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Lanthanoid-catalysed Tishchenko Reaction of Mono- or Di-aldehydes

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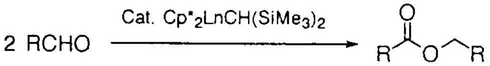
Abstract: Lanthanoid complexes are found to be very active catalysts for the Tishchenko reaction of aldehydes. In the presence of $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = Nd, La), esters are obtained from corresponding monoaldehydes in high yields. This method is applicable to dialdehydes. The reaction of *o*-phthalaldehyde proceeds intramolecularly to give phthalide quantitatively. Terephthalaldehyde and di(4-formylphenyl) ether are cleanly converted into the poly[*p*-(carboxymethylene)phenylene] (**II**) and poly[*p*-(carboxymethylene)(*p*-phenylenoxy)phenylene] (**III**), respectively. On the other hand, isophthalaldehyde polymerizes first and then the polymer is transformed into a macrocyclic lactone 1,5,11-trioxo-2,4;8,10;14,16-tribenzo-6,12,18-trioxacyclooctadecane (**I-a**) in high yields. The 18-membered macrocyclic structure of **I-a** was determined by the X-ray analysis. Stoichiometric reactions of the La complex with benzaldehyde indicated the intermediacy of alkoxo complexes in the catalysis.

Development of new catalysis with early transition metal complexes and its application to organic synthesis have been intensively and extensively investigated these days.[1] We have also reported a few reactions such as dehydrogenative condensation of hydrosilanes and hydrosilation of olefins and dienes catalysed by pentamethylcyclopentadienyl (Cp*) lanthanoid complexes.[2] During the study about the hydrosilation of carbonyl compounds catalysed by $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = La or Nd), we have found that these complexes serve as catalyst for the Tishchenko reaction of aldehydes (1).[3]



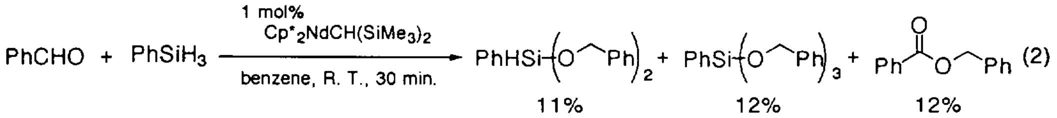
(1)

The Tishchenko reaction is well known as the method for preparation of esters from aldehydes and has been usually carried out using aluminium alkoxides or boron alkoxides.[4] However, there are only a few papers reported for the reaction catalysed by transition metals.[5] Studies on the Tishchenko reaction of dialdehydes are also rare, and only intramolecular versions have been reported.[5d, g, h] This paper deals with the reaction of mono- and dialdehydes catalysed by $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = La or Nd), inclusive of polymer synthesis.

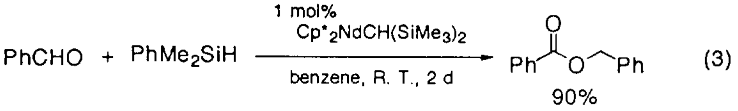
Results and Discussion

1. Dimerization of Monoaldehyde

During the investigation of the catalysis by lanthanoid metal comlexes such as $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = La or Nd), we tried hydrosilation of benzaldehyde. In the presence of a catalytic amount of $Cp^*{}_2NdCH(SiMe_3)_2$, di- and tribenzyloxysilanes were obtained in the reaction with phenylsilane. Unexpectedly however, benzyl benzoate, a Tishchenko-type dimer, was also formed in an unnegligible yield (2: yields were based on benzaldehyde charged).



In the reaction with dimethylphenylsilane, which was less active in the hydrosilation of olefins catalysed by lanthanoid complexes,[2b] hydrosilation adducts were not formed at all. Instead, benzyl benzoate was obtained as major product in a high yield and phenylsilane was quantitatively recovered (3), indicative of the ester formation having taken place without involvement of the hydrosilane in the catalysis. Indeed, an experiment under similar conditions without the hydrosilane also gave the dimer in a good yield (4).



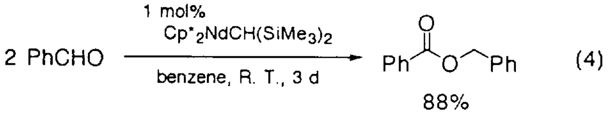
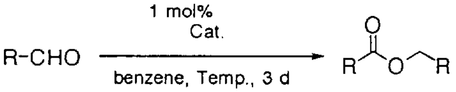
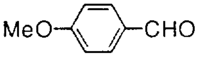
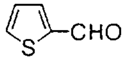
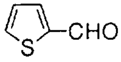
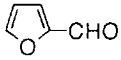
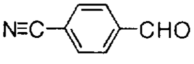
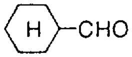
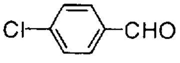
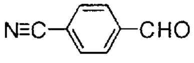
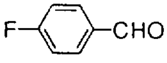
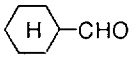
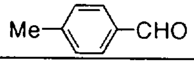


Table 1 shows the dimerization of various aldehydes to corresponding esters by the lanthanoid metal complexes. In general, $Cp^*_2LaCH(SiMe_3)_2$ was more active than the Nd complex (entries 1-4, 10 and 12). In

Table 1. Dimerization of Monoaldehydes by Lanthanoid-catalysts.



