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Studies on organolanthanide complexes

XXXVII *. Reaction of dicyclopentadienylyttrium chloride with acyl chlorides in tetrahydrofuran. Acylative cleavage of the Cp–Y π-bond and tetrahydrofuran ring

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Abstract

Dicyclopentadienylyttrium chloride reacts with aromatic and aliphatic acid chlorides in tetrahydrofuran at room temperature, resulting in cleavage of the Cp–Y π-bond to produce 1,5-diacylcyclopentadienes, and the acylative ring-opening of tetrahydrofuran. A possible reaction mechanism is proposed.

Introduction

Cyclopentadienyl is considered as an excellent stabilizing ligand for organolanthanide complexes, as in *d*-block organometallic compounds. In fact, most of the known stable organolanthanide complexes have one or more cyclopentadienyl ligands. Cp_2LnR (Cp = cyclopentadienyl, Ln = lanthanide metals including yttrium) type compounds are often used to study the reaction of the Ln–C σ-bond, such as hydrogenolysis [1], C–H bond activation [2], insertion of alkenes [3] and carbon monoxide [4], on the assumption that the Cp–Ln π-bond is stable and intact. Kagan and co-workers [5] even used Cp_2SmCH_2Ar to study the reaction of Sm–C σ-bond with benzyl bromides, aldehydes, ketones and acid chlorides. In all of these reactions, there was no indication of any reactivity attributable to the Cp–Ln π-bond.

However, it has been known for a long time that cyclopentadienyllanthanide complexes are sensitive to moisture and can easily be protolysed with active hydrogen-containing molecules such as H_2O, ROH, HCN, etc. to release cyclopentadiene [6]. This indicates that the Cp–Ln π-bond can indeed be broken. In a

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previous paper [7], we reported for the first time that a Cp–Ln π-bond (Ln = Y) can be cleaved in the presence of an electrophilic reagent, e.g. an aldehyde or a ketone. This result prompted us to propose that other electrophilic reagents might also cleave the Cp–Ln π-bond. On the other hand, we think that studies on the reactivity of Cp–Ln π-bond are of significance for the following three reasons (i) to exploit the degree of the stability of Cp–Ln π-bond; (ii) to provide some understanding of the nature of this bond; and (iii) to provide a possible new method for preparing some five membered ring-containing molecules. So as a further study we have been investigating the reaction of dicyclopentadienylyttrium chloride with acyl chlorides, which are more active electrophilic reagents than aldehydes and ketones. We found that acyl chlorides can cleave the Cp–Y π-bond more easily than aldehydes or ketones, and the products are also different. Diacylcyclopentadienes were formed in the present reaction in addition to the hydrocarbon fulvenes we reported previously [7]. Moreover, it is interesting that the solvent tetrahydrofuran (THF) also participates in the present reaction.

Results and discussion

Reaction of dicyclopentadienylyttrium chloride with acyl chlorides (**1**) in THF at room temperature affords two different products at the same time. They are 1,5-diacylcyclopentadienes (**2**) and 4-chlorobutyl esters (**3**). The reaction is shown in Scheme 1.

The ratio of **2** to **3** varies with the acyl chlorides used. Moreover, it takes longer for the aromatic acyl chlorides to react than the aliphatic ones. These results are summarized in Table 1.

1,5-Diacylcyclopentadienes exist only in the enol form, so it is perhaps more appropriate to use the names 1-aroyl-6-hydroxy-6-arylfulvenes [8] and 1-acyl-6-hydroxy-6-alkylfulvenes. The hydroxyl proton has a chemical shift at 17–18, indicating that the molecule contains an intramolecular hydrogen bond. ^{1}H NMR and ^{13}C NMR indicate that the molecule has a symmetric structure with the equivalence of the two R group at ambient temperature. We have also recorded the ^{1}H NMR spectrum of **2a** at $-50\,^{\circ}C$, which shows little difference from that at room temperature. The real structure might be expressed as Scheme 2. But for the sake of simplicity and uniformity, we continue to use the name 1,5-diacylcyclopentadienes in the present paper.

