Lanthanide catalysts for the hetero Diels–Alder reaction: effect of ligand structure and acidity

Claude Spino, Laurel L. Clouston, and David J. Berg

Abstract: A series of yttrium, ytterbium, and lanthanum hexa- or heptacoordinate complexes were prepared and their catalytic activities tested in the hetero Diels–Alder reaction between crotonaldehyde and ethyl vinyl ether. It was found that a pK_a below 7 of the ligand was necessary but not sufficient for catalytic activity. It was determined that the ligand should possess a perfluoromethyl-β-diketonate functionality. Other factors such as bite angle and hinging motion may also play a determining role.

Key words: lanthanide, catalyst, hetero Diels–Alder, yttrium, ytterbium, lanthanum.

Résumé : L'activité catalytique d'une série de complexes d'yttrium, d'ytterbium et de lanthanum fait à partir de ligands hexa ou heptadentates a été mesurée pour la réaction d'hétéro Diels–Alder entre la crotonaldéhyde et l'éthyl vinyl éther. Nous en avons conclus qu'un pK_a inférieur à 7 du ligand est nécessaire mais pas suffisant pour engendré une activité catalytique. Nous avons déterminé que le ligand doit posséder la fonctionalité perfluorométhyl β-dicétone. D'autres facteurs tel que l'angle de mordage et une action de type charnière des ligands peuvent aussi jouer un rôle déterminant.

Mots clés : lanthanide, catalyseur, Diels–Alder hétéro, yttrium, ytterbium, lanthanum.

The hetero Diels–Alder cycloaddition has proven extremely useful in the synthesis of a multitude of heterocycles (1). The cycloaddition of α,β-unsaturated aldehydes with electron-rich dienes such as vinyl ethers is in the forefront of hetero Diels–Alder reactions due to the importance and prevalence of the dihydropyran and tetrahydropyran (2) substructures contained in such natural compounds as sugars and polyether antibiotics (3, 4). Lanthanide(III) complexes have demonstrated clear effectiveness and mildness in catalyzing this and other reactions (1, 5). The prototypical case of crotonaldehyde reacting with ethyl vinyl ether under $Yb(fod)_3$ catalysis serves to demonstrate this point with an isolated yield greater than 95% of a single *endo* cycloadduct at room temperature (6). In comparison, the thermal reaction of crotonaldehyde and ethyl vinyl ether proceeds at 175°C in sealed tube conditions to give 87% of cycloadducts (7) whereas under high pressure conditions (15 kbar (1 bar = 100 kPa), 75°C, 24 h) one obtains 89% of the *endo* product (8). Also, stronger Lewis acids give reduced yields of product, presumably because of product decomposition (vide infra). We have ourselves observed the high tolerance of lanthanide catalysts for sensitive functional groups such as acetals, silyl ethers, and esters (9).

So far, though, the asymmetric catalysis of the hetero [4+2]-cycloaddition has met with only limited success (10), especially in the case of lanthanide catalysts (1, 10, 6*b*, 11). In the latter case, the lability of the chiral ligands may be partly to blame. As part of a project directed at the preparation of efficient chiral lanthanide catalysts, we initiated a study of the ligand effect on the catalytic activity of ytterbium, lanthanum, and yttrium complexes. The focus of the study was to determine if ligands other than perfluoro-β-diketones could confer catalytic activity on the lanthanide complexes so as to ease the preparation of effective chiral ligands. Also, to address the ligand lability issue, complexes with multidentate ligand systems were investigated. The study not only provided helpful and incisive information on necessary structural features of the ligand for catalytic activity, it also provided novel, air-stable, and effective yttrium and ytterbium catalysts for the hetero Diels–Alder reaction (12). The well-defined and characterized tripodal structures of these catalysts will provide a solid model from which to design and develop highly effective chiral catalysts. Their stability in air is a good indication of low ligand lability.

Figure 1 provides a list of the structural formula of the different ligands prepared or purchased. Compounds **1a**–**d**, **3a**,**b**, **7b**, and **7c** were purchased (available from Aldrich). Compound **2** is commercially available but was purchased as its ytterbium complex (Aldrich). Ligand **1e** was prepared as per Morris and Koob (13). Ligands **4a** (14), **4b**, and **5** (14) were prepared by refluxing tris(aminoethyl)amine and **1a**, **1b**, or **3b**, respectively, in benzene with azeotropic removal of water.