Entry	Aldehyde	Cat.	Temp. (°C)	Yield (%)	Entry	Aldehyde	Cat.	Temp. (°C)	Yield (%)
1	Ph-CHO	A	R. T.	88	9		B	60	95 [c]
2		A	60	31	10		B	60	quant
3	${}^tBu$-CHO	A	60	46	11		B	60	77
4	Ph-CHO	B	R. T.	94	12	${}^tBu$-CHO	B	60	quant
5		B	R. T.	96 [b]	13		B	R. T.	95
6		B	R. T.	89 [c]	14		C	R. T.	70 [b]
7		B	R. T.	95	15		C	60	84 [c]
8		B	60	88 [c]					

[a] A = $Cp^*_2NdCH(SiMe_3)_2$; B = $Cp^*_2LaCH(SiMe_3)_2$; C = $La(O^iPr)_3$; [b] 1 h; [c] 2 d.

the lanthanocene complex catalysed reactions, all of the *p*-substituted benzaldehydes gave the esters in high yields (entries 4-9). Recently, Ishii et al. have reported that benzaldehyde was reluctant to be converted to benzyl benzoate in the presence of Cp_2ZrH_2 complex.[5b] Accordingly we can conclude that the lanthanocene complexes are more active than the zirconocene complex. Dimerization of heteroaromatic aldehydes such as 2-thiophene-carboxaldehyde and furfural also proceeded smoothly (entries 10 and 11). The dimerization of furfural was reported to be difficult in the aluminium alkoxide- or tetracarbonylferrate(-II)-catalysed reaction.[4a, 6] In the latter case, the ester was obtained only when crown ethers were added to the reaction system.[5d] In our new method however, 2-furylmethyl 2-furancarboxylate was easily formed in a good yield.

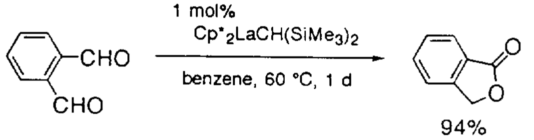
As for aliphatic aldehydes, only those having branching at the α-carbon such as pivalaldehyde and cyclohexanecarboxaldehyde gave the corresponding dimers in high yields (entries 12 and 13). The reaction of simple aldehydes such as heptanal and 3-phenylpropanal that did not have α-branching did not afford the dimers. GC-MS analyses of the reaction mixture suggested that aldol-type dehydrated trimers were the major products in the latter reaction.[7]

As anticipated through the mechanistic consideration (*vide infra*), the reaction could be promoted by commercial $La(OCHMe_2)_3$. However, its activity proved to be very sensitive to the structure of the starting aldehyde. Thus, 4-cyanobenzaldehyde smoothly dimerized at room tempelature (entry 14) and cyclohexanecarboxaldehyde required heating at 60 °C (entry 15). On the other hand, the dimerization reaction of benzaldehyde or 2-thiophenecarboxaldehyde did not proceed even at 60 °C. In general, $La(OCHMe_2)_3$ was less active than $Cp^*_2LaCH(SiMe_3)_2$ although the reason is ambiguous.

In the case of aromatic aldehydes, the nature of *p*-substituents very much influenced the reaction rate. In the presence of 1 mol% $Cp^*_2LaCH(SiMe_3)_2$, the reacivities of *p*-substituted benzaldehydes were compared based on the yields of the dimer obtained in 1 h at room temperature. The yield (*p*-substituent) increased as follows: 3% (MeO-) < 20% (Me-) < 43% (Cl-) < 96% (NC-). Thus, the reactivity of aldehydes is enhanced by electron attracting groups. This seems to suggest that the rate-determining step of this Tishchenko reaction is the nucleophilic addition of the lanthanoid complexes to the carbonyl group of aldehydes (*vide infra*). Yamashita et al. have also reported the same tendency in the Tishchenko reaction catalysed by tetracarbonylferrate(-II).[6]

2. Reaction of Dialdehyde

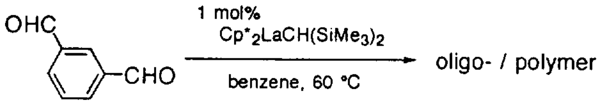
When *o*-phthalaldehyde was treated with the La complex (1 mol%) at 60 °C, the mixture immediately became dark red and then the colour turned gradually to yellow to result in the formation of a white precipitate in a few hours. After continued heating under the same conditions for 20 h, the crude solid obtained after evaporation of the solvent was purified by TLC, and phthalide was obtained in 94% yield (5). Intermolecular dimerization products were not observed by GC-MS analysis.



(5)

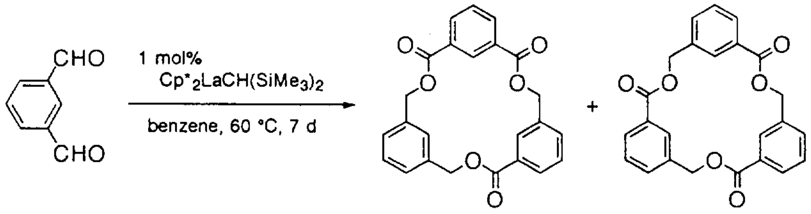
When the reaction of isophthalaldehyde was run under the same conditions, the starting material was completely consumed in 3 h to give a polymeric material. The time course of the reaction was monitored by GPC analysis (polystyrene standards) of the reaction mixture (Table 2). The distribution of the molecular weight was bimodal; the products at the 3 h reaction time were comprising of oligomers (*M*w = 300) and polymers (*M*w = 6300), the latter being the main product. When the reaction mixture was further heated, the Mw of the polymer increased to 18000 after 24 h, but the amount of the polymer decreased. Continued heating at 60 °C for 7 days resulted in a reversal of the major component; the oligomers that were the major products were isolated in 86% yield (6). This phenomenon suggests that the ester exchange reaction occurred by the La complex and that the polyester formed at first was being converted into the more thermodynamically stable oligoesters.

Table 2. Reaction of Isophthalaldehyde Catalysed by $Cp^*_2LaCH(SiMe_3)_2$.



