Chiral Polysiloxane-Fixed Metal 1,3-Diketonates (Chirasil-Metals) as Catalytic Lewis Acids for a Hetero Diels-Alder Reaction – Inversion of Enantioselectivity Upon Catalyst–Polymer Binding

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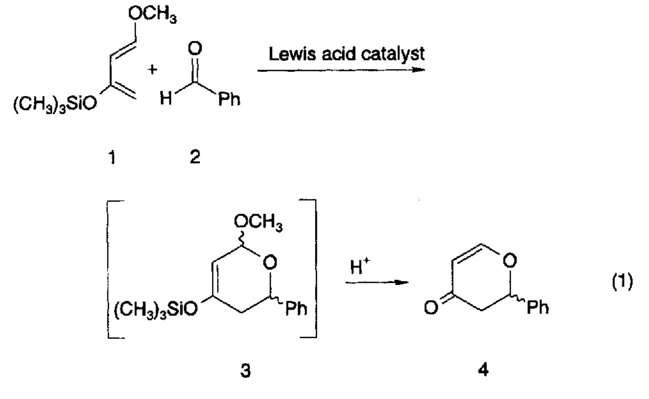
A dimethylpolysiloxane chain is covalently bound to the monomeric Lewis acid catalyst (1*R*)-(+)-oxovanadium(IV) bis[3-heptafluorobutanoylcamphorate] [(+)-**5a**] at the C-10 position of the camphor moiety yielding the novel chiral polymeric (1*S*)-(+)-oxovanadium(IV) bis[3-heptafluorobutanoylcamphorate]–dimethylpolysiloxane [(+)-**6a**][1]. The Lewis acid promoted hetero Diels-Alder reaction of *trans*-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (**1**) and benzaldehyde (**2**) is studied in the presence of the enantiomerically pure monomeric (**5a**, **5b**) and polymeric (**6a**, **6b**) catalysts. The monomeric and polymeric catalysts of identical chirality[1] invoke opposite enantioselectivities toward the formation of 2-phenyl-2,3-dihydro-4*H*-pyrone (**4**). This remarkable result is corroborated by numerous control experiments. Thus, it is demonstrated that the environment of the active site of the catalyst is changed when the complex is fixed to a polymeric chain. In contrast to **5** and **6**, the monomeric **12** and polymeric **13** europium(III) tris[3-heptafluorobutanoylcamphorates] of identical chirality invoke the same enantioselectivity toward the formation of **4**. The concept of polymer attachment is utilized to recover the catalyst from the reaction mixture by precipitation and to recycle it for subsequent catalytic runs.

The catalytic influence of chiral Lewis acids on enantioselective [2 + 4] cycloadditions between prochiral aldehydes and activated dienes (hetero Diels-Alder reaction) [cf. eq. (1)] has been investigated in the past[2].



(1)

Suitable Lewis acids are lanthanides[3], transition metals[4,6], and main-group elements[5] coordinated to chiral ligands such as 3-heptafluorobutanoylcamphorates[3,4], binaphthol[5], and phosphanes (CHIRAPHOS, DIOP)[6].

Apart from modest enantioselectivities, a drawback of the hetereo Diels-Alder reaction catalysed by metal-3-heptafluorobutanoylcamphorates such as **5a** or **12a** is the loss of the chiral auxiliary after work-up. We therefore tried to employ soluble polymeric catalysts which can be recovered from the reaction mixture by precipitation and can thus be recycled in subsequent catalytic runs as it has been previously demonstrated for soluble polymeric polystyrene–phosphane rhodium(I) catalysts by Schurig and Bayer[7] and in more recent work[8].

Fixing metal 3-heptafluorobutanoylcamphorates to a dimethylpolysiloxane chain via the C-10 position of the camphor moiety has been described earlier[9]. The resulting polymers, Chirasil-Metals, have been used as versatile chiral stationary phases for enantiomer separation by complexation gas chromatography[10]. Recently, the analogous dimethylpolysiloxane-linked europium(III) tris[3-heptafluorobutanoylcamphorate] (**13a**) has been synthesized[11]. Chirasil-Europium (**13a**) can be employed in four different modes, i.e., as chiral stationary phase for enantiomer separation by complexation gas chromatography, as polymeric paramagnetic chiral lanthanide shift reagent (which can be recovered by precipitation) in NMR spectroscopy[11], as coating material of quartz microbalance sensors for the detection of organic σ-donor molecules[12] and as chiral catalyst for the hetero Diels-Alder reaction[11]. This latter aspect will be addressed in the present contribution. The impetus of this work arose from the notion that the microenvironment of the apolar polymeric backbone may alter the self-association properties of the metal chelates and may change the chiral recognition pattern by either enhancing, lowering, or even inverting enantioselectivity. Quite unexpectedly, the latter case has been observed in the present work with Chirasil-Oxovanadium (**6a**) as polymeric catalyst.

