

Insertion of ketenes into lanthanocene *n*-butylamide and imidazolate complexes

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Abstract

Reaction of $\text{Cp}_2\text{LnNH}^n\text{Bu}$ with 1 equiv. of Ph_2CCO in toluene affords dimeric complexes $[\text{Cp}_2\text{Ln}(\text{OC}(\text{CHPh}_2)\text{N}^n\text{Bu})_2]$ [$\text{Ln} = \text{Yb}$ (**1**), Dy (**2**)], derived from a formal insertion of the $\text{C}=\text{C}$ bond of the ketene into the $\text{N}-\text{H}$ bond. Treatment of CpErCl_2 with 2 equiv. of LiNH^nBu followed by reacting with Ph_2CCO affords a rearrangement product $[\text{Cp}_2\text{Er}(\text{OC}(\text{CHPh}_2)\text{N}^n\text{Bu})_2]$ (**3**). Treatment of $[\text{Cp}_2\text{Ln}(\mu\text{-Im})_3]$ ($\text{Im} = \text{imidazolate}$) with PhRCCO gives $[\text{Cp}_2\text{Ln}(\mu\text{-OC}(\text{Im})=\text{CPhR})_2]$ [$\text{R} = \text{Et}$, $\text{Ln} = \text{Yb}$ (**4**); $\text{R} = \text{Ph}$, $\text{Ln} = \text{Yb}$ (**5**), Er (**6**)]. In contrast to the previous observations that $[\text{Cp}_2\text{ErN}^i\text{Pr}_2]_2$ and $[\text{Cp}_2\text{ErNHet}]_2$ react with ketenes to give di-insertion products, in the present cases the presence of excess of ketenes has no influence on the final product even with prolonged heating and only mono-insertion products are isolated. All these complexes were characterized by elemental analysis, IR and mass spectroscopies. The structures of complexes **1** and **3–6** were also determined through X-ray single crystal diffraction analysis.

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Keywords: Organolanthanide; Insertion; Ketene; Amide complexes; Crystal structures

1. Introduction

The insertion of unsaturated substrates into organolanthanide complexes is regarded as one of the most fundamental organometallic reactions and has attracted great interest [1]. Among these, steady and increasingly attention has been focused on the addition reactions of organolanthanide amide complexes to unsaturated substrates such as CO_2 [2a], CS_2 [3], isocyanates [2a,4a–c], isothiocyanates [3,4b,5], and carbodiimides [4b,5,6a–g], because of the potential for facilitating carbon–nitrogen bond formation. Such stoichiometric insertions have resulted in access to a

wide variety of new organolanthanides. Additionally, catalytic transformation of unsaturated amines via the $\text{Ln}-\text{N}$ bond insertion mechanism has rendered available organic products that would only be accessible, often less selectively, by lengthy alternative synthetic routes [7]. We are interested in contributing to this field by developing new insertion reactions. We recently reported that reactions of ketenes with organolanthanide amide complexes led to interesting patterns of reactivity compared to their transition metal counterparts and demonstrated that the products strongly depended on the nature of amide ligands. For example, the reaction of $[\text{Cp}_2\text{ErN}^i\text{Pr}_2]_2$ with 4 equiv. of PhEtCCO affords the unprecedented enolizative dearomatization/rearomatization product $[\text{Cp}_2\text{Er}\{\text{OC}(\text{C}_6\text{H}_4(p\text{-CHEtCON}^i\text{Pr}_2))=\text{CEtPh}\}]_2$, while $[\text{Cp}_2\text{ErNHet}]_2$ reacts with excess of PhEtCCO to give the non-coupling double insertion product $[\text{Cp}_2\text{Er}(\text{PhEtCHCON}(\text{Et})\text{COEtPh})_2]$ under the same conditions [8]. In seeking to broaden further the scope of this work and to better understand the

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influence of the amide ligand, herein we describe the reactions of lanthanocene *n*-butylamide and imidazolate complexes with ketenes, which lead to the isolation and characterization of a series of lanthanocene amido complexes.

