(Table 1). The coordinates of Arg 62$_{(n)}$, Arg 62$_{(l)}$, Ala-Pro, W$_{a}$, W$_{b}$, W$_{c}$, and W$_{d}$ were fixed during occupancy refinement. Arg 62$_{(n)}$ represents the Arg 62 conformation without Ala-Pro bound and Arg 62$_{(l)}$ represents the Arg 62 conformation with Ala-Pro bound to ceCyp3. The B-factors of Arg 62$_{(n)}$, W$_{a}$, W$_{b}$, W$_{c}$, and W$_{d}$ were fixed to the same B-factor values as those of the native structure. Individual atomic B-factors for Arg 62$_{(l)}$ and Ala-Pro were refined together with occupancy (Figure 4). The restraints applied in the occupancy refinement are summarized below:

$Q_{\mathrm{Arg62(n)}} + Q_{\mathrm{Arg62(l)}} = 1$

$Q_{\mathrm{Arg62(l)}} = Q_{\mathrm{l}}$

$Q_{\mathrm{Arg62(n)}} = Q_{\mathrm{Wa}} = Q_{\mathrm{Wb}} = Q_{\mathrm{Wc}} = Q_{\mathrm{Wd}}$

where

$Q_{\mathrm{Arg62(n)}}$: is the occupancy of the Arg 62 conformation with no Ala-Pro binding, $Q_{\mathrm{Arg62(l)}}$: is the occupancy of the Arg 62 conformation with Ala-Pro binding, and Q_{l}: is the occupancy of Ala-Pro.

PPIase assay:[13] α-chymotrypsin selectively hydrolyzes the C-terminal *p*-nitroanilide bond of the substrate in the *trans* X-Pro conformer only. This hydrolysis releases the chromophore 4-nitroaniline, the accumulation of which is recorded by measuring the absorbance at 400 nm as a function of time. Substrate (*N*-succinyl-Ala-Ala-Pro-Phe-p-nitroanilide, Bachem AG) was dissolved in LiCl/2,2,2-trifluoroethanol (LiCL/TFE) to give a stock solution of 100 mM. The experiment took place at 4 °C. Constant temperature was maintained within the cuvette by a Peltier (PTP-1) temperature control unit. A Perkin–Elmer UV/Vis Lambda 20 spectophotometer was used.

Proteins: ceCyp3 solution was freshly prepared before the experiment from frozen stock solution, at the appropriate concentration, by dilution in buffer 50 mM 2-[4-[2hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES), 100 mM NaCl, pH 8.0 (buffer A).

α-chymotrypsin (Sigma): In a typical experiment 10 µL of 20 nM ceCyp3 was made up to 870 µL with buffer A and the appropriate volume of Ala-Pro in a 1-mL cuvette. The cuvette was then preincubated for 30 min on ice. Immediately before the assay, 100 µL of chymotrypsin solution (50 mg mL^{-1} in 10 mM HCl) was added, followed by 30 µL of a 3.7 µM stock solution of Suc-Ala-Ala-Pro-PNA in LiCl (470 mM)/TFE. The reaction progress was monitored by the absorbance change at 400 nm that accompanies the hydrolysis of the amide bond and the release of 4-nitroaniline.

Received: September 8, 2000 [Z 15779]

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A Heterogeneous *cis*-Dihydroxylation Catalyst with Stable, Site-Isolated Osmium–Diolate Reaction Centers**

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Osmium tetroxide is by far the most versatile catalyst for *cis*-dihydroxylation (DH) of double bonds.[1, 2] When homogeneous catalysts are used, free OsO_4 is always present in some step of the catalytic cycle, and the high toxicity and volatility of OsO_4 have hitherto obstructed industrial application. Previous attempts to immobilize OsO_4 used polymers, for example, with coordination of OsO_4 on polyvinylpyridine.[3, 4] However, hydrolysis of the intermediate Os^{VI} diolate complex requires that Os is detached from the polymeric Lewis base,[5] and this implies an inherent liability to Os leaching. Similarly, reports on immobilized alkaloids for asymmetric DH mention that Os leaching necessitates Os supplementation in subsequent runs.[6] In another attempt, OsO_4 was entrapped in polystyrene microspheres, but the mechanism by which OsO_4 is retained within the polymer is not understood.[7] Herein we report a solid with Os^{VIII} type reactivity, and with a persistent bond between Os and the support. Rigorous heterogeneity tests and reactions with 12 olefins substantiate the value of the new Os catalyst.

