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Reaction of $(Cp^*_2LnH)_2$ (Ln = Y, La) and $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ with Esters and Amides and Molecular Structure of $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$

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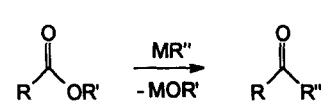
The activation of esters and amides by $(Cp^*_2LnH)_2$ [Ln = Y (1a), Ln = La (1b), Cp* = C_5Me] and $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (2) is described. Compounds 1a and 1b react with ethyl acetate to form Cp^*_2YOEt (3a) and Cp^*_2LaOEt (3b). With 1a and ethyl benzoate a 1:1 mixture of 3a and $Cp^*_2YOCH_2Ph$ (4a) is produced and the corresponding 1:1 mixture of 3b and $Cp^*_2LaOCH_2Ph$ (4b) is observed with 1b. Ethyl acrylate is polymerized rapidly by both 1a and 1b. The reaction of 1a with *N,N*-dimethylacetamide leads to a mixture of the carbonyl insertion product $Cp^*_2Y(OCH(NMe_2)Me)$ (5) and the aldol condensation product $Cp^*_2Y(OC(NMe_2)(Me)CH_2C(O)NMe_2)$ (6). Formation of the condensation product $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (7) occurred when 2 was reacted with ethyl acetate. The molecular structure of 7 was determined by X-ray diffraction: $a = 10.129(1)$ Å, $b = 10.650(1)$ Å, $c = 12.093(1)$ Å, $\alpha = 77.642(6)°$, $\beta = 79.402(7)$, $\gamma = 86.408(9)$, $V = 1252.2(2)$ Å^3, space group $P\bar{1}$, $Z = 1$. Anisotropic least-squares refinement based on 4871 reflections converged to $R_F = 0.034$ and $R_w = 0.041$ for 428 refined parameters. The more sterically hindered ester ethyl 2-methylpropanoate reacted with 2 to produce the enolate complex $Cp^*_2Y\{OC(2\text{-}C_6H_4CH_2NMe_2){=}CMe_2\}$ ($Me_2CHCOOEt$) (8). With *N,N*-dimethylacetamide 2 gives a clean aldol condensation to form 6.

Keywords: lanthanide catalysis; polymerization; activation; aldol condensation

INTRODUCTION

The recent interest in the use of organolanthanides for organic synthesis[1] has led to the discovery of some useful C–C bond formation reactions mediated by these complexes. For instance, aldol coupling of enolizable ketones could be induced by $Cp^*_2LnCH(SiMe_3)_2$ ($Cp^* = C_5Me_5$), as has been found by Heeres.[2] Samarium-based C–C bond forming reactions with aldehydes, ketones and acid chlorides have been reported by Kagan and co-workers and have a broad scope.[3] Recently, interesting work on stereoselective aldol condensations using lanthanide alkoxides has been published.[4]

In this study we focus on the reactions of $(Cp^*_2LnH)_2$ [Ln = Y (**1a**), La (**1b**)], and the intramolecularly stabilized aryl $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (**2**)[5] with esters and amides, since condensation of these compounds by yttrium or lanthanide complexes is to our knowledge unprecedented. The intramolecularly stabilized aryl complex was chosen because of the lower steric congestion at the yttrium center compared with that in $Cp^*_2YCH(SiMe_3)_2$.[6] Esters are especially interesting because of the possible addition–elimination sequence depicted in Eqn [1], which would lead to the alkylation of esters to produce ketones. Another possibility would be enolization of the ester leading to Claisen-type condensation with a second equivalent of ester. In addition, we are interested in the effect of the intramolecularly coordinated amine function of **2** on its reactivity.



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RESULTS AND DISCUSSION

Activation of esters and amides by $(Cp^*_2LnH)_2$ [Ln = Y (1a) and La (1b)]