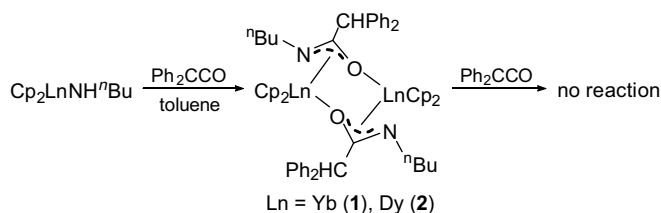
2. Results and discussion

2.1. Reaction of Cp_2LnNH^iBu with diphenylketene

Cp_2LnNH^iBu were prepared by reaction of $LiNH^iBu$ with Cp_2LnCl [9]. As illustrated in Scheme 1, the reaction of Cp_2LnNH^iBu with Ph_2CCO provided the products from formal Ph_2CCO insertion into the N–H bond, $[Cp_2Ln(\mu-\eta^1:\eta^3-OC(CHPh_2)N^iBu)_2]$ [$Ln = Yb$ (**1**), Dy (**2**)], as determined by X-ray crystal analysis. In contrast to $[Cp_2ErN^iPr_2]_2$ and $[Cp_2ErNH^iEt]_2$ that react with ketenes to give the di-insertion products [8], in the present reaction the presence of excess of Ph_2CCO has no influence on the final product even with prolonged heating.

Complexes **1** and **2** are moderately sensitive to air and moisture, they are readily dissolved in THF and toluene, but sparingly soluble in *n*-hexane. Complexes **1** and **2** were characterized by elemental analysis, IR, and mass spectroscopies, which were in good agreement with the proposed structures. The structure of complex **1** was also confirmed by X-ray single crystal diffraction analysis.

The bonding mode of the resulting amido ligand was verified by the X-ray analysis of complex **1** (Fig. 1). A



Scheme 1.

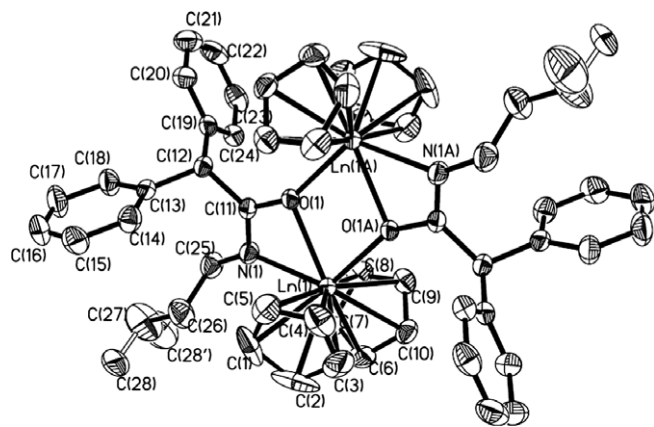


Fig. 1. ORTEP diagram of $[Cp_2Ln(OC(CHPh_2)N^iBu)_2]$ [$Ln = Yb$ (**1**), Er (**3**)] with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 1
Select bond lengths (Å) and angles (°) for **1** and **3**

	Ln = Yb (1)	Ln = Er (3)
Ln(1)–O(1A)	2.285(3)	2.299(4)
Ln(1)–O(1)	2.374(3)	2.399(4)
Ln(1)–N(1)	2.406(4)	2.435(5)
C(11)–C(12)	1.521(5)	1.543(7)
Ln–C _{ave} (Cp)	2.623(5)	2.638(8)
O(1)–C(11)	1.325(5)	1.313(7)
N(1)–C(11)	1.282(5)	1.282(7)
C(11)–O(1)–Ln(1A)	151.4(3)	151.9(4)
C(11)–O(1)–Ln(1)	95.5(2)	95.1(4)
Ln(1A)–O(1)–Ln(1)	111.51(11)	111.34(15)
O(1)–C(11)–C(12)	116.1(4)	116.2(6)
N(1)–C(11)–Ln(1)	58.0(2)	58.9(3)
O(1)–C(11)–Ln(1)	56.73(19)	57.5(3)

C=N stretching frequency in the IR spectrum at approximately 1580 cm^{-1} is in agreement with the bidentate η^3 -bonding mode of the amido ligand [10]. The mass spectra of **1** and **2** displays a series of peaks representing fragments derived from the parent molecules and are characterized by the $[M/2-Cp]$.

The structure of **1** is shown in Fig. 1 and selected bond distances and angles are given in Table 1. All the distances and angles of complex **1** are in normal range, and the OCN fragment of the amido ligand acts as both a bridging and side-on chelating group. The C(11)–C(12) distance, 1.521(5) Å, is in the observed range for the C–C single bond distance. Both the O(1)–C(11) and the N(1)–C(11) distances of 1.325(5) and 1.282(5) Å lie between the corresponding single and double bond distances [11], which suggests electronic delocalization over the OCN unit.