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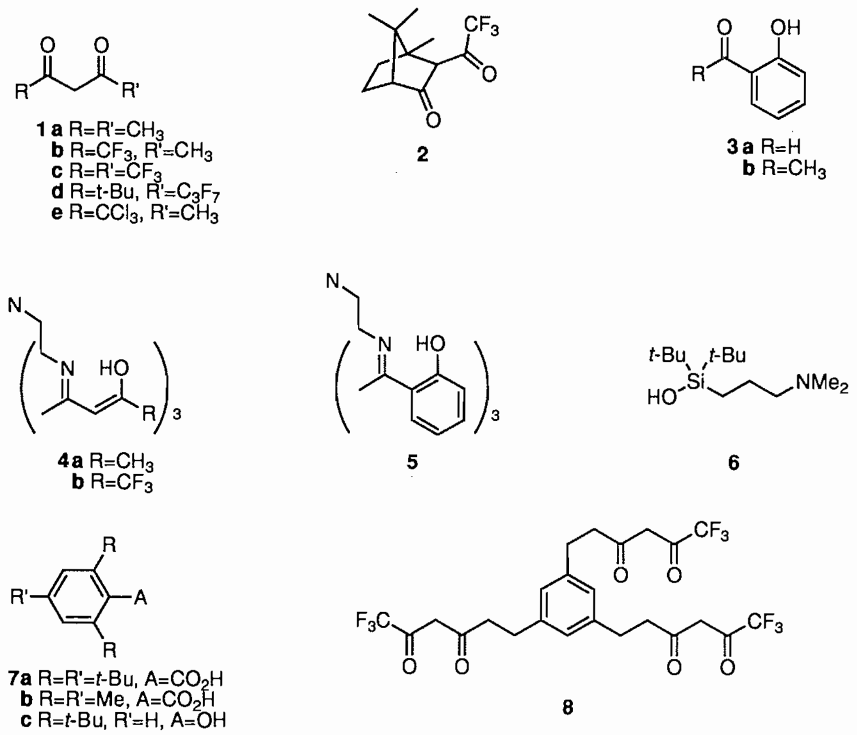
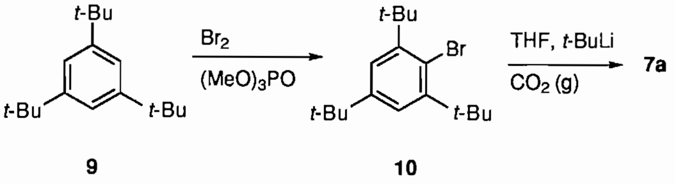
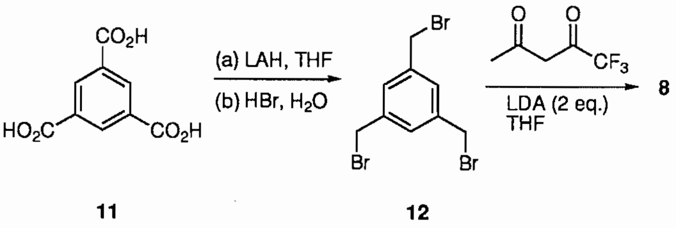
Fig. 1. Ligands tested as their lanthanide complexes.



Scheme 1.



Scheme 2.



Their purification was done by sublimation under reduced pressure. Compound **6** was prepared in four steps as described in the literature (15). Ligand **7a** was prepared by monobromination of 1,3,5-tri-*tert*-butylbenzene (16) followed by lithium–halogen exchange with *tert*-butyllithium in THF and quenching with gaseous carbon dioxide (Scheme 1) (17). Finally, ligand **8** was prepared by the reaction sequence shown in Scheme 2. Starting from 1,3,5-benzenetricarboxylic acid **11** using a one-pot procedure where the aluminium salts resulting from the reduction with LAH are directly treated with aqueous hydrobromic acid, we obtained an 80% yield of **12** (18). The dianion of 1,1,1-trifluoroacetylacetone was generated using slight modifications of a standard procedure (19). Though its reactivity was lower than that of non-fluorinated β-diketones, effective alkylation in THF at room temperature with tribromomesitylene **12** could be achieved. The tripodal ligand **8** was thus obtained in 40% yield after recrystallization and sublimation at 140°C / 10^{-2} Torr (1 Torr = 133.3 Pa).

Except for the ytterbium complex of **2**, which was purchased (Aldrich), all other complexes were made by adding the ligand to a toluene solution of the lanthanide tris(bis(trimethylsilyl)amide) at 0°C (20). The complexes precipitated out from solution and were collected and sublimed whenever possible. When the reaction was carried out in THF or other coordinating solvents, the solution was first concentrated under reduced pressure to remove the solvent. Ytterbium complexes of **4a** (21), **5** (21), **6** (15) and the yttrium complex of **4b** were monomeric and characterized by single-crystal X-ray analysis.[2] The yttrium complexes **17a**, **17b**, and **19**·THF were shown to be monomeric by proton NMR spectroscopy. All other complexes were characterized by NMR (in the case of yttrium) and (or) by mass spectrometry and could be

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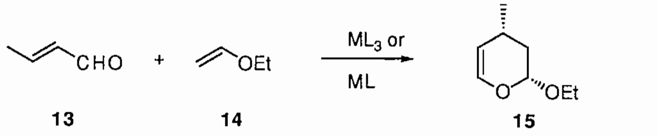
[2] X-ray crystal data and tables of atomic coordinates, isotropic thermal equivalents, bond lengths and angles, torsion angles, and anisotropic displacement factors have been deposited and can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. With the exception of the torsion angles and anisotropic displacement factors, this material has also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Table 1. Reaction of crotonaldehyde with ethyl vinyl ether catalysed by the different lanthanide complexes.