Entry	Time	Oligomer : Polymer (*Mw* (*Mw*/*Mn*)) [a]
1	3 h	19 : 81 (6300 (2.7))
2	24 h	47 : 53 (18000 (4.0))
3	4 d	53 : 47 (17000 (4.6))
4	7 d	80 : 20 (18000 (3.3))

[a] Area ratio of GPC peaks. *Mw* and *Mw*/*Mn* based on polystylene standards are given for the polymer, exclusive of the oligomer fraction.



I-a **I-b**

86% (**I-a** : **I-b** = 96 : 4) (6)

The oligomers were separated into two isomers (**I-a** and **I-b**) by recycling preparative HPLC. Since aldehyde proton signals were not observed in ^1H NMR and the molecular weight (determined by HRMS) of the oligomers corresponded to the trimers of isophthalaldehyde, the structures of these products are likely to be cyclic triesters. The microstructure of the main isomer (**I-a**) appears irregular because three (1 : 1 : 1) methylene signals and three (1 : 1 : 1) carbonyl signals were observed in ^{13}C NMR. The structure of **I-a** was finally confirmed by X-ray analysis. ORTEP representation of **I-a** is shown in Figure 1, and selected bond distances, angles and atomic coordinates are listed in Table 3, 4 and 5. The ratio of these isomers were about 96 : 4, based on the integral ratio in ^1H NMR.

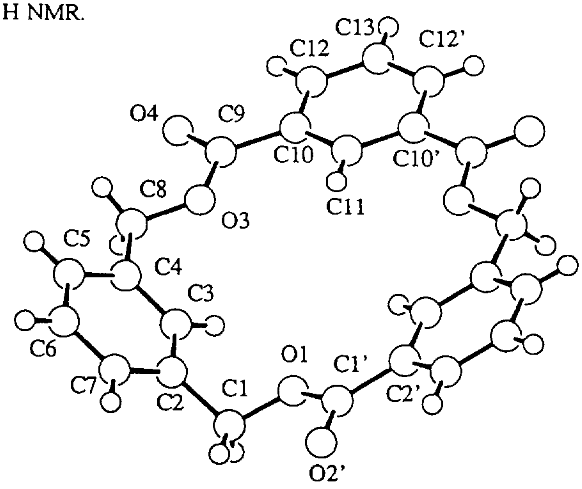


Figure 1. Molecular Structure of **I-a**.

Table 3. Selected Bond Lengths (Å) for I-a.

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.349(5)	O(2)	C(1)	1.235(8)
O(3)	C(8)	1.445(4)	O(3)	C(9)	1.344(4)
O(4)	C(9)	1.204(4)	C(1)	C(2)	1.480(6)
C(2)	C(3)	1.401(5)	C(2)	C(7)	1.370(6)
C(3)	C(4)	1.370(5)	C(4)	C(5)	1.372(6)
C(4)	C(8)	1.498(6)	C(5)	C(6)	1.363(6)
C(6)	C(7)	1.365(7)	C(9)	C(10)	1.477(5)
C(10)	C(11)	1.385(4)	C(10)	C(12)	1.389(5)
C(12)	C(13)	1.371(4)			

Table 4. Selected Bond Angles (°) for I-a.

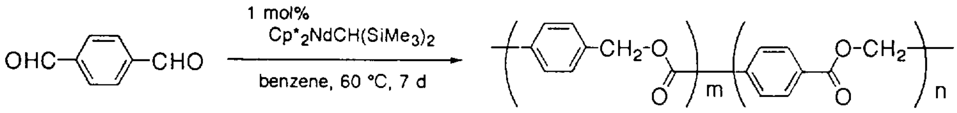
atom	atom	atom	angle	atom	atom	atom	angle
C(1)	O(1)	C(1')	115.8(4)	C(8)	O(3)	C(9)	115.1(3)
O(1)	C(1)	O(2)	114.9(5)	O(1)	C(1)	C(2)	112.9(4)
O(2)	C(1)	C(2)	124.1(5)	C(1)	C(2)	C(3)	121.7(4)
C(1)	C(2)	C(7)	119.5(4)	C(3)	C(2)	C(7)	118.8(4)
C(2)	C(3)	C(4)	120.5(3)	C(3)	C(4)	C(5)	119.1(3)
C(3)	C(4)	C(8)	122.5(3)	C(5)	C(4)	C(8)	118.3(3)
C(4)	C(5)	C(6)	120.8(4)	C(5)	C(6)	C(7)	120.3(4)
C(2)	C(7)	C(6)	120.5(4)	O(3)	C(8)	C(4)	110.1(3)
O(3)	C(9)	O(4)	121.6(3)	O(3)	C(9)	C(10)	113.8(3)
O(4)	C(9)	C(10)	124.5(4)	C(9)	C(10)	C(11)	123.2(4)
C(9)	C(10)	C(12)	117.3(3)	C(11)	C(10)	C(12)	119.6(3)
C(10)	C(11)	C(10')	119.8(5)	C(10)	C(12)	C(13)	120.6(4)
C(12)	C(13)	C(12')	119.8(5)				

Table 5. Selected Atomic Coordinates and B_{iso}/B_{eq} for I-a.