2.2. Reaction of $CpLnCl_2$ with $LiNH^iBu$ and subsequent treatment with diphenylketene

It is well-known that cyclopentadienyl co-ligands play an important role in controlling the reactivity of organo-lanthanide amide complexes, but the study has been mainly focused dicyclopentadienyl lanthanide amides and cyclopentadienyl-bridged lanthanide amides complexes [12]. To gain more insight into the insertion of ketene into the Ln–N bond, the reaction of $CpEr(NH^iBu)_2$, prepared in situ, with Ph_2CCO was also studied. It was found that $CpEr(NH^iBu)_2$ reacted with 2 equiv. of diphenylketene, leading to the isolation of $[Cp_2Er(OC(CHPh_2)N^iBu)_2]$ (**3**). Complex **3** structurally resembles **1** and **2**, although they are obtained by different approaches. Presumably, complex **3** could result from the rearrangement of the di-insertion product $CpEr[(OC(CHPh_2)N^iBu)_2]$. Regrettably, efforts for the separation and characterization of the di-insertion intermediate $CpEr[(OC(CHPh_2)N^iBu)_2]$ and another rearrangement product were unsuccessful.

Complex **3** crystallized from toluene in the orthorhombic *Pbc*a space group. As shown in Fig. 1, complex **3** are isomorphous to **1**. All bond parameters for **3** (Table 1) fall

in the normal ranges. The bond distances associated with the metal in **3** are similar to the corresponding values in **1**, if the difference in metal radii is considered [13] (see Scheme 2).

2.3. Reaction of $[\text{Cp}_2\text{Ln}(\mu\text{-Im})_3]$ with ethylphenylketene and diphenylketene

In contrast to the extensive studies on the rich chemistry of non-cyclic amide lanthanide complexes, reports on reactions involving aromatic nitrogen ligands bonded to the lanthanide metal are scarce. In most cases, aromatic nitrogen ligands serve as ancillary ligands for the construction of the coordination geometry of the metal ions but do not participate in organometallic reactions [14–17]. Very recently, we found that treatment of $[\text{Cp}_2\text{Ln}(\mu\text{-Im})_3]$ (Im = imidazolate) with phenyl isocyanate could lead to the formation of unusual ring expansion products [4a]. To better understand the influence of the nature of amide ligands and further develop the ketene insertion, reactions of $[\text{Cp}_2\text{Ln}(\mu\text{-Im})_3]$ with ethylphenylketene and diphenylketene have been studied. The results indicated that PhRCCO can only be mono-inserted into the lanthanide–imidazolate bond to yield $[\text{Cp}_2\text{Ln}(\mu\text{-OC}(\text{Im})=\text{CPhR})_2]$ [R = Et, Ln = Yb (**4**); R = Ph, Ln = Yb (**5**), Er (**6**)] (Scheme 3), even in presence of excess PhRCCO with a higher reaction temperature and a longer reaction time.

Complexes **4–6** are readily dissolved in THF, but sparingly soluble in toluene and *n*-hexane. They were characterized by elemental analysis, IR, mass spectroscopies. Their mass spectra display a series of peaks clearly representing fragments derived from the parent molecule. In the IR spectra of **4–6**, the characteristic absorption at ca. 2097 cm^{-1} for the stretch of free PhEtCCO is absent, but

a new strong absorption at ca. 1620 cm^{-1} is present, which is attributable to a C=C stretch [18]. The structures of complexes **4–6** were further confirmed by X-ray single-crystal structure determinations.

The X-ray structural analysis results show that **4** (Fig. 2) and **5–6** (Fig. 3) are solvent-free cyclic dimeric structures with the lanthanide atom bonded to two η^5 -cyclopentadienyl rings, one nitrogen atom of the imidazolate and one oxygen of enolate unit to form a distorted tetrahedron geometry. The coordination number of the central Ln^{3+} is 8. Selected bond distances and angles for complex **4**, **5** and **6** are given in Tables 2 and 3, respectively.