Our approach is rooted in the mechanism of the *cis*-dihydroxylation, which comprises two stages: 1) attack of the Os^{VIII} *cis*-dioxo complex on the olefin (osmylation), 2) reoxidation of Os^{VI} to Os^{VIII} and hydrolytic release of the diol. Two points are particularly relevant. First, if the hydrolytic conditions are not too drastic, *tetrasubstituted* olefins are not converted into *cis*-diols.[8, 9] These olefins are smoothly osmylated to an osmate(VI) ester, but the rate of subsequent hydrolysis is zero (0% yield for a tetrasubstituted olefin vs. 83% for a trisubstituted olefin, ref. [8]). Second, an Os^{VI} monodiolate complex can be reoxidized to *cis*-dioxo Os^{VIII} without release of the diol; subsequent addition of a second olefin results in an Os bisdiolate complex.[10] These two properties make it possible to immobilize a catalytically active Os compound by the addition of OsO_4 to a tetrasubstituted olefin that is covalently linked to a silica support (**1a**, Scheme 1). The tetrasubstituted diolate ester (**1b**) which is

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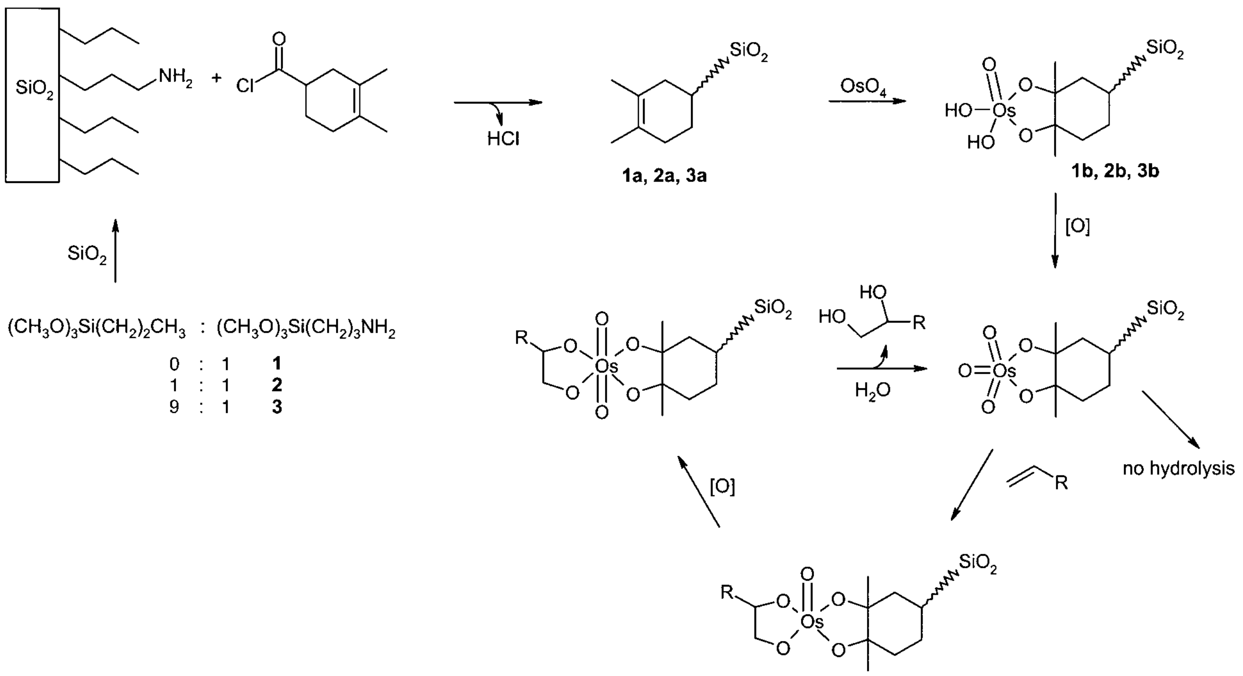
[**] This work was supported by the Belgian Federal Government in the frame of an Interuniversitary Attraction Pole on Supramolecular Catalysis. We are indebted to FWO for fellowships (A.S., D.D.V.) and for a research grant (D.D.V., F.V., P.A.J.).