In Scheme 1 the prepared monomeric and polymeric Chirasil-Metal catalysts including transition metals, lantha-

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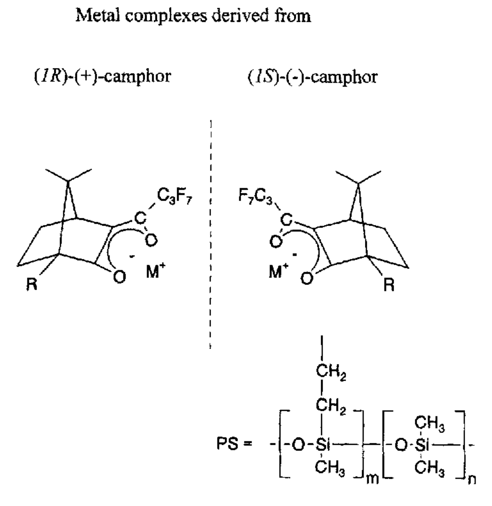
Scheme 1



	M	R		M	R
5a	$VO_{1/2}$	$-CH_3$	**5b**	$VO_{1/2}$	$-CH_3$
6a	$VO_{1/2}$	-PS	**6b**	$VO_{1/2}$	-PS
7	$VO_{1/2}$	$-CH=CH_2$			
8	$VO_{1/2}$	$-CH=CH-CH(CH_3)_2$			
9	$Ni_{1/2}$	$-CH_3$			
10	$Ni_{1/2}$	-PS			
11	$Pr_{1/3}$	$-CH_3$			
12a	$Eu_{1/3}$	$-CH_3$	**12b**	$Eu_{1/3}$	$-CH_3$
13a	$Eu_{1/3}$	-PS	**13b**	$Eu_{1/3}$	-PS
14	$UO_{2\ 1/2}$	$-CH_3$	**15**	$UO_{2\ 1/2}$	-PS

nides and an actinide are summarized. According to Table 1, the most versatile catalysts are derived from oxovanadium(IV) (**5**, **6**) and europium(III) (**12**, **13**) ions. Both have been obtained in either enantiomeric forms **a** and **b**. The hetero Diels-Alder reaction depicted in eq. (1) was selected to test the catalytic reaction in regard to the degree of enantioselectivity (*ee* of **4**) and of the sign of enantioselectivity [(+)/(−)-**4**] (cf. Table 1). The catalytic activity of the oxovanadium(IV) complexes **5**, **6** is significantly higher than that of the europium(III) complexes **12**, **13** (cf. Table 1).

Table 1. Enantioselective formation of (+)-**4** or (−)-**4** catalyzed by various metal complexes, reaction time 3 d, temperature −33°C, solvent 3 ml of *n*-hexane

Catalyst	Chemical yield of **4** [%]	(+)-4 [%]	(-)-4 [%]	ee [%]
5a	98.0	20.5	79.5	59.0
6a	77.9	70.3	29.8	40.5
9	34.5	44.2	55.8	11.6
10	< 5	38.0	62.0	24.0
11	10.3	30.8	69.2	38.4
12a	77.0	29.0	71.0	42.0
13a	6.4	28.5	71.5	43.0
14	97.4	44.4	55.6	11.2
15	66.1	54.7	45.3	9.4

In the course of the investigation an unexpected result was observed in the enantioselectivity generated by oxovanadium(IV) bis[3-heptafluorobutanoylcamphorate] employed either as monomeric (+)-**5a** or polymeric catalyst (+)-**6a** of identical chirality (cf. Figure 1 and Table 2[1]).

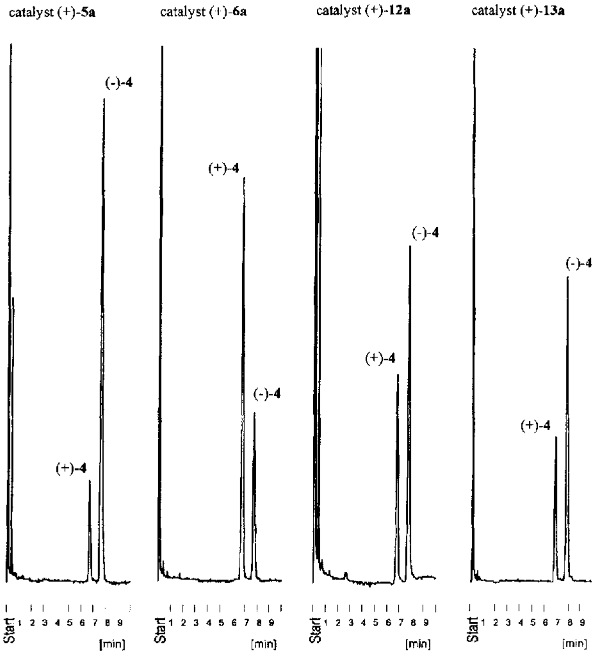
(+)-**5a** was reported by Togni to furnish (−)-**4** with an *ee* = 68% in a high yield[4]. In our hands, the *ee* amounted to only 59.0% (at −33°C) but an excess of the levorotatory (−)-**4** was indeed formed when dextrorotatory and monomeric (+)-**5a** was employed as catalyst. However, an excess of the dextrorotatory (+)-**4** was obtained with *ee* = 40.4% (at −33°C) when dextrorotatory and polymeric (+)-**6a** was used. Upon enantiomer analysis of **4**, this surprising result was unequivocally proved by the opposite sign of the optical rotation using polarimetry and by the reversal of the elution order using chiral gas chromatography (cf. Figure 1).

