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Synthesis and crystal structure of 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) *ansa*-lanthanocene chlorides

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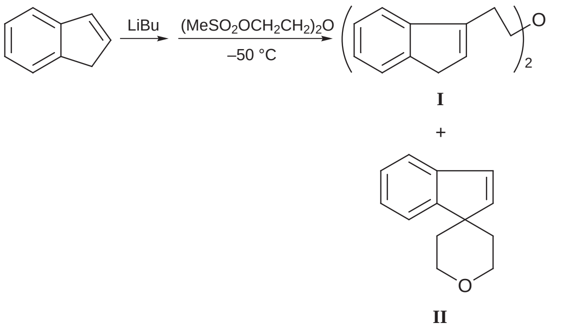
Several representative chiral *ansa*-lanthanocene chlorides have been synthesized and characterised with a *rac*:*meso* ratio of 6:1 using an ether-bridged bis(indenyl) ligand. The structure of these complexes was identified by X-ray crystallography in the solid state or ^{1}H NMR spectroscopy in solution. The ligand proved to be rather rigid leading to the favoured unsymmetric *rac* isomer. The ^{1}H NMR spectra indicated that the configuration of the *rac* isomer in solution agrees well with that in the solid state and, interestingly, the two bridged indenyl rings of the *rac* isomers slowly oscillated.

Over recent years considerable efforts have been devoted to exploring organometallic chemistry of chiral *ansa*-metallocenes of lanthanoids.[1] However, current examples of such compounds are predominantly those with short bridges (one or two atoms) and bulky substituents on the cyclopentadienyl rings to achieve rigid ligands and high *rac*/*meso* selectivity. This is probably due to the implications of the chiral long-bridged Group IV *ansa*-metallocene complexes which showed poor selectivities and reactivities in the polymerisation of olefins, attributed to the flexibility of the bridges, although there are sharp differences between Group III and IV elements.[2] Our previous work demonstrated that pentamethylene-bridged cyclopentadienyl lanthanide complexes showed low reactivities. Interestingly, when the central atom of the bridge was replaced with an oxygen or nitrogen atom the corresponding complexes exhibited higher reactivities.[3] However, the decisive structure of these sorts of complexes is still elusive, except for some deduction from spectra and a few hydrolysis derivatives.[4] Although triindenyllanthanide complexes were reported *ca.* 30 years ago,[5] the indenyl ligand has not found wide application in the organometallic chemistry of lanthanoids,[6] especially compared with the other transition-metal elements. Considering the unique features of the indenyl ligand in exploring the chemistry of sandwich organometallic complexes, such as its diversity of bonding modes (η^1, η^3 and η^5) and the so-called 'indene effect', *etc.*,[7] we believed that replacement of cyclopentadienyl with indenyl would help to explore the chemistry of *ansa*-lanthanocene complexes. In connection with our previous work, we chose 1,1′-(3-oxapentamethylene)bis(indenyl) as ligand. The sterically demanding but planar indenyl rings were expected to serve dual functions: satisfying the requirement of steric saturation, but leaving more easily accessible the central metals relative to some substituted cyclopentadienyl ligands such as *tert*-butylcyclopentadienyl, *etc.* Here we report the synthesis and structure of some representative 1,1′-(3-oxopentamethylene)bis(indenyl) *ansa*-lanthanoid chlorides.

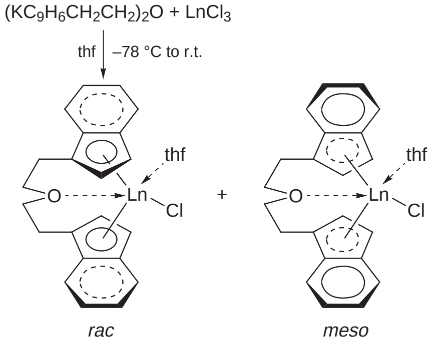
Results and Discussion

Synthesis

The initial attempt to prepare 1,5-bis(indenyl)-3-oxapentane by using indenyl alkali-metal salts (Li, Na or K) and bis(2-chloroethyl) ether led to complex mixtures including compounds **I**, **II** and unidentified polymers. Considering that the by-products were due to rapid proton exchange between indenyl salts and the intermediate nucleophilic substitution products, we turned to a combination of indenyllithium with diethylene glycol dimesylate and obtained the desired indene derivatives in *ca.* 34% yield under optimized conditions: low temperature, slow addition of indenyllithium to diethylene glycol dimesylate in thf (Scheme 1). Deprotonation of **I** with potassium metal followed by exposure to equimolar amounts of lanthanide chlorides suspended in thf provided the desired complexes **1**–**7** in moderate yields with a *rac*:*meso* ratio up to 6:1 determined from the integration of the ^{1}H resonance of the five-membered portion of the indenyl rings (Scheme 2). Interestingly, recrystallisation from thf did not appear to change the ratio of the *rac*:*meso* isomers. All complexes were soluble in thf at room temperature, but just slightly soluble in toluene. It was surprising that one tetrahydrofuran molecule was co-ordinated for both the light and heavy lanthanoid complexes, considering that the corresponding cyclopentadienyl analogues exist as unsolvated complexes.[3] The co-ordinated tetrahydrofuran could be partly removed when these complexes were heated *in vacuo*