  1433-7851/01/4003-0586 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2001**, *40*, No. 3



Scheme 1. Immobilization of Os in a tertiary diolate complex, and proposed catalytic cycle for *cis*-dihydroxylation ([O] = *N*-methylmorpholine *N*-oxide).

formed at one side of the Os atom is stable, and keeps the catalyst fixed to the support material. The catalytic reaction can then take place at the free coordination sites of Os.

For the preparation of a silica-anchored tetrasubstituted olefin, silica is first functionalized with 3-aminopropyltrimethoxysilane (Scheme 1).[11] Next 3,4-dimethylcyclohex-3-enylcarbonyl chloride is added, which reacts with the grafted amino groups to form an amide. The 3,4-dimethylcyclohex-3-enylcarbonyl chloride is prepared by the Diels–Alder reaction of 2,3-dimethyl-1,3-butadiene and ethyl acrylate, and conversion of the ester into the acid chloride.[12] Next, OsO_4 adds to the double bond in the functionalized support **1a** (→**1b**). To avoid handling the poisonous OsO_4, hexavalent $K_2OsO_2(OH)_4$ is used as an Os source, and oxidized in situ to OsO_4 with *N*-methylmorpholine *N*-oxide (NMO) in *tert*-butyl alcohol:dichloromethane (2:1).[13] Excess OsO_4 is removed from **1b** by threefold washing with the same solvent mixture.

Physicochemical observations confirm that Os is immobilized in surface-linked diolate complexes. In solution chemistry, reaction of OsO_4 with an olefin gives rise to dark brown Os^{VI} complexes. In the reaction of the solid support **1a** with OsO_4, the solid (**1b**) turns dark brown, while no color develops in solution. Diffuse reflectance spectroscopy measurements of the solid show intense absorptions at wavelengths shorter than 700 nm. More detailed information is obtained from solid-state ^{13}C NMR spectrometry (Figure 1). The amide signal at δ=177 (for **1a**) confirms the successful attachment of the acyl group to the surface. The spectrum of the Os-free material (**1a**) shows a C=C signal at $\delta = 124$, characteristic for the tetrasubstituted olefin. When OsO_4 is added (→**1b**), this signal is replaced by a new signal at δ=92. The tertiary alcohol groups in Os(VI) diolate complexes (prepared from OsO_4 and 3,4-dimethylcyclohex-3-enylcarboxylic acid) have a resonance signal in solution NMR spectroscopy between $\delta = 90$ and 95. Thus, the intense peak at $\delta = 92$ in the solid-state spectrum of **1b** confirms that Os is bound by esters of tertiary diols. The immobilized Os is easily observed with X-Ray photoelectron spectroscopy (XPS). Os $4f_{7/2}$ lines at 53.6 eV and 51.2 eV demonstrate that osmium is in the +VI and +IV state. Based on reported values, this is clear evidence that the octavalent OsO_4 is reduced in the reaction with the covalently linked double bond.[14]

Catalysis with the new solid Os materials reveals that the activity strongly depends on the concentration of the Os ester groups on the surface: the highest activity is observed for the lowest concentration of Os-binding groups! (Table 1, entries 1–3). The Os loading is easily controlled by performing the surface functionalization with mixtures of silylating agents