The possible mechanism to form 1,5-diacylcyclopentadienes (**2**) may be expressed as Scheme 3. Coordination to Y atom and electrophilic attack to one cyclopentadienyl ring of Cp_2YCl by acyl chlorides would afford chloroalkoxylyttrium complexes (**4**), which might eliminate $CpYCl_2$ (**5**) to produce monoacylcyclopentadienes (**6**) [9]. **6** are more acidic than cyclopentadiene and would protolyse cyclopentadienylyttrium dichloride (**5**) to form complexes (**7**), which would react with a

$$\underset{(\mathbf{1})}{Cp_2YCl + RCOCl} \xrightarrow{THF,\ r.t.} \mathbf{2} + \underset{(\mathbf{3})}{RCO_2CH_2CH_2CH_2CH_2Cl}$$

(R = C_6H_5 (**a**); $p-ClC_6H_4$ (**b**); o-BrC_6H_4 (**c**); $C_6H_5CH{=}CH$ (**d**); $C_6H_5CH_2$ (**e**); CH_3 (**f**); C_2H_5 (**g**))

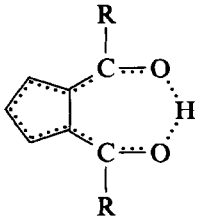
Scheme 1.

Table 1

Reaction of Cp_2YCl with acyl chlorides in THF [a]

Acyl chloride	Reaction time (h)	Yield [b] (%)	
		2	3
1a	11	62	30
1b	25	78	10
1c	15	15	63
1d	21	16	64
1e	7	32	40
1f	7	34	52
1g	7	47	45

[a] Molar ratio: $Cp_2YCl/1 = 1:1$; Temperature: r.t. [b] Isolated yields based on the starting acyl chlorides 1.



(2)

Scheme 2

second molecule of acyl chlorides to produce diacylcyclopentadienes (2). That the two acyl groups are at ortho-position probably results from the chelate coordination of the two oxygen atoms of the acyl groups to the Y atom in the intermediate **8**.

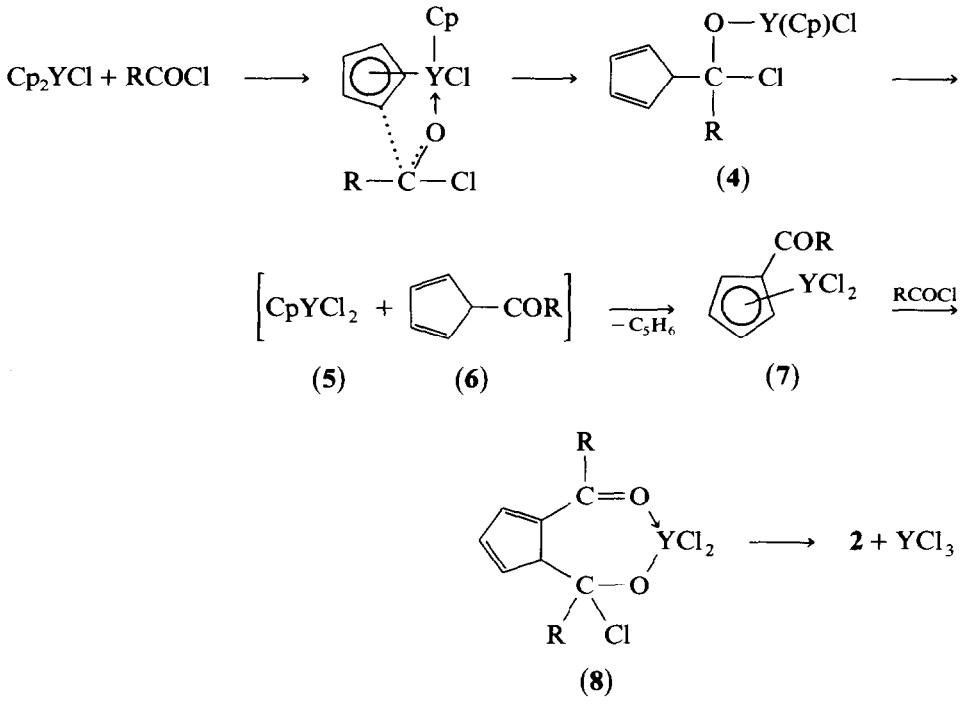
How does the acylative ring-opening of THF occur? It is not very clear. But it is obvious that this ring-opening reaction results from the interaction of a Y complex with THF or with acyl chlorides, and such a Y complex can be considered as a catalyst for the ring-opening reaction. The classical cleavage reaction of ethers by an acid chloride in the presence of a Lewis acid [10a] suggests to us that YCl_3 produced *in situ* would have acted as the catalyst. In order to confirm this, we have investigated the reaction of acyl chlorides with THF in the presence of anhydrous

