

Synthesis, Characterisation of Carbon-Bridged (Diphenolato)lanthanide Complexes and Their Catalytic Activity for Diels–Alder Reactions

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The synthesis and structures of new lanthanide complexes supported by the carbon-bridged diphenolato ligand 2,2'-methylenebis(6-*tert*-butyl-4-methylphenolato) (MBMP²⁻) are described. Reactions of anhydrous lanthanide trichlorides with Na₂MBMP in a 1:2 molar ratio in THF at room temperature afforded the corresponding "ate" (diphenolato)lanthanide complexes [(THF)_nLn(MBMP)₂Na(THF)₂] [Ln = Nd (**1**), Sm (**2**), *n* = 2; Ln = Yb, *n* = 1 (**3**)]. Recrystallisation of complexes **1–3** from toluene in the presence of DME gave the discrete ion-pair complexes [(MBMP)₂Ln(THF)₂][Na(DME)₂(THF)₂] [Ln = Nd (**4**), Sm (**5**), Yb (**6**)]. These complexes have

been fully characterised. The single-crystal structural analyses of **1**, **3** and **6** revealed that the coordination geometries of the lanthanide ions can be best described as distorted octahedral in complexes **1** and **6** and distorted trigonal-bipyramidal in complex **3**. It was found that these lanthanide complexes are able to act as Lewis acids to catalyse the Diels–Alder reactions of cyclopentadiene with substituted dienophiles with good activity and stereoselectivity.

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Introduction

Of the possible alternatives to the traditional ancillary bis(cyclopentadienyl) ligand set in lanthanide chemistry, alkoxides (aryloxides) have received much attention and become increasingly popular since they are easily available, tuneable and even potentially recyclable ancillary ligand sets for mediating the reactivity of electropositive cations.^[1] The synthesis and structural characterisation of a variety of di-^[2] and trivalent^[3] lanthanide complexes supported by monodentate aryloxides have been published and some of them have shown good catalytic activities for the polymerisation of polar and nonpolar monomers.^[4] To date, the chelate diphenolates have been seldom used as ancillary ligands in lanthanide chemistry.^[5]

Chelate ligands have played a remarkable role in the development of coordination chemistry. They may stabilise complexes either by thermodynamic or kinetic means and they may serve in the exploration of reaction mechanisms.^[6] Carbon-bridged diphenols such as 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (MBMPH₂) and 2,2'-ethyldienebis(4,6-di-*tert*-butylphenol) (EDBPH₂) have been found to be able to act as dianionic ligands which have the advantage of avoiding ligand redistribution reactions and providing a stereochemically rigid framework for the metal centre which could affect stereospecific transformations. The use

of these carbon-bridged diphenolato ligands in transition and main-group metal complexes has attracted considerable attention in recent years and some of these complexes have shown interesting catalytic activity.^[7] For example, the corresponding titanium complexes are able to catalyse not only the polymerisation of α -olefins in the presence of MAO^[7a,7c,7d] but also the living anionic polymerisation of ϵ -caprolactone.^[7b] The aluminium complexes can effectively catalyse the controllable polymerisation of propylene oxide^[7f] and ϵ -caprolactone^[7g,7h,7k] as well as MPV hydrogen transfer reactions.^[7i] In view of this, it can be anticipated that organolanthanide complexes supported by carbon-bridged diphenolato ligands could lead to the activation of a range of small molecules and act as new types of Lewis acid catalysts for organic synthesis. However, these kinds of ligands have not been used in lanthanide coordination chemistry except for our recent report of the synthesis of divalent lanthanide complexes.^[5i] Here we report the synthesis and characterisation of trivalent lanthanide complexes supported by the MBMP²⁻ group and their catalytic activity for Diels–Alder reactions.

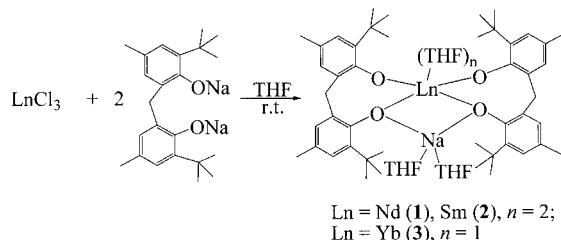
Results and Discussion

Synthesis and Characterisation of Carbon-Bridged (Diphenolato)lanthanide Complexes

Since the organolanthanide or organolanthanoid chlorides are important precursors for lanthanide derivatives, we tried to synthesise the mono(diphenolato)neodymium complex [(MBMP)NdCl(THF)_x] by the general salt metath-

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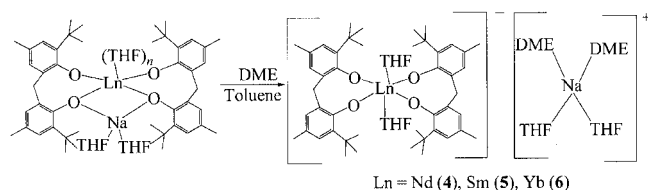
esis reaction of anhydrous NdCl_3 with MBMPNa_2 in a 1:1 molar ratio in THF at ambient temperature but this attempt was unsuccessful. The resultant complex, isolated in moderate yield, was characterised as a ligand-redistributed product $[(\text{THF})_2\text{Nd}(\text{MBMP})_2\text{Na}(\text{THF})_2]$ (**1**). The reaction was repeated with the stoichiometry appropriate for complex **1** and a yield of >78% was obtained. Thus, the isostructural complexes $[(\text{THF})_n\text{Ln}(\text{MBMP})_2\text{Na}(\text{THF})_2]$ [$\text{Ln} = \text{Sm}$ (**2**), $n = 2$; Yb (**3**), $n = 1$] were synthesised by the reaction of LnCl_3 with MBMPNa_2 in 1:2 molar ratio in THF as shown in Scheme 1.



