Chemical Impact on a Seemingly "Inert" Material: An Electron Microscopic Case Study of Titanium Activated by Chlorosilanes

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Commercial titanium powder, after pretreatment with chlorosilanes, can be used as an "off-the-shelf" McMurry reagent for various types of carbonyl coupling reactions. Electron microscopic studies (SEM, TEM, HRTEM, and electron diffraction) of the activated titanium now reveal the morphological basis for the observed reactivity, which stems from a partial degradation of the passivating oxide layer on the surface as well as from a severe change of the inner structure of the particles. Therefore, altered surface *and* altered bulk properties cooperatively account for the chemical reactivity of titanium metal activated by purely chemical means. ^{29}Si NMR investigations fully support this view.

Introduction

The "organic chemistry" of titanium is known only since methods have been devised which allow the preparation of highly activated forms of this metal.[1] All of these procedures essentially rely on the reduction of $TiCl_x$ ($x = 3, 4$) with an appropriate reducing agent in rigorously anhydrous solvents under argon. Although this concept was very successful in preparative terms and has reached a high degree of sophistication,[2,3] it suffers from the inherent inconvenience of requiring advanced preparative techniques and hazardous reagents.

In striking contrast, the use of *commercial* titanium as a "chemical" was in vain for decades. Because of an exceptional resistance to almost any kind of chemical attack in combination with a high mechanical strength and low density, this material is ideally suited for applications in industrial plants, marine equipment, aircraft frames, surgical implants, etc.[4] Titanium mimics the stability of the noble metals due to the formation of a thin, dense, adherent, nonporous, and repairable oxide layer on its surface which renders it inert against hot alkali, mineral acids, and even aqua regia in the cold, just to mention a few. Moreover, it is protected against amalgamation and resists cavitation by ultrasound.[4]

Only recently, this chemical insensitivity was mastered. During a study on low-valent titanium-catalyzed intramolecular oxo−amide cyclization reactions we discerned that titanium oxides formed in situ as the inorganic byproducts of this process react reasonably well with admixed chlorosilanes, most likely by a metathetic ligand exchange.[5] Since a similar process may also allow degradation of the passivating layer on commercial titanium, we have reevaluated its capacity as an off-the-shelf reagent for reductive C−C-bond formations of the McMurry type.[5] In fact, it turned out that mixtures of commercial titanium powder and simple chlorosilanes (Me_3SiCl, Et_3SiCl, $Ph_2MeSiCl$, etc.) in boiling THF or DME efficiently induce various intermolecular as well as intramolecular coupling reactions of aromatic or α,β-unsaturated aldehydes and ketones. Among others, retinal **1** can be dimerized to β-carotene **2** in high yield,[5] diketones will undergo efficient macrocyclization reactions (e.g. **3 → 4**),[5,6] and benzofurans and indoles are formed from oxo ester or oxo amide precursors (e.g. **5 → 6**),[5,7] respectively (Scheme 1). These preparative data pinpoint the fact that commercial titanium can be conveniently activated and

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(3) (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513−1524. (b) Lectka, T. in ref 10a, p 85−131. (c) Robertson, G. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 563−611.

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(6) For a comparison of Ti/TMSCl with conventional McMurry reagents, see: Fürstner, A.; Seidel, G.; Kopiske, C.; Krüger, C.; Mynott, R. *Liebigs Ann.* **1996**, 655−662.

(7) For titanium-induced heterocycle syntheses, see: (a) Fürstner, A.; Hupperts, A.; Ptock, A.; Janssen, E. *J. Org. Chem.* **1994**, *59*, 5215−5229. (b) Fürstner, A.; Weintritt, H.; Hupperts, A. *J. Org. Chem.* **1995**, *60*, 6637−6641. (c) Fürstner, A.; Ernst, A.; Krause, H.; Ptock, A. *Tetrahedron* **1996**, *52*, 7329−7344. (d) Fürstner, A.; Ptock, A.; Weintritt, H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 678−681. (e) Fürstner, A.; Jumbam, D. N. *Tetrahedron* **1992**, *48*, 5991−6010. (f) Fürstner, A.; Jumbam, D. N.; Weidmann, H. *Tetrahedron Lett.* **1991**, *32*, 6695−6696. (g) Fürstner, A.; Jumbam, D. N. *J. Chem. Soc., Chem. Commun.* **1993**, 211−212. (h) Fürstner, A.; Jumbam, D. N.; Seidel, G. *Chem. Ber.* **1994**, *127*, 1125−1130. (i) Fürstner, A.; Ernst, A. *Tetrahedron* **1995**, *51*, 773−786.