atom	x	y	z	B_{eq}	occ
O(1)	0.6367(3)	0.2500	0.5000	5.9(1)	0.5000
O(2)	0.4924(5)	0.2028(3)	0.514(2)	8.1(2)	0.5000
O(3)	0.9492(2)	0.1341(1)	0.4014(10)	4.62(6)	1.0000
O(4)	1.0935(2)	0.0820(1)	0.395(1)	6.36(8)	1.0000
C(1)	0.5840(3)	0.1962(2)	0.518(1)	8.3(2)	1.0000
C(2)	0.6372(3)	0.1406(2)	0.439(1)	5.30(10)	1.0000
C(3)	0.7414(3)	0.1351(2)	0.450(1)	5.0(1)	1.0000
C(4)	0.7887(3)	0.0831(2)	0.376(1)	4.36(8)	1.0000
C(5)	0.7328(3)	0.0365(2)	0.289(1)	5.7(1)	1.0000
C(6)	0.6314(4)	0.0415(2)	0.277(1)	7.0(1)	1.0000
C(7)	0.5838(3)	0.0929(2)	0.353(1)	5.8(1)	1.0000
C(8)	0.8994(3)	0.0738(2)	0.390(1)	4.95(9)	1.0000
C(9)	1.0495(3)	0.1314(2)	0.404(1)	4.52(9)	1.0000
C(10)	1.0981(3)	0.1935(2)	0.424(1)	4.04(8)	1.0000
C(11)	1.0470(4)	0.2500	0.407(1)	4.1(1)	0.5000
C(12)	1.2001(3)	0.1941(2)	0.462(1)	5.0(1)	1.0000
C(13)	1.2502(4)	0.2500	0.485(1)	5.4(1)	0.5000

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

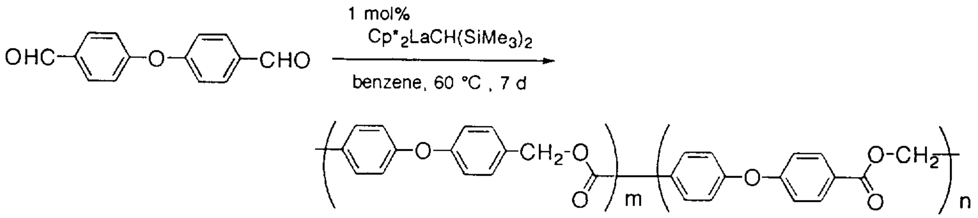
In the reaction of terephthalaldehyde, neither intramolecular reaction (like the *o*-isomer) nor oligomerization (like the *m*-isomer) is envisioned to occur easily. Indeed, the reaction at 60 °C using the Nd catalyst started forming a white polymer in a few minutes. After 2 days, a polyester (*M*w = 5000, *M*n = 2900) was quantitatively obtained (7). To enhance the molecular weight, the reaction was continued for 7 days under the same conditions. The resulting solid was filtlated and washed with hexane to give a quantitative amount of the polyester **II**. The molecular weight of the polymer was calculated to be *M*w = 7000 (*M*n = 3800), based on the polystyrene standard, indicative of a slight increase in the molecular weight. This polymer was soluble in chloroform but not in benzene, toluene and tetrahydrofuran. The number-average molecular weight (*M*n) was estimated at 4000 by the integral ratio of methylene and terminal aldehyde groups in ^{1}H NMR. This estimation agrees well with the *M*n determined by GPC with polystyrene standards. The microstructure of the polymer appears irregular because two (1 : 1) and three (1 : 1 : 1) methylene signals were observed in ^{1}H and ^{13}C NMR, respectively.



(7)

II
Mw = 7000 (Mw/Mn = 1.8)
97%

In the foregoing reaction of terephthalaldehyde, the molecular weight of the polymer was rather low. This is likely to be due, at least partly, to the low solubility of the polymer. In agreement with this consideration, the polymerization of di(4-formylphenyl) ether that has a flexible ether linkage gave a polymer of a higher molecular weight (*M*w = 15000, *M*n = 4000) after 1 day. Further heating for 7 days, followed by evapolation gave crude products, which were purified by reprecipitation (from benzene-hexane). The desired polymer **III** (*M*w = 19000, *M*n = 7600) was obtained in 86% yield (8).

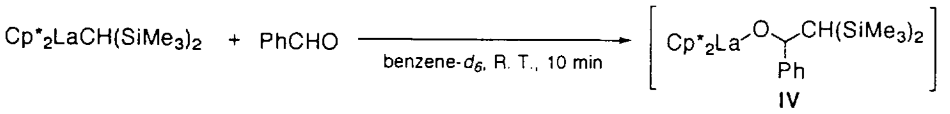


(8)

III
Mw = 19000 (Mw/Mn = 2.5)
86%

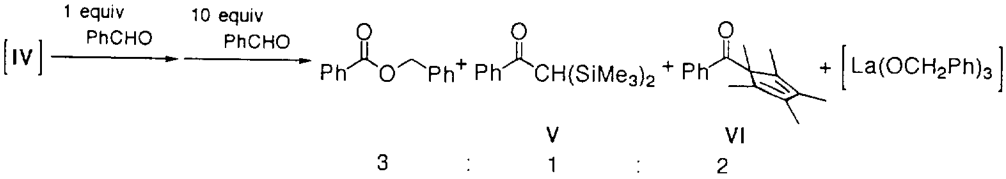
3. Reaction Mechanism

To obtain mechanistic information of the reaction, Cp*$_2$LaCH(SiMe$_3$)$_2$ was allowed to react with 1 equiv of benzaldehyde in C$_6$D$_6$ at room temperature. Upon mixing the two components, the colour of reaction mixture immediately turned to deep red from pale yellow and the aldehyde proton signal in ^{1}H NMR declined, possibly because of the coordination of a benzaldehyde molecule to the La complex. Then, the colour of this solution turned to light red over a few minutes, and new ^{1}H NMR signals emerged at δ 0.94 and δ 5.33 ppm. The signals are mutually coupled doublets (J = 10.8 Hz); the one at δ 0.94 is assigned to a methine connected to the two silicon atoms and the other at δ 5.33 is due to a benzylic proton. Accordingly the NMR data suggest the formation of an alkoxo complex **IV** (70% NMR yield after 5 minutes) (9).