Scheme 1.

These complexes gave satisfactory elemental analyses and the lanthanide and sodium analyses indicated a molar ratio of 1:1 for Ln and Na in these complexes. The definitive structures of complexes **1** and **3** were determined by X-ray diffraction studies which revealed them to be “ate” complexes in which a sodium atom is connected to one oxygen atom from each of the diphenolato ligands.

It is interesting that recrystallisation of complexes **1–3** from toluene in the presence of DME gave the discrete ion-pair complexes $[(\text{MBMP})_2\text{Ln}(\text{THF})_2][\text{Na}(\text{DME})_2(\text{THF})_2]$ [$\text{Ln} = \text{Nd}$ (**4**), Sm (**5**), Yb (**6**)] which were confirmed by elemental analysis and ^1H NMR spectroscopy as well as by a structural determination in the case of **6**.^[8] In the anionic (aryloxo)lanthanide complexes, most of the anions are connected to the cations by bridging ligands and the ion-pair complexes are rare. Previously reported ion-pair (aryloxo)lanthanide complexes are limited to $[\text{Na}(\text{DME})_3][\text{Ln}(\text{OC}_6\text{H}_3\text{-Ph}_2\text{-2,6})_4]$, $[\text{Na}(\text{diglyme})_2][\text{Ln}(\text{OC}_6\text{H}_3\text{-Ph}_2\text{-2,6})_4]$ [diglyme = bis(2-methoxyethyl) ether, $\text{Ln} = \text{Nd}$, Er],^[3e] $[\text{Nd}(\text{OC}_6\text{H}_3\text{-}t\text{Bu}_2\text{-2,6-Me-4})_4][\text{Na}(\text{THF})_6]$ ^[3d] and $[(\text{C}_5\text{Me}_5)\text{-Y}(\text{OC}_6\text{H}_3\text{-Me}_2\text{-2,6})_3][\text{Na}(\text{THF})_6]$.^[9] Due to the competition between coordinating solvents and oxygen atoms in the MBMP^{2-} groups for complexation of the sodium atom, addition of DME broke the bridges between the sodium atom and the diphenolato ligands and formed a sodium cation coordinated by two DME groups and two THF groups as shown in Scheme 2. This can be attributed to the fact that



Scheme 2.

the bidentate DME has a relatively stronger coordinating ability than the bridging phenolate.^[3e]

Complexes **1–3** are moderately air- and moisture-sensitive. The crystals can be exposed to air for a few hours without apparent decomposition but the colours of the solutions changed gradually in a few minutes. However, complexes **4–6** are air- and moisture-sensitive and the crystals decompose in a few minutes when exposed to air. These complexes are freely soluble in donor solvents such as THF and DME, slightly soluble in toluene and benzene but insoluble in hexane. The neodymium complexes (**1** and **4**) did not provide any resolvable ^1H NMR spectra due to the strong paramagnetism of the neodymium ion.

Crystal Structure Analyses

Although there are many structurally characterised (dinaphtholato)lanthanide complexes in the literature,^[5c,10] there are only a few examples of structurally characterised lanthanide complexes supported by diphenolato ligands. The diphenolato ligand $[1,1'-(2\text{-OC}_6\text{H}_2\text{-}t\text{Bu}_2\text{-3,5})]_2$, in which two phenols are linked directly, was first used as an ancillary ligand in organolanthanide chemistry.^[5a] Recently, other (diphenolato)lanthanide complexes containing donor-functionalised linkers have been reported.^[5c–5h] The crystal structures of trivalent lanthanide complexes supported by carbon-bridged diphenolate have not been reported until now.^[5i] To elucidate the influence of the carbon-bridged diphenolates on the lanthanide coordination spheres, the X-ray crystal structures of complexes **1**, **3** and **6** were determined.

Crystals of complex **1** suitable for an X-ray diffraction study were grown by cooling a concentrated toluene solution to -10°C . An ORTEP diagram with the atom-numbering scheme of **1** is shown in Figure 1, selected bond lengths and angles are given in Table 1. Complex **1** has a C_2 -symmetric dinuclear structure. The overall molecular geometry consists of a six-coordinate neodymium metal centre which is coordinated by the four oxygen atoms of the two MBMP^{2-} groups and two oxygen atoms from the THF molecules in a distorted octahedron as well as a four-coordinate sodium cation which is coordinated by two oxygen atoms from the MBMP^{2-} groups and two THF ligands in a distorted tetrahedron. The coordination geometry around the neodymium atom is similar to that of the yttrium atom in $[(2,6\text{-Me}_2\text{-C}_6\text{H}_3\text{O})_2\text{Y}(\text{THF})_2(\mu\text{-OC}_6\text{H}_3\text{-Me}_2\text{-2,6})_2\text{(THF)}_3]$.^[9] The terminal phenolate $[\text{O}(2), \text{O}(2_2)]$, one bridging phenolate $[\text{O}(1)]$ and one THF molecule $[\text{O}(3)]$ can be viewed as occupying equatorial positions within the octahedron about the neodymium centre with $\Sigma(\text{O–Nd–O}) = 360.53^\circ$. The oxygen atom from another bridging phenolate ligand $[\text{O}(1_2)]$ and one oxygen atom from the THF $[\text{O}(3_2)]$ occupy axial positions and the $\text{O}(1_2)\text{–Nd–O}(3_2)$ angle is slightly distorted away from the idealised 180° to $172.466(4)^\circ$.