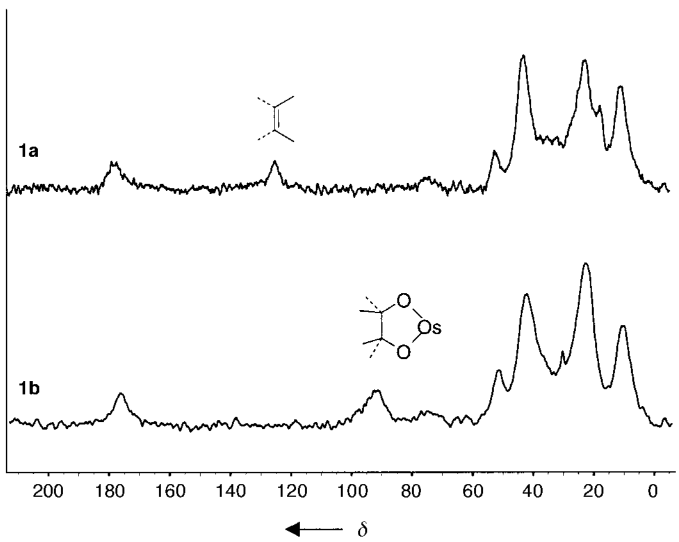


Figure 1. Solid state ^{13}C MAS NMR spectra of **1a** (top), with immobilized tetrasubstituted olefin, and **1b** (bottom), that is, **1a** after addition of OsO_4 to the double bond (high power proton decoupling; 45° pulses with 10 s recycle time; spinning rate 10 kHz).

  1433-7851/01/4003-0587 $ 17.50+.50/0

Table 1. Heterogeneous *cis*-dihydroxylation of 1-hexene: effect of the dilution of active sites with propyltrimethoxysilane (PrTMS);[a] comparison with homogeneous dihydroxylation with or without 2,3,4-trimethyl-2-pentene.

Entry	Catalyst	PrTMS:NH_2PrTMS	*t* [h]	Conversion [%]
1	**1b**	0:1	24	1
2	**2b**	1:1	24	5
3	**3b**	9:1	24	66
4	OsO_4[b]	–	10	98
5	OsO_4[c]	–	10	0

[a] 100 mg supported catalyst, 1-hexene (1.6 mmol), NMO (1.6 mmol), solvent (3 mL), and RT unless otherwise stated. [b] NMO:1-hexene:Os = 400:400:1 [c] NMO:1-hexene:2,3,4-trimethyl-2-pentene:Os = 400:400:10:1; 1-hexene is added 4 h after the other reagents.

(Scheme 1). The highest activity is obtained after silylation with a 9:1 mixture of propyltrimethoxysilane (PrTMS) and 3-aminopropyltrimethoxysilane (NH_2PrTMS). This results in a material (**3b**) with the Os centers diluted by propyl groups (Si:Os = 270, as determined by XPS). In contrast, the material is practically inactive when the surface coverage with Os-binding tetrasubstituted alkene groups is raised (for **1b**: Si:Os = 36, XPS). The deactivation of Os by a high surface concentration of Os-binding alkene groups is explained by double-sided binding of Os by two adjacent tetrasubstituted alkenes. This situation is easily mimicked in homogeneous catalytic experiments, by adding 10 equivalents of the tetrasubstituted 2,3,4-trimethyl-2-pentene per Os to the catalytic dihydroxylation of 1-hexene with NMO (Table 1, entries 4 and 5). Product formation from 1-hexene is fully blocked by a small amount of the tetrasubstituted alkene, since the latter forms bisdiolate complexes that are not hydrolyzed in the mild conditions of our experiments. A similar situation arises in the heterogeneous catalyst if the Os-binding tetrasubstituted alkene groups are too close to each other. In contrast, appropriate site isolation, as in **3b**, ensures that a nonhydrolyzable ester is only formed at one side of the Os atom; at the other side, an olefin such as 1-hexene is dihydroxylated at a high rate.

