$[C_{450}H_{456}Cd_{24}N_{120}O_{66}]\cdot x\,H_2O\cdot y\,DMF$ (**4**): $Cd(NO_3)_2\cdot 4H_2O$ (48.3 mg, 0.16 mmol) and **1**·HCl (46.0 mg, 0.10 mmol) were dissolved in DMF (10 mL). Water (10 mL) followed by triethylamine (2 mL) in methanol (8 mL) were carefully layered on top. Over a period of two months orange crystals of **4** grew. Yield: 6.2 mg (0.55×10^{-3} mmol, 8.2 %); elemental analysis found (%): C 45.51, H 3.85, N 14.46; calcd (for $x=30$, $y=10$): C 45.82, H 4.66, N 14.48.

Crystallography: Intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing the ω-2θ scan method, the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied for **2** and **4**.[13] All structures were solved using direct methods (SHELXS-97)[14] and refined using a full-matrix least-squares refinement procedure (SHELXL-97).[15] The data of **4** were corrected using the "SQUEEZE" routine in PLATON.[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146818–146821 for **1**, **2**, **3**, and **4**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[5] $0.33\times0.14\times0.03$ mm^3, triclinic, $P\bar{1}$, $a=12.848(1)$, $b=13.0504(6)$, $c=15.158(2)$ Å, $\alpha=92.667(7)$, $\beta=102.81(1)$, $\gamma=110.512(6)^\circ$, $V=2299.6(5)$ Å^3, $\rho_{calcd}=1.644$ g cm^{-3}, $2\theta_{max}=120^\circ$, $\lambda=1.54178$ Å, $T=293$ K, 7858 measured reflections, 6818 independent reflections ($R_{int}=0.0568$), $\mu=11.343$ mm^{-1}, min./max. transmission factors 0.141/0.698, 591 parameters, $R_1=0.0669$, $wR2=0.1424$, max. residual electron density 1.219 e Å^{-3}.

[6] $0.54\times0.46\times0.34$ mm^3, trigonal (hexagonal settings), $R\bar{3}$, $a=16.310(2)$, $c=21.552(3)$ Å, $V=4965(1)$ Å^3, $\rho_{calcd}=1.610$ g cm^{-3}, $2\theta_{max}=54.9^\circ$, $\lambda=0.71073$ Å, $T=140$ K, 3173 measured reflections, 2537 independent reflections ($R_{int}=0.0273$), numerical absorption correction, $\mu=2.296$ mm^{-1}, min./max. transmission factors 0.314/0.490, 181 parameters, $R_1=0.0391$, $wR2=0.1204$, max. residual electron density 1.141 e Å^{-3}.

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[9] $0.46\times0.43\times0.34$ mm^3, trigonal (hexagonal settings), $R\bar{3}$, $a=33.838(7)$, $c=46.23(1)$ Å, $V=45845(18)$ Å^3, $\rho_{calcd}=1.227$ g cm^{-3}, $2\theta_{max}=100^\circ$, $\lambda=1.54178$ Å, $T=130$ K, 11 987 measured reflections, 10 394 independent reflections ($R_{int}=0.1104$), $\mu=7.051$ mm^{-1}, min./max. transmission factors 0.120/0.264, 473 parameters, $R_1=0.1064$, $wR2=0.3105$, max. residual electron density 0.385 e Å^{-3}.

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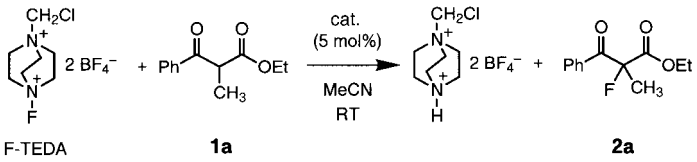
Catalytic Enantioselective Fluorination of β-Ketoesters**