Scheme 1



Ln = Y **1**, Pr **2**, Nd **3**, Gd **4**, Dy **5**, Ho **6**, Lu **7**

Scheme 2

Table 1 Selected two-dimensional ^{1}H NMR data for complex **1** (*rac* isomer)

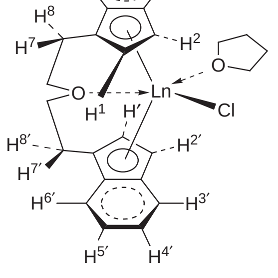
Proton (δ, *J*/Hz)	Cross-peaks in NOESY	Exchange cross-peaks in NOESY	Cross-peaks in COSY
$H^{6'}$ (7.80, 1 H, d, $J = 7.8$)	$H^{6'}$–H^1, $H^{6'}$–$H^{7'}$	$H^{6'}$–H^6	$H^{6'}$–$H^{5'}$
$H^{3'}$ (7.70, 1 H, q, $J = 7.5$, 1.5)	$H^{3'}$–H^2	$H^{3'}$–H^3	$H^{3'}$–$H^{4'}$
H^6 (7.35, m)*	H^6–CH_2	H^6–$H^{6'}$	H^6–H^5
H^3, $H^{4'}$, $H^{5'}$ (7.10–7.25, m)*	$H^{4'}$($H^{5'}$)–H^1	$H^{4'}$–H^4, $H^{5'}$–H^5	H^4–$H^{3'}$, $H^{5'}$–$H^{6'}$
H^4, H^5 (6.80, m)*	H^4–H^3, H^5–H^6	H^4–$H^{4'}$, H^5–$H^{5'}$	H^4–H^3, H^5–H^6
$H^{1'}$ (6.40, 1 H, d, $J = 3.4$)	$H^{1'}$–$H^{2'}$, $H^{1'}$–$H^{8'}$	$H^{1'}$–H^1	$H^{1'}$–$H^{2'}$
$H^{2'}$ (5.95, 1 H, d, $J = 3.4$)	$H^{2'}$–$H^{3'}$, $H^{2'}$–$H^{1'}$	$H^{2'}$–H^2	$H^{2'}$–$H^{1'}$
H^1 (5.05, 1 H, d, $J = 3.1$)	H^1–H^7, H^1–H^2, $H^{4'}$($H^{5'}$)–H^1	H^1–$H^{1'}$	H^1–H^2
H^2 (4.90, 1 H, d, $J = 3.1$)	H^2–H^1, H^2–H^3	H^2–$H^{2'}$	H^2–H^1

* Overlapped with *meso* isomer.

or immersed in toluene or hexane, but the resulting complexes became less soluble. The exact reason is not clear. These complexes are not only sensitive to air and moisture but also to light and are less thermally stable relative to the cyclopentadienyl complexes. Attempts to prepare the corresponding lanthanum complex met with failure.

Spectroscopic properties

The ^{1}H NMR spectra of diamagnetic complexes **1** and **7** were recorded in [$^2H_8$]thf. Owing to the complexity of the spectra, *e.g.* overlap of peaks of the diastereotopic protons on the bridge, unsymmetric structure (see below) and isomers, the discussion is restricted to the resonances of the five-membered ring protons of the indenyl rings. To our surprise, the *rac* isomer of **1** and **7** assumed an unsymmetric structure: the two bridged indenyl rings displayed sharply different resonances as four sets of doublets (1 : 1 : 1 : 1) at δ 6.40 ($H^{1'}$), 5.95 ($H^{2'}$) and 5.05 (H^1), 4.90 (H^2) (the other ring), respectively, while the *meso* isomer showed a symmetric structure for which just one set of small signals appeared at δ 6.55 and 6.20. The assignment was based on the chemical shifts, splitting pattern and two-dimensional COSY and NOESY spectra of complex **1** (Table 1). From these spectra the predominant set of signals was assigned to the *rac* isomer. The ratio of *rac*:*meso* was about 6 : 1 determined from the integration of the well resolved peaks of protons on the five-membered ring of the indenyl groups. The cross-peaks between H^1–H^2, $H^{1'}$–$H^{2'}$ (*rac*) and H^1–H^2 (*meso*) in COSY and the exchange cross-peaks of H^1–$H^{1'}$, H^2–$H^{2'}$ (*rac*) and aromatic protons in NOESY were observed; the latter were attributed to a slow oscillation of the two bridged indenyl rings of the *rac* isomer. The NOESY spectrum unmistakably confirmed the assignment of the *rac* isomer showing cross-peaks (dipolar interaction) between H^1–$H^{4'}$ ($H^{5'}$), H^1–$H^{6'}$ and H^2–$H^{3'}$. Since the lanthanide complexes have similar properties, we believe these assignments are also applicable to **7** and the paramagnetic complexes **2**–**6**.