Table 2. Enantioselective formation of (+)-**4** or (−)-**4** catalyzed by various oxovanadium(IV) complexes at different temperatures, reaction time 3 d, solvent 3 ml of *n*-hexane

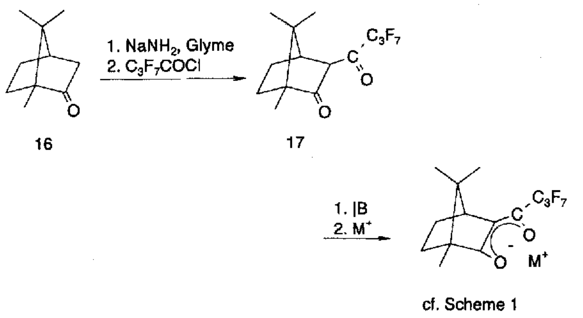
Catalyst	Temperature [°C]	Chemical yield of **4** [%]	(+)-4 [%]	(-)-4 [%]	ee [%]
5a	-33	98.0	20.5	79.5	59.0
5a	-78	98.4	15.5	84.5	69.0
6a	-33	89.0	70.2	29.8	40.4
6a	-78[a]	76.4	66.0	34.0	32.0
7	-33	66.6	34.2	65.8	31.6
7	-78	78.5	29.3	70.7	41.4
8	-33	50.8	33.3	66.6	33.3
5b	-33	91.7	77.1	22.9	54.2
6b	-33	72.6	32.0	68.0	36.0

[a] The catalyst precipitates in a gelatinous form.

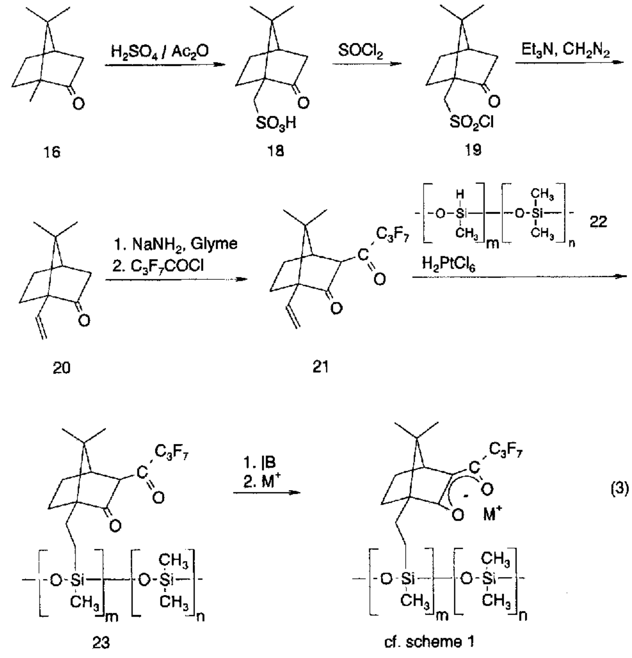
Figure 1. Enantiomer separation of **4** by GC (fused silica column coated with Chirasil-β-Dex[8b], 10 m × 0.25 mm i.d., film thickness 0.2 μm, carrier 1 bar He, temperature 120°C) obtained by the catalysis of various metal complexes, reaction time 3 d, −33°C, solvent 3 ml of *n*-hexane



The inversion of enantioselectivity when changing from the monomeric to the polymeric catalysts was further scrutinized by a number of control experiments. In order to exclude an accidental confusion in the catalytic specimens, it was first shown that no change in the sign of the optical rotation occurred during all reaction steps when (1*R*)-(+)-camphor was transformed to either monomeric **5a** or polymeric **6a** according to the reaction sequences of eq. (2) and eq. (3).



(2)



(3)

Before catalysis, the dextrorotatory sign of the optical rotation of the catalysts was checked. The results were then confirmed using the levorotatory catalysts with opposite chirality obtained from (1*S*)-(−)-camphor. In line with the previous results, (+)-**4** with *ee* = 54.2% (at −33°C) was formed when (−)-**5b** was employed while (−)-**4** was obtained with *ee* = 36.0% (at −33°C) when (−)-**6b** was used (cf. Table 2).

In contrast to the oxovanadium(IV) system, no change of enantioselectivity between the monomeric and polymeric europium(III) tris[3-heptafluorobutanoylcamphorates] **13a** was observed (cf. Figure 1, Table 3). Both dextrorotatory catalysts, (+)-**12a** and (+)-**13a**, gave rise to an enantiomeric excess of (−)-**4**.

Table 3. Enantioselective formation of (+)-**4** or (−)-**4** catalyzed by various monomeric and polymeric europium(III) complexes at different temperatures, reaction time 3 d, solvent 3 ml of *n*-hexane

Catalyst	Reaction temperature [°C]	Chemical yield of 4 [%]	(+)-4 [%]	(-)-4 [%]	ee [%]
12a	20	91.6	35.0	65.0	30.0
12a	-33	77.0	29.0	71.0	42.0
13a	20	95.5	30.2	69.8	39.6
13a	-33	6.4	28.5	71.5	43.0
12b	-33	73.0	70.0	30.0	40.0
13b	20	86.0	70.5	29.5	41.0

This observation offered another decisive control experiment. Both (+)-**6a** and (+)-**13a** were prepared from the same dextrorotatory polymeric ligand batch (+)-**23**. Both specimens were tested as catalysts and the inversion of enantioselectivity for **4** formed according to eq. (1) was again observed. Thus, with (+)-**6a** an excess of (+)-**4**, and with (+)-**13a** an excess of (−)-**4** was formed (cf. Table 4).