Lukas Hintermann and Antonio Togni*

Although in nature organofluorine metabolites are extremely rare, bioactive fluoroorganic compounds are eminently important in medicinal chemistry.[1] Therefore, it is not surprising that research in the field of synthetic organofluorine chemistry is flourishing more than ever.[2, 3] Protocols for the introduction of the fluorine atom into organic molecules rely upon the use of dozens of different reagents,[4] the most successful of which contain the N–F fragment.[5, 6] Methods for the enantioselective fluorination (C–F bond-forming reactions) of organic molecules are quite rare, and catalytic methods are not known. An important breakthrough occurred when Differding and Lang reported the first example of enantioselective electrophilic fluorination of a β-ketoester enolate in up to 70 % *ee* by using an *N*-fluorosultam derived from camphor.[7] This strategy, requiring the intermediate generation of the enolate from an activated methylene compound, has been further developed more recently.[8–13] Another impetus in this field came also from the discovery and commerical availability of new N–F reagents, such as 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis{tetrafluoroborate} (F-TEDA; also called Selectfluor, see Scheme 1; TEDA = triethylenediamine).[14, 15] However, the total absence of an efficient catalytic reaction for stereoselective fluorination prompted us to embark in a study aimed at developing such a reaction. Recent reports had indicated



F-TEDA **1a** **2a**

Scheme 1. The catalytic fluorination of **1a** with F-TEDA.

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that N–F reagents were capable of fluorinating unactivated ketones in the α-position in refluxing acetonitrile, whereas activated ketones, notably β-ketoesters and β-diketones, were already fluorinated at room temperature.[16] As these reactions proceed via the enol form of the substrate, we reasoned that substochiometric amounts of a Lewis acid might accelerate the reaction by catalyzing the enolization process.[17] Thus, we started a systematic study with model compound **1a** (Scheme 1), a monosubstituted β-ketoester, and found that it does not react with a saturated solution of F-TEDA in acetonitrile at room temperature, in accordance with its low enol content ($<0.5\,\%$ in CD_3CN by ^1H NMR spectroscopy). However, the addition of a range of Lewis acids[18, 19] (5 mol % level) effectively catalyzed the reaction (Table 1).

Table 1. Qualitative ordering of catalytic activity of several Lewis acids for the reaction shown in Scheme 1.[a]

Very fast (<1 h)	Fast (<1 d)	Slow (≤2 w)	Very slow or no reaction (>2 w)
$TiCl_4$	$[CpTiCl_3]$	$[Cp_2Ti(OTf)_2]$	$[Cp_2TiCl_2]$
$AlCl_3$	$[TiCl_2(diolato)]$	HBF_4	HCl
		BF_3	$ZnCl_2$
		Me_3SiOTf	$Cu(ClO_4)_2$
			$[Cp_2Zr(OTf)_2]$
			TiF_4
			$TaCl_5$
			$Yb(OTf)_3$

[a] OTf = trifluoromethanesulfonate.

It is evident that titanium-based Lewis acids constitute the most potent catalysts, with $TiCl_4$ driving the reaction to completion in less than 1 h at room temperature. Since many chiral, enantiopure Lewis acidic Ti complexes are known, we were in the comfortable situation of being able to screen a large number of known catalysts[20] for the enantioselective version of this reaction. We found that with 5 mol % of in situ prepared $[TiCl_2(R,R\text{-TADDOLato})]$ ((*R*)-**3a**)[21] as catalyst, a quite fast reaction of racemic β-ketoester **1a** with F-TEDA took place (quantitative conversion in less than 5 h), yielding the fluoro-β-ketoester **2a** in good yield and with 28 % *ee*. Notably, $[TiCl_2(TADDOLato)]$ catalysts have been extensively used by Seebach and others[22] but these were typically prepared in situ and not used in isolated form. We found that the two prototypical catalysts (*R*)-**3a** and (*R*)-**3b**,[23] that have been mainly exploited for this study as catalysts, may be isolated in high yields (85–90 %) as air-stable highly crystalline materials as dimethoxyethane (DME) or acetonitrile adducts, respectively, in the latter case with a varying number of acetonitrile molecules per titanium. Furthermore, these isolated materials gave more reliable results than the corresponding forms generated in situ, in terms of both reproducibility and enantioselectivity of catalytic experiments (see below). Compound [(*R*)-**3a**(DME)] and the bis(acetonitrile) adduct [(*R*)-**3b**$(NCMe)_2$] were characterized by X-ray crystallography[24] and ORTEP views of the octahedral complexes are shown in Figure 1.