The terminal $\text{Nd–O}(\text{Ar})$ bond lengths are $2.278(2) \text{ \AA}$ which compare well with the previously reported terminal

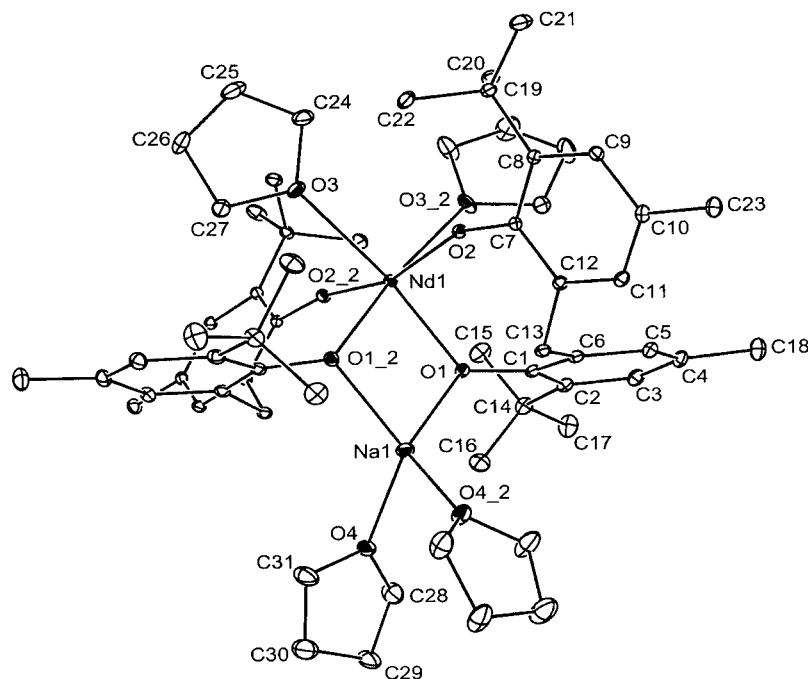


Figure 1. ORTEP diagram of **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**.

Nd(1)–O(1)	2.315(2)	Nd(1)–O(2)	2.278(2)
Nd(1)–O(3)	2.559(3)	Nd(1)–Na(1)	3.543(2)
C(1)–O(1)	1.352(4)	C(7)–O(2)	1.339(4)
Na(1)–O(1)	2.305(2)	Na(1)–O(4)	2.287(3)
O(1)–Nd(1)–O(2)	95.51(8)	O(2)–Nd(1)–O(3)	90.09(8)
O(3)–Nd(1)–O(2_2)	77.92(6)	O(1)–Nd(1)–O(2_2)	97.61(6)
O(1_2)–Nd(1)–O(3_2)	172.466(4)	Nd(1)–O(1)–C(1)	127.3(2)
Nd(1)–O(2)–C(7)	158.5(2)		

Nd–O(Ar) distances when the difference in coordination number is considered.^[3d] The bridging Nd–O(Ar) bond length is only 0.04 Å longer than the terminal Nd–O(Ar) bond length which is comparable with that in [Na{Nd(OC₆H₃-Ph₂-2,6)₄}]^[3e] but apparently shorter than that in [(THF)La(OC₆H₃-*i*Pr₂-2,6)₂(μ-OC₆H₃-*i*Pr₂-2,6)₂Na(THF)₂].^[3] The O(2)–Nd–O(2_2) bond angle between the two terminal phenolato ligands is 162.90(6)° whereas the O(1)–Nd–O(1_2) angle between the two bridging phenolato ligands is dramatically smaller at 79.62(5)°. The Nd(1)–O(1)–C(1) bond angle for the bridging phenolato ligand is rather acute at 127.3(2)° reflecting its interaction with the sodium cation while the Nd(1)–O(2)–C(7) bond angle for the terminal phenolato ligand is more obtuse [158.5(2)°] and is comparable with the corresponding bond angles in K[Nd(OC₆H₃-*i*Pr₂-2,6)₄].^[3i] The bite angle O(1)–Nd–O(2) of 95.51(8)° for the diphenolato ligand is apparently larger than those found in [{Ln[P1,1'-(2-OC₆H₃-*t*Bu-3-Me₂-5,6)₂][N(SiHMe₂)₂](THF)₂}] [Ln = Y 88.79(6)°; La 88.83(7)°]^[5b] and [La{1,1'-(2-OC₆H₃-*t*Bu₂-3,5)₂}CH-

(SiMe₃)₂}(THF)₃] [88.1(3)°]^[5a] reflecting the fact that addition of a methylene linker between two phenolates increases the flexibility of the diphenolato ligand. Nd(1), Na(1), O(1) and O(1_2) are exactly coplanar (plane 1) as required by the crystallographic symmetry. The dihedral angles between plane 1 and plane 2 [C(1) to C(6)], and between plane 1 and plane 3 [C(7) to C(12)] are 90.64(8) and 81.79(9)°, respectively, indicating that the orientations of plane 1 and the arene rings of the diphenolato ligands are approximately perpendicular. The dihedral angle between two arene rings of the MBMP²⁻ group is 68.9(1)°.

The sodium cation is coordinated to two THF oxygen atoms and an oxygen atom from each of the two MBMP²⁻ groups. This coordination geometry is different from that in [(THF)La(OC₆H₃-*i*Pr₂-2,6)₂(μ-OC₆H₃-*i*Pr₂-2,6)₂Na(THF)₂], in which one carbon atom from one of the bridging aryloxy ligands is directed to the fifth coordination site of the sodium cation,^[3] as well as in [Na{Nd(OC₆H₃-Ph₂-2,6)₄}], in which the sodium atom is surrounded by three bridging aryloxy oxygen atoms and three phenyl groups.^[3e] The Na–O(Ar) bond length of 2.305(2) Å lies within the range previously reported for Na–O(Ar) bond lengths.^[3] The O(1)–Na–O(1_2) bond angle between the bridging phenolato ligands is 80.02(7)° while the O(4)–Na–O(4_2) bond angle between two THF molecules is 88.40(9)°.