Entry	L	pK_a of L	Ref.	M	Yield (%)[a]
1	**1a**	9	21*a*	Y, Yb	19
2	**1b**	6.3	21*a*	Y, Yb	86
3	**1c**	4.5	21*b*	Y, Yb	86
4	**1d**	5.1	21*c*	Yb	90
5	**1e**	8.5[b]		Y	17
6	**2**	6[c]		Yb	88
7	**3a**	8.2	21*a*	Yb	21
8	**3b**	10	21*a*	Yb	6
9	**4a**	12[c]		Y, Yb	9
10	**4b**	9[c]		Y, La	8
11	**5**	11	21*d*	Yb	0
12	**6**	13.6	21*e*	Y	0
13	**7a**	6.25	21*f*	Y, Yb	0
14	**7b**	5.25	21*g*	Y, Yb	0
15	**7c**	>11	21*h*	Y	0
16	**8**	6[c]		Y, Yb	96

[a] As measured by G.C.
[b] Measured in 40% dioxane/H_2O.
[c] Estimated.

oligomeric. β-Diketonate complexes of a variety of metals, including the lanthanides, are well known and mentioned throughout the literature (22–25). However, few β-diketonate lanthanide complexes have been rigorously characterized. The ytterbium complexes of **1d** (6), **4a** (21), **5** (21), and **6** (15) are known, while those of the remaining ligands are new. The yttrium complexes of all ligands except **1a** are new.

Starting from the observation that lanthanide complexes derived from β-diketone-type ligands are effective catalysts for the hetero Diels–Alder reaction, we initially believed that ligands such as **4a** and **5** would be well suited for our purpose, because they are heptadentate in nature, easily prepared (14), and easily altered for the eventuality of chiral design. Such tripodal ligands form stable complexes with lanthanides (21). In fact, the rationale for using these heptadentate ligands was to confer extra stability to the complex, in effect "locking" the ligand in place. Monomeric, tripodal structures would provide a solid base from which to design and develop highly effective chiral catalysts with well-defined coordination sites.

Catalytic activities were tested on the hetero Diels–Alder cycloaddition of crotonaldehyde **13** and ethyl vinyl ether **14**, the latter serving as solvent, with 2 mol% of catalyst (Table 1). Each reaction was monitored by GC at specific time intervals. As expected, the product isolated was regiochemically and diastereomerically pure (racemic) and was derived from the *endo* approach of the dienophile as verified by proton NMR (6). We were surprised to find that neither the yttrium nor the ytterbium complexes of **4a** and **5** displayed significant catalytic behaviour toward the cycloaddition reaction of crotonaldehyde and ethyl vinyl ether (Table 1, entries 9 and 11). Careful examination of the literature revealed that in fact only perfluoro-β-diketone-type ligands are known to be involved in the successful catalysis of the hetero Diels–Alder reaction by lanthanide complexes. We thus reasoned that lanthanide complexes of ligand **4b**, the 1,1,1-trifluoro analog of **4a**, should indeed catalyse the desired reaction. To our surprise, the yield of cycloadduct obtained with the yttrium and lanthanum complexes remained negligible even after several days (entry 10). Several factors could be responsible for this lack of activity and we suspected that either the imine nitrogens or the coordinating amine nitrogen could electronically saturate the metal thereby lowering its Lewis acidity.

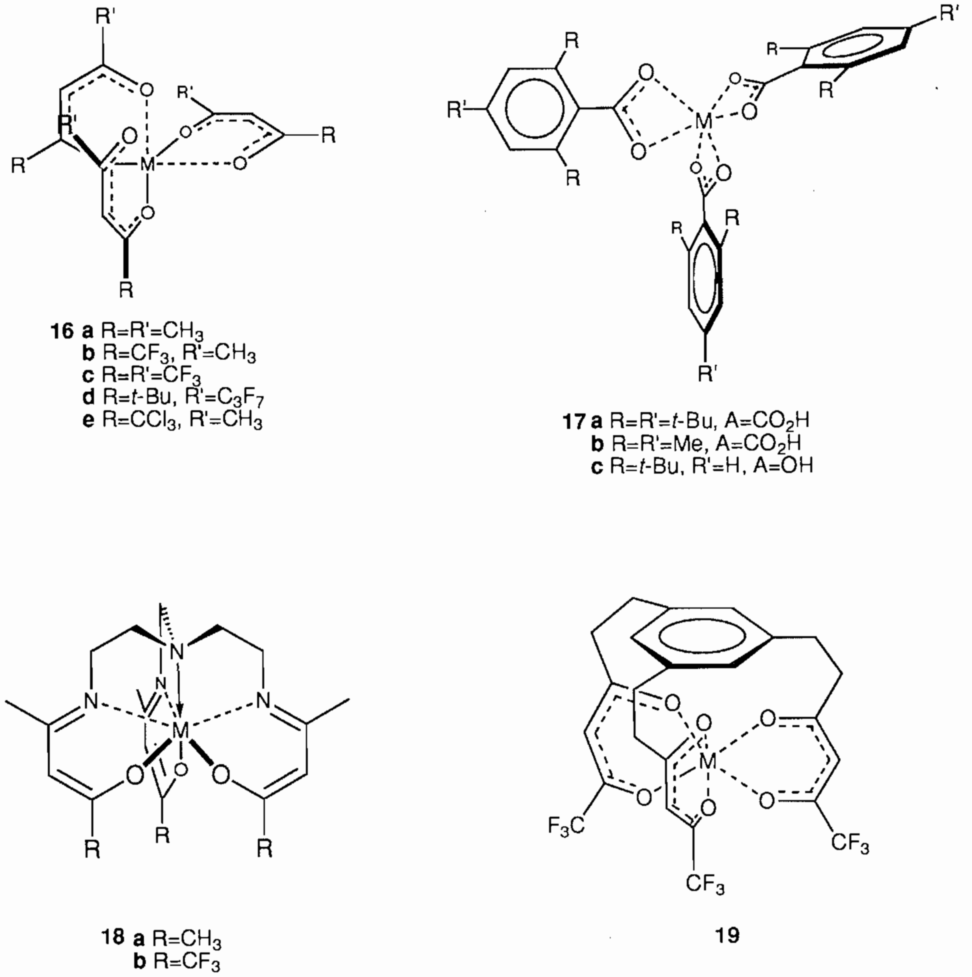
The degree of Lewis acidity at the metal had to be established and therefore we began studying the effect of pK_a of the ligand on the catalytic activity of the resulting lanthanide complex. Although a direct correlation between the pK_a of the ligand and the Lewis acidity of the corresponding complex is only speculative, it is likely that a rough correlation exists among ligands of similar structure. We attempted to determine the Lewis acidity of some complexes by the method of Childs et al. using crotonaldehyde as the complexing agent (26). However, the low solubility of the catalysts in non-coordinating solvents precluded meaningful results.

