58 (10H, $O(CH_2)_2(CH_2)_2$, $CH(CH_3)_2$), 2.18 (2H, NH_2), 0.82–1.43 (20H, $O(CH_2)_2(CH_2)_2$, $CH(CH_3)_2$). IR (Nujol) ν/cm^{-1}: 3382 m, 3047 w, 1598 s, 1535 s, 1404 m, 1271 s, 1243 s, 1059 m, 1028 s, 914 m, 881 s, 762 w, 679 w. MS (70 eV): *m*/*z* (%): 644 (18) [M – 2THF – L] (L = $SC_6H_4N{=}C(NH^iPr)N^iPr$).

Synthesis of $[Cp_2Gd(o\text{-}H_2NC_6H_4S)]_2$ (7). Following the procedure described for **4**, reaction of Cp_3Gd (0.978 g, 2.78 mmol) with *o*-aminothiophenol (0.348 g, 2.78 mmol) gave **7** as colourless crystals. Yield: 0.891 g (78%). C, H, N analysis (%): calcd for $C_{32}H_{32}N_2S_2Gd_2$: C 46.69, H 3.92, N 3.40; found: C 46.93, H 4.10, N 3.18. IR (Nujol) ν/cm^{-1}: 3306 s, 3238 m, 1591 s, 1555 m, 1447 s, 1440 s, 1270 m, 1057 s, 1014 s, 906 m, 781 s, 754 s, 679 m. MS (70 eV): *m*/*z* (%): 824(7) [M].

Synthesis of $\{Cp_2Gd[SC_6H_4N{=}C(NHCy)_2]\}{\cdot}\{CpGd(THF)[\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4N{=}C(NHCy)NCy)][\mu\text{-}\eta^2{:}\eta^1\text{-}SC_6H_4NH_2]GdCp_2{\cdot}THF\}$ (8). A THF solution of DCCI (0.310 g, 1.50 mmol in 10 mL THF) was slowly dropped into a 30 mL THF solution of **7** (0.616 g, 0.75 mmol) at room temperature. After stirring for 24 h, the solution was clear. All volatile substances were removed under vacuum to give white powder. The colourless crystal samples of complex **8** have been obtained from the mixture solvent of *n*-hexane and THF. Yield: 0.496 g (55%). C, H, N analysis (%): calcd for $C_{81}H_{110}N_7O_2S_3Gd_3$: C 54.12, H 6.17, N 5.45; found: C 53.75, H 6.04, N 5.80. IR (Nujol) ν/cm^{-1}: 3354 m, 3285 w, 1573 m, 1540 s, 1315 s, 1259 s, 1237 s, 1146 s, 1062 s, 1013 s, 890 s, 762 s. MS (70 eV): *m*/*z* (%): 618 (17) [M_1], 964 (3) [M_2 – 2THF] (M_1,**8a**; M_2, **8b**).

Synthesis of $CpYb[SC_6H_4NC(NH^iPr)_2]_2(THF)$ (9). Cp_3Yb (0.453 g, 1.23 mmol) and *o*-aminothiophenol (0.308 g, 2.46 mmol) were mixed in 20 mL of THF. After stirring for 12 h at room temperature, *N*,*N*′-diisopropylcarbodiimide (0.310 g, 2.46 mmol) was added into the solution. After stirring for 48h, all volatile substances were removed under vacuum to give orange powder. Orange crystals of **9** were obtained by recrystallization from THF at –20 °C for several days. Yield: 0.855 g (86%). C, H, N analysis (%): calcd for $C_{35}H_{53}N_6OS_2Yb$: C 51.84, H 6.59, N 10.36; found: C 51.98, H 6.53, N 10.21; ^{1}H NMR δ/ppm: 7.00–7.28 (8H, C_6H_4), 6.53 (5H, C_5H_5), 3.10–3.57 (8H, $O(CH_2)_2(CH_2)_2$, $CH(CH_3)_2$), 4.00 (4H, N*H*), 0.83–1.41 ($O(CH_2)_2(CH_2)_2$, 28H, $CH(CH_3)_2$). IR

Table 6 Crystal and data collection parameters of complexes **2**, **5** and **6**

	2	**5**	**6**
Formula	$C_{29}H_{38}N_3SYb$	$C_{56}H_{80}N_6O_2S_2Y_2$	$C_{42}H_{56}N_4O_2S_2Y_2$
Molecular weight/g mol^{-1}	633.72	1111.20	890.85
Crystal colour	Orange	colorless	colorless
Crystal dimensions/mm	0.10 × 0.08 × 0.05	0.15 × 0.10 × 0.08	0.10 × 0.15 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$
a/Å	15.321(4)	10.340(3)	14.520(4)
b/Å	11.728(3)	20.754(5)	19.120(5)
c/Å	15.762(4)	15.309(4)	30.856(8)
β/°	103.182 (4)	99.351(3)	96.055(4)
V/Å^3	2757.7(13)	3241.6(13)	8518(4)
Z	4	2	8
D_c/g cm^{-3}	1.526	1.138	1.389
μ/mm^{-1}	3.488	1.884	2.848
F(000)	1276	1168	3696
Radiation (λ = 0.710730 Å)	MoKα	MoKα	MoKα
T/K	297(2)	293(2)	298(2)
Scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
θ range/°	1.37–26.01	1.96–25.01	1.77–25.01
h,k,l range	$-18 \le h \le 17, -14 \le k \le 12 -19 \le l \le 18$	$-12 \le h \le 12\ 0 \le k \le 24\ 0 \le l \le 18$	$-14 \le h \le 17 -15 \le k \le 22 -36 \le l \le 29$
No. of reflections measured	15 818	5702	17 785
No. of unique reflections completeness to θ	5412 (R_{int} = 0.0604) 99.7% (θ = 26.01)	5702 (R_{int} = 0.0000) 99.7% (θ = 25.01)	7524 (R_{int} = 0.0700) 100.0% (θ = 25.01)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5412/2/291	5702/2/310	7524/0/469
Goodness-of-fit on F^2	1.004	0.934	0.968
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0453, wR_2 = 0.1158	R_1 = 0.0470, wR_2 = 0.1069	R_1 = 0.0517, R_1 = 0.0453, wR_2 = 0.1158, wR_2 = 0.0918
R indices (all data)	R_1 = 0.0782, R_1 = 0.0453, wR_2 = 0.1158, wR_2 = 0.1416	R_1 = 0.0791, R_1 = 0.0453, wR_2 = 0.1158, wR_2 = 0.1157	R_1 = 0.1125, R_1 = 0.0453, wR_2 = 0.1158, wR_2 = 0.1087
Largest diffraction peak and hole (e Å^{-3})	2.530 and –1.059	0.518 and –0.364	0.417 and –0.267