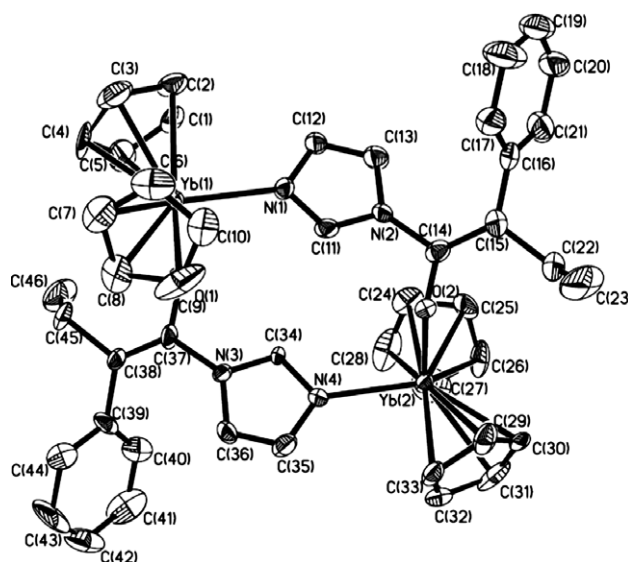


Fig. 2. ORTEP diagram of $[\text{Cp}_2\text{Yb}(\mu\text{-OC}(\text{Im})=\text{CPhEt})_2]$ (**4**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

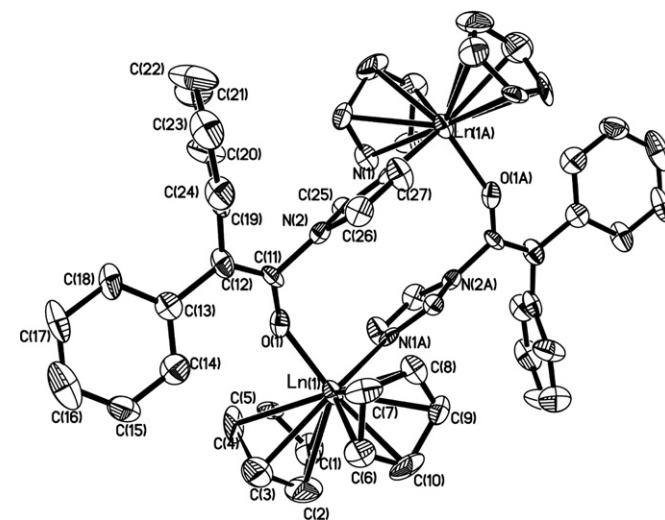
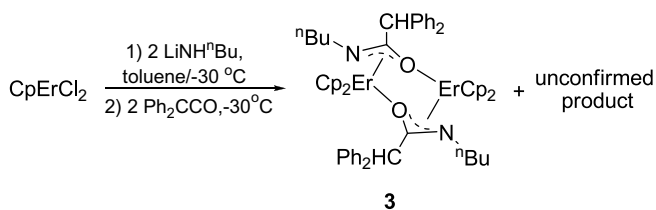
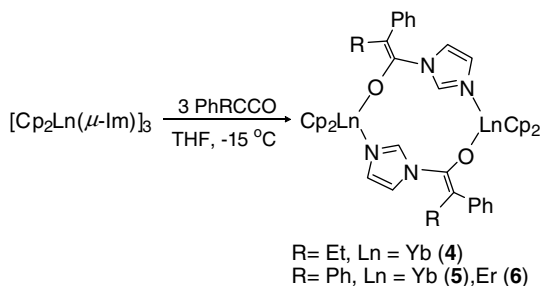


Fig. 3. ORTEP diagram of $[\text{Cp}_2\text{Ln}(\mu\text{-OC}(\text{Im})=\text{CPh}_2)_2]$ (Ln = Yb (**5**), Er (**6**)) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.



Scheme 2.



Scheme 3.