Scheme 1
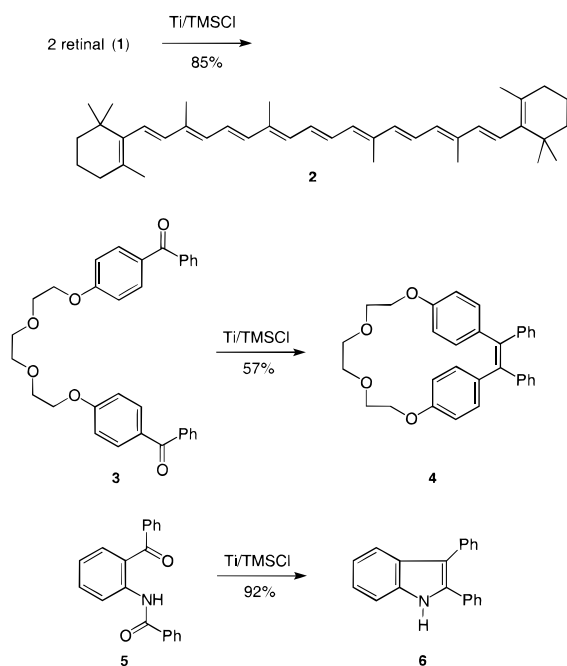
kept active under unprecedentedly mild conditions which are compatible with the requirements of sensitive organic compounds.

This constitutes a significant preparative advancement compared to existing methodology.[2,3] The origin of the observed chemical reactivity of bulk titanium in the presence of Me₃SiCl, however, remains highly speculative on a molecular level perspective. Moreover, comparisons with other metal/activator systems are elusory since (i) commonly used depassivation methods[8] completely fail when applied to titanium and (ii) only a few conclusive reports are known in the literature which explain the effects of additives on the reactivity of a given metal on a morphological basis.[9,10] Therefore, we undertook a detailed electron microscopic and spectroscopic investigation of the Ti/chlorosilane reagent combination. The results of this study shed some light on the intricate ties between the structural features and the chemical response of an activated metal system.

Results and Discussion

Commercial titanium used as the starting material for this investigation does not show any structural peculiarities, as can be seen from the micrographs depicted in Figure 1. Thus, scanning electron microscopy (SEM) at different magnifications (Figure 1a,b) shows the irregular shapes and the rather smooth surface of the particles. The transmission electron micrograph (TEM, Figure 1c) as well as the electron diffraction pattern (Figure 1d) indicate large crystalline domains characteristic for α-Ti.

This situation changes dramatically upon treatment of this sample with an excess of a chlorosilane (Me₃SiCl or Et₃SiCl, vide infra) in an ethereal solvent at reflux for 70 h. For analytical purposes, some of the activations have been carried out in THF-d_8. The samples were filtered under argon, the insoluble material was carefully rinsed with the same solvent, and the activated titanium powder and the filtrate thus obtained were analyzed independently. Control experiments in which oxo amide **5** was added to the greenish filtrate did not lead to the formation of indole **6**, even after prolonged heating. This excludes that a reactive titanium species has been solubilized during the activation phase and makes sure that it is the slurry of commercial Ti in combination with R₃SiCl which accounts for the observed results.

SEM images of the activated particles show that their overall size is more or less unchanged and remains in the micron range (Figure 2a). However, all other features evident from Figures 2 and 3 denote substantial perturbations of the entire particles caused by this chemical treatment. Specifically, their rough appearance, clearly visible in the SEM image at higher resolution (Figure 2b), reflects the impact of the chlorosilane on the surface oxide coating. Much more striking are the *profound morphological changes of the inner structure* of the particles (TEM, Figure 2c). It is apparent that the chlorosilane attacks grain boundaries and leads to a significant shrinking or even the breakdown of the crystalline domains, thus giving rise to a matrix containing only few and fairly small ordered zones in the subsurface area (cf. lattice fringes in Figure 3a).[11] To assess the effective range of this morphological perturbation, the activated titanium powder was embedded in an epoxy resin and then cut with an ultramicrotome. TEM investigations of samples thus prepared reveal that the R₃SiCl treatment disturbs the crystal structure throughout the particles, although they are several microns in diameter. In addition, EDX (energy dispersive X-ray) analyses detect traces of chlorine and silicon in all areas of such cross sections (Figure 3b), i.e. at the border as well as in the core. These chemically induced topotactic changes are also evident from the substantial alterations of the electron diffraction pattern of the sample, which confirms its microcrystalline and in some parts even amorphous character (Figure 2d).