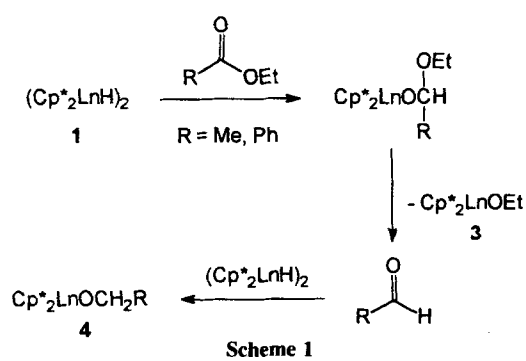
Both hydrides **1a** and **1b** reacted with ethyl acetate to form rapidly the alkoxide complexes Cp^*_2LnOEt (Ln = Y (**3a**) and La (**3b**)) through a reductive ester cleavage (Eqn [2]). Even at −80 °C no intermediates could be detected (^1H NMR). With ethyl benzoate an analogous ester cleavage was observed, resulting in a 1 : 1 mixture of alkoxides **3** and **4** (Eqn [3]). No metallation of the phenyl ring takes place, which is remarkable when compared with other functionalized arenes PhX (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, PPh_2=CH_2) which are metallated very easily in the *ortho* position by the same system.[7] It is clear that activation of the carbonyl group by nucleophilic attack of the hydride ligand is the dominant reaction taking place here.

$$(Cp^*_2LnH)_2 + MeCOOEt \longrightarrow 2\ Cp^*_2LnOEt \quad [2]$$
1 **3**

$$(Cp^*_2LnH)_2 + PhCOOEt \longrightarrow Cp^*_2LnOEt + Cp^*_2LnOCH_2Ph \quad [3]$$
1 **3** **4**

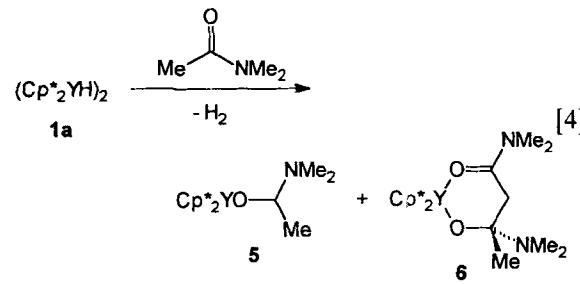
The first step in the ester reduction is most probably insertion of the carbonyl group in the Ln–H bond, as has been observed for **1b** with di-t-butyl ketone to form $Cp^*_2LaOCH(^tBu)_2$[2b] (Scheme 1). Elimination of the ethoxy group and formation of **3a** and aldehyde HC(O)R seems to be a plausible second step. The aldehyde formed can then be attacked by another molecule of **1** to form $Cp^*_2LnOCH_2R$.

To test whether activation of the carbonyl group is still the main reaction with α,β-unsaturated esters, **1a** and **1b** were allowed to react with ethyl acrylate. This resulted in fast polymerization of the acrylate, whereas the bulk of **1a** or **1b** remained intact. This indicates that only minor amounts of **1a** and **1b** are involved in the catalytic polymerization, which can be explained by slow initiation. The poly(ethyl acrylate) formed is apparently completely atactic, as is shown by the ^1H NMR spectrum, which shows two types of methylene and methine protons.[8] However, it is clear that alkoxide formation, which would lead to complete deactivation of the catalyst, is not taking place here. From this it can be concluded that insertion of C–C double bonds into Ln—H can in principle compete successfully with alkoxide elimination. Since polymerization of methyl methacrylate (MMA) has been investigated extensively[9] we did not look further into this aspect of organolanthanide chemistry.



Scheme 1

The —NR_2 groups of organic amides are poor leaving groups compared with alkoxy groups of esters. We therefore anticipated that reaction with *N*,*N*-dimethylacetamide would lead to the carbonyl insertion products of **1a** and **1b**. However the reaction was not clean owing to competitive α-H abstraction and aldol condensation of acetamide (Eqn [4]). This resulted in a mixture of carbonyl insertion product **5** (40%) and condensation product **6** (60%). No attempts were made to isolate the aldol-coupled product since the reaction of **2** with *N*,*N*-dimethylacetamide produced **6** in much better yield (*vide infra*).

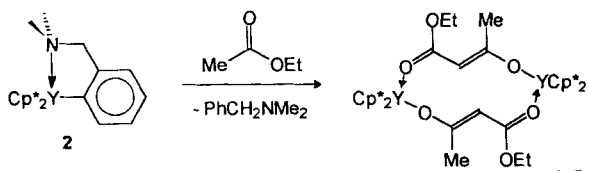


[4]

Activation of esters and amides by $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (2)