Table 4. Comparison of the catalytic properties of the polymeric europium(III) and oxovanadium(IV) complexes, prepared from the same batch of dextrorotatory ligand (+)-**23**, reaction time 3 d, temperature −33°C, solvent 3 ml of *n*-hexane

Catalyst	$[\alpha]_{22}^{D}$ of catalyst	Chemical yield of 4 [%]	(+)-4 [%]	(-)-4 [%]	ee [%]	Sign of optical rotation of 4
6a[a]	+15.7[b]	99.8	67.6	32.4	35.2	+
13a	+23.8[c]	6.4	28.5	71.5	43.0	-

[a] The used batch of **6a** differs from that mentioned in Table 2. − [b] c = 0.23 in CH_2Cl_2. − [c] c = 2.06 in CH_2Cl_2.

The observed inversion of enantioselectivity of **4** invoked by monomeric (+)-**5a** and polymeric (+)-**6a** may be the result of the increase of steric bulk at the C-10 position of the camphor moiety (cf. also ref.[13]). In order to corroborate this tentative steric argument, the two oxovanadium(IV) catalysts (+)-**7** and (+)-**8** were prepared from the corresponding ligands (+)-**21** and (1*S*)-(+)-3-heptafluorobutanoyl-10-isobutylidenecamphor **24**[14] and their enantioselectivity compared to that of (+)-**5a** (cf. Table 2). Indeed with increased steric constraint in the C-10 position of camphor the *ee* dropped from 59.0% for (+)-**5a** to 33.3% for (+)-**8** and 31.6% for (+)-**7**. It is open to speculation why the change of enantioselectivity between monomeric and polymeric catalysts occurs only in bis-chelated oxovanadium(IV) but not in tris-chelated europium(III) complexes.

Due to modest enantioselectivities, the hetero Diels-Alder route of eq. (1) (Danishefsky reaction) would not appear attractive for the enantioselective synthesis of natural products with the 5,6-dihydro-4*H*-pyran-4-one (5,6-dihydropyranone) structure unless recrystallization steps are utilized at the expense of the chemical yield. Yet, the principle of recycling a polymeric catalysts (i.e. **6**, **13**) by precipitation in subsequent enantioselective catalytic runs without appreciable loss of activity and enantioselectivity is demon-

Figure 2. Enantiomeric excess (*ee*) [%] of (+)-**4** obtained with new (run 1) or recycled catalyst (run 2–7) **6a**

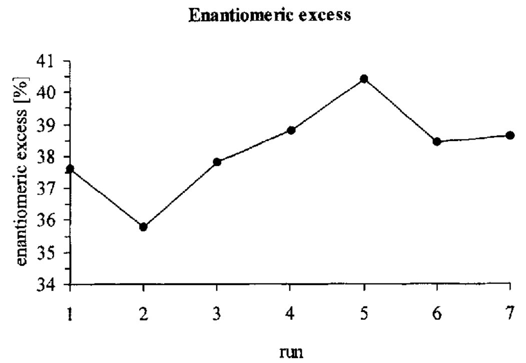
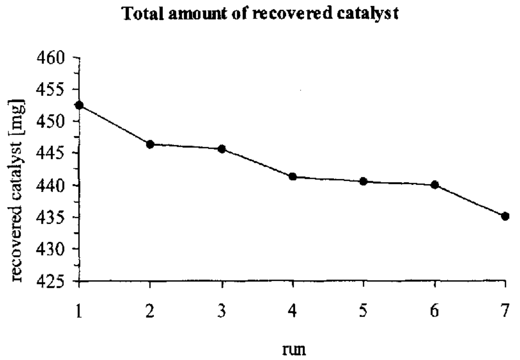


Figure 3. Recovered catalyst **6a** [mg] starting at the first run with 496.1 mg **6a**



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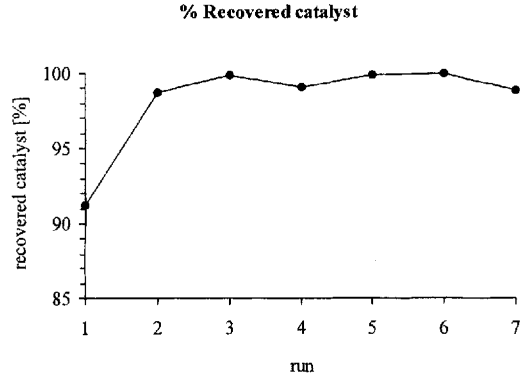
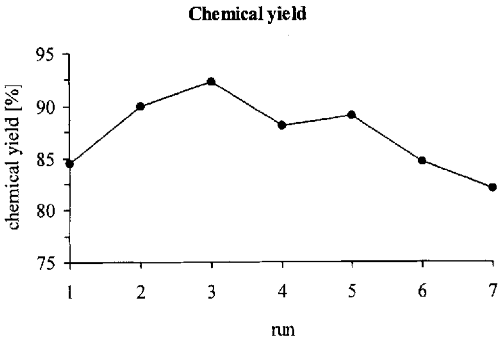


strated in the present work. This strategy is of interest in its own right and may be useful for related catalytic reactions.