Yb(fod)$_3$ is known to be a mild and effective catalyst for the hetero Diels–Alder reaction and it provided a reference point against which all other reactions were compared (6). The complexes having acac-type ligands with pK_a's lower than approximately 6.3 were effective as catalysts (Table 1, entries 2–4, and 6) (27). Other ligands with higher pK_a were less effective or ineffective in the time period studied (entries 1, 5, 7–15). Interestingly, there was no difference between the yttrium, ytterbium, and lanthanum complexes (entries 9–11, 13, 14, and 16). Yttrium and ytterbium have similar van der Waals radii and Lewis acidity but lanthanum is substantially larger and is a weaker Lewis acid. The high catalytic activity of the ytterbium complex of **2** suggests that steric bulk around the metal is not an important factor (entry 6). Complexes of ligands **3** gave modest catalytic activity in line with pK_a values (entries 7 and 8) and the complex of silanol **6** gave no activity at all (entry 12). A catalytic run was also performed with the yttrium complex of ligand **1a** in trifluoroethanol as solvent with no success. It therefore seems unlikely that the fluorines are playing a role other than simply lowering the pK_a of the diketone ligand.

Confident that the Lewis acidity of the metal could be tuned by adjusting the pK_a of the ligand, we surmised that complexes of carboxylic acids would be efficient catalysts because of their low pK_a. We had in mind to eventually use linked amino acids to make chiral tripodal complexes of ytterbium and yttrium, thereby obtaining easy access to chiral catalysts. Before embarking on the synthesis of an elaborate ligand we decided to test the catalytic activity of the lanthanide complexes of acids **7**. The results were unequivocal: no catalysis whatsoever was observed (entries 13 and 14). All of the acids **7** have a pK_a below that of trifluoroacac **1b**. The Yb and Y complexes **17b** (Fig. 2) were tested to verify that the bulky *tert*-butyl groups in **17a** were not sterically blocking the active site; they were also inactive. Not surprisingly, the Y complex made with phenol **7c** did not lead to a better result (entry 15). Finally, the commercially available yttrium tris(hexanoate) was also screened and found to be inactive.

These results are reminders that the mechanism of catalysis

Fig. 2. Lanthanide complexes. No definite geometry intended for **17** and **19**.



16 a $R=R'=CH_3$
b $R=CF_3$, $R'=CH_3$
c $R=R'=CF_3$
d $R=t\text{-}Bu$, $R'=C_3F_7$
e $R=CCl_3$, $R'=CH_3$

17 a $R=R'=t\text{-}Bu$, $A=CO_2H$
b $R=R'=Me$, $A=CO_2H$
c $R=t\text{-}Bu$, $R'=H$, $A=OH$

18 a $R=CH_3$
b $R=CF_3$

19

may involve more than just a simple chelation of the Lewis acid to the aldehyde with concurrent lowering of the oxadiene LUMO (28). We considered solubility as a possible explanation for the lack of activity of complexes **17**. However, they are more soluble than many active catalysts in ethereal solvents. The geometry, bulk, and bite angle of the ligand may of course affect the effective Lewis acidity of the metal independently of its pK_a. As stated earlier, a direct measurement of the Lewis acidity of the metal is possible by the method of Childs et al. (26), though Laszlo and Teston pointed out that NMR measurements of Lewis acidities of metals fail to accurately predict the chemical activity of Lewis acids as catalysts (28*a*). In any case, the generally low solubility of these complexes in non-coordinating solvents prevented meaningful measurements by the NMR method. Unfortunately the semiempirical MNDO calculations by the method of Laszlo could not be carried out on lanthanides because the parameters do not yet exist (28*a*). Nevertheless, the difference of catalytic activity between complexes **17** and **16** could not be due to ligand pK_a, steric bulk, or solubility. We considered three alternative explanations, namely, that the catalytic activity may be due to trace impurities emanating from the experimental preparation of the catalysts, or that the effective Lewis acidity of complexes **17** may be lower than that of complexes **16b–d** because of ligand geometry or oligomer formation, or last, that the displacement or, possibly, hinging of one of the ligands may be necessary to free a coordination site for catalysis (hinging specifically refers to partial dissociation of one arm, i.e., bidentate to monodentate for that arm). A hinging motion would be more favorable, from a geometric standpoint, in β-diketone-type ligands than in carboxylic acids.