Stringent heterogeneity tests were performed with the **3b** catalyst, by splitting the reaction suspension in the dihydroxylation of 1-hexene at a conversion of 21%, and monitoring the conversion in the suspension and in the clear supernatant. Zero activity was found in the supernatant, while the reaction continues in the suspension (21% in the clear solution vs. 60% in the suspension; Table 2, entry 13). This test was successfully performed for the reaction of **3b** with several olefins, however, it fails for OsO_4 bound on polyvinylpyridine; this is because of the dissociation of the coordinate bond between Os and the nitrogen base in the hydrolytic release of the diol.

With **3b**, we succeeded in oxidizing olefins to the corresponding *cis*-diols with an excellent conversion and selectivity (Table 2). Monosubstituted, *cis* and *trans* disubstituted aliphatic olefins and cyclic olefins are stereoselectively converted to *cis* diols with good conversions and selectivities over 98% (entries 1–7). Note that the excellent chemoselectivity of the homogeneous reactions with NMO is preserved in the heterogeneous system;[15] overoxidation products such as the ketol make up less than 1% of the products. Aromatic olefins such as styrene and indene are suitable substrates as well (entries 8–9). The reaction proceeds more slowly with a trisubstituted olefin. This is not unexpected, since in our mild conditions, the hydrolysis of the trisubstituted diolate is slow because of steric hindrance. Note that an even greater steric hindrance is at the basis of the stable association between Os and the surface-bound tetrasubstituted diolate. Nevertheless, after a somewhat increased reaction time, 98% yield is obtained from the trisubstituted 2-methyl-2-pentene. While it is known that more electron-rich double bonds are osmylated at a higher rate,[16] the reactivity of Os^{VIII} dioxo species is sufficient to even react with relatively deactivated double bonds. Thus, unsaturated esters such as cinnamates or crotonates are dihydroxylated in high yields (entries 11–12).

Table 2. *Cis*-dihydroxylation of olefins with NMO and the heterogeneous **3b** catalyst.[a]

Entry	Olefin	*t* [h]	Conversion [%]	Selectivity [%]
1	1-pentene	48	83	99
2[b]	1-hexene	48	99	98
3	1-heptene	48	96	99
4	cyclopentene	48	83	98
5	cyclohexene	48	99	99
6	*cis*-2-hexene	48	99	99
7	*trans*-2-hexene	48	98	98
8	styrene	48	99	96
9	indene	48	72	99
10	2-methyl-2-pentene	48	50	99
		150	99	99
11	ethyl *trans*-cinnamate	24	65	99
12	ethyl *trans*-crotonate	48	85	99
13[c]	1-hexene	10	21	
		20, filtrate	21	
		20, suspension	60	

[a] reaction conditions: 100 mg heterogeneous catalyst (4×10^{-6} mol Os), olefin (1.6 mmol), NMO (1.6 mmol), solvent (3 mL), H_2O (200 μL), RT. [b] A second run was performed with the used catalyst from entry 2. After 48 h, conversion and selectivity were again 99 and 98% respectively. [c] Filtrate test: the reaction mixture is splitted after 10 h; further conversion in filtrate and suspension is determined 20 h later.

As is highlighted by the heterogeneity tests, our Os-immobilization concept, and the formation of a stable tetrasubstituted diolate complex, is to date the only solution to the problem of producing such Os supported heterogeneous catalysts. The concept can be expanded to other catalyst carriers that form nonhydrolyzable bonds with Os in the conditions of the catalytic dihydroxylation. Site isolation has been demonstrated to be crucial to obtain an active and truly heterogeneous Os catalyst.

Experimental Section

The support material was commercial SiO_2 60 from Fluka, predried at 150 °C. Surface functionalization was performed by standard reported techniques.[11] For the functionalization of the support with Os, a solution containing OsO_4 (4×10^{-3} mmol) was treated for 4 h with the support (100 mg, containing 10^{-2} mmol of double bonds in the case of catalyst **3b**). After all the OsO_4 had reacted with the support, the catalyst was thoroughly washed with *t*BuOH:CH_2Cl_2 (2:1) to remove traces of unbound OsO_4.