Table 2

Reaction of acyl chlorides with THF catalyzed by YCl_3 [a]

Acyl chloride	Temperature (°C)	Reaction time (h)	Yield [b] of 3 (%)
1a	65	18	99
1b	65	49	85
1c	65	10	89
1f	r.t.	24	86
1g	r.t.	24	82

[a] 10% mole equivalent of YCl_3 (relative to acyl chlorides) was used, THF itself was the solvent. [b] Isolated yields based on acyl chlorides.



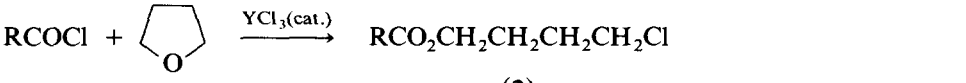
Scheme 3

YCl_3, showing that YCl_3 is a good catalyst for the acylative ring-opening of THF. The reaction is shown as Scheme 4, and the results are listed in Table 2.

The THF acylative ring-opening reaction catalyzed by YCl_3 may follow the general mechanism of cleavage reaction of ethers with acid chlorides catalyzed by a Lewis acid [10b].

It is noteworthy that in the reaction of Scheme 4, when R represents aryl groups, the reaction proceeded very slowly at room temperature and a higher temperature (see Table 2) was needed. But we have known that in the reaction of Scheme 1, room temperature is enough even in the cases of aroyl chlorides. These results suggest that YCl_3 produced *in situ* is more active and that Cp_2YCl is a good catalyst precursor for the acylative cleavage of THF ring and the present reaction differs from the ring opening observed in the reaction of $(C_5Me_5)_2Yb(THF)_2$ with Me_3SiCl which provides $(C_5Me_5)(CH_2)_4OSiMe_3$ [9].

In conclusion, we have shown that in the presence of acyl chlorides, Cp–Y π-bond can easily be cleaved to produce 1,5-diacylcyclopentadienes, and Cp_2YCl



(3)

(R = C_6H_5 (**a**); *p*-ClC_6H_4 (**b**); *o*-BrC_6H_4 (**c**); CH_3 (**f**); C_2H_5 (**g**))

Scheme 4

can be considered as a good catalyst precursor for the acylative ring-opening of THF.

Experimental

Melting points were determined on a hot plate melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR440 spectrometer. ^1H NMR spectra were recorded on a Varian EM360A (60 MHz) instrument in CCl_4 or on a Varian XL-200 (200 MHz) instrument in CD_3COCD_3 with $SiMe_4$ as internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-90Q (90 MHz) instrument. Mass spectra were determined on a Finnigan 4021 spectrometer (low resolution) and on a Finnigan-MAT 8430 spectrometer (high resolution).

Anhydrous yttrium chloride was prepared from the hydrate by a published method [11]. Dicyclopentadienylyttrium chloride was prepared according to Maginn's procedure [12]. Because it is sensitive to air and moisture, Schlenk techniques were used. Tetrahydrofuran was refluxed and distilled over blue sodium benzophenone under argon immediately before use.