The results obtained by using the isolated forms of (*R*)-**3a** or (*R*)-**3b** as catalyst precursors for the fluorination of

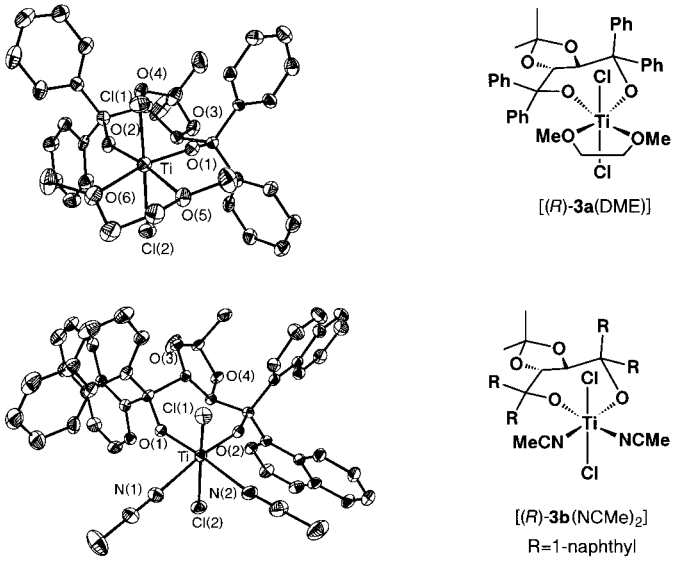

Figure 1. Structures of the complexes [*R*-**3a**(DME)] and [*R*-**3b**$(NCMe)_2$] (ORTEP views; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: [*R*-**3a**(DME)]: Ti-O(1) 1.752(5), Ti-O(2) 1.765(5), Ti-O(5) 2.224(5), Ti-O(6) 2.164(6), Ti-Cl(1) 2.337(2), Ti-Cl(2) 2.342(3), O(1)-Ti-O(2) 98.6(2), O(1)-Ti-O(5) 90.9(2), O(2)-Ti-O(6) 96.8(2), O(5)-Ti-O(6) 73.7(2), Cl(1)-Ti-Cl(2) 164.97(10); [*R*-**3b**$(NCMe)_2$]: Ti-O(1) 1.780(3), Ti-O(2) 1.773(3), Ti-N(1) 2.283(4), Ti-N(2) 2.264(4), Ti-Cl(1) 2.3343(13), Ti-Cl(2) 2.3622(13), O(1)-Ti-O(2) 97.18(12), O(1)-Ti-N(1) 90.74(13), O(2)-Ti-N(2) 88.86(13), N(1)-Ti-N(2) 83.24(14), Cl(1)-Ti-Cl(2) 162.11(5).

different β-ketoesters are presented in Table 2. We so far restricted this reaction to substrates bearing an α-methyl group, thus leading to products having a quaternary stereogenic center. The reactions have been typically conducted at room temperature in a closed vessel and with a slight excess of a saturated F-TEDA solution in acetonitrile (this proved to be more reactive than, e.g., *N*-fluorobenzenesulfonimide or *N*-fluoropyridinium tetrafluoroborate). Products were isolated in analytically pure form after column chromatography, in all cases in yields between 80 % and more than 95 %.[25] It is apparent from Table 2 that the steric bulk of the catalyst is important with regard to the stereoselectivity. Thus, the better enantioselectivities for all substrates under study were obtained by using catalysts **3b**, bearing 1-naphthyl groups. Also the nature of the ester group clearly influences enantioselectivity; the best results have been obtained with the substituted benzyl ester of substrate **2f** (90 % *ee*; using the in situ prepared catalyst a maximum of 85 % *ee* was obtained). This level of stereoselectivity compares favorably with the highest enantioselectivity obtained by using chiral enantiopure fluorinating agents.

The fluorination of cholesteryl ester **2g** using $[CpTiCl_3]$ as catalyst gave a diastereoisomeric product ratio of 55:45. This poor selectivity was gradually improved in the reactions catalyzed by the complexes (*R*)-**3a** (60:40), (*R*)-**3b** (80:20), and (*S*)-**3b** (16:84), indicating that for this doubly stereodifferentiating reaction both the sense and the extent of asymmetric induction are dominated by the catalyst.