Table 2
Select bond lengths (Å) and angles (°) for **4**

Yb(1)–O(1)	2.107(8)	Yb(2)–O(2)	2.123(9)
Yb(1)–N(1)	2.379(12)	Yb(2)–N(4)	2.404(11)
O(1)–C(37)	1.363(15)	C(14)–C(15)	1.389(16)
O(2)–C(14)	1.279(15)	C(37)–C(38)	1.317(14)
Yb(1)···Yb(2)	6.951(18)		
O(1)–Yb(1)–N(1)	90.2(4)	C(13)–N(2)–C(14)	127.6(12)
O(2)–Yb(2)–N(4)	90.8(3)	C(34)–N(3)–C(36)	105.9(10)
C(37)–O(1)–Yb(1)	142.9(8)	C(34)–N(3)–C(37)	124.6(10)
C(14)–O(2)–Yb(2)	144.2(9)	C(36)–N(3)–C(37)	129.5(11)
C(11)–N(1)–C(12)	105.0(11)	C(34)–N(4)–C(35)	103.6(11)
C(11)–N(1)–Yb(1)	125.4(9)	C(34)–N(4)–Yb(2)	124.2(8)
C(12)–N(1)–Yb(1)	129.4(9)	C(35)–N(4)–Yb(2)	131.6(9)
C(11)–N(2)–C(13)	107.0(12)	O(2)–C(14)–C(15)	127.7(12)
C(11)–N(2)–C(14)	125.3(11)	O(2)–C(14)–N(2)	112.7(12)

Table 3
Bond lengths (Å) and angles (°) for complex **5** and **6**

	Ln = Yb	Ln = Er
Ln(1)–O(1)	2.078(18)	2.152(9)
Ln(1)–N(1A)	2.367(18)	2.404(10)
O(1)–C(11)	1.31(3)	1.279(17)
N(2)–C(11)	1.43(3)	1.463(16)
C(11)–C(12)	1.37(4)	1.357(19)
O(1)–Ln(1)–N(1A)	96.0(6)	96.6(4)
C(11)–O(1)–Ln(1)	147.5(16)	147.7(8)
O(1)–C(11)–C(12)	127(2)	129.4(12)
O(1)–C(11)–N(2)	115(2)	112.4(11)
C(12)–C(11)–N(2)	117(2)	118.1(12)

For complex **4**, the Yb–N distances, 2.379(12) and 2.404(11) Å, are intermediate between the values observed for the Yb–N single-bond and donor-bond distances (2.19–2.69 Å) [19] and are comparable to the corresponding values found in $[(C_5H_4Me)Yb(PzMe_2)(OSiMe_2PzMe_2)]_2$ (Yb–N(bridge pyrazolate)) 2.402(7) Å [19b]. Consistent with this case, the C–O distances, 1.363(15) and 1.279(15) Å, are between those expected for a $C_{sp^2}=O$ (1.214 Å) and $C_{sp^2}-O$ (1.41 Å). The Yb–O(1) distance (2.107(8) Å) is slightly longer than that observed for the μ -oxide group in $[(C_5H_4Me)_2Yb(THF)]_2(\mu-O)$ (2.02(1) Å) [20], but is shorter than that found in $[(C_5H_4Me)Yb(PzMe_2)(OSiMe_2PzMe_2)]_2$ (2.250(5) Å) [19b] and $[Cp_2Ln(\mu-\eta^1:\eta^2-OC(Im)NPh)]_3$ (2.352(8) Å) [4a]. The C(37)–C(38) distance, 1.317(14) Å, is in the observed range for carbon–carbon double bond distances [11].

As shown in Fig. 3, complex **6** is isostructural to complex **5**. Selected bond distance and angles for **6** are listed in Table 3. The structural parameters of **5** and **6** are very similar to those for complex **4**.

3. Conclusions

We have demonstrated that the reactivity of lanthanocene amide complexes toward ketenes is susceptible to the

nature of amide ligands. In contrast to the observation that for secondary amide complexes, such as $[Cp_2LnN^iPr_2]_2$, the second ketene molecule can be incorporated into the first insertion product [8], the use of the imidazolate ligand can only lead to the mono-insertion product. Furthermore, it has been found that replacement of NHEt with NH^tBu also affects the overall reactivity of lanthanocene amides toward ketenes due to the steric effect. All these results indicate that the nature of the amide ligands have great influence on the ketene insertion into the lanthanide–nitrogen bond.

4. Experimental

4.1. General procedures

All operations dealing with air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques. The solvents of THF, toluene and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen prior to use. 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 300 °C. The values of *m/z* are referred to the isotopes ¹H, ¹²C, ¹⁴N, ¹⁶O, ¹⁷⁴Yb, ¹⁶⁶Er, and ¹⁶⁴Dy.

$CpLnCl_2(THF)_3$ [21], Cp_3Ln [22], $[Cp_2Ln(\mu-Im)]_3$ [4a], diphenylketene [23], and ethylphenylketene [24] were prepared according to the procedures described in the literatures. Cp_2LnNH^tBu were prepared by reaction of ^tBuNHLi with Cp_2LnCl [9]. *n*-Butyllithium, *n*-butylamine, and imidazole were purchased commercially and used without further purification.