Reaction of dicyclopentadienylyttrium chloride with acyl chlorides in tetrahydrofuran

General method. To a solution of dicyclopentadienylyttrium chloride (about 1 mmol) in THF (6.5 ml) the acyl chloride (about 1 mmol) was introduced from a syringe under argon. The mixture was stirred at room temperature until reaction had ceased (TLC). The solvent was evaporated under reduced pressure and the residue was chromatographed on a column of silica gel with petroleum ether–ethyl acetate (100 : 5) as solvent. Thus the 1,5-diacylcyclopentadiene and the 4-chlorobutyl ester were separated and collected. The 1,5-diacylcyclopentadienes obtained were an orange yellow solid or an oil. The 4-chlorobutyl esters were colourless oils and became light yellow in some cases probably because of contamination by the corresponding 1,5-diacylcyclopentadienes.

1,5-Dibenzoylcyclopentadiene (**2a**) [8]. Orange yellow solid, m.p. 100–102°C (from hexane); δ(H) 6.43 (t, 1H); 7.23 (d, 2H); 7.50–7.92 (m, 10H); 17.77 (s, 1H); δ(C) (CD_3COCD_3): 125.5, 126.4, 130.4, 131.7, 133.7, 139.6, 143.8, 187.0; MS *m/z* 274 (M^+, 66.36%), 197 (8.85), 169 (11.73), 119 (14.71), 105 (100) Found: C, 83.33; H, 5.26. $C_{19}H_{14}O_2$ calc.: C, 83.19; H, 5.14%).

4-Chlorobutyl benzoate (**3a**) [13]. Oil, δ(H) 1.94 (m, 4H); 3.52 (m, 2H); 4.26 (m, 2H); 7.33–7.48 (m, 3H); 7.94–8.03 (m, 2H); IR ν_{max} (film) 1720 cm^{-1}; MS *m/z* 215 (6.59%), 213 (M^+, 17.36), 177 (20.93), 123 (59.68), 106 (100), 91 (36.18).

1,5-Di-*p*-chlorobenzoylcyclopentadiene (**2b**) [8]. Orange yellow solid, m.p. 173–175°C (from hexane–benzene); δ(H) 6.56 (t, 1H, *J* 3.9 Hz); 7.30 (d, 2H, *J* 3.9 Hz); 7.62 (d, 4H, *J* 8.6 Hz); 7.82 (d, 4H, *J* 8.6 Hz); 17.30 (s, 1H); MS *m/z* 342 (M^+, 52.23%), 230 (24.33), 139 (100), 141 (26.47), 119 (26.29) Found: C, 66.14; H, 3.07 $C_{19}H_{12}Cl_2O_2$ calc.: C, 66.50; H, 3.50%).

4-Chlorobutyl *p*-chlorobenzoate (**3b**). Oil, δ(H) 1.88 (m, 4H); 3.55 (m, 2H); 4.29 (m, 2H); 7.36 (d, 2H); 7.93 (d, 2H); IR ν_{max} (film) 1725 cm^{-1}; MS *m/z* 246 (M^+, 7.56%), 211 (24.57), 158 (32.60) 156 (81.16), 141 (36.47), 139 (100), 91 (36.18).

1,5-Di-*o*-bromobenzoylcyclopentadiene (**2c**). Orange yellow solid, δH 6.45 (t, 1H); 7.00 (d, 2H); 7.42–7.83 (m, 8H); 18.43 (s, 1H); MS *m/z* 430 (M^+, 17.67%),

353 (94.23), 351 (76.36), 185 (100), 183 (88.80) (Found: 52.55; H, 2.44 $C_{19}H_{12}Br_2O_2$ calc.: C, 52.81; H, 2.80%).

4-Chlorobutyl *o*-bromobenzoate (**3c**). Oil, δ(H) 1.80–2.00 (m, 4H); 3.57–3.72 (m, 2H); 4.26–4.43 (m, 2H); 7.17–7.80 (m, 4H); IR ν_{max} (film) 1730 cm^{-1}; MS *m/z* 290 (M^+, 4.2%), 257 (10.3), 255 (10.2), 202 (68.4), 200 (68.6), 185 (97.5), 183 (100), 157 (25.9), 155 (26.0), 91 (8.4) (HRMS Found: 289.9756 $C_{11}H_{12}BrClO_2$ 289.9710).