Crystals of complex **3** suitable for an X-ray diffraction study were obtained from a concentrated toluene solution at room temperature. The molecular structure of complex **3** is shown in Figure 2 with selected bond lengths and bond angles listed in Table 2. The difference in the molecular

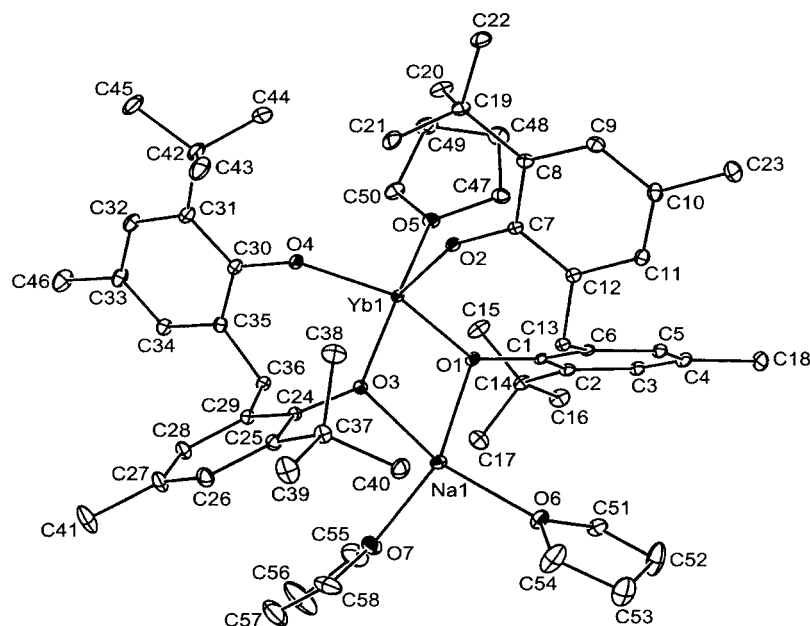


Figure 2. ORTEP diagram of **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level and hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **3** and **6**.

	3	6a	6b
Yb(1)–O(1)	2.160(3)	2.157(5)	2.148(5)
Yb(1)–O(2)	2.059(3)	2.130(5)	2.107(4)
Yb(1)–O(3)	2.134(3)	2.156(5)	2.161(5)
Yb(1)–O(4)	2.088(3)	2.119(5)	2.118(4)
Yb(1)–O(5)	2.333(3)	2.419(5)	2.421(5)
Yb(1)–O(6)	–	2.427(5)	2.399(5)
C(1)–O(1)	1.350(5)	1.330(8)	1.328(8)
C(7)–O(2)	1.340(5)	1.317(8)	1.325(8)
C(24)–O(3)	1.349(5)	1.331(9)	1.333(8)
C(30)–O(4)	1.351(5)	1.331(8)	1.324(8)
Yb(1)–O(1)–C(1)	135.8(3)	152.1(5)	149.9(5)
Yb(1)–O(2)–C(7)	151.6(2)	154.2(5)	156.0(5)
Yb(1)–O(3)–C(24)	134.4(3)	147.1(5)	151.7(4)
Yb(1)–O(4)–C(30)	149.6(3)	156.7(5)	155.7(5)

structures of complexes **3** and **1** is that only one THF molecule is coordinated to the central metal atom in the former. Thus, the ytterbium centre is five-coordinate by four oxygen atoms from the two MBMP^{2–} groups and one oxygen atom from a THF molecule in a somewhat distorted trigonal-bipyramidal geometry. The oxygen atoms O(5) and O(3) occupy axial positions and the oxygen atoms O(2), O(4) and O(1) can be considered to occupy equatorial positions. The overall molecular structure is similar to that of the previously reported [(THF)La(OC₆H₃-*i*Pr₂-2,6)₂(μ-OC₆H₃-*i*Pr₂-2,6)₂Na(THF)₂].^[3] The coordination geometry of the sodium cation is identical to that observed in complex **1**.

The terminal Yb–O(Ar) bond lengths are 2.059(3) and 2.088(3) Å, respectively, giving an average of 2.073(8) Å which is comparable with those previously reported terminal Yb–O(Ar) bond lengths.^[3b] Yb–O(Ar) distances to

the bridging ligands are, as expected, somewhat longer at 2.147(3) Å (av.). The Na–O(Ar) and Na–O(THF) bond lengths are comparable with those found in complex **1**. As previously observed in the structure of complex **1**, the O–Yb–O angle between the bridging phenolato ligands [O(1)–Yb(1)–O(3) = 82.2(1)°] is apparently smaller than that between the two terminal phenolato ligands [O(2)–Yb(1)–O(4) = 112.6(1)°]. The average Yb–O–C bond angle for the bridging phenolato ligands is 135.1(3)° while the Yb–O–C angles for the terminal phenolato ligands average 150.6(2)° which is comparable with the corresponding bond angles in complex **1**. The dihedral angles between two arene rings in the MBMP^{2–} groups are quite different, i.e. 57.4(1)° for the ligand containing O(1) and O(2) but 94.8(2)° for that containing O(3) and O(4).