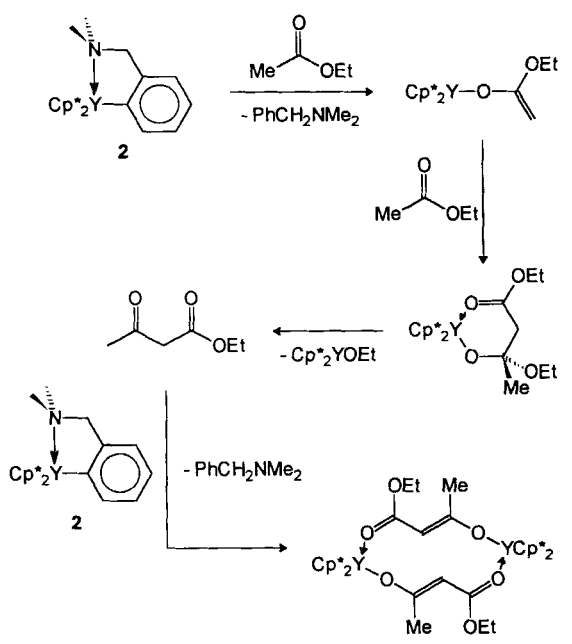
In contrast to the hydrides **1a** and **1b**, which react by nucleophilic attack on the carbonyl function of esters, the aryl **2** behaves like a base and abstracts an α-H of ethyl acetate which subsequently leads to $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (**7**) as the isolated product (Eqn [5]). Formation of this

compound can be explained as shown in Scheme 2. The enolate $Cp^*_2YOC(OEt)=CH_2$, which is formed by α-H abstraction from ethyl acetate, enters a condensation with another molecule of ethyl acetate, similarly to the mechanism proposed for aldol condensations with $Cp^*_2LnCH(SiMe_3)_2$.[2b] The condensation product then eliminates Cp^*_2YOEt, producing a β-keto ester and turning the overall process into a Claisen condensation. The final step is enolization of the β-keto ester by **2** to form **7**.



2 **7** [5]

Compound **7** could be isolated in good yield and was fully characterized. Also, the elimination product Cp^*_2YOEt could be detected in the mother liquor as the ethyl acetate adduct after isolation of **7**. The IR spectrum of **7** exhibits a band at 1568 cm^{-1} indicative of a severely reduced carbonyl bond order. Compared with β-keto esters for which $\nu_{C=O}$ occurs at 1650 cm^{-1},[10] this value is significantly shifted to lower frequency.



2 **7**

Scheme 2

This carbonyl shift can be explained by coordination to the Lewis acidic yttrium center, which causes reduction of the carbonyl double bond character. Also, the delocalized bonding within the OCMe=CHC(OEt)O causes significant reduction of the C=O bond order (*vide infra*). The low carbonyl stretching frequency compares well with those observed for tris(acetylacetonate) complexes $Ln(acac)_3(H_2O)_n$ (1600 cm^{-1}).[11]

The molecular structure of **7** was determined by X-ray diffraction and the resulting geometry is depicted in Fig. 1. For selected bond distances and angles, see Table 1. The molecule is a dimer consisting of two equivalent $Cp^*_2Y\{\mu\text{-}OCMe=CHC(OEt)O\}$ units. The arrangement of the Cp* ligands on yttrium with a Cp*–Y–Cp* angle of 138.6° is normal for bent yttrocene compounds.[12] The Y1–O3a distance is significantly longer than the terminal Y–OR distances in the alkoxides $Cp^*Y(OC_6H_3{}^tBu_2)_2$ [2.096(4) and 2.059(3) Å][13] and $[Cp^*Y(\mu\text{-}O^tBu)(O^tBu)]_2$ [1.995(10) and 2.018(9) Å].[14] However, the almost linear angle Y1–O3a–C23, which is due to π-overlap of the oxygen lone pairs with metal orbitals, was also observed for one of the aryloxy ligands in $Cp^*Y(OC_6H_3{}^tBu_2)_2$. In fact the Y1–O3a distance is intermediate between the Y–O distances in these alkoxides and that of the enolate $[(C_5H_4Me)_2Y(\mu\text{-}OCH_2=CH_2)]_2$ (2.275(3) and 2.290(2) Å).[15]

The Y1–O1 distance is significantly longer than Y1–O3a whereas the O1–C21 distance is slightly shorter than O3a–C23. This can be interpreted as a carbonyl function interacting coordinatively with yttrium. The fact that Y1, O1, C21, C22, C23 and O3 lie almost within the same plane, as follows from the torsion angles O3a–Y1–O1–C21, C22–C21–O1–Y1, O1–C21–C22–C23 and C21–C22–C23–O3a, shows that there is significant π-overlap between these atoms resulting in delocalized bonding. This is supported by the distances O1–C21, C21–C22, C22–C23, O3–C23 which all indicate significant double bond character (bonding distances for pure double and single bonds: C—C = 1.54 Å, C=C = 1.34 Å, C—O = 1.43 Å, C=O = 1.20 Å).[16] The delocalized bonding within the μ-OCMe=CHC(OEt)O ligands could also explain the elongation of the Y–O3a distance relative to the Y–O distances of $Cp^*Y(OC_6H_3{}^tBu_2)_2$ and $[Cp^*Y(\mu\text{-}O^tBu)(O^tBu)]_2$.