Whatever the explanation, we concluded that an effective catalyst should possess the unaltered perfluoromethyl-β-diketone functionality on the ligand. Such units could be linked by the end methyl group via a number of linkers, thereby leaving the γ-perfluoro-β-diketone unit intact. 1,3,5-Tribromomesitylene **12** caught our attention as being a useful linker because of its relative ease of preparation and high reactivity toward alkylation. The yttrium and ytterbium complexes of **8** were prepared by mixing the ligand with a solution of yttrium or ytterbium tris(bis(trimethylsilyl)amide) in toluene as described earlier. In each case, an instantaneous reaction occurred with concomitant precipitation of the complex, which was washed several times with toluene. Unfortunately, we could not grow crystals of adequate quality to perform a single-crystal X-ray crystallographic analysis on either of the complexes and neither were soluble in non-coordinating solvents. To secure the structure of the yttrium complex **19**

Table 2. Compared efficiency of catalysts **19** on the hetero Diels–Alder reaction of **13** and **14**.

Entry	Catalyst	M	Conditions[a]	Time (h)	Conversion[b]	Yield (%)[c]
1	**19**	Y	A	72	98	95
2	**19**	Yb	A	96	80	80
3	Yb(fod)$_3$		A	96	98	90
4	ZnCl$_2$		A	48	98	46
5	BF$_3$·Et$_2$O		A	48	98	12
6	**19**	Y	B	96	69	69
7	Yb(fod)$_3$		B	96	69	65
8	**19**	Y	C	96	89	89
9	**19**	Yb	C	96	89	89
10	Yb(fod)$_3$		C	96	0	0

[a] Method A = ethyl vinyl ether as solvent, 2 mol% catalyst, 25°C; Method B = method A + dioxane (0.5 equiv.) (similar results if **19** is prepared in a coordinating solvent); Method C = method A + deliberately exposed to air for 7 days.

[b] Disappearance of starting materials analysed by gas chromatography.

[c] Isolated yield after distillation.

(Fig. 2, M = Y), we prepared it in THF and isolated the powdery material by reduced pressure evaporation of the solvent. Although no X-ray quality crystals could be grown, the proton NMR analysis of the complex in benzene-d_6 was unequivocal and established the coordination of a molecule of THF (12). Mass spectral data and exact mass measurement on this compound were satisfactory. The structure of the ytterbium complex **19** (M = Yb) was inferred only from mass spectral data and by analogy to its yttrium analogue.

Catalytic activities of these new ligands were tested on the hetero Diels–Alder cycloaddition of crotonaldehyde and ethyl vinyl ether as described earlier (Table 2). In each example involving ytterbium or yttrium catalysts the isolated yields of the respective dihydropyran product **15** were excellent, testimony to their mildness (entries 1–3). In contrast, zinc chloride and BF$_3$-etherate gave 46% and 12% isolated yield, respectively, of **15** (entries 4 and 5). The yttrium catalyst **19** was superior to all others, including the commonly used Yb(fod)$_3$ (6), having the fastest conversion rate and giving a good isolated yield of **15** (entry 1). If dioxane was utilized as an internal standard for quantitative work, the reaction rate between **13** and **14** dropped (entries 6 and 7), indicating a competition for the active site between the coordinating solvent and crotonaldehyde. We found that when the complexes **19** were prepared in, or came in contact with, coordinating solvents, the reaction rate also dropped, presumably due to the incorporation of a coordinating solvent molecule. This coordinating solvent molecule may compete with crotonaldehyde for the active site or simply reduce the Lewis acidity of the complex. This outcome convinced us that in the case of complexes of **4** and **5** the coordinating amine nitrogen is playing the same role, only more efficiently, and no or very low conversion rates are observed. More importantly though, both catalysts **19** remained active even after several days of exposure to the ambient air (entries 8 and 9), even though the complexes may have picked up water molecules from exposure to air. Moreover, a 3-month-old sample of yttrium complex **19** stored in an opened vial still retained complete catalytic activity and the complex can be stirred in water (it is insoluble in water), extracted with THF, recovered, and used as a catalyst. The activity of the complex, even after exposure to air, is probably due to significantly reduced ligand lability. Multidentate ligands are known to exhibit this phenomenon. In contrast, all other catalysts including Yb(fod)$_3$ had to be kept in a rigorously dry atmosphere to remain active (entry 10).

In conclusion, we have prepared the first lanthanide complexes possessing a hexadentate ligand that are active catalysts. Their high stability, even in air, is not only desirable in terms of handling but is also very promising as a base from which to develop chiral catalysts showing high asymmetric induction. Our results clearly demonstrate that the ligand around the lanthanide should possess the unaltered perfluoromethyl-β-diketone functionality. It would seem that the role of the fluorines is to bring the pK_a of the β-diketone below a minimal level for catalysis and that, possibly, their hinging motion allows access to the catalytic site.