We assume that the interaction of the β-ketoester with the catalyst triggers an enolization reaction, and that the coordinated enol or enolate is the reactive form of the substrate,

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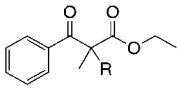
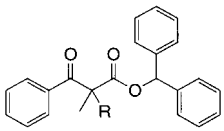
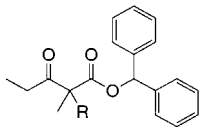
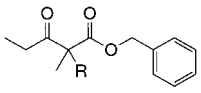
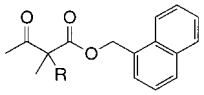
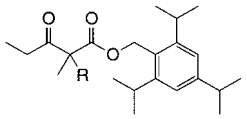
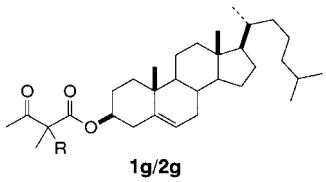
Table 2. Selected results of catalytic enantioselective fluorination reactions using isolated [$TiCl_2$(TADDOLato)] complexes.

1 (R = H) (racemic) **2** (R = F)	Selectivity (Reaction time) cat. = (*R*)-**3a**	 cat. = (*R*)-**3b**	$[\alpha]_D^{20}$(**2**)[a] [*ee* [%]]	$\delta(^{19}F)$(**2**)[b]	HPLC analysis[c]	
 **1a/2a**	28% *ee* (*S*) (4 h)	62% *ee* (40 min)	+53.8 (c = 0.545) [61.7]	−152.3	OB 0.5	96/4 *13.5*/**16.0**
 **1b/2b**	59% *ee* (1 d)	82% *ee* (1 d)	+19.0 (c = 1.83) [56]	−152.5	OJ 1	95/5 **14.1**/*18.9*
 **1c/2c**	58% *ee* (2 h)	81% *ee* (20 min)	+38.2 (c = 1.02) [81.2]	−159.5	OJ 0.25	70/30 **36.1**/*39.4*
 **1d/2d**	48% *ee* (15 min)	71% *ee* (< 7 min)	+32.5 (c = 0.905) [70.8]	−159.5	OJ 1	96/4 *11.7*/**15.3**
 **1e/2e**	51% *ee* (< 15 min)	68% *ee* (< 15 min)	+19.6 (c = 1.14) [68.8]	−157.4	OJ 1	96/4 *24.0*/**27.7**
 **1f/2f**	55% *ee* (1 h)	90% *ee* (< 15 min)	+24.1 (c = 1.11) [85.6]	−159.2	OD-H 0.3	99.8/0.2 **27.8**/*29.8*
 **1g/2g**	d.r. = 60:40	d.r. = 80:20[d]	n.d.[e]	−157.3[f]	–	–

[a] Measured in MeOH at room temperature on a sample of given *ee* [value in square brackets]. [b] Measured in $CDCl_3$, relative to $CFCl_3$. [c] Daicel Chiralcel 25 cm column type; solvent mixture: hexane/*i*PrOH (v/v); flow rate in mL min^{-1}. Retention times (HPLC) in min of *minor*/**major** enantiomer (UV detection at λ = 210 nm and 254 nm). [d] (*S*)-**3b**: d.r. = 16:84. [e] Not determined. [f] The difference of the shifts between the two diastereomers is $\Delta\delta$ = 0.01.

susceptible to external electrophilic attack by the fluorinating agent. Thus, the role of the Lewis acid consists in activating the nucleophile and not, as it is more common in reactions involving carbonyl compounds, in enhancing the electrophilicity of the coordinated carbonyl group. We are currently exploring these mechanistic aspects, in order to better understand this quite unique and novel catalytic reaction. Furthermore, the extension of this convenient and expeditious fluorination process to other enolizable substrates, as well as to the corresponding asymmetric chlorination reaction[26] using *N*-chlorosuccinimide (NCS) are the object of current and future work.[27]