rac isomer

Table 2 Selected bond lengths (Å) and angles (°) for complexes **3**, **4** and **6**

	3 (Nd)	**4** (Gd)	**6** (Ho)
Ln–Cl	2.668(2)	2.612(1)	2.573(2)
Ln–O(1)	2.507(4)	2.470(4)	2.448(4)
Ln–O(2)	2.511(4)	2.474(4)	2.440(4)
Ln–C(3)	2.766(5)	2.717(5)	2.680(6)
Ln–C(4)	2.750(6)	2.709(5)	2.666(6)
Ln–C(5)	2.751(6)	2.710(5)	2.678(6)
Ln–C(6)	2.796(5)	2.753(5)	2.724(5)
Ln–C(11)	2.801(5)	2.746(4)	2.726(5)
Ln–C(14)	2.773(6)	2.730(6)	2.684(6)
Ln–C(15)	2.719(6)	2.665(5)	2.624(6)
Ln–C(16)	2.746(6)	2.697(5)	2.674(6)
Ln–C(17)	2.854(6)	2.831(4)	2.812(6)
Ln–C(22)	2.843(5)	2.816(5)	2.804(5)
Cl–Ln–O(1)	80.6(1)	79.69(10)	79.3(1)
Cl–Ln–O(2)	83.4(1)	82.53(9)	82.1(1)
O(1)–Ln–O(2)	164.0(1)	162.2(1)	161.3(2)
Cl–Ln–C(4)	87.5(1)	87.5(1)	87.3(1)
Cl–Ln–C(15)	133.6(2)	133.4(1)	133.2(2)
C(6)–Ln–C(17)	114.7(2)	114.6(1)	113.8(2)
C(11)–Ln–C(22)	129.6(2)	130.7(1)	131.5(2)

Although the thermal stability of these complexes was relatively poor, their EI mass spectra showed characteristic fragments such as $[M - \text{thf}]^+$ and $[M - \text{thf} - \text{Cl}]^+$, *etc*. The IR spectra of all complexes exhibited similar patterns with characteristic bands at *ca*. 3060, 3030, 1000 and 770 cm^{-1} for η^5-indenyl moieties and 1060 cm^{-1} for the co-ordinated O–C–O stretching.[8] A split of the aromatic portion (3030 cm^{-1}) into two peaks at *ca*. 3035 and 3030 (3025) cm^{-1} was tentatively attributed to the unsymmetric structure of these complexes.

Molecular structure

X-Ray-quality crystals were grown from thf solution. All complexes are *rac* isomers with one tetrahydrofuran molecule co-ordinated and crystallise in the monoclinic system, space group $P2_1/n$, as discrete molecules in the unit cell. Since these complexes are isostructural a representative ORTEP[9] drawing of **3** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The co-ordination geometry can be described as distorted trigonal bipyramidal with O(1) and O(2) apical if a indenyl ring is regarded as occupying a single polyhedral vertex. The η^5-indenyl groups are bound to the metal at normal bond distances ranging from 2.719(6) to 2.854(6) Å [for the other ring 2.750(6) to 2.80(5) Å] falling within the range of reported Nd–C (η^5-indenyl) bond lengths, such as 2.730(9)–3.016(8) Å in $[Na(thf)_6][Nd(C_9H_7)_3(\mu\text{-}Cl)Nd(C_9H_7)_3]$,[6d] 2.694(12)–2.960(16) Å in $[Nd(C_9H_7)_3(thf)]$,[6a] 2.71(2)–2.92(2) Å in $[\{Nd(C_9H_7)(\mu\text{-}OCH_2C_4H_7O)\}_2]$.[10] These bond lengths also follow the general pattern established for indenyl systems, that is the distances between the metal and bridged carbons of the indenyl group are greater than those of the other three. However, the range of Nd–C bond lengths of the two bridged η^5-indenyl ligands is significantly different, consistent with the unsymmetric structure in solution observed by ^{1}H NMR spectroscopy for complexes **1** and **7**, indicating the bridge is rather