Experimental section

All solvents were distilled from sodium–benzophenone with the exception of di- and tetrachloromethane and dimethyl sulfoxide, which were distilled from calcium hydride. All reactions were performed under an atmosphere of argon unless otherwise stated. Flash column chromatography was done using Merck 60 silica gel. NMR spectra were taken in CDCl$_3$ at 250 or 360 MHz, and IR spectra were recorded in CHCl$_3$. ^{13}C NMR signal multiplicities were determined by DEPT experiments. Gas chromatography was performed on a DB-1 capillary column with FID detector. 2,4-Pentanedione (**1a**), 1,1,1-trifluoroacetylacetone (**1b**), and 1,1,1,5,5,5-hexafluoroacetylacetone (**1c**), were purchased and subsequently purified by distillation. Salicylaldehyde (**3a**), hydroxyacetophenone (**3b**), 2,4,6-trimethylbenzoic acid (**7a**), and 2,6-di-*tert*-butylphenol (**7c**) were purchased and purified by sublimation under vacuum. 1,1,1-Trichloroacetylacetone (**1e**) was synthesized as outlined in ref. 13. Tris(3-aza-4-methyl-6-oxohept-3-

en-1-yl)amine (**4a**), tris(3-aza-4-(2-hydroxyphenyl)-3-penten-1-yl)amine (**5**), and each of their respective yttrium and ytterbium complexes were synthesized and purified as outlined by Orvig and co-workers (14, 21). (*N,N*-Dimethyl-3-aminoprop-1-yl)di-*tert*-butylsilanol (**6**) and its tris-yttrium salt were prepared and isolated as outlined in Shao et al. (15). The yttrium complex of **7c** was prepared and isolated as outlined in Lappert et al. (29). The ytterbium complexes of **1d** and **2** were purchased from Aldrich.

Tris(3-aza-4-methyl-6-oxo-7,7,7-trifluorohept-3-en-1-yl)amine (4b)

In a 25 mL round-bottom flask equipped with a stirbar and a Dean Stark trap, 0.1 g (0.68 mmol) of tris(aminoethyl)amine was dissolved in 10 mL of dry benzene. Then 4.0 mL (5.1 g, 33.0 mmol) of 1,1,1-trifluoroacetylacetone was added via syringe and the reaction mixture was refluxed for 16 h. The resulting solution was concentrated under reduced pressure to obtain a sticky, golden powder. Purification by repeated triturations with Et_2O gave an isolated yield of 0.38 g (85%) of the desired tripodal ligand. ^1H NMR (300 MHz, C_6D_6) δ: 11.11 (br s, 3H), 5.24 (s, 3H), 3.48 (q, 6H, J = 7 Hz), 2.84 (t, 6H, J = 7 Hz), 2.06 (s, 3H). ^{13}C NMR (90 MHz, C_6D_6) δ: 175.45 (q, 2C, J_{CF} = 31 Hz), 170.02 (q), 117.63 (q, J_{CF} = 281 Hz), 89.73 (d), 54.36 (t), 42.41 (t), 19.38 (q). ^{19}F NMR (338 MHz, $CDCl_3$) δ: −76.84 (s). HRMS, calcd. for $C_{21}H_{27}F_9N_4O_3$: 152.1201; found: 152.1205.

2,4,6-Tri-*tert*-butylbenzoic acid (7a)

An oven-dried Schlenk tube was charged with 1.4 g (6.3 mmol) of 1-bromo-2,4,6-tri-*tert*-butylbenzene (16) in 125 mL of dry hexanes. Then 3.7 mL (6.3 mmol) of 1.7 M *t*-BuLi in pentanes was added and the resulting mixture was left to stir at −78°C for 1 h. Then, carbon dioxide was bubbled through the solution for 4 h. The mixture was quenched with 3 N aqueous HCl until the water layer was approximately at pH 1. The two phases were separated and the aqueous phase was extracted with ether. The combined organic portions were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Washing the product repeatedly with hexanes yielded 0.4 g (35%) of the desired product (16). ^1H NMR (250 MHz, $CDCl_3$) δ: 7.40 (s, 2H), 1.57 (s, 18H), 1.34 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ: 179.24 (s), 150.69 (s), 146.39 (s), 127.46 (s), 122.16 (d), 35.06 (s), 32.22 (s), 31.56 (q), 31.26 (q).

1,3,5-Tribromomesitylene (12)

In an oven-dried 1 L round-bottom flask equipped with a stirbar, was added 2.0 g (74 mmol) of lithium aluminum hydride in 200 mL of dry THF. Then, 5.0 g (23.8 mmol) of 1,3,5-benzenetricarboxylic acid in 200 mL of dry THF was added dropwise into the stirring slurry over 2 h under an atmosphere of N_2 while cooling with an ice bath. The resulting slurry was heated to reflux for 16 h using a condenser equipped with a drying tube. Enough water was then added to destroy excess reagent and the resulting salts were dried under high vacuum. To this vessel was added 150 mL of a 48% HBr solution and 250 mL of benzene. The mixture was heated to reflux for 16 h. The organic layer was separated and the aqueous portion was extracted with Et_2O; the organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. Recrystallization from hot cyclohexanes yielded 6.9 g (80%) of the desired product (18). ^1H NMR (360 MHz, $CDCl_3$) δ: 7.33 (s, 3H), 4.43 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ: 139.03 (s), 129.56 (d), 32.18 (t).