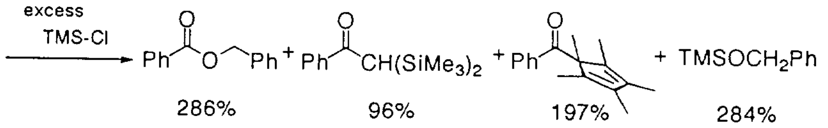


(9)

Addition of 1 equiv benzaldehyde to this solution developed a complicated products mixture that displayed ^1H NMR signals of several Cp* rings. Bis(trimethylsilyl)methyl phenyl ketone **V** and benzylic species (several signals at δ 4.5-5.5) were observed in the mixture. Addition of an excess amount (10 equiv) of benzaldehyde to the complicated mixture resulted in the formation of benzyl benzoate, ketone **V** and pentamethylcyclopentadienyl phenyl ketone **VI** (10). The **V** to **VI** molar ratio calculated by integration in ^1H NMR was 1 to 2. The result clearly indicates that all ligands in $Cp^*{}_2LaCH(SiMe_3)_2$ were converted into corresponding ketones in the reaction with benzaldehyde. In addition to these ketones, ^1H NMR of the reaction mixture displayed a broad signal centered at δ 6.9 ppm, indicative of $PhCH_2OLa$ species being generated. To confirm the generation, a large excess of chlorotrimethylsilane was added to the mixture. GC-MS and ^1H NMR analyses of the resulting mixture revealed that the species was converted to trimethylsilyl benzyl ether (11: yields were based on La metal). These results strongly suggest that the benzyloxo-La species is the possible active species in this Tishchenko reaction. Indeed, commercial $La(OCHMe_2)_3$ could catalyse the reaction of isophthalaldehyde at 60 °C and the lactone and the polymer were obtained in 78% combined yield after 24 h.

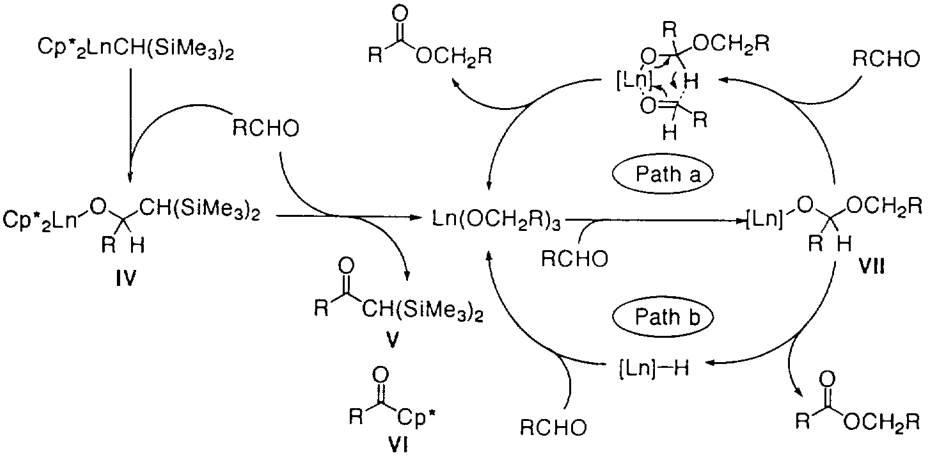


(10)



(11)

Based on the foregoing results, one can consider the mechanism of the catalysis as illustrated in Scheme 1. The first event in the catalytic cycle is envisioned to be aldehyde insertion into the Ln-OR bond to form hemiacetal-Ln species **VII**. There are two alternative pathways after **VII**. One (path a) involves coordination of



Scheme 1

an aldehyde to **VII**. Resulting species is likely to undergo hydride migration *via* a six-membered intermediate, followed by extrusion of a product molecule. In the other (path b), the reaction involves direct β-hydride elimination from the intermediate **VII** and the resulting Ln-H species may undergo insertion of an aldehyde. At the moment, we are unable to determine which is the real one (path a or b). Both mechanistic posibilities were proposed by Ishii et al. for the group 4 metallocene complex-catalysed reactions, although the Cp rings were considered to continue ligating to the central metal throughout the catalysis.[5b]

Experimental

General. All manipulations were carried out under argon or nitrogen using a dry box and/or the Schlenk tube technique. Solvents were dried and purified by the standard method and stored under nitrogen. ^{1}H, ^{13}C and ^{29}Si NMR spectra were measured on a Bruker ARX-300 spectrometer. Chemical shifts were referred to C_6D_5H (7.16 ppm) or $CHCl_3$ (7.25 ppm) for ^{1}H NMR, $CDCl_3$ (77.0 ppm) for ^{13}C NMR and tetramethylsilane (0 ppm) for ^{29}Si NMR. Infrared spectra were recorded on a JASCO FT/IR-5000 spectrometer. MS and HRMS analyses (EI, 70eV) were carried out using Shimadzu QP-5000 and JEOL DX-303 spectrometers. GC and GC-MS analyses were carried out using columns of OV-101 (3 m) and capillary CBP1-M25 (25 m), respectively. Molecular weights of polymers were measured using polystyrene standards on a GPC system equipped with a Shimadzu LC-6A high-pressure pump, Shodex KF-801, KF-802 and KF-80M columns and a GL Sciences Model 504R RI detector or an Waters 150-C GPC system with Shodex HT-803 and HT-804 columns. Products were purified by preparative TLC (Merk, silica gel $60GF_{254}$) or preparative HPLC using a model LC-908-G30 equipped with JAIGEL-1H and JAIGEL-2H columns (Japan Analytical Industry Co., Ltd.). $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Nd) were synthesized as reported.[8]

The Reaction of Benzaldehyde with Hydrosilanes. To a benzene solution (1 ml) containing $Cp^*_2NdCH(SiMe_3)_2$ (0.01 mmol) and octadecane (100 mg) in a Schlenk tube, benzaldehyde (1 mmol) and phenylsilane (1 mmol) were added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. Yields of alkoxysilanes and benzyl benzoate were determined by GC analysis of the resulting solution.