Thus, according to Figures 2–5, seven consecutive catalytic runs (at a constant reaction time) lead essentially to no change in the *ee* of **4** (within experimental error) (cf. Figure 2). Except for the first run which results in some loss of catalyst upon precipitation (cf. Figure 3), possibly due to the removal of low-molecular weight contaminants of the polymeric catalyst, no serious loss of catalyst is observed in subsequent cycles and recovery is >98% (cf. Figure 4). The slight decrease of the >82% chemical yield of **4** is ascribed to a small loss of activity of the catalyst containing the metal in a very diluted form (0.23% vanadium, 1.17% europium) (cf. Figure 5).

Figure 5. Chemical yield of **4** [%] obtained with new (run 1) or recycled catalyst (run 2–7) **6a**



Comparable results are obtained when (+)-**13b** is used as catalyst (Table 5).

Table 5. Recovery of the catalyst **12b** and enantiomeric excess *ee* of (+)-**4** in subsequent catalytic runs, 0.62 mmol of **1** and 0.59 mmol of **2**, reaction time 3 d, temperature 20°C, solvent 5 ml of *n*-hexane

Run	Amount of catalyst used [mg]	Amount of catalyst recovered [mg]	Catalyst recovered [%]	Chemical yield of 4 [%]	ee of (+)-4 [%]
1	120.0	111.1	92.6	86.0	41.0
2	111.1	109.9	98.9	57.7	38.4
3	109.9	102.7	93.4	74.3	41.0
4	102.7	97.4	94.8	72.3	38.8
5	97.4	88.5	90.9	57.2	40.4

Attempts to immobilize the ligand **21** on silica particles as described by Matlin et al.[15] were successful, however, the catalytic properties of the complexes of oxovanadium(IV) and europium(III) with the heterogenic ligand were poor.

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Experimental Section

Instrumentation: Optical rotation: Perkin Elmer 241. – ^{1}H NMR and ^{13}C NMR: Bruker AC 250. MS: Finnigan MAT TSQ 70. – Melting points (uncorrected) were determined with a Büchi Tottoli apparatus (sealed glass capillaries). – The metal content was determined after acid hydrolysis by ICP-MS or AAS[16]. The fluorine content was determined by Schoeninger pyrolysis[16]. – The enantiomeric excess (*ee*) of **4** was determined by enantioselective gas chromatography on a fused silica column coated with Chirasil-β-Dex[9] (10 m × 0.25 mm i.d., film thickness 0.2 μm), carrier: 1 bar He at 120°C.

Starting Compounds and Reagents: (1*R*)-(+)-Camphor, >97% (GC), distilled in a Kugelrohr apparatus before use, $[\alpha]_D^{22}$ = 44.7 (*c* = 10, methanol); (1*S*)-(–)-camphor, >95% (GC), distilled before use, $[\alpha]_D^{22}$ = –40.7 (*c* = 10, methanol); *trans*-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (all Fluka, Buchs, Switzerland); heptafluorobutanoyl chloride (Riedel-de Haën); europium(III) trichloride hydrate, 99.9% (Aldrich); oxovanadium(IV) sulfate pentahydrate, >96% (Merck); silica gel 32–63 μm; *n*-hexane HPLC-Grade (Aldrich); all other solvents reagent grade. – All reactions were carried out under nitrogen (99.996%). Solvents were carefully dried by using standard procedures and were distilled prior to use.

Camphor-10-sulfonic Acid (**18**) was prepared as described[17] from camphor (**16**), sulfuric acid and acetic anhydride. (1*S*)-(+)-Camphor-10-sulfonic acid [(+)-**18**]: yield 60.5%; $[\alpha]_D^{22}$ = 21.5 (*c* = 2 in H_2O); mp 196°C. – (1*R*)-(–)-Camphor-10-sulfonic acid [(–)-**18**]: yield 44.7%; $[\alpha]_D^{22}$ = –20.2 (*c* = 2 in H_2O); mp 196°C. – ^1H NMR (250 MHz, D_2O): δ = 0.68 (s, 3H), 0.88 (s, 3H), 1.25–1.54 (m, 2H), 1.79–2.03 (m, 3H), 2.20–2.32 (m, 2H), 2.70 (d, 1H, *J* = 15.0 Hz), 3.16 (d, 1H, *J* = 15.0 Hz). – ^{13}C NMR (62.9 MHz, D_2O): δ = 21.4, 21.5, 27.2, 28.8, 44.9, 45.2, 49.8, 50.7, 61.1, 224.3. – MS (70 eV), *m/z* (%): 233 (10) [M + 1^+], 188 (10), 168 (11), 123 (25), 109 (100), 107 (34), 93 (24), 81 (61), 67 (28), 55 (15), 41 (25).

Camphorsulfonyl Chloride (**19**) was prepared from camphor-10-sulfonic acid (**18**) with thionyl chloride and was recrystallized from diethyl ether/petroleum ether (boiling range 30–50°C). – (1*S*)-(+)-Camphor-10-sulfonyl chloride [(+)-**19**]: yield 80.0%; $[\alpha]_D^{22}$ = 25.1 (*c* = 1 in $CHCl_3$); mp 66°C. – (1*R*)-(–)-Camphor-10-sulfonyl chloride [(–)-**19**]: yield 80.5%; $[\alpha]_D^{22}$ = –23 (*c* = 1 in $CHCl_3$); mp 67–8°C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.92 (s, 3H), 1.14 (s, 3H), 1.40–1.55 (m, 1H), 1.70–1.84 (m, 2H), 1.93–2.18 (m, 3H), 2.36–2.54 (m, 2H), 3.72 (d, 1H, *J* = 14.6 Hz), 4.30 (d, 1H, *J* = 14.6 Hz). – MS (70 eV); *m/z* (%): 253 (12) [M^+], 251 (23), 215 (8), 151 (57), 133 (12), 123 (40), 109 (100), 93 (32), 81 (10), 41 (35).