1,3,5-Tris(3,5-dioxo-6,6,6-trifluorohexan-1-yl)benzene (8)

A solution of 2.0 mL (2.6 g, 16.8 mmol) of 1,1,1-trifluoroacetylacetone in 20 mL of dry THF in an oven-dried Schlenk tube equipped with a stirbar was cooled to −78°C. In a separate oven-dried Schlenk tube was prepared an LDA solution in 10 mL of dry THF using 2.6 mL (2.0 g, 20.2 mmol) of dry diisopropylamine and 12.6 mL (20.2 mmol) of 1.6 M *n*-butyllithium in hexanes. After cooling to −78°C the trifluoroacetylacetone solution was transferred by cannula to the LDA solution while maintaining the temperature at −78°C. In a third oven-dried Schlenk tube was prepared a second LDA solution in 20 mL of dry THF using 2.0 mL (1.5 g, 15.2 mmol) of dry diisopropylamine and 9.5 mL (15.2 mmol) of 1.6 M *n*-butyllithium in hexanes. After cooling to −78°C this LDA solution was transferred into the previous one, while maintaining the temperature at −78°C. The mixture was stirred for 20 min and a solution of 1 g (2.8 mmol) of 1,3,5-tribromomesitylene in 20 mL of dry THF was added via cannula into the the dianion solution at −78°C. The reaction was stirred for 4 h while slowly warming to room temperature. The work-up consisted in adding a 3 M aqueous HCl solution, separating the layers, and, after ensuring that the water layer was acidic, extracting exhaustively with dichloromethane. The combined organic fractions were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Recrystallizing the resulting golden oil using a dry THF–hexanes mixed solvent system gave pale yellow crystals that could be further purified by sublimation at 140°C/10^{-2} Torr, yielding 0.63 g (40%) of the desired benzene-capped tripodal ligand **8**. ^1H NMR (250 MHz, C_6D_6) δ: 6.86 (s, 3H), 5.85 (s, 3H), 3.45 (t, 6H, J = 7 Hz), 2.87 (t, 6H, J = 7 Hz). ^{13}C NMR (63 MHz, C_6D_6) δ: 196.24 (q), 174.69 (q, $^2J_{CF}$ = 36 Hz), 140.57 (q), 126.51 (d), 117.01 (q, $^1J_{CF}$ = 282 Hz), 96.18 (d), 40.17 (t), 31.00 (t). ^{19}F NMR (338 MHz, C_6D_6) δ: −76.76 (s). HRMS, calcd. for $C_{24}H_{21}F_9O_6$: 576.1194; found: 576.1194.

Metal complexes

General procedure for the preparation of Y and Yb complexes of all ligands

Preparation was carried out in a similar manner for all complexes. β-Diketonates have been extensively investigated (22–25) and were previously prepared in high yields using this anhydrous method (23*a*). Hence various metal derivatives of **1a** (23), **1b** (23, 24), **1c** (23, 25), and **1e** (23) had been previously prepared and were used for comparison. In a Schlenk tube equipped with a stirbar, under an inert atmosphere, the ligand was dissolved in dry THF. In a separate oven-dried Schlenk tube equipped with a stirbar, under an inert atmosphere, $Y(N(SiMe_3)_2)_3$ (20) was dissolved in dry THF and transferred via cannula into the ligand solution while stirring. Stirring was continued for 20 min before removing the solvents and the resulting $Y(N(SiMe_3)_2)_3$ under reduced pressure, thereby isolating the desired product as a powder. The insoluble powders were repeatedly washed with toluene and hexanes to give free-flowing powders. The same procedure was used with $Yb(N(SiMe_3)_2)_3$ and $La(N(SiMe_3)_2)_3$ for those complexes.

*Yttrium and ytterbium tris(acetylacetone) (**16a**)*: Prepared using the general procedure above. The reaction of 1.38 g (2.1 mmol) $Yb(N(SiMe_3)_2)_3$ with 0.65 mL (6.3 mmol) of dry acetylacetone yielded 0.51 g (52%) of the desired material. LRMS: 471 (M^+) with the expected isotopic pattern for ytterbium. Similar quantities, yields, and characterization for the yttrium complex.

*Yttrium and ytterbium tris(1,1,1-trifluoroacetylacetone) (**16b**)*: Prepared using the general procedure above. The reaction of 1.38 g (2.1 mmol) $Yb(N(SiMe_3)_2)_3$ with 0.77 mL (6.3 mmol) of dry trifluoroacetylacetone yielded 0.65 g (50%) of the desired material, purified by sublimation at 90°C at 10^{-4} Torr. LRMS: 633 (M^+) with the expected isotopic pattern for ytterbium. Similar quantities, yields, and characterization for the yttrium complex.

*Ytterbium tris(1,1,1,5,5,5-hexafluoroacetylacetone) (**16c**)*: Prepared using the general procedure above. The reaction of 1.38 g (2.1 mmol) $Yb(N(SiMe_3)_2)_3$ with 0.90 mL (6.3 mmol) hexafluoroacetylacetone yielded 0.83 g (50%) of the desired material, purified by sublimation at 120°C at 10^{-2} Torr. LRMS: 795 (M^+) with the expected isotopic pattern for ytterbium.

*Yttrium tris(1,1,1-trichloroacetylacetone) (**16e**)*: Prepared using the general procedure above. The reaction of 0.71 g (1.3 mmol) of $Y(N(SiMe_3)_2)_3$ with 0.76 g (3.9 mmol) of dry trichloroacetylacetone yielded 0.42 g (49%) of orange powder.

*Ytterbium tris(salicylaldehyde) (Yb of **3b**)*: Prepared using the general procedure above. The reaction of 1.38 g (2.1 mmol) $Yb(N(SiMe_3)_2)_3$ with 0.76 g (6.3 mmol) of dry salicylaldehyde yielded 0.58 g (51%) of pale yellow powder.