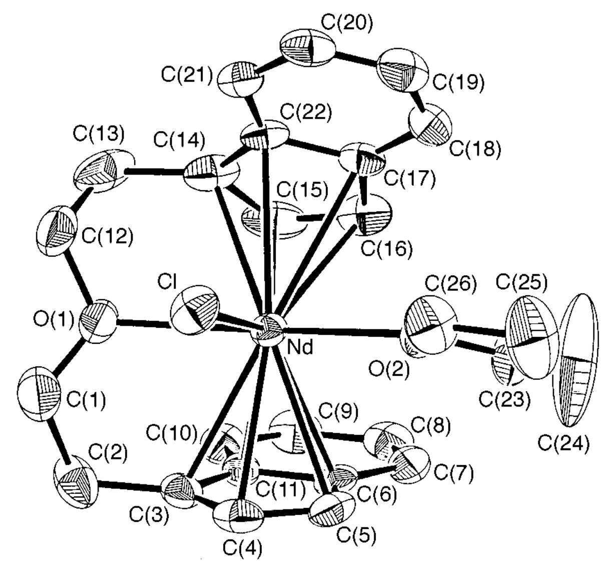


Fig. 1 An ORTEP drawing of complex **3** showing the numbering scheme employed

rigid. The Nd–Cl bond length 2.668(2) Å is in good agreement with those, 2.667(3) and 2.669(3) Å, in $[AsPh_4][Nd\{C_5H_3(SiMe_3)_2\}_2Cl_2]$[11] and comparable to the terminal Nd–Cl distances 2.712(4) and 2.719(4) Å, in $[Nd(C_5H_5)Cl_2(thf)_3]$,[12] but shorter than the bridging ones, such as 2.787(4) and 2.861(4) Å in $[\{Nd(C_5H_5)_2Cl(thf)\}_2]$,[13] 2.754(2) and 2.802(1) Å in $[Li(thf)_2][\{Nd[(C_5Me_4)_2SiMe_2]\}_2]Cl$[14] and 2.757(4)–2.800(13) Å in $[(C_5H_5)Nd(thf)(\mu\text{-}Cl)_4Li_2(thf)_4]$.[15] In general, the Ln–O bond lengths vary with the changes in co-ordination environments. In the present case the two Nd–O distances are closely equivalent 2.507(4) and 2.511(4) Å and comparable to those 2.51(1) Å in $[\{Nd(C_9H_7)_2(\mu\text{-}OCH_2C_4H_7O)\}_2]$,[10] 2.552(7) Å in $[\{Nd(C_5H_5)_2Cl(thf)\}_2]$,[13] 2.543(6) Å in $[Nd(C_5H_5)_2(OC_6H_3Ph_2\text{-}2,6)(thf)_2]$,[16] 2.445(9)–2.529(10) Å in $[Nd(C_5H_5)Cl_2(thf)_3]$,[12] 2.519(8) Å in $[(C_5H_5)Nd(thf)(\mu\text{-}Cl)_4Li_2(thf)_4]$,[15] 2.557(21) Å in $[Nd(C_9H_7)_3(thf)]$,[6a] 2.54(1) [2.56(4)] Å in $[Nd(C_5H_5)_3(thf)]$,[17] and 2.553(13) and 2.566(17) Å in $[Nd(C_5H_4CH_2CH_2OMe)_2(BH_4)]$[18] but substantially shorter than those 2.724(3) and 2.839(3) Å in the formal 11-co-ordinated complex $[Nd(C_5H_4CH_2CH_2OMe)_3]$.[19] The structures of complexes **4** and **6** are essentially identical with that of **3** after ionic radius corrections.

Conclusion

The synthesis, characterisation and structure of several representative chiral *ansa*-lanthanocene chlorides using a long but rigid bridged indenyl ligand with *rac*:*meso* ratio up to 6:1 are reported. The remaining chloride ligand in these complexes promises a wide range of derivatives such as those containing Ln–H, Ln–N and Ln–C, *etc*. Further investigations are in hand.

Experimental

All operations involving organometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium–benzophenone prior to use. Diethylene glycol dimesylate[20] and anhydrous lanthanide chlorides[21] were prepared according to the literature; *n*-butyllithium and indene were from Aldrich, the latter distilled prior to use. $[^2H_8]$Tetrahydrofuran was degassed and dried over Na/K alloy. All chemical shifts are reported in ppm relative to the residues of the deuteriated solvent. Infrared spectra were recorded using a Perkin-Elmer 983 spectrometer with Nujol and Fluorolube mulls prepared in an argon-filled glove-box between disc-shaped CsI crystals, mass spectra on a HP5989A spectrometer (50–400 °C, 1.3 kV) and ^1H NMR spectra on Am-300 (300 MHz) spectrometers. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Preparations