²⁹Si NMR investigations of the supernatant liquid collected after the activation phase and after carrying

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(9) See the following for leading studies on the morphology of activated metal systems: (a) Hill, C. L.; Vander Sande, J. B.; Whitesides, G. M. *J. Org. Chem.* **1980**, *45*, 1020−1028. (b) Root, K. S.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 5475−5479. (c) Teerlinck, C. E.; Boyer, W. J. *J. Org. Chem.* **1996**, *61*, 1059−1064. (d) Koon, S. E.; Oyler, C. E.; Hill, J. H. M.; Bowyer, W. J. *J. Org. Chem.* **1993**, *58*, 3225−3226. (e) Suslick, K. S.; Doktycz, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 2342−2344. (f) Suslick, K. S.; Casadonte, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 3459−3461. (g) Suslick, K. S.; Casadonte, D. J.; Doktycz, S. J. *Chem. Mat.* **1989**, *1*, 6−8. (h) Pétrier, C.; Luche, J. L.; Lavaitte, S.; Morat, C. *J. Org. Chem.* **1989**, *54*, 5313−5317. (i) Souza-Barboza, J.; Pétrier, C.; Luche, J. L. *J. Org. Chem.* **1988**, *53*, 1212−1218. (j) Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. *J. Org. Chem.* **1991**, *56*, 698−703. (k) Fürstner, A.; Weidmann, H.; Hofer, F. *J. Chem. Soc., Dalton Trans.* **1988**, 2023− 2026. (l) Fürstner, A.; Hofer, F.; Weidmann, H. *Carbon* **1991**, *29*, 915− 919. (m) Klabunde, K. J.; Efner, H. F.; Murdock, T. O.; Ropple, R. *J. Am. Chem. Soc.* **1976**, *98*, 1021−1023 and literature cited.

(10) Reviews: (a) *Active Metals. Preparation, Characterization, Applications;* Fürstner, A., Ed.; VCH: Weinheim, 1996. (b) Fürstner, A. *Angew. Chem.* **1993**, *105*, 171−197. Fürstner, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 164−189.

(11) BET analyses shows that the chlorosilane activation also leads to a significant increase of the specific surface area of the titanium from 5.8 to 48.1 m² g⁻¹.
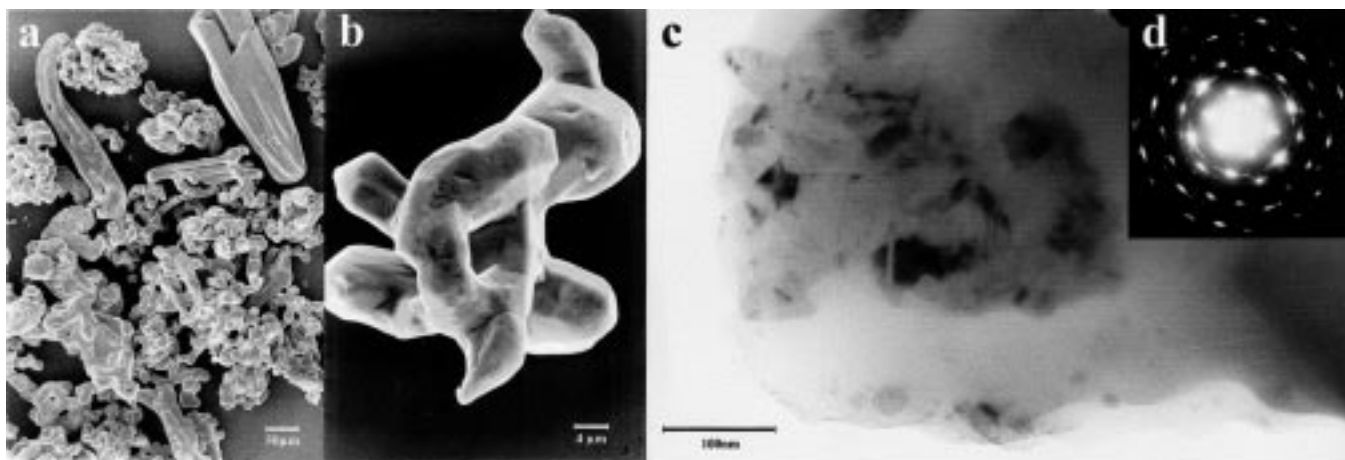
Figure 1. Electron microscopic investigation of commercial titanium powder: (a) SEM image (low resolution), (b) SEM image (high magnification), (c) TEM image, (d) electron diffraction.
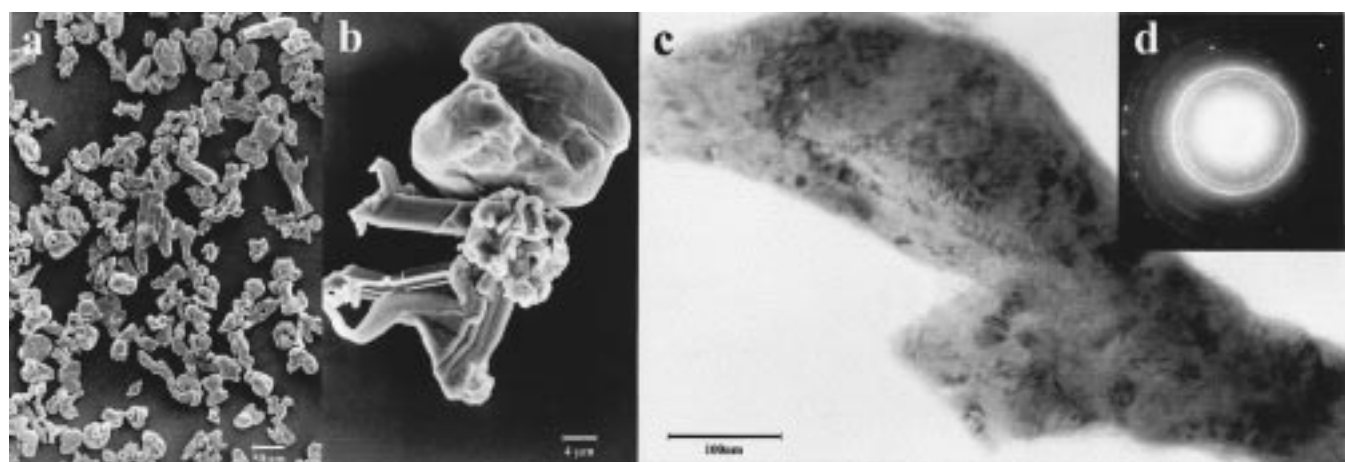
Figure 2. Electron microscopic investigation of commercial titanium powder activated with triethylchlorosilane: (a) SEM image (low resolution), (b) SEM image (high magnification), (c) TEM image, (d) electron diffraction.