Authentic samples di(benzyloxy)phenylsilane and tri(benzyloxy)phenylsilane were synthesized from phenylsilane and benzyl alcohol by a method similar to that reported by Corriu et al.[9]

Di(benzyloxy)phenylsilane. IR (neat) 2168 cm^{-1} (SiH); ^{1}H NMR ($CDCl_3$) δ 5.18 (s, 4H, CH_2O), 5.48 (s, 1H, SiH), 7.52-7.70 (m, 13H, aromatic), 8.02 (dd, J = 1.7, 7.7 Hz, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 66.0 (CH_2O), 127.1, 127.8, 128.4, 128.7, 131.2, 132.6, 134.6, 140.2 (aromatic); ^{29}Si NMR ($CDCl_3$) δ -28.2; MS m/z (%) 320 (M^+, 0.2), 229 (63), 211 (24), 199 (50), 151 (24), 91 (100); HRMS calcd for $C_{20}H_{20}O_2Si$ 320.1227, found 320.1247.

Tri(benzyloxy)phenylsilane. ^{1}H NMR ($CDCl_3$) δ 4.96 (s, 6H, CH_2O), 7.30-7.55 (m, 18H, aromatic), 7.79-7.83 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 65.1 (CH_2O), 126.7, 127.3, 128.0, 128.3, 130.8, 135.0, 140.1 (aromatic); ^{29}Si NMR ($CDCl_3$) δ -56.6; MS m/z (%) 426 (M^+, 0.3), 335 (52), 257 (21), 229 (24), 199 (20), 167 (31), 151 (25), 91 (100), 65 (27). Anal. Calcd for $C_{27}H_{26}O_3Si$: C, 76.02; H, 6.14; Found: C, 76.09; H, 6.52.

General Procedure for the Dimerization of Monoaldehydes. To a benzene solution of $Cp^*_2LnCH(SiMe_3)_2$ (0.01 mmol) and octadecane (100 mg) in a Schlenk tube was added an aldehyde at room temperature, and the reaction mixture was stirred at room temperature for 3 d. Yields of esters were determined by GC analysis of the resulting solution. Products were purified by preparative TLC.

2-Thienylmethyl 2-thiophenecarboxylate. IR (neat) 1711 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.48 (s, 2H, CH_2O), 7.00 (dd, J = 3.3, 5.1 Hz, 1H, aromatic), 7.09 (dd, J = 3.8, 4.9 Hz, 1H, aromatic), 7.17 (dd, J = 0.9, 3.3 Hz, 1H, aromatic), 7.34 (dd, J = 0.9, 5.1 Hz, 1H, aromatic), 7.55 (dd, J = 1.3, 4.9 Hz, 1H, aromatic), 7.82 (dd, J = 1.3, 3.8 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 61.1 (CH_2O), 126.9, 127.0, 127.8, 128.4, 132.7, 133.4, 133.8, 137.8 (aromatic), 161.9 (C=O); MS m/z (%) 224 (M^+, 18), 111 (53), 97 (100). Anal. Calcd for $C_{10}H_8O_2S_2$: C, 53.55; H, 3.59. Found C, 53.41; H, 3.43.

4-Cyanobenzyl 4-cyanobenzoate.[10] IR (KBr) 1731 cm^{-1} (CO), 2230 cm^{-1} (NC); ^{1}H NMR ($CDCl_3$) δ 5.43 (s, 2H, CH_2O), 7.54 (d, J = 8.3 Hz, 2H, aromatic), 7.69 (d, J = 8.3 Hz, 2H, aromatic), 7.75 (d, J = 8.5 Hz, 2H, aromatic), 8.16 (d, J = 8.5 Hz, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 66.3 (CH_2O), 112.4, 116.9 (aromatic), 117.8, 118.4 (NC), 128.5, 130.3, 132.4, 132.6, 133.3, 140.6 (aromatic), 164.6 (C=O).

4-Chlorobenzyl 4-chlorobenzoate.[10] IR (KBr) 1717 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 2H, CH_2O), 7.37 (s, 4H, aromatic), 7.41 (d, J = 8.6 Hz, 2H, aromatic), 7.99 (d, J = 8.6 Hz, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 66.1 (CH_2O), 128.4, 128.8, 128.9, 129.7, 134.3, 139.7 (aromatic), 165.5 (C=O).

4-fluorobenzyl 4-fluorobenzoate. IR (neat) 1725 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 2H, CH_2O), 7.03-7.14 (m, 4H, aromatic), 7.39-7.45 (m, 2H, aromatic), 8.03-8.11 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 66.2 (CH_2O), 115.6 (d, J = 21.9 Hz, aromatic), 126.3 (d, J = 3.0 Hz, aromatic), 130.3 (d, J = 8.3 Hz, aromatic), 131.8 (d, J = 3.0 Hz, aromatic), 132.3 (d, J = 9.1 Hz, aromatic), 162.7 (d, J = 247.6 Hz, aromatic), 165.4 (C=O), 165.9 (d, J = 253.6 Hz, aromatic); MS m/z (%) 248 (M^+, 20), 123 (100), 109 (94), 108 (21), 95 (37). Anal. Calcd for $C_{14}H_{10}F_2O_2$: C,67.74; H, 4.06. Found C, 67.87; H, 4.12.

4-Methylbenzyl 4-methylbenzoate.[11] IR (neat) 1719 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 5.31 (s, 2H, CH_2O), 7.18-7.26 (m, 4H, aromatic), 7.32-7.36 (m, 2H, aromatic), 7.94-7.98 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH3), 21.7 (CH_3), 66.5 (CH_2O), 127.5, 128.3, 129.1, 129.3, 129.7, 133.2, 138.0, 143.7 (aromatic), 166.6 (C=O).