1,5-Dicinnamoylcyclopentadiene (**2d**). Red solid, m.p. 169–170 °C; δ(H) 6.23 (t, 1H); 7.13–7.80 (m, 16H); 18.45 (s, 1H); MS *m/z* 326 (m^+, 54.41%); 233 (5.40), 195 (29.73), 131 (100), 119 (17.26), 103 (39.03) (HRMS Found: 326.1310. $C_{23}H_{18}O_2$ calc.: 326.1307).

4-Chlorobutyl cinnamate (**3d**). Oil, δ(H) 1.77–1.97 (m, 4H); 3.45–3.68 (m, 2H); 4.10–4.29 (m, 2H); 6.35 (d, 1H); 7.28–7.53 (m, 5H); 7.66 (d, 1H); IR ν_{max} 1715 and 1640 cm^{-1}; MS *m/z* 240 (5.01%), 238 (M^+, 15.09), 203 (21.08), 148 (68.69), 131 (100), 103 (50.54), 91 (14.95).

1,5-Diphenylacetylcyclopentadiene (**2e**). Orange yellow oil, δ(H) 4.00 (s, 4H); 6.32 (t, 1H); 7.20 (s, 10H);7.38 (d, 2H); 18.45 (s, 1H); MS *m/z* 302 (M^+, 17.57%), 274 (73.14), 211 (43.15), 197 (15.84), 169 (22.01), 119 (39.04), 105 (100) HRMS Found: 302.1291. $C_{21}H_{18}O_2$ calc.: 302.1307).

4-Chlorobutyl phenylacetate (**3e**). Oil, δ(H) 1.60 (m, 4H); 3.30 (m, 2H); 3.40 (s, 2H); 3.95 (m, 2H); 7.15 (s, 5H); IR ν_{max} 1745 cm^{-1}; MS *m/z* 226 (M^+, 9.02%), 136 (10.33), 91 (100) (HRMS) Found: 226.0785. $C_{12}H_{15}ClO_2$ calc.: 226.0760).

1,5-Diacetylcyclopentadiene (**2f**) [14]. Orange yellow oil, δ(H) 2.52 (s, 6H); 6.31 (t, 1H); 7.25 (d, 2H); 17.28 (s, 1H); MS *m/z* 150 (M^+, 77.74%), 135 (27.04), 117 (12.25), 43 (100) (HRMS Found: 150.0649. $C_9H_{10}O_2$ calc.: 150.0681).

4-Chlorobutyl acetate (**3f**) [13]. Oil, δ(H) 1.80 (m, 4H); 2.00 (s, 3H); 3.53 (m, 2H); 4.04 (m, 2H); IR ν_{max} 1740 $cm^{-}N^{1}$; MS *m/z* 153 (4.21%), 151 (M^+, 11.94), 115 (5.65), 91 (23.41), and 44 (100).

1,5-Dipropionylcyclopentadiene (**2g**). Orange yellow oil, δ(H) 1.30 (t, 6H); 2.90 (q, 4H); 6.30 (t, 1H); 7.28 (d, 2H), 17.54 (s, 1H); MS *m/z* 180 ($M + 2$, 65.10%), 179 ($M + 1$, 64.85), 150 (100), 119 (16.93), 58 (93.22).

4-Chlorobutyl propionate (**3g**). Oil, δ(H) 1.11 (t, 3H), 1.65–1.90 (m, 4H), 2.26 (q, 2H), 3.53 (m, 2H) 4.05 (m, 2H); IR ν_{max} 1740 cm^{-1}; MS *m/z* 165 ($M + 1$, 3.78%), 129 (13.59), 107 (11.14).

Reaction of acyl chlorides with tetrahydronfuran catalyzed by YCl_3

General method. To a suspension of YCl_3 (0.1 mmol) in THF (1 ml) the acyl chloride (1 mmol) was added by a syringe. The mixture was stirred at room temperature or at 65 °C (see Table 2) until reaction had ceased (TLC). The solvent was evaporated under reduced presure and the residue was chromatographed on a short column of silica gel with petroleum ether–ethyl acetate (100 : 5) as solvent. The 4-chlorobutyl esters thus obtained were colourless oils. Their spectra were identical with those listed above.

Acknowledgements

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