1,5-Bis(inden-3-yl)-3-oxapentane I. To a solution of *n*-butyllithium (1.6 M in hexane, 100 cm^3) thf (250 cm^3) was added dropwise freshly distilled indene (18 g, 155 mmol) in thf (50 cm^3) with rigorous stirring at 0–10 °C. The mixture was stirred for 3 h at room temperature until no gas was given off, then added slowly to a diethylene glycol dimesylate (23 g, 88 mmol, slight excess) solution in thf (100 cm^3) at −50 °C. The resulting pink mixture was stirred for 2 h, allowed to warm to room temperature, stirred for 2 h and then quenched with water. The organic phase was separated and the aqueous phase extracted with diethyl ether (2 × 50 cm^3). The combined organic solution was dried over anhydrous $MgSO_4$ overnight. The solvent was removed *in vacuo* and the residue chromatographed using light petroleum (b.p. 60–90 °C) as eluent providing compounds **I** (7.9 g, 34%) and **II** (1.5 g). Compound **I**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C) $\delta(J/Hz)$ 7.45 (d, $J = 7.3$, 2 H, aromatic), 7.35 (d, $J = 7.4$, 2 H, aromatic), 7.25 (m, 2 H, aromatic), 7.15 (m, 2 H, aromatic), 6.25 (t, $J = 1.5$, 2 H, olefin), 3.80 (t, $J = 7.3$, 4 H, OCH_2), 3.30 (d, $J = 1.9$, 4 H, allylic) and 2.85 (m, 4 H, CH_2); EI mass spectrum (70 eV, eV ≈ 1.60×10^{-19} J) *m*/*z* 302 (2.55, M^+) and 128 (100%). Compound **II**: $\delta(J/Hz)$ 7.35 (m, 2 H, aromatic), 7.20 (m, 2 H, aromatic), 6.95 (d, $J = 5.7$, 1 H, olefin), 6.75 (d, $J = 5.7$, 1 H, olefin), 4.10 (ddd, $J_1 = 11.9$, $J_2 = 4.4$, $J_3 = 2.5$, 2 H, OCH_2), 3.75 (td, $J_1 = 11.9$, $J_2 = 2.2$, 2 H, OCH_2), 2.20 (ddd, $J_1 = 13.9$, $J_2 = 12.1$, $J_3 = 4.6$, 2 H, CH_2) and 1.30 (dd, $J_1 = 13.4$, $J_2 = 2.1$, 2 H, CH_2); EI mass spectrum (70 eV) *m*/*z* 186 (70.94, M^+) and 128 (100%).

$(KC_9H_6CH_2CH_2)_2O$. A solution of compound **I** (8.6 g, 28 mmol in 50 cm^3 thf) was added dropwise to a stirred suspension of potassium sand in 80 cm^3 thf (1.5 g, excess) at 0 °C. The resulting mixture was stirred for 5 h, then warmed to room temperature and stirred overnight. After centrifugation a clear yellow-green solution was obtained and titrated prior to use.

$[Ln\{(C_9H_6CH_2CH_2)_2O\}Cl(thf)]$. *Complex* **1**. To a suspension of YCl_3 (0.88 g, 4.5 mmol in 50 cm^3 thf) at −78 °C was added by syringe a solution of the dipotassium salt of compound **I** (20.5 cm^3, 0.22 M). The mixture was stirred for 2 h, then warmed to room temperature and stirred for 2 d. The precipitate was separated and the clear solution concentrated until a solid appeared. The product was washed with cool thf (10 cm^3) and dried *in vacuo* at room temperature affording **1** (1.45 g, 65%) (Found: C, 62.87; H, 4.99. Calc. for $C_{26}H_{28}ClO_2Y$: C, 62.84; H, 5.64%). ^1H NMR (300 MHz, $[^2H_8]$thf, 25 °C) (*rac* + *meso*): δ (*J*/Hz) 7.80 (1 H, d, $J = 7.8$, $H^{6'}$, *rac*), 7.70 (1 H, q, $J = 7.5, 1.5$, $H^{3'}$, *rac*), 7.35 (m, H^6, overlapped with *meso*), 7.25–7.10 (m, H^3, $H^{4'}$, $H^{5'}$, overlapped with *meso*), 6.80 (m, H^4, H^5, overlapped with *meso*), 6.55 (d, H^1, *meso*), 6.40 (1 H, d, $J = 3.4$, $H^{1'}$, *rac*), 6.20 (d, H^2, *meso*), 5.95 (1 H, d, $J = 3.4$, $H^{2'}$, *rac*), 5.05 (1 H, d, $J = 3.1$, H^1, *rac*), 4.90 (1 H, d, $J = 3.1$, H^2, *rac*), 4.50 (m, OCH_2, overlapped with *meso*), 4.05, 3.95 (m, OCH_2, overlapped with *meso*), 3.70 (4 H, m, thf), 3.45 (m, $H^{7'}$, $H^{8'}$, overlapped with *meso*), 3.05, 2.90 (m, H^7, H^8, overlapped with *meso*) and 1.85 (4 H, m, thf). EI mass spectrum (70 eV, 50–400 °C): *m*/*z* 424 (0.61, $[M - thf]^+$) and 128 (100%). IR (cm^{-1}): 3065m, 3035m, 3030 (sh), 2930 (sh), 2901s, 1460m, 1440w, 1360m, 1341m, 1121s, 1057m, 1024m, 1005w, 873m, 860m, 772s, 722s and 440m.