4-Methoxybenzyl 4-methoxybenzoate.[11] IR (neat) 1713 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 5.27 (s, 2H, CH_2O), 6.90 (d, J = 8.9 Hz, 2H, aromatic), 6.91 (d, J = 8.6 Hz, 2H, aromatic), 7.38 (d, J = 8.6 Hz, 2H, aromatic), 8.01 (d, J = 8.9 Hz, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 55.3 (CH3O), 55.4 (CH3O), 66.3 (CH_2O), 113.6, 114.0, 122.7, 128.4, 130.0, 131.7, 159.6, 163.4 (aromatic), 166.3 (C=O).

2-Furylmethyl 2-furancarboxylate.[11] IR (neat) 1725 cm^{-1} (CO); ^{1}H NMR (CDCl3) δ 5.27 (s, 2H, CH_2O), 6.36 (dd, 1H, J = 1.8, 3.3 Hz, aromatic), 6.46-6.49 (m, 2H, aromatic), 7.18 (dd, 1H, J = 0.6, 3.3 Hz, aromatic), 7.42 (dd, 1H, J = 0.7, 1.7 Hz, aromatic), 7.56 (dd, 1H, J = 0.7, 1.7 Hz, aromatic); ^{13}C NMR ($CDCl_3$) δ 58.3 (CH_2O), 110.6, 111.2, 111.9, 118.4, 143.4, 144.3, 146.5, 149.1 (aromatic), 158.3 (C=O).

General Procedure for the Reaction of Dialdehydes. To a benzene solution (1 ml) containing $Cp^*{}_2LaCH(SiMe_3)_2$ (0.01 mmol) in a Schlenk tube, isophthalaldehyde (1 mmol) was added at room temperature, and then the reaction mixture was warmed to 60 °C. The reaction mixture was stirred for 7 days and was evaporated *in vacuo*. A 3 mg portion of the resulting crude products was dissolved in 1 ml of THF, and the THF solution was subjected to GPC analysis to determine Mw of polyesters and oligoesters. The products **I-a** and **I-b** were separated by the recycling preparative HPLC.

1,5,11-Trioxo-2,4;8,10;14,16-tribenzo-6,12,18-trioxacyclooctadecane (I-a). IR (KBr) 1707, 1717 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.43- 5.46 (m, 6H, CH_2), 7.28-7.65 (m, 6H, aromatic), 7.91 (s, 1H, aromatic), 8.10-8.13 (m, 1H, aromatic), 8.32-8.38 (m, 2H, aromatic), 8.41 (s, 1H, aromatic), 8.79-8.80 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 66.01, 66.60, 66.86 (CH_2), 126.55, 127.14, 127.52, 127.82, 128.60, 128.70, 129.05, 129.64, 129.87, 130.30, 130.44, 130.77, 131.45, 134.76, 134.78, 136.13, 136.28, 136.65 (aromatic), 165.41, 165.51, 166.05 (C=O); HRMS calcd for $C_{24}H_{18}O_6$ 402.1098, found 402.1136. Anal. Calcd for $C_{24}H_{18}O_6$: C,71.64; H, 4.51. Found C, 71.89; H, 4.56.

X-ray Structure Determination of I-a. A colourless crystal with dimension 0.2 x 0.2 x 0.3 mm was used for data collection. The lattice parameters and intensity data were measured on a Rigaku AFC7R diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54178 Å). Crystal data: $C_{24}H_{18}O_6$, M = 402.40, orthorhombic, Abm2, a = 13.387(7), b = 21.228(4), c = 6.796(2) Å, U = 1932(1) Å^3, Z = 4, D = 1.384 g/cm^3, u = 8.29 cm^{-1}, F(000) = 840, T = 20 °C. A total of 856 unique reflections in the range of $2\theta \leq$ 120 ° was collected.

Systematic absences indicated the space group to be Abm2 or Cmma, of which the number of asymmetric units is 8 or 16, respectively. The former one was initially assumed, which would mean that the molecules adopt the C_s or C_2 molecular symmetry because of Z = 4. Such molecular structures, however, were not acceptable on the basis of the spectral data, so that we supposed the molecules to be disordered at the two locations related by a mirror plane or two-fold axis in the crystal. The latter space group seemed not to be available, because the molecules might exhibit higher molecular symmetries than in the former case. The structure was solved by direct methods[12] and refined by a full-matrix least-squares technique to R = 0.041, Rω = 0.061, and S = 1.64 for 711 observed reflections with I > 3σ(I). All calculations were performed using the teXsan[13] crystallographic software package.

Molecular structure is shown in Figure 2: the atoms of O(1), C(11) and C(13) lie on a mirror plane in the crystal. Atoms of one half of the molecule are represented by the corresponding primed numbers of the other half. However, the molecular structure containing an anhydride moiety is inconsistent with the spectral data. In addition, the geometry in the O(1), O(2) and C(1) part is unrealistic: the distance between O(2) and O(2') is too short (2.0 Å); the bonds around C(1) is not coplanar (sum of the bond angles = 352 °). Moreover, temperature factor of O(2) was abnormally large as compared with those of the other atoms. We thus supposed that two ester moieties oriented in relatively opposite directions, i. e. $-CH_2OC(=O)-$ and $-C(=O)OCH_2-$, would be superimposed. For this model, the carbonyl O atom might statistically be distributed at the two locations named O(2) and O(2') with an occupancy ratio of 0.5 : 0.5. This partially disordered structure was successfully refined to R = 0.041. The temperature factor of O(2) approached that of C(1) at the last stage of refinement.