10-Methylidenecamphor (**20**) was obtained by reaction of camphor-10-sulfonyl chloride (**19**) and diazomethane as described[18]. – (1*S*)-(+)-10-Methylidenecamphor [(+)-**20**]: Yield 85%; $[\alpha]_D^{22}$ = 18.5 (*c* = 2 in methanol); mp 62°C. – (1*R*)-(–)-10-Methylidenecamphor [(–)-**20**]: Yield 64%; $[\alpha]_D^{22}$ = –18.2 (*c* = 2 in methanol); mp 62–4°C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85 (s, 3H), 0.86 (s, 3H), 1.27–1.47 (m, 2H), 1.76–2.11 (m, 4H), 2.3–2.44 (m, 1H), 5.14 (dd, 1H, *J* = 17.6 Hz, *J'* = 1.7), 5.30 (dd, 1H, *J* = 11.1 Hz, *J'* = 1.7 Hz), 5.73 (dd, 1H, *J* = 17.6 Hz, *J'* = 11.1 Hz). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.3, 20.1, 26.0, 26.9, 43.4, 43.6, 48.5, 64.0, 118.9, 132.2, 217.1. – MS (70 eV); *m/z* (%): 164 (37) [M^+], 135 (15), 120 (100), 107 (47), 95 (30), 93 (90), 81 (30), 79 (39), 67 (36), 65 (11), 53 (22), 41 (20).

Heptafluorobutanoylation of Camphor Derivatives[19]: To a stirred suspension of 0.24 mol of sodium amide in 20 ml of dimethoxyethane, 0.24 mol of the camphor derivative in 300 ml dimethoxyethane were added. The resulting mixture was slowly brought to gentle boiling. After reaching the boiling point, the reaction started with the evolution of gaseous ammonia and the heating mantle was removed. After the exothermic reaction subsided, the reaction mixture was heated for about 3 h with a gentle nitrogen flow through the solution until no further ammonia was detectable. Then the reaction mixture was cooled to –10°C with an ice/salt mixture. With stirring, 0.1 mol of heptafluorobutanoic chloride in 80 ml of dimethoxyethane was slowly added over 4 h. The temperature was then allowed to rise to 20°C and the deep red mixture was stirred for another 12 h, then poured on 300 g of crushed ice, acidified with HCl and extracted four times with 100 ml of diethyl ether. The combined extracts were washed with water and two times with brine, dried over $MgSO_4$ and the solvent was removed in vacuo. 10 g of the crude 1,3-diketone was dissolved in 500 ml of methanol and placed onto an ion-exchange column (300 mm × 50 mm i.d.) filled with Amberlyst A-26 (preconditioned with 500 ml of 1% methanolic KOH and washed with 500 ml of methanol). The solution was passed through the column very slowly (500 ml/2 h). The excess of camphor was washed from the column with 500 ml of methanol. The 1,3-diketone was eluted with 500–600 ml of acidified methanol (1 ml HCl 10 N/500 ml methanol). The methanol was removed under reduced pressure. The resulting dark red oil was dissolved in 50 ml of diethyl ether and washed two times with water to remove the hydrochloric acid and excess of heptafluorobutanoic acid. The diethyl ether solution was dried with anhydrous $MgSO_4$ and the diethyl ether was evaporated. The crude product was distilled yielding a colorless to slightly yellow oil. To recover the excess camphor derivative, the methanol of the solution containing the camphor derivative was removed in vacuo and the residue was dried and dissolved in 100 ml of diethyl ether, washed twice with 1 N HCl with diluted $NaHCO_3$ solution and with water. The crude camphor derivative was purified by flash chromatography on silica gel with petroleum ether (boiling range 30–50°C)/diethyl ether (9:1, v/v) as eluent. The recovered camphor derivative was then distilled in a Kugelrohr apparatus to obtain colorless crystals of the pure camphor starting compound which could be used for subsequent acylation reactions.

Table 6. Heptafluorobutanoylation of camphor derivatives

Product	Starting compound	$[\alpha]_{22}^{D}$ [a]	Product yield [%] [b]	Recovered starting compound [%][c]
(+)-**17**	(+)-**16**	+17.1	66.4	[d]
(-)-**17**	(-)-**16**	-15.6	35.0	48.3
(+)-**21**	(+)-**20**	+13.9	69.0	47.2
(-)-**21**	(-)-**20**	-14.0	33.6	74.8

[a] Neat, 0.1 dm. – [b] Based on heptafluorobutanoic chloride. – [c] Base on total amount of camphor derivative. – [d] Not recovered.

3-Heptafluorobutanoylcamphor (**17**): ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80 (s, 3H), 0.94 (s, 3H), 0.99 (s, 3H), 1.37–1.51 (m, 2H), 1.68–1.81 (m, 1H), 2.00–2.14 (m, 1H), 2.81–2.86 (m, 1H) 11.70 (s, 1H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.4, 18.1, 20.2, 26.6, 30.0, 47.4, 49.0, 58.0, 120.5, 147.9, 148.4, 148.9, 213.9. – MS (70 eV); *m/z* (%): 348 (93) [M^+], 320 (49), 305 (33), 179 (18), 151 (100), 123 (57), 108 (53), 91 (27), 69 (46), 55 (49), 43 (55).