By using a more sterically hindered ester, ethyl 2-methylpropanoate, we tried to isolate

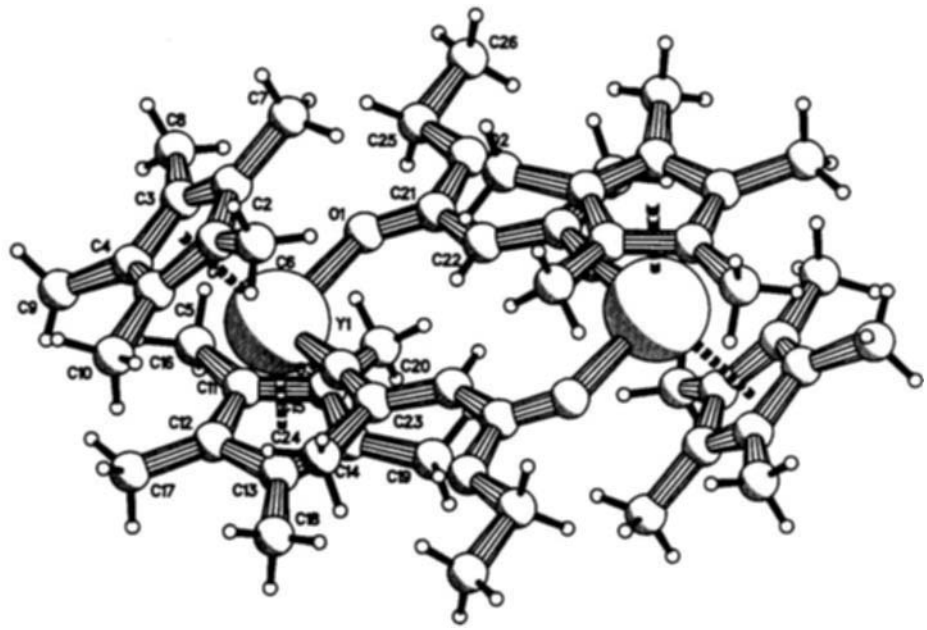
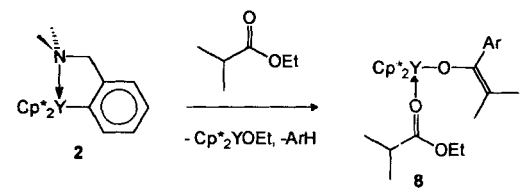


Figure 1 PLUTO drawing of $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (**7**).

the anticipated enolate intermediate. This ester has still one acidic α-H proton but, due to the methyl groups in the α-position, nucleophilic attack of the enolate on a second equivalent of ethyl 2-methylpropanoate would be sterically highly unfavorable. However, we did not find the expected enolate complex $Cp^*_2Y(O{-}C(OEt){=}CMe_2)$. Instead the product obtained was $Cp^*_2Y\{OC(2\text{-}C_6H_4CH_2NMe_2){=}CMe_2\}$ ($Me_2CHCOOEt$) (**8**) (Eqn [6]), which could be fully characterized by standard techniques.



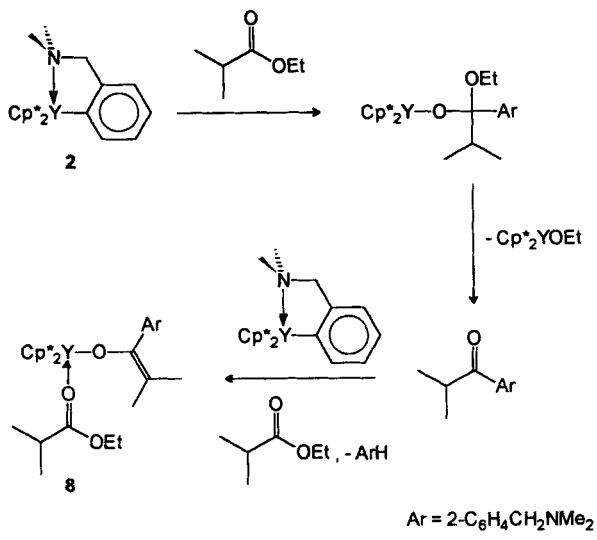
[6]