Crystals of complex **6** suitable for an X-ray diffraction study were obtained from a toluene/DME solution at –5 °C. This complex is composed of a discrete six-coordinate [(MBMP)₂Yb(THF)₂][–] anion and an [Na(DME)₂(THF)₂]⁺ cation. Complex **6** crystallises with two crystallographically independent but chemically similar molecules (**6a** and **6b**) in the unit cell. The selected bond lengths and angles are provided in Table 2 for both molecules. The structure of the anion of complex **6a** with the atom-numbering scheme is shown in Figure 3.

In the cation, the sodium atom is coordinated to four oxygen atoms from two DME molecules and two oxygen atoms from two THF molecules to form a slightly distorted octahedral geometry. In the anion, the coordination geometry around the ytterbium atom is different from that in complex **3**. The ytterbium atom is located in the centre of an octahedron comprised of two MBMP^{2–} groups and two THF molecules in which the oxygen atoms from the MBMP^{2–} groups [O(1), O(3), O(4)] and one THF molecule

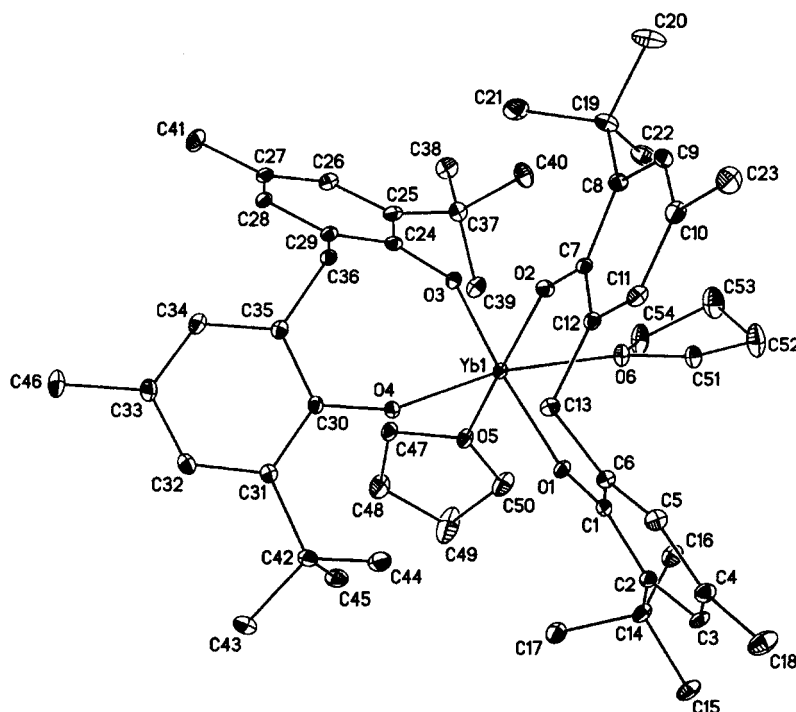


Figure 3. ORTEP diagram of the anion of **6a** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level and hydrogen atoms are omitted for clarity.

[O(6)] can be considered as occupying equatorial positions with $\Sigma(\text{O}-\text{Yb}-\text{O}) = 359.0^\circ$. Two oxygen atoms from one MBMP²⁻ group [O(2)] and the THF molecule [O(5)] occupy axial positions.

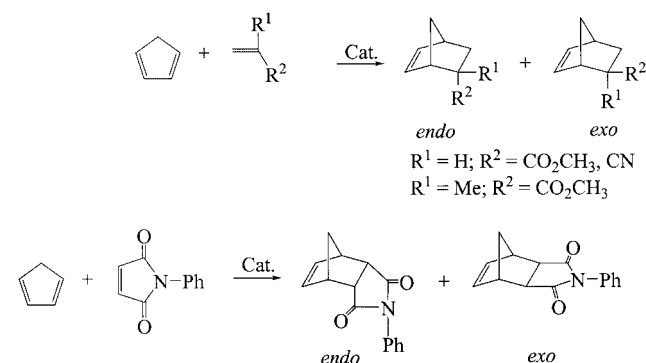
The Yb–O(Ar) bond lengths range from 2.119(5) to 2.157(5) Å, giving an average of 2.140(6) Å which is comparable with the terminal Yb–O(Ar) bond lengths in complex **3** when the difference in coordination number is considered but it is slightly longer than that in [Na(THF)₆][(C₅Me₅)Y(OC₆H₃-Me₂-2,6)₃] (2.094 Å).^[9] The bite angles of O–Yb–O in complex **6a** are 90.45(19)° and 95.72(19)°, respectively, which are comparable with that in complex **1**. The average Yb–O–C bond angle is 152.5(5)° which is similar to the corresponding bond angles in complexes **1** and **3**. The dihedral angles between the arene rings in the two MBMP²⁻ groups are 53.9(3)° and 56.5(2)°, respectively.