*Ytterbium tris(hydroxyacetophenone) (Yb of **3b**)*: Prepared using the general procedure above. The reaction of 1.38 g (2.1 mmol) $Yb(N(SiMe_3)_2)_3$ with 0.75 mL (6.3 mmol) of dry 2-hydroxyacetophenone yielded 0.58 g (48%) of yellow powder.

*Yttrium tris(2,4,6-tri-*tert*-butylbenzoate) (**17a**)*: Prepared as described in the general procedure above using 600 mg (2.1 mmol) of ligand **7a** in 5 mL of dry THF and 0.39 g (0.69 mmol) of $Y(N(SiMe_3)_2)_3$ in 5 mL of dry THF. A white soluble powder was isolated in 75% yield and purified by washing repeatedly with hexanes, giving a 73% overall yield. ^1H NMR (360 MHz, C_6D_6) δ: 7.42 (s, 6H), 1.46 (s, 54H), 1.31. (s, 27H). ^{13}C NMR (90 MHz, C_6D_6) δ: 179.94 (s), 150.68 (s), 146.33 (s), 127.53 (d), 122.16 (s), 37.63 (s), 35.05 (s), 32.22 (q), 31.26 (q).

*Yttrium and ytterbium tris(2,4,6-trimethylbenzoate) (**17b**)*: Prepared as described in the general procedure above using 0.38 g (0.67 mmol) $Y(N(SiMe_3)_2)_3$ with 0.33 g (2.0 mmol) of ligand **7b**. A white powder was isolated in 54% yield after repeated washing with hexanes. ^1H NMR (360 MHz, C_6D_6) δ: 7.23 (s, 6H), 2.43 (s, 18H), 2.24 (s, 9H). ^{13}C NMR (90 MHz, C_6D_6) δ: 177.74 (s), 149.32 (s), 144.42 (s), 126.92 (d), 121.20 (s), 35.55 (q), 33.43 (q). Similar quantities and yields for the ytterbium complex.

*Yttrium tris(3-aza-4-methyl-6-oxo-7,7,7-trifluorohept-3-en-1-yl)amine (**18b**)*: Prepared following the procedure for Y–**4a** complex described by Berg, Rettig, and Orvig (21) using 0.2 g (0.35 mmol) of $Y(N(SiMe_3)_2)_3$ with 0.195 g (0.35 mmol) of ligand **4b** in 20 mL of dry THF, affording a quantitative yield (0.22 g) of creamy white powder. This could be recrystallized from warm toluene upon standing, yielding colourless brick-like crystals in modest quantities. X-ray (see footnote 2), ^1H NMR (360 MHz, C_6D_6) δ: 5.46 (s, 3H), 2.68 (br m, 6H), 1.32 (br m, 6H), 1.29 (s, 9H). ^{13}C NMR (90 MHz, C_6D_6) δ: 173.47 (s), 161.89 (q, $^2J_{CF} = 29$ Hz), 120.92 (q, $^1J_{CF} = 269$ Hz), 98.77 (d), 52.68 (t), 46.72 (t), 21.96 (q). ^{19}F NMR (338 MHz, C_6D_6) δ: −74.76.

*Yttrium and ytterbium 1,3,5-tris(3,5-dioxo-6,6,6-trifluorohexan-1-yl)benzene (**19**)*: Prepared as described in the general procedure above using 76 mg (0.13 mmol) of ligand **8** in 5 mL of dry THF and 75 mg (0.13 mmol) of $Y(N(SiMe_3)_2)_3$ in 5 mL of dry THF to afford a pale yellow powder in quantitative yield. ^1H NMR (250 MHz, C_6D_6) δ: 6.41 (s, 3H), 5.83 (s, 3H), 3.75 (br t, THF), 2.43 (t, 6H, J = 7 Hz), 2.06 (t, 6H, J = 7 Hz), 1.27 (m, THF). ^{13}C NMR (63 MHz, C_6D_6) δ: 201.14 (s), 169.95 (q, $^2J_{CF} = 32$ Hz), 138.55 (s), 128.02 (q), 127.87 (d), 97.35 (d), 69.17 (t, THF), 42.21 (t), 33.20 (t), 25.42 (t, THF). ^{19}F NMR (338 MHz, C_6D_6) δ: −75.66 (s). HRMS, calcd. for $C_{24}H_{18}F_9O_6Y$: 662.0018; found: 662.0000. Similar quantities and yields for the ytterbium complex.

Catalytic test run

Into an oven-dried Schlenk tube equipped with a stirbar was loaded 30.5 mg (2 mol%) of the catalyst metal complex. Then 5.0 mL of freshly distilled ethyl vinyl ether was added via syringe into the tightly capped vessel. The reaction mixture was stirred while adding 0.2 mL of distilled *trans*-crotonaldehyde via a syringe. Every 4 h an aliquot of solution was acquired, diluted in 0.5 mL of diethyl ether, and injected (0.5 μL) into a Fisons E980 gas chromotagraph to detect product formation. A 100 μL (1.2 mmol) dioxane standard can be used in the reaction mixture to better quantify results. However, dioxane slows the reaction rate somewhat as stated above. Upon reaction completion the mixture was quenched with 1 N aquous HCl and stirred for 30 min. Extraction of the organic layer with ether and removal of solvent from the combined organic fractions under reduced pressure gave a crude product that can be further purified (8*a*) by column chromatography using a 4:1 pentanes:ether eluant or by distillation (if crotonaldehyde is no longer present in crude product). NMR spectral data of the adduct were in accord with literature values (6).

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