3-Heptafluorobutanoyl-10-methylidenecamphor (**21**): ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84 (s, 3H), 0.87 (s, 3H), 1.36–1.58 (m, 2H), 1.99–2.16 (m, 2H), 2.84 (s, 1H), 5.27 (dd, 1H, *J* = 17.6 Hz, *J'* = 1.5 Hz), 5.39 (dd, 1H, *J* = 11.1 Hz, *J'* = 1.5 Hz), 5.76 (dd, 1H, *J* = 17.6 Hz, *J'* = 11.1 Hz). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.5, 20.6, 26.5, 26.6, 47.6, 50.7, 64.0, 115.3, 120.1, 120.5, 130.3, 148.9, 211.9. – MS (70 eV); *m/z* (%): 361 (14) [M^+], 360 (100), 317 (17), 191 (30), 163 (44), 135 (41), 120 (46), 107 (53), 91 (46), 67 (39), 41 (47).

Preparation of the Polymeric Ligand. – Hydrosilylation[9a]: To a stirred refluxing mixture of 6 g of **22** {(7%)-hydromethyl-(93%)-dimethyl}polysiloxane (molecular weight approx. 3000 g/mol[9a]) and 3.4 g (9.420 mmol) of 3-heptafluorobutanoyl-10-methylidenecamphor (**21**) in 150 ml of toluene, 1 ml of 0.1% H_2PtCl_6 in tetrahydrofuran as a hydrosilylating catalyst were added. After 10 h, a second portion of the catalyst was added. After another 30 h, toluene was evaporated in vacuo and the residue was refluxed for 3 h in methanol. The turbid mixture was then centrifuged to separate the methanolic solution from the polymer. The polymer was suspended six times in fresh methanol to dissolve the excess of **21** and was then centrifuged. After filtration through celite to remove precipitated platinum, the polymer was heated in a Kugelrohr apparatus at 90°C/3–10 Torr to remove volatiles yielding the slightly grey and viscous polymer **23**.

(1S)-(+)-3-Heptfluorobutanoylcampher–Dimethylpolysiloxane [(+)-**24**]: Yield 5.7 g; $[\alpha]_D^{22}$ = 25.3 (neat, 0.1 dm).

(1R)-(–)-3-Heptafluorobutanoylcampher–Dimethylpolysiloxane [(–)-**24**]: Yield 4.9 g; $[\alpha]_D^{22}$ = –35.0 (neat, 0.1 dm). – ^1H-NMR (250 MHz, $CDCl_3$): δ = 0.00–0.09, 0.79. – IR (film, cm^{-1}): ṽ = 2950, 2895, 1725, 1685, 1630, 1410, 1255, 1235, 1100–1010, 855, 790.

Preparation of the Polymeric Complexes. – Method A: To a solution of 0.6 g of the polymeric ligand in 15 ml of *n*-heptane, 0.8 mmol of the metal salt in 20 ml of methanol were added. The mixture was stirred at 20°C, after 30 min, 0.33 ml of triethylamine were added and the mixture was refluxed for 2 h. The resulting solution was evaporated to leave a residue which was dissolved in 30 ml of *n*-hexane. The solution was filtered from inorganic residues. The organic phase was washed twice with water and dried shortly with Na_2SO_4. After the removal of most of the solvent in vacuo, 20 ml of methanol was added. The resulting suspension was centrifuged and the polymeric complex was separated from the material that dissolved in the methanolic phase. The methanolic solution was decanted and the polymer was treated in this manner for additional three times. The solvent was removed from the polymer in vacuo at 50°C to leave a very viscous to rubber-like material.

Method B: To 0.3 g of NaH in 10 ml of toluene a solution of 1 g of the polymeric ligand **27** in 20 ml of toluene was added. After the evolution of hydrogen gas, the solution was stirred for additional 2 h and then filtered through a G3 glass frit. 1.5 mmol of the metal salt, dissolved in 20 ml of methanol, was added. The mixture was stirred for 30 min at 20°C and refluxed for 2 h. The resulting solution was evaporated to dryness. The residue was worked up as described above.

Table 7. Prepared polymeric metal complexes

Product	Method	Ligand	Metal salt	$[\alpha]_{22}^{D}$
6a	A	(+)-**23**	$VOSO_4 \cdot 5\,H_2O$	+15.7[a]
6b	A	(-)-**23**	$VOSO_4 \cdot 5\,H_2O$	-28.9[a]
10	B	(+)-**23**	$NiCl_2$	+20.1[b]
13a	B	(+)-**23**	$EuCl_3 \cdot H_2O$	+23.8[b]
13b	B	(-)-**23**	$EuCl_3 \cdot H_2O$	-25.0[b]
15	B	(-)-**23**	UO_2ac_2	-16.0[b]

[a] $c = 0.2$ in CH_2Cl_2. – [b] $c = 2.0$ in CH_2Cl_2.

(+)-(1S)-Oxovanadium(IV) Bis[3-heptafluorobutanoylcampher]–Dimethylpolysiloxane (**6a**): Vanadium content 0.23% (two determinations, ICP-MS[16]). Fluorine content 4.98%, (Schöninger method[16]).