Complex **2**. A procedure similar to that for complex **1** was adopted using $PrCl_3$ (1.16 g, 4.68 mmol) and afforded a yellow-green powder (1.69 g, 66%) (Found: C, 57.42; H, 5.10. Calc. for $C_{26}H_{28}ClO_2Pr$: C, 56.88; H, 5.10%). EI mass spectrum (70 eV, 50–400 °C, based on ^{141}Pr): *m*/*z* 476 (89.82, $[M - thf]^+$), 441 (12.22, $[M - thf - Cl]^+$) and 141 (100%). IR (cm^{-1}): 3060m,

Table 3 Details of the crystallographic data and refinements for complexes **3**, **4** and **6***

	3	**4**	**6**
Formula	$C_{26}H_{28}ClNdO_2$	$C_{26}H_{28}ClGdO_2$	$C_{26}H_{28}ClHoO_2$
M	552.20	565.21	572.89
Crystal dimensions/mm	0.20 × 0.20 × 0.30	0.30 × 0.40 × 0.50	0.20 × 0.20 × 0.30
Colour	Green	Yellow	Yellow
a/Å	11.092(8)	11.042(3)	11.007(3)
b/Å	10.219(5)	10.192(4)	10.147(2)
c/Å	20.57(1)	20.510(8)	20.488(7)
β/°	98.81(5)	98.42(3)	98.18(2)
U/Å^3	2303(2)	2283(1)	2264(1)
D_c/g cm^{-3}	1.592	1.644	1.680
F(000)	1108	1124	1136
μ(Mo-Kα)/cm^{-1}	23.88	30.49	36.35
Reflections collected	3637	3832	3946
Independent reflections	3402	3599	3715
Observed data	2660	2929	2974
Parameters	272	272	267
Goodness of fit	1.83	1.57	1.78
R, *R'*	0.027, 0.040	0.027, 0.040	0.027, 0.040
$\Delta\rho_{max, min}$/e Å^{-3}	0.46, −0.66	0.52, −0.61	1.14, −1.43

* Details in common: monoclinic, space group $P2_1/n$ (no. 14); $Z = 4$; $2\theta_{max} = 50°$.

3034m, 3030 (sh), 2905s, 2885s, 1459m, 1438w, 1338m, 1120m, 1054s, 1031s, 1006m, 876m, 862m, 768vs, 722m and 443m.

Complex **3**. Analogously, $NdCl_3$ (1.01 g, 4.03 mmol) afforded complex **3** as a green powder (1.30 g, 59%) (Found: C, 56.23; H, 5.43. Calc. for $C_{26}H_{28}ClNdO_2$: C, 56.57; H, 5.08%). EI mass spectrum (70 eV, 50–400 °C, based on ^{142}Nd): *m*/*z* 477 (6.09, $[M - \text{thf}]^+$), 440 (0.78, $[M - \text{thf} - \text{Cl}]^+$) and 141 (100%). IR (cm^{-1}): 3060m, 3030w, 3025w, 2930m, 2880s, 1460m, 1440m, 1121m, 1055m, 1031m, 1005w, 876m, 860m, 770s, 752s, 722m and 443m.

Complex **4**. Analogously, $GdCl_3$ (0.92 g, 3.49 mmol) provided complex **4** as a yellow powder (1.0 g, 51%) (Found: C, 55.10; H, 5.10. Calc. for $C_{26}H_{28}ClGdO_2$: C, 55.27; H, 4.96%). EI mass spectrum (70 eV, 50–400 °C, based on ^{158}Gd): *m*/*z* 493 (2.55, $[M - \text{thf}]^+$), 458 ($[M - \text{thf} - \text{Cl}]^+$) and 142 (100%). IR (cm^{-1}): 3061m, 3035m, 3030 (sh), 2930m, 2901m, 1459w, 1438w, 1354m, 1339m, 1185m, 1120s, 1056vs, 1030s, 1006m, 875s, 863s, 770s, 722m and 442m.