A comparison of the structural geometry of the (diphenolato)lanthanide complexes with those of the structurally characterised monodentate aryloxy examples enables an evaluation of the MBMP²⁻ ligand set compared with two ArO⁻ ligands. The yttrium centre is six-coordinate in [(2,6-Me₂-C₆H₃O)₂Y(THF)₂(μ-OC₆H₃-Me₂-2,6)₂(THF)₃] and [Na(THF)₆][(C₅Me₅)Y(OC₆H₃-Me₂-2,6)₃]^[9] whereas the lanthanum centre is only five-coordinate in [(THF)La(OC₆H₃-*i*Pr₂-2,6)₂(μ-OC₆H₃-*i*Pr₂-2,6)₂Na(THF)₂]^[3] and the neodymium centre is four-coordinate in [Na(THF)₆]-[Nd(OC₆H₃-*t*Bu₂-2,6-Me-4)₄]^[3d] [Na(diglyme)][Nd(OC₆H₃-Ph₂-2,6)₄], Na[Nd(OC₆H₃-Ph₂-2,6)₄]^[3e] and K[Nd(OC₆H₃-*i*Pr₂-2,6)₄]^[3i]. However, in these (diphenolato)lanthanide complexes, the central metal atom is five- or six-coordinate. Thus, the diphenolato ligand MBMP²⁻ is

sterically less demanding than the two monodentate aryloxy groups [OC₆H₃-*t*Bu₂-2,6-Me-4]⁻, [OC₆H₃-Ph₂-2,6]⁻ and [OC₆H₃-*i*Pr₂-2,6]⁻ but is comparable with two less bulky aryloxy groups [OC₆H₃-Me₂-2,6]⁻. It is because of the sterically less demanding nature of MBMP²⁻ that the desired (diphenolato)lanthanide chloride [(MBMP)LnCl(THF)_x] could not be achieved by the general salt metathesis reaction.

Diels–Alder Reactions Catalysed by the (Diphenolato)lanthanide Complexes

In recent years, as a result of the importance of Diels–Alder reactions in the synthesis of natural products and physiologically active molecules, increased interest has been directed towards the development of efficient methods for



Scheme 3.

Table 3. Diels–Alder reactions of cyclopentadiene with dienophiles catalysed by carbon-bridged (diphenolato)lanthanide complexes.

Run	Cat.	Dienophile	[Cat.]/[Dienophile]	<i>t</i> [h]	Yield [%]	<i>endo/exo</i>
1	–	methyl acrylate	–	24	67	2.7
2	1	methyl acrylate	1:10	4	59	4.6
3	1	methyl acrylate	1:10	8	78	4.3
4	1	methyl acrylate	1:10	24	93	4.6
5	2	methyl acrylate	1:10	4	54	4.3
6	2	methyl acrylate	1:10	8	69	4.3
7	3	methyl acrylate	1:10	2	14	4.0
8	3	methyl acrylate	1:10	4	35	3.9
9	3	methyl acrylate	1:10	24	94	4.0
10	–	methyl methacrylate	–	10	25	0.45
11	1	methyl methacrylate	1:10	4	22	2.2
12	1	methyl methacrylate	1:10	10	58	2.2
13	–	acrylonitrile	–	10	36	1.2
14	1	acrylonitrile	1:10	4	31	1.6
15	1	acrylonitrile	1:10	8	54	1.6
16	–	<i>N</i> -phenyl maleimide	–	10	46	–
17	1	<i>N</i> -phenyl maleimide	1:10	4	35	35
18	1	<i>N</i> -phenyl maleimide	1:10	8	65	35

the purpose of improving the reaction rates and/or stereoselectivities of cycloaddition reactions.^[11] As Lewis-acidic catalysts, lanthanide complexes are well established and have been found to be effective catalysts in numerous Diels–Alder reactions.^[12] We found that these carbon-bridged (diphenolato)lanthanide complexes can also catalyse the Diels–Alder reactions of cyclopentadiene with methyl acrylate, methyl methacrylate, acrylonitrile and *N*-phenylmaleimide with relatively good activities and stereoselectivities as shown in Scheme 3 with preliminary results listed in Table 3.

As shown in Table 3, these (diphenolato)lanthanide complexes accelerate the Diels–Alder reactions of cyclopentadiene with these dienophiles and the product yields increased as a function of time whereas the stereoselectivities remained essentially the same at all reaction times. Reactions with substituted dienophiles produced a mixture of *endo* and *exo* isomers although the stereoselectivity (*endo/exo* ratio) is apparently dependent on the dienophile. For reactions with asymmetrically substituted dienophiles, the reaction with methyl acrylate afforded the best stereoselectivity. The *endo/exo* ratio of 4.6 can be achieved for this reaction at 40 °C in the presence of 10 mol-% of complex **1** as the catalyst (the *endo/exo* ratio is 2.7 for the blank reaction, runs 1 and 2). In comparison with other lanthanide catalysts, the activities and stereoselectivities exhibited by the (diphenolato)lanthanide complexes for the reaction of cyclopentadiene with methyl acrylate are higher than that of anhydrous lanthanide chlorides^[13a] and are comparable with those of SmI₂^[13b] and Sc(OTf)₃ if toluene is used as solvent (using scCO₂ as solvent, the *endo/exo* ratio is up to 10)^[13c] but are lower than those of other Lewis acid catalysts such as aluminium,^[14a–14c] copper^[14d] and ruthenium^[14e] complexes. It is worthy to note that the reaction of cyclopentadiene with methyl methacrylate catalysed by complex **1** is *endo*-selective and gave products with an *endo/exo* ratio of 2.2. The Diels–Alder reaction of cyclopentadiene with methyl methacrylate normally gave a higher amount of the *exo* stereoisomer^[15a] and some organic and

inorganic reagents can increase the yield of the *endo* stereoisomer.^[15b,15c] Recently, there has been one example reported in which this *exo*-selective reaction can be converted to an *endo*-selective process in chloroaluminate ionic liquids.^[15d] Complex **1** showed poor activity and stereoselectivity for the reaction of cyclopentadiene with acrylonitrile, although the result was similar to those reported in the literature.^[16] For the symmetrically substituted dienophile *N*-phenylmaleimide, excellent stereoselectivity was obtained. The reaction with *N*-phenylmaleimide using complex **1** as catalyst gave the *endo* stereoisomer as the major product but the selectivity was lower than those of montmorillonite and alumina.^[17]

Conclusions

In summary, we have successfully synthesised a series of new soluble carbon-bridged (diphenolato)lanthanide complexes and characterised some of their structural features by X-ray crystallography. Moreover, it was found that coordinated solvents dramatically affect the solid-state structures of the (diphenolato)lanthanide complexes. Crystallisation from toluene in the presence of THF afforded the “ate” complexes while in presence of DME discrete ion-pair complexes were formed. Preliminary results revealed that these “ate” (diphenolato)lanthanide complexes have good activities and stereoselectivities for the Diels–Alder reactions of cyclopentadiene with some substituted dienophiles. Further studies of these reactions are in progress in our laboratory.