(+)-(1S)-Nickel(II) Bis[3-heptafluorobutanoylcampher]–Dimethylpolysiloxane (**10**): Nickel content 1.05% (by AAS[16]).

(+)-(1S)-Europium(III) Tris[3-heptafluorobutanoylcampher]–Dimethylpolysiloxane (**13a**): Europium content 1.17% (by AAS[16]).

Preparation of the Monomeric Complexes: Method A was carried out according to Togni[4].

Method B: To 0.4 g of NaH in 50 ml of toluene a solution of 8.3 mmol of the monomeric ligand in 20 ml of toluene was slowly added. After the evolution of hydrogen gas, the solution was stirred for additional 30 min and then filtered through a G3 glass frit. The toluene was removed under reduced pressure leaving the sodium salt of the ligand which was dissolved in 40 ml of methanol. To this solution 20 mmol of the metal salt dissolved in 120 ml of methanol was added. The mixture was stirred for 2 h at 20°C and refluxed for 30 min. The methanol was removed in vacuo, the residue was dissolved in 100 ml of *n*-hexane and the insoluble parts were removed by filtration through Celite. The organic phase was washed twice with water and dried with Na_2SO_4. After removal of *n*-hexane in vacuo at 50°C, the resulting catalyst was obtained as a microcrystalline, colored powder.

Table 8. Prepared monomeric metal complexes

Product	Method	Ligand	Metal salt	$[\alpha]_{22}^{D}$
5a	A	(+)-**17**	$VOSO_4 \cdot 5\,H_2O$	+ 82.4[a]
5b	A	(-)-**17**	$VOSO_4 \cdot 5\,H_2O$	- 84.1[a]
7	A	(+)-**21**	$VOSO_4 \cdot 5\,H_2O$	+ 66.0[a]
8	A	**24**	$VOSO_4 \cdot 5\,H_2O$	+ 95.0[a]
9	B	(+)-**17**	$NiCl_2$	+135.1[b]
11	B	(+)-**17**	$Pr(NO_3)_3$	+138.8[b]
12a	B	(+)-**17**	$EuCl_3 \cdot H_2O$	+130.0[b]
12b	B	(-)-**17**	$EuCl_3 \cdot H_2O$	-120.6[b]
14	B	(+)-**17**	UO_2ac_2	+ 98.0[b]

[a] $c = 0.07$ in $CHCl_3$. – [b] $c = 1.0$ in $CHCl_3$.

Hetero Diels-Alder Reaction. – Method A: General Procedure for the Monomeric Catalysts: To the solution of 5 mol-% of the catalyst of *n*-hexane, 0.06 ml (0.59 mmol) of **2** and 0.12 ml (0.62 mmol) of **1** were added. Under occasional shaking, the mixture was allowed to react 3 d to the initial adduct **3**. For work-up, the reaction mixture was treated at ambient temperature with 4 ml of a 0.5% (v/v) trifluoroacetic acid in dichloromethane, afterwards the solvent was evaporated in vacuo and the residue containing **4** was chromatographed on 30 g of silica gel with *n*-hexane/diethyl ether (3:2, v/v) as eluent, $R_f = 0.27$.

Method B: General Procedure for the Polymeric Catalysts: To the solution of 100 mg of the polymeric catalyst in 3 ml of *n*-hexane, 0.06 ml (0.59 mmol) of **2** and 0.12 ml (0.62 mmol) of **1** were added. Under occasional shaking the mixture was allowed to react three days to the initial adduct **3**. For work-up, the polymeric catalyst was separated by precipitation through addition of 20 ml of methanol. The milky suspension was centrifugated and the methanolic solution was decanted from the polymeric catalyst. The methanol was evaporated under reduced pressure and the residue containing the initial adduct **3** was treated at ambient temperature with 4 ml of a 0.5% (v/v) trifluoroacetic acid in dichloromethane. After 10 min, the solvent was evaporated at reduced pressure and the crude product chromatographed on 30 g of silica gel with *n*-hexane/diethyl ether (3:2, v/v) as eluent, $R_f = 0.27$.

2-Phenyl-2,3-dihydro-4H-pyran-4-one: Chemical yields given in Tables 1–5 and Figure 5 are based on **1**. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.50-2.65$ (m, 1H), 2.81 (dd, 1H, $J = 16.8$ Hz, $J' = 14.3$ Hz), 5.32 (dd, 1H, $J = 14.3$ Hz, $J' = 3.6$ Hz), 5.43 (dd, 1H, $J = 6.0$ Hz, $J' = 1.2$ Hz), 7.31 (s, 5H), 7.38 (d, 1H, $J = 6.0$ Hz). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 43.4$, 81.1, 107.4, 126.1, 128.9, 129.0, 137.9, 163.2, 192.2. – MS (70 eV); *m/z* (%): 174 (7) [M^+], 156 (5), 145 (6), 105 (8), 104 (100), 78 (14), 71 (24), 51, (7), 43 (16).

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[1] The chirality descriptor (1*R*) is changed into (1*S*), and vice versa, respectively, when going from the monomeric to the polymeric catalyst as a result of the priority rule, Si > C. Consequently, to avoid confusion, the catalysts are preferentially characterized by their sign of optical rotation.

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