Complex **5**. Analogously, $DyCl_3$ (1.08 g, 4.01 mmol) provided complex **5** as a yellow powder (1.68 g, 73%) (Found: C, 55.63; H, 4.90. Calc. for $C_{26}H_{28}ClDyO_2$: C, 54.74; H, 4.91%). EI mass spectrum (70 eV, 50–400 °C, based on ^{164}Dy): *m*/*z* 499 (49.09, $[M - \text{thf}]^+$), 464 (2.67, $[M - \text{thf} - \text{Cl}]^+$) and 141 (100%). IR (cm^{-1}): 3062m, 3036m, 3030 (sh), 2930m, 2903m, 1459w, 1439w, 1259m, 1082m, 1056s, 1030s, 1007m, 864m, 774s, 764s, 743s, 722m and 441m.

Complex **6**. Analogously, $HoCl_3$ (1.14 g, 4.20 mmol) provided complex **6** as a yellow powder (1.60 g, 67%) (Found: C, 54.24; H, 4.85. Calc. for $C_{26}H_{28}ClHoO_2$: C, 54.50; H, 4.89%). EI mass spectrum (70 eV, 50–400 °C, based on ^{165}Ho): *m*/*z* 546 (3.08, $[M - 26]^+$) and 128 (100%). IR (cm^{-1}): 3066m, 3030m, 3025m, 2929s, 2850s, 1462m, 1399m, 1124m, 1025m, 1007m, 773s and 722m.

Complex **7**. Analogously, $LuCl_3$ (2.35 g, 8.35 mmol) afforded complex **7** as a white powder (3.33 g, 69%) (Found: C, 53.03; H, 4.84. Calc. for $C_{26}H_{28}ClLuO_2$: C, 53.56; H, 4.81%). ^{1}H NMR (300 MHz, [$^2H_8$]thf, 25 °C) (*rac* + *meso*): δ (*J*/Hz) 7.75 (1 H, d, $J = 9.1$, $H^{6'}$, *rac*), 7.70 (1 H, m, $H^{3'}$, *rac*), 7.30 (m, H^6, overlapped with *meso*), 7.10–7.25 (m, H^3, $H^{4'}$, $H^{5'}$, overlapped with *meso*), 6.80 (m, H^4, H^5, overlapped with *meso*), 6.60 (d, H^1, *meso*), 6.40 (1 H, d, $J = 3.4$, $H^{1'}$, *rac*), 6.20 (d, H^2, *meso*), 5.90 (1 H, d, $J = 3.3$, $H^{2'}$, *rac*), 4.95 (2 H, q, $J = 3.0$, H^1, H^2, *rac*), 4.45 (m, OCH_2, overlapped with *meso*), 4.05, 3.95 (m, OCH_2, overlapped with *meso*), 3.70 (4 H, m, thf), 3.35 (m, CH_2, overlapped with *meso*), 3.10 (m, CH_2, overlapped with *meso*), 2.85 (m, CH_2, overlapped with *meso*) and 1.85 (4 H, m, thf). EI mass spectrum (70 eV, 50–400 °C, based on ^{175}Lu): *m*/*z* 510 (100, $[M - \text{thf}]^+$) and 475 (38.48%, $[M - \text{thf} - \text{Cl}]^+$). IR (cm^{-1}): 3066m, 3035m, 3030 (sh), 2930s, 2901s, 1460m, 1440m, 1360m, 1341m, 1121s, 1057m, 1024m, 1005w, 873m, 860m, 772s, 722s and 440m.

Crystallography

Owing to desolvation, single crystals were sealed in thin-walled glass capillaries with some mother-liquor under argon. Crystal data and details of data collection and structure refinement are given in Table 3. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation λ = 0.710 69 Å using the ω–2θ technique at 20 °C. The data were corrected for Lorentz-polarisation effects; an empirical absorption correction was applied using the program DIFABS[22] for complex **4** and **6** or based on azimuthal scans of several reflections for **3**. The structures were solved by direct methods[23] for **4** and **6** or the heavy-atom Patterson method[24] for **3**, and expanded using Fourier techniques.[25] The non-hydrogen atoms were refined anisotropically by full-matrix least squares except for **6** for which some non-hydrogen atoms were refined isotropically. Hydrogen atoms were included but not refined. All hydrogen atoms were included in calculated position. Scattering factors were taken from ref. 26. All calculations were performed using the TEXSAN crystallographic software package.[27]

CCDC reference number 186/929.

See http://www.rsc.org/suppdata/dt/1998/1607/ for crystallographic files in .cif format.