Ar = 2-$C_6H_4CH_2NMe_2$

Table 1 Selected distances (Å) and angles (°) for $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (**7**)[a]

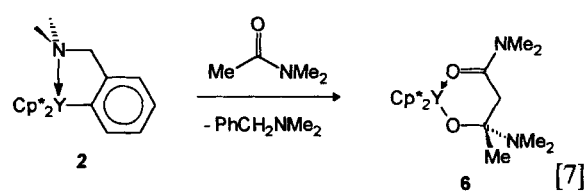
Distances			
Y1–O1	2.292 (2)	O3a–C23	1.281 (4)
Y1–O3a	2.179(2)	C21–C22	1.406(4)
O1–C21	1.260(3)	C22–C23	1.385 (3)
O2–C21	1.341 (4)	C23–C24	1.513 (4)
O2–C25	1.439 (4)	C25–C26	1.509 (5)
Angles			
O1–Y1–O3a	103.30 (7)	O2–C21–C22	117.9 (2)
Y1–O1–C21	137.8 (2)	C21–C22–C23	129.3 (3)
C21–O2–C25	118.2 (2)	O3a–C23–C22	119.8 (3)
C23–O3a–Y1a	174.59 (18)	O3a–C23–C24	116.8 (2)
O1–C21–O2	119.3 (3)	C22–C23–C24	123.4 (3)
O1–C21–C22	122.8 (3)	O2–C25–C26	106.0 (3)
Ct1–Y1–Ct2[b]	138.6		
O3a–Y1–O1–C21	6.7 (3)	O1–C21–C22–C23	176.7 (3)
C22–C21–O1–Y1	−3.6 (5)	C21–C22–C23–O3a	177.9 (3)

[a] label 'a' indicates symmetry operation: $-x, -y, 2-z$. [b] Ct1 = C1 – C5; Ct2 = C11 – C15.



Scheme 3

The presence of the benzyldimethylamine function in **8** suggests that the first step is insertion of the carbonyl function of the ester in the Y–aryl bond of **2** (Scheme 3). Next, the ethoxy group can be eliminated to form Cp^*_2YOEt and $Me_2CHC(O)C_6H_4CH_2NMe_2$. This is supported by the presence of Cp^*_2YOEt in the reaction mixture (^1H NMR). The ketone produced can then be converted into the enolate by another equivalent of **2** and the final product is formed by complexation of one molecule of ester. This reaction shows that by using a sterically more hindered ester, we have indeed prevented aldol condensation, but apparently also, the enolization of the ester to $Cp^*_2YOC(OEt)=CMe_2$ is more difficult. Instead, insertion of the carbonyl group of the ester into the Y–aryl bond of **2** is taking place. Although the C–C coupling reaction is now blocked, the OEt elimination, stimulated by the electrophilicity of yttrium, is still possible, yielding the observed product **8**.



[7]

With *N*,*N*-dimethylacetamide, regular aldol condensation was observed to form $Cp^*_2Y[OC(Me)(NMe_2)CH_2C(O)NMe_2]$ (**6**) (Eqn [7]). In contrast to the reaction with **1a**, the carbonyl addition product was not formed, which indicates that **2** is less nucleophilic and behaves like a base. As stated before, the $—NMe_2$ function is a poor leaving group, which prevents NMe_2 elimination and formation of the β-keto amide. Apparently enolization with another equivalent of **2** is more difficult since formation of the enolate is not taking place here.

CONCLUDING REMARKS

In this study we have seen that organoyttrium complexes can function as versatile synthetic tools in organic chemistry. The C–C bond forming aldol and Claisen condensations could offer opportunities for the development of catalysts for these reactions. However, much work needs to be done to reach this goal. In particular the stereochemistry with α-substituted carbonyls needs to be controlled to make these reactions useful in organic synthesis. Therefore, the development of complexes which induce diastereoselective and enantioselective C–C-forming condensations remains to be worked out. In this study we have shown that organoyttrium compounds could serve as promising candidates for transformations of this type.

EXPERIMENTAL

General considerations

General procedures, techniques and instrumentation have been described elsewhere.[7] Compounds **1a**,[6] **1b**,[17] $Li(2\text{-}C_6H_4CH_2NMe_2)$[5a] and $(Cp^*_2YCl)_2$[18] were prepared as described. Reagents ethyl acetate, ethyl benzoate, ethyl acrylate, *N*,*N*-dimethylacetamide and ethyl 2-methylpropanoate were distilled and stored over molecular sieves (4 Å). Solvents were distilled from Na/K and degassed prior to use.