  1433-7851/01/4003-0588 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2001**, *40*, No. 3

In a typical catalytic dihydroxylation, the **3b** material (100 mg) was added to a mixture of the olefin (1.6 mmol), NMO (1.6 mmol), and water (200 μL) in *t*BuOH:CH_2Cl_2 (3 mL; 2:1) solvent. The mixture was stirred at room temperature and regularly analyzed by GC.

Received: August 18, 2000 [Z15661]

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Stereoselective Nucleophilic Trifluoromethylation of *N*-(*tert*-Butylsulfinyl)-imines by Using Trimethyl(trifluoromethyl)-silane**

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Trifluoromethylated amines are important building blocks for pharmaceutical research.[1] The CF_3 group, because of its strongly electron withdrawing nature, lowers the basicity of the amide bond towards nonspecific proteolysis[2] when these amines are incorporated into peptides, as well as modify the solubility and desolvation properties.[3] In spite of its prime importance in the drugs industry, direct asymmetric synthesis of trifluoromethylated amines is a challenge. Pirkle et al.[4] and Mosher and Wang[5] prepared 2,2,2-trifluoro-1-phenylethylamine, and Soloshonok and Ono[6] recently reported an elegant method for the preparation of perfluorinated amines by a novel [1,3]-proton shift reaction. However, all of these methods require fluorinated ketones. Nucleophilic transfer of "CF_3" to nitrones and imines for direct preparation of trifluoromethylated amines was recently achieved by Nelson et al.[7] and Blazejewski et al.,[8] respectively. These methods suffer from low yield and lack generality. We now report the first stereoselective synthesis of trifluoromethylated amines by using $TMSCF_3$ **2** (TMS = $SiMe_3$).

Our systematic investigation began as an extension of our earlier work,[9] based on the fact that imines are less electrophilic than carbonyl compounds, and that O–Si bonds are stronger than N–Si bonds. We predicted that strongly electrophilic imines might be a solution to this problem under noncatalytic conditions. When *N*-sulfonylaldimines[10] were used as imine sources the reaction indeed proceeded smoothly in the presence of CsF and gave only the trifluoromethylated adducts in 45–95% yield. Next we turned our attention to sulfinylimines **1** to make this reaction stereoselective. When chiral sulfinylimines[11] were subjected to similar reaction conditions little or no products were obtained. Sulfinylimines were recovered intact, but $TMSCF_3$ decomposed. We surmised that sulfinylimines are not reactive enough to add $TMSCF_3$. Use of different aprotic solvents and excess of reagents was not helpful. When an excess of $TMSCF_3$ was used, a number of unidentified fluorinated products with little or none of the expected adduct were obtained. TMS-Imidazole,[8] was recently reported to facilitate addition of $TMSCF_3$ to imines. In our case, however, it was ineffective. In all experiments the starting material was recovered.

The above results indicate that $TMSCF_3$ decomposes prior to reacting with the starting material. Hence, we thought that increasing the substrate concentration might be a solution to this problem. Indeed, when neat $TMSCF_3$ was added to a concentrated solution of the imines, the desired adduct was obtained. The mass balance corresponds to recovered starting material. Attempts to complete the reaction by using excess of reagent in different solvents was, however, unsuccessful. Imines were treated with $TMSCF_3$ in the presence of a stoichiometric amount of CsF to give the corresponding trifluoromethylated sulfinamides in 50–65% yields of isolated products (Table 1, entries 1–7, values in parentheses). Imines with acidic α-hydrogen atoms gave lower yields because of competitive deprotonation. The diastereoselectivity was not very high.

During these investigations we thus encountered two problems: a) Conversion of imines was incomplete even in the presence of excess $TMSCF_3$ and CsF; b) imines with an α-hydrogen atom failed to react with $TMSCF_3$ because of the basic nature of CsF. However, we overcame these problems by employing a nonmetallic fluoride source. DeShong et al. reported that tetrabutylammonium difluorotriphenylsilicate (TBAT),[12] a soluble fluoride source, is very effective for nucleophilic displacement reactions. We found that TBAT is also effective in our system. Reaction of *N*-sulfonylaldimines

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[**] Support of our work by Loker Hydrocarbon Research Institute is gratefully acknowledged.

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