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[23] (*R*)-**3a** = dichloro[4*R*, 5R-2,2-dimethyl-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,3-dioxolane-4,5-dimethanolato(2-)-*O*,*O*′]titanium. (*R*)-**3b** = dichloro[4*R*,5*R*-2,2-dimethyl-$\alpha,\alpha,\alpha',\alpha'$-tetra(1-naphthyl)-1,3-dioxolane-4,5-dimethanolato(2-)-*O*,*O*′]titanium. The two corresponding TADDOL ligands are commercially available.
[24] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145414 ([(*R*)-**3a**(DME)]) and CCDC-145415 ([(*R*)-**3b**-$(NCMe)_2$]). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[25] A representative experimental procedure is as follows: Complex **3b** (10.3 mg, 0.0125 mmol) was added to a solution of β-ketoester **1d** in acetonitrile (0.25 mmol in 1 mL), and the mixture was stirred until a clear yellow solution was obtained (5 min). To this was added a saturated F-TEDA solution (2.0 mL; 0.145 mol L^{-1}; 0.29 mmol) in MeCN. After 7 min, TLC (TBME/hexane 1/5, R_f(starting material) = 0.36, R_f(product) = 0.50; detection by UV and/or phosphomolybdic acid; TBME = *tert*-butyl methyl ether) indicated complete conversion. The reaction mixture was extracted with water (50 mL) and TBME (30 mL), the organic phase was filtered through Al_2O_3 (1 g; washed with additional TBME) and evaporated. Liquid chromatography (TBME/hexane 1/20) gave **2d** (49 mg; 82 %) of as colorless oil (70.8 % *ee* by HPLC).
[26] L. Hintermann, A. Togni, *Helv. Chim. Acta* **2000**, *83*, 2425 – 2435.
[27] Note added in proof (27. October 2000): After this work was submitted the first Lewis acid catalyzed asymmetric ring opening of epoxides by fluoride was reported. See: S. Bruns, G. Haufe, *J. Fluorine Chem.* **2000**, *104*, 247 – 254.

Octahedral SeO_6^{6-} and Square-Pyramidal SeO_5^{4-}, Two New Oxoselenate Anions**

Helmut Haas and Martin Jansen*

For kinetic as well as thermodynamic reasons cations in tetrahedral and octahedral complexes usually show a lower Lewis acidity than in three- or fivefold coordination. We have therefore considered the main driving force for the surprisingly smooth acid – base reaction of the addition of O^{2-} to SeO_4^{2-} in the synthesis of Li_4SeO_5[1] to be the formation of a collective solid-state structure $A_4A'B_5$, thus the order variant of an AB structure type,[2] and the associated gain in lattice energy. Also the unexpected coordination polyhedron (CN = 5, trigonal-bipyramidal) was attributed to this overriding structure-chemical argument. That such explanations are not applicable, is confirmed by the preparation of two other oxoselenates, for which at first glance there are no structural features apparent that stabilize a hexaoxo- or pentaoxo anion.

For the Na_2O/Na_2SeO_4 system the solid-state reaction at a molar ratio of the starting materials of 1:2[3] under standard pressure gave $Na_6Se_2O_9$, which contains hexaoxoselenate(VI) and tetraoxoselenate(VI) anions, whereas at a ratio of 1:1 under hydrostatic pressure Na_4SeO_5 was formed. The single-crystal structure analysis[4] confirmed in the first case that according to the formulation $Na_{12}(SeO_6)(SeO_4)_3$ an octahedral orthoselenate anion had been obtained for the first time (Figure 1). This displays the point symmetry O_h within the margins of error of the structure determination. The dimensions of the tetrahedral SeO_4^{2-} ions ($\bar{d}_{Se\text{-}O}$ = 163.6 pm, O-Se-O = 109.53°) are comparable with those of already known oxoselenates(VI) with tetrahedral anions (cf. Na_2SeO_4[6] with $\bar{d}_{Se\text{-}O}$ = 164.8 pm). The increase of the average Se–O bond

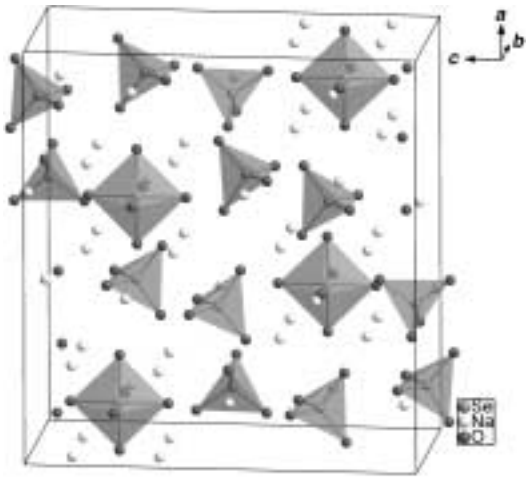

Figure 1. Crystal structure of $Na_6Se_2O_9$ (perspective representation).

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