4.2. Synthesis of $[Cp_2Yb(\mu-\eta^1:\eta^3-OC(CHPh)_2)N^tBu]_2$ (**1**)

Diphenylketene (0.410 g, 2.12 mmol) was added to a solution of Cp_2YbNH^tBu (0.396 g, 1.06 mmol) in toluene at –30 °C. The mixture was warmed to room temperature and was stirred overnight. The solution was concentrated by reduced pressure to saturation and added 1 mL THF and then cooled at –18 °C to give **1** as orange crystals. Yield: 0.432 g (72%). IR (Nujol, cm^{-1}): 1583 s, 1494 m, 1344 s, 1216 s, 1190 s, 1155 m, 1120 m, 1077 m, 1011 m, 923 m, 901 m, 890 m, 644 s, 617 m. EI-MS: *m/z* [fragment, relative intensity (%)] = 505 (M/2-Cp, 20), 304 (Cp_2Yb , 70), 195 (Ph_2CCO+1 , 3), 66 (CpH, 40). Anal. Calc. for $C_{56}H_{60}N_2O_2Yb_2$, $M_w = 1139.14$: C, 59.05; H, 5.31; N, 2.46. Found: C, 59.17; H, 5.22; N, 2.40%.

4.3. Synthesis of $[Cp_2Dy(\mu-\eta^1:\eta^3-OC(CHPh_2)N^mBu)]_2$ (**2**)

By the procedure described for **1**, reaction of Cp_2DyNH^mBu (0.408 g, 1.12 mmol) with Ph_2CCO (0.215 g, 1.11 mmol) gave yellow solution. The solution was concentrated to 1 mL and then washed by 20 mL hexane twice to give **2** as pale yellow powder. Yield: 0.369 g (59%). IR(Nujol, cm^{-1}): 1560 s, 1490 s, 1344 s, 1250 s, 1215 s, 1155 m, 1120 m, 1078 m, 1011 m, 901 m, 890 s, 649 s, 610 m. EI-MS: m/z [fragment, relative intensity (%)] = 495 (M/2-Cp, 24), 294 (Cp_2Dy , 56). Anal. Calc. for $C_{56}H_{60}N_2O_2Dy_2$, $M_w = 1118.10$: C, 60.16; H, 5.41; N, 2.50. Found: C, 60.56; H, 5.30; N, 2.61%.

4.4. Synthesis of $[Cp_2Er(\mu-\eta^1:\eta^3-OC(CHPh_2)N^mBu)]_2$ (**3**)

nBuLi (1.72 M, 0.71 mL in cyclohexane) was added to a solution of nBuNH_2 (0.09 g, 1.22 mmol) in 30 mL toluene at $-30^\circ C$. After being stirred for 3 h at this temperature, the mixture solution was added to the toluene solution of $CpErCl_2(THF)_3$ (0.317 g, 0.61 mmol) at $-20^\circ C$. After stirring for 30 min at the low temperature, the mixture was warmed to room temperature and stirred for 2 h. Then it was cooled $-30^\circ C$ and Ph_2CCO (0.237 g, 1.22 mmol)

was added to the solution. The mixture was warmed to room temperature and was stirred overnight. After centrifugation, the filtrate was concentrated to ca. 4 mL and cooled at $-18^\circ C$ to give **3** as orange crystals. Yield: 0.109 g. IR(Nujol, cm^{-1}): 1667 s, 1493 m, 1347 s, 1217 s, 1190 m, 1155 w, 1122 m, 1077 w, 1011 s, 923 w, 901 w, 890 w, 702 s, 644 s. Anal. Calc. for $C_{56}H_{60}N_2O_2Er_2$, $M_w = 1127.58$: C, 59.65; H, 5.37; N, 2.48. Found: C, 60.79; H, 5.54; N, 2.29%.