Reactions of $(Cp^*_2LnH)_2$ [Ln = Y(1a), La (1b)] with ethyl acetate

Ethyl acetate (1.4 µl, 0.015 mmol) was added to a solution of 11 mg (0.015 mmol) **1a** in 0.5 ml of cyclohexane-d_{12}. ^1H NMR spectroscopy after 5 min at room temperature showed the quantitative formation of **3a**. For ^1H NMR data of **3a**, see Ref. 7(b). A similar procedure was used for reaction of **1b** with 0.5 equivalent of ethyl acetate

per La. Quantitative formation of **3b** was observed within several minutes at room temperature.

^{1}H NMR (300 MHz, benzene-d_6): δ 3.87 (broad, s, $lw_{1/2}$ = 20 Hz, 2H, $LaOCH_2$), 2.07 (s, 30H, C_5Me_5), 1.24 (t, $^3J_{HH}$ = 7.12 Hz, 3H, OCH_2CH_3).

Reactions of $(Cp^*_2LnH)_2$ [Ln = Y (1a), La (1b)] with ethyl benzoate

Similarly to the reaction of **1a** with ethyl acetate, 1 equivalent of ethyl benzoate per Y was added to a solution of **1a** in cyclohexane-d_{12}. ^{1}H NMR showed the quantitative formation of a 1:1:1 mixture of **3a**, **4a** and ethyl benzoate.

^{1}H NMR for **4a** (200 MHz, cyclohexane-d_{12}): δ 7.60 (d, $^3J_{HH}$ = 7.0 Hz, 2H, *ortho*-H), 7.34 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *meta*-H), 5.36 (s, 2H, OCH_2) 2.07 (s, 30H, C_5Me_5); *para*-H not found due to overlap with signals of unreacted ester. In a similar procedure for **1b**, using 1 equivalent of ethyl benzoate per La, quantitative formation of a 1:1:1 molar mixture of **3b**, **4b** and ethyl benzoate was observed within 5 min at room temperature. ^{1}H NMR for **4b** (200 MHz, benzene-d_6): δ 7.55 (d, $^3J_{HH}$ = 6.8 Hz, 2H, *ortho*-H), 7.16 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *meta*-H), 5.32 (s, 2H, OCH_2), 2.12 (s, 30H, C_5Me_5); *para*-H not found due to overlap with signals of unreacted ester.

Reaction of 1a with ethyl acrylate

To a solution of 0.025 g (0.035 mmol) of **1a** in 20 ml of cyclohexane was added 1.40 mmol of ethyl acrylate. The reaction mixture was stirred for 2 h at room temperature after which the reaction was quenched with 1 ml of methanol. After the mixture had been filtered and volatiles had been removed, a sticky substance remained.

^{1}H NMR (200 MHz, chloroform-d_1): δ 4.11 (q, $^3J_{HH}$ = 6.8 Hz, OCH_2CH_3), 2.30 (broad s, CH—CH_2—CH), 1.95 (broad s, CH_2—CH—CH_2), 1.65 (broad s, CH—CH_2—CH), 1.52 (broad s, CH_2—CH), 1.25 (t, $^3J_{HH}$ = 6.8 Hz, OCH_2CH_3), relative integrated intensities 4:2:1:2:1:6 respectively.

Reaction of 1a with *N,N*-Dimethylacetamide

To a stirred solution of 0.20 g (0.28 mmol) of **1a** in 30 ml of pentane was added 104 µl (1.12 mmol), *N,N*-dimethylacetamide. Gas evolution was observed. After 5 min at room temperature, stirring was stopped and the mixture was left to crystallize at room temperature. Yield: 0.236 g. ^{1}H and ^{13}C NMR showed that this material consisted of **5** (0.23 mmol) and **6** (0.34 mmol).

^{1}H NMR for **5** (200 MHz, benzene-d_6): δ 5.01 (q, $^3J_{HH}$ = 5.6 Hz, 1H, OC*H*(Me), 2.35 (s, 6H, NMe_2), 2.14 (s, 30H, C_5Me_5), 1.26 (d, $^3J_{HH}$ = 5.6 Hz, 3H, OCH*Me*). ^{13}C NMR for **5** (75.4 MHz, benzene-d_6): δ 114.97 (s, C_5Me_5), 87.61 (dd, $^1J_{CH}$ = 144 Hz, $^2J_{CY}$ = 5 Hz, YOCH), 39.17 (t, $^1J_{CH}$ = 134 Hz, NMe_2), 18.08 (q, $^1J_{CH}$ = 125 Hz, OCH*Me*), 11.68 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5). For NMR data of **6**, see synthesis of this compound from ethyl acetate and **2**.

$Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (2)

A suspension of 15.9 g (20 mmol) of $(Cp^*_2YCl)_2$ and 5.68 (40 mmol) of Li-2-$C_6H_4CH_2NMe_2$ in 50 ml of toluene was stirred at room temperature for 15 h. Volatiles were removed in vacuum and the remaining solid was stripped three times with pentane. Extraction with pentane and crystallization at −80 °C afforded 9.82 g (20 mmol, 50%) of **2** as yellow crystals. NMR data were identical to those reported before.[7]

$[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (7)

To a stirred solution of 1.13 g (2.29 mmol) of **2** in 20 ml of benzene was added 0.45 ml (4.6 mmol) of ethyl acetate. The mixture was heated to 50 °C for 3 h. Cooling to room temperature gave white crystals which were washed with benzene. Yield: 0.44 g, (0.45 mmol, 39%).

IR: ν 1730 (m), 1568 (s), 1537 (m), 1396 (sh), 1323 (m), 1271 (s), 1067 (m), 1020 (m) cm^{-1}. ^{1}H NMR (300 MHz, benzene-d_6): δ 5.37 (s, 1H, C=CH), 4.16 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.46 [s, 3H, $C(O)CH_3$], 2.01 (s, 30H, C_5Me_5), 1.10 (t, $^3J_{HH}$ = 7.3 Hz, 3H, OCH_2CH_3). ^{13}C NMR (75.4 MHz, benzene-d_6): δ 190.08 (d, $^2J_{CY}$ = 5 Hz, Y–O–C), 174.01 (d, $^2J_{CY}$ = 2 Hz, Y—O = C), 116.42 (s, C_5Me_5), 91.26 (d, $^1J_{CH}$ = 154 Hz, C=CH), 61.14 (t, $^1J_{CH}$ = 145 Hz, OCH_2), 28.23 (q, $^1J_{CH}$ = 127 Hz, C(O)*Me*), 14.40 (q, $^1J_{CH}$ = 127 Hz, OCH_2CH_3), 11.06 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5).

Analysis: calcd for $C_{26}H_{39}O_3Y$: C, 63.93; H, 8.05; Y, 18.20. Found: C, 63.80; H, 8.29; Y, 18.43%.

The mother liquor was evaporated to dryness and the residue was identified as $Cp^*_2YOEt(MeCOOEt)$ and traces of **7** by ^1H NMR.

^1H NMR (300 MHz, benzene-d_6): δ 4.19 (q, $^3J_{HH}=6.8$ Hz, 2H, $YOCH_2$), 3.97 (q, $^3J_{HH}=7.3$ Hz, $C(O)OCH_2$), 2.04 (s, 30H, C_5Me_5), 1.97 [s, 3H, C(O)Me], 1.32 (t, $^3J_{HH}=6.8$ Hz, 3H, $YOCH_2CH_3$), 0.88 (t, $^3J_{HH}=7.3$ Hz, 3H, OCH_2CH_3). Crystal data for **7**: $[C_{26}H_{39}O_3Y]_2$, $M=977.00$, triclinic with $a=10.129(1)$ Å, $b=10.650(1)$ Å, $c=12.093(1)$ Å, $\alpha=77.642(6)°$, $\beta=79.402(7)°$, $\gamma=86.408(9)°$, $V=1252.2(2)$ Å^3, space group $P\bar{1}$, $Z=1$, μ(Mo Kα) = 23.6 cm^{-1}. Anisotropic least-squares refinement based on 4871 reflections converged to $R_F=0.034$ and $R_w=0.041$ for 428 refined parameters.

$Cp^*_2Y\{OC(2\text{-}C_6H_4CH_2NMe_2)=CMe_2\}(Me_2CHCOOEt)$ (8)

To a stirred solution of 0.42 g (0.85 mmol) of **2** in 10 ml of toluene was added 250 µl (1.87 mmol) of ethyl 2-methylpropanoate. The reaction mixture was heated at 100 °C for three days. Volatiles were evaporated in vacuum and the residue was washed with pentane. Crystallization at −80 °C afforded 0.13 g (0.19 mmol, 22%) of white crystals.