Experimental Section

General Procedures: All manipulations were performed under argon using standard Schlenk techniques. THF, DME and toluene were distilled from sodium benzophenone ketyl before use. Anhydrous lanthanide trichlorides were prepared according to the literature procedures^[18] and Na₂(MBMP) was prepared from the reac-

tion of MBMPH₂ with Na in THF [MBMPH₂ = 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol)]. Lanthanide analyses were performed by EDTA titration with xylenol orange indicator and hexamine buffer^[19] and chloride analyses were carried out using the Volhard method. The sodium content was determined with a Hitachi 180-80 polarised Zeeman atomic absorption spectrophotometer. Carbon and hydrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. Uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Methyl acrylate, methyl methacrylate and acrylonitrile were washed with diluted NaOH solution three times, dried with anhydrous Na₂SO₄ for 24 h and distilled before use. *N*-Phenylmaleimide was prepared according to the literature.^[20] Cyclopentadiene was freshly prepared by thermally cracking dicyclopentadiene. Other reagents were commercially available.

Synthesis of [(THF)₂Nd(MBMP)₂Na(THF)₂] (1). **Method A:** To a suspension of NdCl₃ (1.63 g, 6.50 mmol) in THF (50 mL) was slowly added a THF solution of Na₂(MBMP) (27.6 mL, 6.50 mmol) at room temperature. After being stirred for 24 h, the precipitate was separated from the reaction mixture using a centrifuge, the solvent was completely removed in vacuo and toluene was added to extract the product. The dissolved portion was removed with a centrifuge. Light-blue microcrystals were obtained from the concentrated toluene solution. Yield: 2.41 g, 32%. M.p. 165–166 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2955 (s), 2871 (m), 1632 (m), 1474 (s), 1389 (m), 1055 (w), 861 (m) cm⁻¹. C₆₂H₉₂NaO₈Nd (1132.64): calcd. C 65.75, H 8.19, Nd 12.73, Na 2.03; found C 65.43, H 8.01, Nd 12.55, Na 1.91. **Method B:** To a suspension of NdCl₃ (1.28 g, 5.10 mmol) in THF (40 mL) was slowly added a THF solution of Na₂(MBMP) (43.3 mL, 10.2 mmol) at room temperature. After the reaction solution had been stirred for 24 h, complex **1** was isolated as described above (4.53 g, 78%).

Synthesis of [(THF)₂Sm(MBMP)₂Na(THF)₂] (2): The synthesis of complex **2** was carried out as described above for complex **1** (Method B) but anhydrous SmCl₃ (1.3 g, 5.06 mmol) was used instead of NdCl₃. Colourless microcrystals were obtained from toluene. Yield: 4.21 g, 73%. M.p. 144–145 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2955 (s), 2920 (s), 2870 (m), 1604 (w), 1435 (s), 1385 (m), 1250 (s), 1087 (w), 860 (m) cm⁻¹. ¹H NMR (C₆D₆): δ = 1.47 [36 H, C(CH₃)₃], 2.01–2.58 (br., 28 H, THF and ArCH₃), 3.66 (16 H, THF), 3.78 (4 H, ArCH₂), 6.93–7.08 (4 H, C₆H₂) ppm. C₆₂H₉₂NaO₈Sm (1138.76): calcd. C 65.39, H 8.14, Sm 13.18, Na 2.02; found C 65.27, H 7.93, Sm 13.47, Na 1.98.

Synthesis of [(THF)₂Yb(MBMP)₂Na(THF)₂] (3): The synthesis of complex **3** was carried out as described for complex **1** but anhydrous YbCl₃ (1.31 g, 4.69 mmol) was used instead of NdCl₃. Yellow microcrystals were obtained from toluene. Yield: 4.07 g, 75%. M.p. 142–143 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2954 (s), 2909 (s), 2869 (m), 1605 (m), 1526 (m), 1434 (s), 1240 (s), 1156 (s), 1050 (m), 862 (m) cm⁻¹. ¹H NMR (C₆D₆): δ = 1.45 (48 H, C(CH₃)₃ and THF), 2.17 (12 H, ArCH₃), 3.42–3.81 (br., 16 H, THF and ArCH₂), 6.93–7.08 (8 H, C₆H₂) ppm. C₅₈H₈₄NaO₇Yb (1089.33): calcd. C 63.95, H 7.77, Yb 15.88, Na 2.11; found C 63.56, H 7.74, Yb 15.60, Na 1.93.

Synthesis of [(THF)₂Nd(MBMP)₂][Na(DME)₂(THF)₂] (4): To a solution of complex **1** (3.27 g, 2.8 mmol) in toluene (50 mL) was added DME (1 mL). After stirring the solution for about 30 min, blue-purple microcrystals were obtained upon concentration and subsequent cooling of the solution to –5 °C for 3 d. Yield: 3.11 g, 85%. M.p. 109–110 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2951 (s), 2912 (s), 1608 (w), 1466 (s), 1435 (s), 1385 (m), 1084 (s), 860 (m) cm⁻¹.