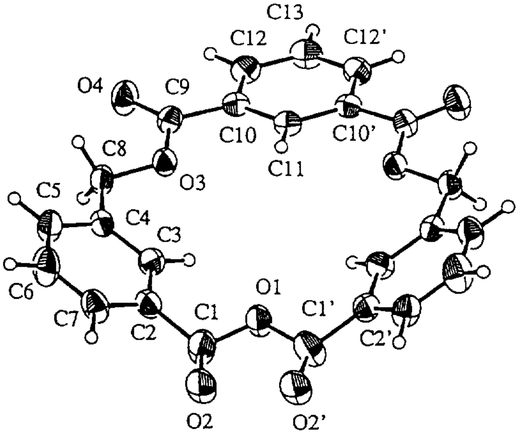


Figure 2. Molecular Structure of I-a by 30% Probability.

The optimized molecular structure of **I-a** is shown in Figure 1. In the crystal, the molecule occupies the location where O(1), C(11) and C(13) lie on a mirror as a symmetry element of the crystal, so that one molecule appears to be superposed with another one related by the mirror. Such imaginary molecular structure was solved in this work. The atoms of each molecule, excluding O(2), were paired so close that the positions of respective atoms could not be distinguished on Fourier maps.

1,7,13-Trioxo-2,4;8,10;14,16-tribenzo-6,12,18-trioxacyclooctadecane (I-b). IR (KBr) 1717 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 5.45 (s, 6H, CH_2), 7.46-7.56 (m, 6H, aromatic), 8.10 (d, J = 7.4 Hz, 3H, aromatic), 8.42 (s, 3H, aromatic); ^{13}C NMR ($CDCl_3$) δ 65.81 (CH_2), 127.27, 128.73, 129.87, 130.57, 131.75, 136.57 (aromatic), 165.93 (C=O); HRMS calcd for $C_{24}H_{18}O_6$ 402.1098, found 402.1111. Anal. Calcd for $C_{24}H_{18}O_6$: C, 71.64; H, 4.51. Found C, 71.58; H, 4.48.

Poly[*p*-(carboxymethylene)phenylene] (II). Mw = 7000 (Mw/Mn = 1.84); mp 130-140 °C; IR (KBr) 1718 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 5.38 and 5.42 (each s, 2H, CH_2), 7.25-8.12 (m, 4H, aromatic), 10.03 (0.07H, s, tarminal CHO); ^{13}C NMR ($CDCl_3$), δ 66.0, 66.4, 66.8 (CH_2), 127.4-141.4 (20 signals, aromatic), 165.4, 165.5, 165.8, 166.0 (C=O). Anal. Calcd for $(C_8H_6O_2)_n$: C, 71.64; H, 4.51. Found: C, 72.27; H, 4.63.

Poly[*p*-(carboxymethylene)(*p*-phenylenoxy)phenylene] (III). Mw = 19000 (Mw/Mn = 2.5); mp 113-125 °C; IR (KBr) 1715 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 5.33-5.38 (m, 2H, aromatic), 7.00-7.10 (m, 4.4H, aromatic), 7.37 (s, 1.6H, aromatic), 7.42-7.50 (m, 2H, aromatic), 8.05-8.13 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 66.0, 66.2, 66.3 (CH_2), 117.0-162.0 (17 signals, aromatic), 165.7, 165.9 (C=O). Anal. Calcd for $(C_{14}H_{10}O_3)_n$: C, 74.33; H, 4.45. Found C, 74.31; H, 4.93.

Complex (IV). ^1H NMR (C_6D_6) δ -0.16, 0.23 (18H, each s, CH_3Si), 0.94 (1H, d, J = 10.8 Hz, $CHSi_2$), 1.95 (30H, s, $C_5(CH_3)_5$), 5.33 (1H, J = 10.8 Hz, OCH), 7.00-7.50 (m, 5H, aromatic); ^{13}C NMR (C_6D_6) δ 1.6, 2.0 (CH_3Si), 11.0 ($C_5(\underline{C}H_3)_5$), 29.5 ($CHSi_2$), 78.9 (OCH), 119.3 ($\underline{C_5}(CH_3)_5$), 126.4, 127.5, 128.2, 150.7 (aromatic).

Bis(trimethylsilyl)methyl phenyl ketone (V). IR (KBr) 1644 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 0.14 (s, 18H, CH_3Si), 2.99 (s, 1H, $CHSi_2$), 6.95-7.23 (m, 3H, aromatic), 7.89-7.93 (m, 2H, aromatic); ^1H NMR ($CDCl_3$) δ 0.12 (s, 18H, CH_3Si), 3.09 (s, 1H, $CHSi_2$), 7.38-7.52 (m, 3H, aromatic), 7.85-7.88 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 0.4 (CH_3Si), 37.1 ($CHSi_2$), 128.0, 128.4, 132.0, 140.1 (aromatic), 202.2 (C=O); ^{29}Si NMR ($CDCl_3$) δ 3.0; MS m/z (%) 264 (M^+, 9), 147 (100), 73 (37). Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.14. Found C, 63.18; H, 8.96.

Pentamethylcyclopentadienyl phenyl ketone (VI). IR (KBr) 1665 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 1.45 (s, 3H, CH_3), 1.63 (s, 12H, CH_3), 6.96-7.08 (m, 3H, aromatic), 7.76-7.80 (m, 2H, aromatic); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H, CH_3), 1.68 (s, 6H, CH_3), 1.83 (s, 6H, CH_3), 7.18-7.26 (m, 2H, aromatic), 7.34-7.40 (m, 1H, aromatic), 7.50-7.54 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 10.6, 11.4, 19.2 (CH_3), 70.3 ($CH_3\underline{C}(C{=}O)$), 127.3, 127.9, 131.9 (aromatic), 138.1 ($\underline{C}CH_3$), 138.3 (aromatic), 140.0 ($\underline{C}CH_3$), 202.3 (C=O); MS: m/z (%) 240 (M^+, 8), 105 (100), 77 (23). Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found C, 84.72; H, 8.33.

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