4.5. Synthesis of $[Cp_2Yb(\mu-OC(Im)=CPhEt)]_2$ (**4**)

To a 30 mL THF solution of $[Cp_2Yb(\mu-Im)]_3$ (0.487 g, 0.439 mmol) was added $PhEtCCO$ (0.193 g, 1.32 mmol) with a syringe at $-15^\circ C$. The reaction mixture was slowly warmed to ambient temperature and stirred for 24 h. The solution was added toluene 8 mL and then evaporated to ca. 5 mL. Orange yellow crystals of **4** were slowly formed at room temperature. Yield: 0.510 g (75%). M.p. $170-172^\circ C$. IR (Nujol, cm^{-1}): 2418 w, 1969 w, 1951 w, 1898 w, 1737 m, 1620 s, 1589 s, 1222 s, 1198 s, 1155 s, 1073 s, 1013 s, 939 s, 913 m, 841 m, 694 s, 661 s. EI-MS: m/z [fragment, relative intensity (%)] = 304 (Cp_2Yb , 2), 239 ($CpYb$, 5), 213 ($PhEtCCO+C_3H_3N_2$, 5), 146 ($PhEt-$

Table 4
Crystal and data collection parameters of complexes **1**, **3-6**

	1	3	4	5	6
Formula	$C_{56}H_{60}N_2O_2Yb_2$	$C_{56}H_{60}Er_2N_2O_2$	$C_{46}H_{46}N_4O_2Yb_2$	$C_{54}H_{46}N_4O_2Yb_2$	$C_{54}H_{46}N_4O_2Er_2$
Molecular weight	1139.14	1127.58	1032.95	1129.03	1117.47
Crystal color	Orange red	Orange	Orange red	Orange red	Pink
Crystal dimensions (mm)	$0.35 \times 0.15 \times 0.10$	$0.25 \times 0.20 \times 0.15$	$0.25 \times 0.15 \times 0.10$	$0.20 \times 0.15 \times 0.10$	$0.20 \times 0.15 \times 0.10$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pna2</i> ₁	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	19.469(5)	19.554(7)	15.215(5)	32.793(14)	33.029(5)
<i>b</i> (Å)	9.559(3)	9.574(3)	13.448(4)	8.315(4)	8.356(4)
<i>c</i> (Å)	25.792(7)	25.848(9)	24.858(8)	23.057(10)	23.155(7)
α (°)	90	90	90	90	90
β (°)	90	90	90	122.289(5)	122.994(5)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	4800(2)	4839(3)	5086(3)	5315(4)	5360(3)
<i>Z</i>	4	4	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.576	1.548	1.349	1.411	1.358
μ (mm ⁻¹)	3.915	3.487	3.688	3.537	3.149
Radiation ($\lambda = 0.710730$ Å)	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ Range (°)	1.58–25.01	1.58–25.01	1.64–26.00	1.80–25.01	1.79–25.01
<i>h, k, l</i> Range	$-23 \leq h \leq 21$ $-11 \leq k \leq 11$ $-30 \leq l \leq 27$	$-20 \leq h \leq 23$ $-11 \leq k \leq 11$ $-28 \leq l \leq 30$	$-18 \leq h \leq 12$ $-16 \leq k \leq 15$ $-30 \leq l \leq 30$	$-38 \leq h \leq 38$ $-9 \leq k \leq 9$ $-23 \leq l \leq 27$	$-39 \leq h \leq 33$ $-9 \leq k \leq 5$ $-26 \leq l \leq 27$
Number of reflections measured	18,940	19,146	22,232	10,519	9944
Number of unique reflections (<i>R</i> _{int})	4235 (0.0310)	4269 (0.0839)	9991 (0.0367)	4678 (0.0824)	4701 (0.0341)
Completeness to θ	99.9% ($\theta = 25.01$)	100.0% ($\theta = 25.01$)	100.0% ($\theta = 26.00$)	99.9% ($\theta = 25.01$)	99.8% ($\theta = 25.01$)
Maximum and minimum transmission	0.6955 and 0.3411	0.6228 and 0.4760	0.7093 and 0.4591	0.7187 and 0.5381	0.7436 and 0.5716
Data/restraints/parameters	4235/6/273	4269/6/273	9991/1/436	4678/18/258	4701/0/280
Goodness-of-fit on <i>F</i> ²	1.033	1.032	1.125	1.346	1.253
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0281 <i>wR</i> ₂ = 0.0634	<i>R</i> ₁ = 0.0423 <i>wR</i> ₂ = 0.0601	<i>R</i> ₁ = 0.0462 <i>wR</i> ₂ = 0.1432	<i>R</i> ₁ = 0.1531 <i>wR</i> ₂ = 0.3112	<i>R</i> ₁ = 0.0766 <i>wR</i> ₂ = 0.2095
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0422 <i>wR</i> ₂ = 0.0684	<i>R</i> ₁ = 0.0781 <i>wR</i> ₂ = 0.0658	<i>R</i> ₁ = 0.0690 <i>wR</i> ₂ = 0.1608	<i>R</i> ₁ = 0.1958 <i>wR</i> ₂ = 0.3292	<i>R</i> ₁ = 0.1031 <i>wR</i> ₂ = 0.2300
Largest difference in peak and hole (e Å ⁻³)	0.909 and -0.447	1.171 and -0.623	1.866 and -0.965	2.448 and -3.620	2.853 and -1.384