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References

1 E. B. Coughlin and J. E Bercaw, *J. Am. Chem. Soc.*, 1992, **114**, 7606; J. P. Mitchell, S. Hajela, S. K. Brookhart, K. I. Hardcastle, L. M. Henling and J. E. Bercaw, *J. Am. Chem. Soc.*, 1996, **118**, 1045; C. M. Haar, C. L. Stern and T. J. Marks, *Organometallics*, 1996, **15**, 1765; W. A. Herrmann, J. Eppinger, M. Spiegler, O. Runte and R. Anwander, *Organometallics*, 1997, **16**, 1813.

2 R. L. Halterman, *Chem. Rev.*, 1992, **92**, 965; H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.

3 C. Qian, Z. Xie and Y. Huang, *J. Organomet. Chem.*, 1987, **323**, 285; C. Qian, G. Zou and L. Gao, *J. Organomet. Chem.*, 1996, **525**, 23; Z. Xie, C. Qian and Y. Huang, *J. Organomet. Chem.*, 1991, **412**, 61; C. Qian and D. Zhu, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1599.

4 H. Schumann, J. Loebel, J. Pickardt, C. Qian and Z. Xie, *Organometallics*, 1991, **10**, 215; H. Schumann, F. H. Görlitz, F. E. Hahn, J. Pickardt, C. Qian and Z. Xie, *Z. Anorg. Allg. Chem.*, 1992, **609**, 131.

5 M. Tsutsui and H. J. Gysling, *J. Am. Chem. Soc.*, 1969, **91**, 3175.

6 (*a*) J. Xia, Z. Jin, G. Lin and W. Chen, *J. Organomet. Chem.*, 1991, **408**, 173; (*b*) A. Zazzetta and A. Greco, *Acta Crystallogr.*, *Sect. B*, 1979, **35**, 457; (*c*) Z. Ye, S. Wang, D. Kong and X. Huang, *J. Organomet. Chem.*, 1995, **491**, 57; (*d*) M. Chen, G. Wu, W. Wu, S. Zhuang and Z. Huang, *Organometallics*, 1988, **7**, 802; (*e*) Y. Su, Z. Jin and W. Chen, *J. Chin. Rare Earths Soc.*, 1990, **8**, 106; (*f*) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865.

7 J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.

8 (*a*) F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, 1969, **91**, 7281; (*b*) K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 3rd edn., 1978, pp. 388–409; (*c*) C. Qian, C. Ye, H. Lu, Y. Li, J. Zhou, Y. Ge and M. Tsutsui, *J. Organomet. Chem.*, 1983, **247**, 161.

9 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge, National Laboratory, Oak Ridge, TN, 1976.

10 W. Ma, Z. Wu, R. Cai, Z. Huang and J. Sun, *Polyhedron*, 1997, **16**, 3723.

11 M. F. Lappert, A. Singh, J. L. Atwood, W. E. Hunter and H.-M. Zhang, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 69.

12 G. Yang, Y. Fan, Z. Jin, Y. Xing and W. Chen, *J. Organomet. Chem.*, 1987, **322**, 57.

13 Z. Jin, Y. Liu and W. Chen, *Sci. Sin. Ser. B*, 1987, **30**, 1136.

14 G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8103.

15 Z. Jin, N. H. Hu, Y. Li, X. Xu and G. Liu, *Inorg. Chim. Acta*, 1988, **142**, 333.

16 G. B. Deacon, S. Nickel and E. R. T. Tiekink, *J. Organomet. Chem.*, 1991, **409**, Cl.

17 F. Benetollo, G. Bombieri, C. B. Castellani, W. Jahn and R. D. Fischer, *Inorg. Chim. Acta*, 1984, **95**, L7; Y. Fan, P. Lu, Z. Jin and W. Chen, *Sci. Sin. Ser. B*, 1984, **27**, 993.

18 D. Deng, X. Zheng, C. Qian, J. Sun and L. Zhang, *J. Organomet. Chem.*, 1994, **466**, 95.

19 C. Qian, B. Wang, D. Deng, J. Sun, F. E. Hahn, J. Chen and P. Zheng, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 955.

20 L. Qian, Z. Sun, J. Gao, B. Movassagh, L. Morales and K. B. Mertes, *J. Coord. Chem.*, 1991, **23**, 155.

21 J. B. Reed, B. S. Hopkins and L. F. Audrieth, *Inorg. Synth.*, 1939, **1**, 28.

22 DIFABS, N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.

23 SAPI 91, Fan Hai-Fu, Structure analysis programs with intelligent control, Rigaku, Tokyo, 1991.

24 PATTY, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF system, Technical report of the crystallography laboratory, University of Nijmegen, 1992.

25 DIRDIF 92, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF system, Technical report of the crystallography laboratory, University of Nijmegen, 1992.

26 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press. Birmingham, 1974, vol. 4, Table 2.2A.

27 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

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