IR: ν: 3056 (w), 2780 (m), 2723 (w), 1663 (s), 1642 (s), 1591 (w), 1568 (w), 1536 (w), 1404 (m), 1308 (s), 1292 (s), 1265 (w), 1213 (m), 1196 (m), 1175 (s), 1094 (s), 1068 (w), 1028 (s), 949 (w), 895 (w), 858 (m), 777 (s), 638 (m), 567 (w), 532 (w), 422 (w) cm^{-1}. ^1H NMR (300 MHz, benzene-d_6): δ 7.83 (d, $^3J_{HH}=7.6$ Hz, 1H, aryl H), 7.46 (d, $^3J_{HH}=6.8$ Hz, 1H, aryl H), 7.10 (m, 2H, aryl H), 3.79 (m, 4H, overlapping OCH_2 and NCH_2 signals), 2.29 (s, 6H, NMe_2), 2.03 (s, 30H, C_5Me_5), 1.94 (s, 3H, Me), 1.54 (s, 3H, Me), 0.71 (m, 9H, overlapping signals of OCH_2CH_3 and $CHMe_2$); $CHMe_2$ signal not found, presumably due to overlap with the C_5Me_5 signal. ^{13}C NMR (75.4 MHz, benzene-d_6): δ 184.76 (s, C=O), 151.40 (Y—OC), 143.82 (s, aryl C), 137.95 (s, aryl C), 130.2 (d, $^1J_{CH}=149$ Hz, aryl CH), 127.75 (aryl C, overlapping with solvent signal), 126.17 (d, $^1J_{CH}=147$ Hz, aryl CH), 116.28 (s, C_5Me_5), 97.25 (s, $=CMe_2$), 62.95 (t, $^1J_{CH}=148$ Hz, OCH_2), 61.44 (t, $^1J_{CH}=132$ Hz, NCH_2), 46.05 (q, $^1J_{CH}=132$ Hz, NMe_2), 35.31 (d, $^1J_{CH}=136$ Hz, $CHMe_2$), 20.17 (q, $^1J_{CH}=124$ Hz, Me), 19.86 (q, $^1J_{CH}=124$ Hz, Me), 19.42 (q, $^1J_{CH}=128$ Hz, $CHMe_2$), 13.62 (q, $^1J_{CH}=128$ Hz, Me), 11.68 (q, $^1J_{CH}=125$ Hz, C_5Me_5); one aryl CH not found due to overlap with solvent signal.

Analysis: calcd for $C_{39}H_{60}O_3NY$: C, 68.91; H, 8.90; Y, 13.08. Found: C, 68.11; H, 8.85; Y, 13.74%.

$Cp^*_2Y(OC(Me)(NMe_2)CH_2C(O)NMe_2)$ (6)

To a stirred solution of 1.33 g (2.69 mmol) of **2** in 10 ml of benzene was added 0.50 ml (5.2 mmol) of *N,N*-dimethylacetamide. The reaction mixture was stirred for 15 h at 50 °C and volatiles were removed in vacuum. The residue was washed with pentane and crystallization from toluene at −80 °C yielded 0.59 g (1.13 mmol, 42%) of white crystals.

IR: ν 1606 (s), 1587 (s), 1410 (m), 1325 (m), 1264 (w), 1224 (m), 1215 (m), 1018 (s), 985 (m), 594 (m) cm^{-1}. ^1H NMR (200 MHz, benzene-d_6): δ 3.21 (s, 2H, $C(O)CH_2$), 2.77 (s, 6H, NMe_2), 2.45 (s, 3H, Me), 2.17 (s, 30H, C_5Me_5), 1.82 (s, 3H, NMe), 1.80 (s, 3H, NMe). ^{13}C NMR (75.4 MHz, benzene-d_6): δ 167.50 (s, C=O), 115.96 (s, C_5Me_5), 60.99 (t, $^1J_{CH}=155$ Hz, $C(O)CH_2$), 40.44 (q, $^1J_{CH}=134$ Hz, NMe_2), 37.46 (q, $^1J_{CH}=139$ Hz, NMe), 35.98 (q, $^1J_{CH}=140$ Hz, NMe), 21.90 (q, $^1J_{CH}=130$ Hz, Me), 11.53 (q, $^1J_{CH}=125$ Hz, C_5Me_5); Y–O–C carbon not found.

Analysis: calcd for $C_{28}H_{47}O_2N_2Y$: C, 63.14; H, 8.89; N, 5.26; Y, 16.69. Found: C, 63.47; H, 8.99; N, 5.44; Y, 17.13%.

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Note X-ray supplementary crystallographic details are available from the authors.

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