CCO, 85), 117 (PhCCO, 100), 66 (CpH, 30). Anal. Calc. for $C_{46}H_{46}O_2N_4Yb_2$, $M_w = 1032.95$: C, 53.49; H, 4.49, N, 5.42. Found: C, 53.79; H, 4.60; N, 5.36%.

4.6. Synthesis of $[Cp_2Yb(\mu-OC(Im)=CPh_2)]_2$ (**5**)

By the procedure described for **4** reaction of $[Cp_2Yb(\mu-Im)]_3$ (0.510 g, 0.46 mmol) with Ph_2CCO (0.267 g, 1.38 mmol) gave **5** as orange crystals. Yield: 0.646 g (83%). M.p. 218–220 °C. IR (Nujol, cm^{-1}): 1736 w, 1619 s, 1586 s, 1442 m, 1298 s, 1212 s, 1136 s, 1104 s, 1072 s, 1012 s, 940 m, 912 m, 846 m, 795 m, 768 s, 701 s. EI-MS: m/z [fragment, relative intensity (%)] = 304 (Cp_2Yb , 2), 265 ($Ph_2CCO + C_3H_3N_2$, 2), 239 ($CpYb$, 5), 194 (Ph_2CCO , 45), 165 (Ph_2C-1 , 100), 66 (CpH , 45). Anal. Calc. for $C_{54}H_{46}O_2N_4Yb_2$, $M_w = 1129.03$: C, 57.44; H, 4.11, N, 4.96. Found: C, 57.26; H, 4.17; N, 5.04%.

4.7. Synthesis of $[Cp_2Er(\mu-OC(Im)=CPh_2)]_2$ (**6**)

By the procedure described for **4** reaction of $[Cp_2Er(\mu-Im)]_3$ (0.390 g, 0.357 mmol) with Ph_2CCO (0.206 g, 1.07 mmol) gave **6** as pink crystals. Yield: 0.507 g (85%). IR (Nujol, cm^{-1}): 1746 w, 1617 s, 1585 s, 1443 m, 1293 s, 1212 s, 1135 s, 1104 s, 1073 s, 1012 s, 939 m, 912 w, 847 w, 795 m, 768 s, 701 s. EI-MS: m/z [fragment, relative intensity (%)] = 296 (Cp_2Er , 2), 265 ($Ph_2CCO + C_3H_3N_2$, 2), 165 (Ph_2C-1 , 100), 194 (Ph_2CCO , 45), 66 (CpH , 45). Anal. Calc. for $C_{54}H_{46}O_2N_4Er_2$, $M_w = 1117.47$: C, 58.04; H, 4.15, N, 5.01. Found: C, 58.21; H, 4.31; N, 4.96%.

4.8. X-ray data collection, structure determination and refinement

Suitable single crystals of complexes **1**, **3–6** were selected and sealed in a thin-walled glass capillary under N_2 for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated $Mo\ K\alpha$ ($\lambda = 0.71073\text{ \AA}$) 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 [25]. The structures were solved by the direct method using the SHELXL-97 program [26]. 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 Bruker SMART program. A summary of the crystallographic data and selected experimental information is given in Table 4.

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Appendix A. Supplementary material

CCDC 663949, 663950, 663946, 663948 and 663947 contain the supplementary crystallographic data for **1**, **3**, **4**, **5** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2007.12.018](https://doi.org/10.1016/j.jorgchem.2007.12.018).

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- group: Ama_2 , $a = 8.384(3)$, $b = 21.027(8)$, $c = 10.079(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 1776.7(11)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.384$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 4.704$ mm⁻¹, $T = 293(2)$ K, $2\theta = 54.16$, $R_1 = 0.0511$, $wR_2 = 0.1416$ for 4377 reflections with $I > 2\sigma(I)$.
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