Table 7 Crystal and data collection parameters of complexes **7**, **8** and **9**

	7	**8**	**9**
Formula	$C_{32}H_{32}N_2S_2Gd_2$	$C_{81}H_{110}N_7S_3O_2Gd_3$	$C_{35}H_{53}N_6S_2OYb$
Molecular weight/g mol^{-1}	823.22	1797.69	810.99
Crystal colour	Colourless	Colourless	Red
Crystal dimensions/mm	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	16.413(6)	25.853(9)	16.186(8)
b/Å	10.832(4)	12.257(4)	14.485(7)
c/Å	17.526(6)	28.459(10)	16.207(8)
β/°	111.808(4)	91.485(5)	98.977(8)
V/Å^3	2890.5(18)	9015(5)	3753(3)
Z	4	4	4
D_c/g cm^{-3}	1.892	1.271	1.435
μ/mm^{-1}	4.718	2.292	2.683
F(000)	1592	3476	1660
Radiation (λ = 0.710730 Å)	MoKα	MoKα	MoKα
T/K	293(2)	293(2)	293(2)
Scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
θ range/°	1.45–25.01	1.05–20.59	1.65–25.01
h,k,l range	$-18 \le h \le 19$ $-11 \le k \le 12$ $-20 \le l \le 20$	$-25 \le h \le 22$ $-11 \le k \le 12$ $-28 \le l \le 25$	$-19 \le h \le 16$ $-17 \le k \le 17$ $-17 \le l \le 19$
No. of reflections measured	11 749	30 400	15 596
No. of unique reflections	5077 (R_{int} = 0.0327)	9117 (R_{int} = 0.1800)	6610 (R_{int} = 0.0837)
Completeness to θ	99.6% (θ = 25.01)	99.7% (θ = 20.59)	99.8% (θ = 25.01)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5077/0/343	9117/44/403	6610/13/406
Goodness-of-fit on F^2	0.950	1.010	0.909
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0333, wR_2 = 0.0684	R_1 = 0.0731, wR_2 = 0.1835	R_1 = 0.0619, wR_2 = 0.1456
R indices (all data)	R_1 = 0.0595, wR_2 = 0.0765	R_1 = 0.1929, wR_2 = 0.2705	R_1 = 0.0980, wR_2 = 0.1581
Largest diffraction peak and hole (e Å^{-3})	1.460 and –0.661	1.348 and –1.298	3.807 and –2.319

(Nujol) ν/cm^{-1}: 3409 s, 3051 m, 1591 s, 1568 s, 1528 s, 1428 s, 1032 s, 882 m, 769 s, 733 s. m/z (%): 811 (29) [M].

Synthesis of [CpYb(THF)(μ-η^2:η^1-SC$_6$H$_4$N=C(NH^{i}Pr)N^{i}Pr)]$_2$ (3). A 20 mL THF solution of Cp_3Yb (0.196 g, 0.53 mmol) was slowly added to a 20 mL THF solution of **9** (0.559 g, 0.53 mmol) at room temperature and stirred for 24 h. The reaction solution was concentrated to *ca.* 5 mL by reduced pressure. Orange crystals of **3** were obtained at –20 °C for several days. Yield: 0.439 g (74%). C, H, N analysis (%): calcd for $C_{44}H_{64}N_6O_2S_2Yb_2$: C 47.22, H 5.76, N 7.51; found: C 47.19, H 5.80, N 7.74. IR (Nujol) ν/cm^{-1}: 3380 m, 1533 s, 1423 s, 1066 m, 1031 s, 922 m, 773 s, 744 s, 598 w. MS (70 eV): m/z (%): 488 (13) [1/2M – THF]. The identify of **3** was confirmed by comparison of X-ray crystallographic analysis data with literature values.[10a]

Crystal data and refinement details

Suitable single crystals of complexes **2**, and **5–9** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated MoKα (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS program.[15] The structures were solved by the direct method using the SHELXL-97 program.[16] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. All calculations were performed using the SHELXL program. A summary of the crystallographic data and selected experimental information are given in Tables 6 and 7.

Due to the poor quality of data for compound **8** that it was appropriate to leave most of the atoms isotropic as could only show the overall connectivity. The diffraction intensity is too weak in the remote sets during the crystal data collection due to the poor quality of crystal sample **8**. In **2**, the disorder and isotropic of the atoms C6–C10 (one Cp ring) have been done. Compounds **5** and **8** have large voids in the crystal structure should be the result of the highly disordered solvent. However, this problem cannot be solved by the use of the SQUEEZE program. It maybe attributed to the low occupations of these solvent molecules.

Acknowledgements

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