C₇₀H₁₁₂NaO₁₂Nd (1312.88): calcd. C 64.04, H 8.60, Nd 10.99, Na 1.75; found C 63.74, H 8.39, Nd 10.72, Na 1.68.

Synthesis of [(THF)₂Sm(MBMP)₂][Na(DME)₂(THF)₂] (5): To a solution of complex **2** (2.84 g, 2.5 mmol) in toluene (50 mL) was added DME (1 mL). After stirring the solution for about 30 min, pale-yellow microcrystals were obtained upon concentration and subsequent cooling of the solution to –5 °C for 2 d. Yield: 2.83 g, 86%. M.p. 98–99 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2951 (s), 2921 (s), 2870 (m), 1605 (w), 1466 (s), 1431 (s), 1385 (m), 1292 (s), 1084 (s), 860 (m) cm⁻¹. ¹H NMR (C₆D₆): δ = 1.47 [36 H, C(CH₃)₃], 1.97 (16 H, THF), 2.17 (12 H, ArCH₃), 2.78–3.61 (br., 40 H, DME, THF and ArCH₂), 6.93 (4 H, C₆H₂), 7.08 (4 H, C₆H₂) ppm. C₇₀H₁₁₂NaO₁₂Sm (1319.01): calcd. C 63.76, H 8.56, Sm 11.41, Na 1.74; found C 63.83, H 8.63, Sm 11.02, Na 1.62.

Synthesis of [(THF)₂Yb(MBMP)₂][Na(DME)₂(THF)₂] (6): To a solution of complex **3** (3.21 g, 2.95 mmol) in toluene (50 mL) was added DME (1 mL). After stirring the solution for about 30 min, light-yellow microcrystals were obtained upon concentration and subsequent cooling of the solution to –5 °C for 2 d. Yield: 2.28 g, 61%. M.p. 62–63 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2955 (s), 2920 (m), 2870 (m), 1635 (w), 1466 (m), 1442 (s), 1234 (m), 1157 (m), 1049 (w), 864 (m) cm⁻¹. ¹H NMR (C₆D₆): δ = 1.45 [36 H, C(CH₃)₃], 1.87 (16 H, THF), 2.16 (12 H, ArCH₃), 3.12–3.85 (br., 40 H, THF DME and ArCH₂), 6.92 (4 H, C₆H₂), 7.07 (4 H, C₆H₂) ppm. C₇₀H₁₁₂NaO₁₂Yb (1341.68): calcd. C 62.66, H 8.41, Yb 12.91, Na 1.71; found C 63.03, H 8.81, Yb 12.98, Na 1.68.

Diels–Alder Reactions Catalysed by the (Diphenolato)lanthanide Complexes: In a typical run, methyl acrylate (0.25 mL, 2.7 mmol) was added to a toluene solution of the catalyst (3.7 mL, 0.27 mmol). After stirring the solution at 40 °C for 5 min, freshly cracked cyclopentadiene (0.30 mL, 3.3 mmol) was added with a syringe and stirring was continued for the desired time. Methanol was added to the mixture to terminate the reaction and acetylbenzene was immediately added as an internal standard for quantitative analysis. The product yields and *endo/exo* ratios were determined using GC or NMR spectroscopy as described in the literature for different dienophiles.^[13a,15c,16a,17]

X-ray Crystallography: Crystals of complexes **1**, **3** and **6** suitable for X-ray diffraction were sealed in thin-walled glass capillaries under argon. Diffraction data were collected with a Rigaku Mercury CCD area detector. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealised contributions. The structures were solved and refined using the CRYSTALS (for **1** and **3**) and SHELXS-97 (for **6**) programs. Crystal and refinement data are listed in Table 4. CCDC-239852 to -239854 for **1**, **3** and **6**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 4. Details of the crystallographic data and refinements for **1**, **3** and **6**.

	1	3 ·C ₇ H ₈	6 ·C ₄ H ₈ O
Empirical formula	C ₆₂ H ₉₂ NaNdO ₈	C ₇₉ H ₁₀₈ NaO ₇ Yb	C ₇₄ H ₁₂₀ NaO ₁₃ Yb
Formula mass	1132.63	1365.75	1413.73
<i>T</i> [K]	193(2)	193(2)	193(2)
λ [Å]	0.7107	0.7107	0.7107
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit-cell dimensions:			
<i>a</i> [Å]	18.421(2)	12.9822(4)	13.7108(7)
<i>b</i> [Å]	17.955(1)	15.3241(5)	17.1666(12)
<i>c</i> [Å]	18.099(2)	19.3690(5)	36.308(3)
α [°]	90	79.089(7)	89.862(11)
β [°]	96.269(5)	80.662(7)	80.019(9)
γ [°]	90	78.608(6)	79.611(9)
<i>V</i> [Å ³]	5950.6(8)	3677.7(2)	8276.2(9)
<i>Z</i>	4	2	4
Density [Mg m ⁻³]	1.264	1.233	1.135
Absorption coefficient [mm ⁻¹]	0.930	1.328	1.187
<i>F</i> (000)	2396	1438	2996
$\theta_{\max}$ [°]	27.48	27.48	27.49
Reflections collected	58952	36994	87226
Independent reflections	6953	16575	35903
Observed reflections	6046	14039	33673
Parameters refined	372	796	1366
Final <i>R</i> [<i>I</i> > 3σ(<i>I</i>)]	0.0390	0.0450	0.0862
<i>wR</i>	0.1110	0.1330	0.2066
<i>GoF</i> on <i>F</i> ²	1.004	1.034	1.189

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