out a carbonyl coupling reaction, respectively, provide additional information. Thus, treatment of Ti powder with Et$_3$SiCl (δ 35.4 ppm) in refluxing THF-d_8 for 70 h under Ar reproducibly leads to the formation of small amounts of Et$_3$SiOSiEt$_3$ (δ 8.9 ppm) and of Et$_3$SiSiEt$_3$ (δ −22.9 ppm) (Figure 4). While the disiloxane may result from the degradation of the oxidic passivating layer by the chlorosilane, the presence of the disilane indicates that Et$_3$SiCl gets access to a highly reducing and hence "low-valent" titanium species at the solid/liquid interface. NMR inspection of the same reaction mixture after addition of substrate **5** and its complete conversion into indole **6** clearly shows that only the disiloxane signal gains intensity at the expense of the chlorosilane during the coupling process, whereas the disilane peak does not increase any further.

Control experiments made sure that the Et$_3$SiOSiEt$_3$ detected by NMR neither derives from extraneous OH-containing contaminants nor from a reaction of the chlorosilane with the glassware. Note also that Et$_3$SiCl rather than Me$_3$SiCl was chosen for these spectroscopic investigations: the higher boiling points of this compound and derivatives thereof strictly preclude that any silicon-containing byproduct formed upon reaction with the titanium powder is lost during sample preparations. The results summarized in Table 1, however, demonstrate that Et$_3$SiCl and Me$_3$SiCl are equally efficient

activating agents for titanium in preparative terms, with the latter being preferred in large-scale reactions due to its low cost.

It is known that the reaction of *alkyl* chlorides with metallic titanium at ≤250 °C leads to the formation of a titanium hydride phase at the surface of the metal and the concomitant release of an alkene/alkane mixture.[12] Although the distinctly different chemistry of silyl chlorides make a similar process unlikely,[13] we investigated if gas evolves from titanium activated by Me$_3$SiCl under thermal desorption conditions (→350 °C). Only minute amounts of hexamethyldisiloxane, hexamethyl(cyclotrisiloxane), and HCl have been observed by MS, but no H$_2$ evolution at all could be detected, thus making a significant amount of a hydridic phase rather unlikely.

The chemical resistance of titanium has been empirically probed in great detail,[4] but very little is known about the native superficial oxide film which is responsible for it.[14,15] The thickness of this layer remains in

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(13) β-Hydride elimination, which seems to be resonsible for the release of alkenes from alkyl chlorides/Ti, is unlikely in the case of R$_3$SiCl/Ti, due to the reluctance of silicon to form Si=C bonds; see: Weber, W. P. *Silicon Reactions in Organic Synthesis*; Springer: Berlin, 1983 and literature cited.
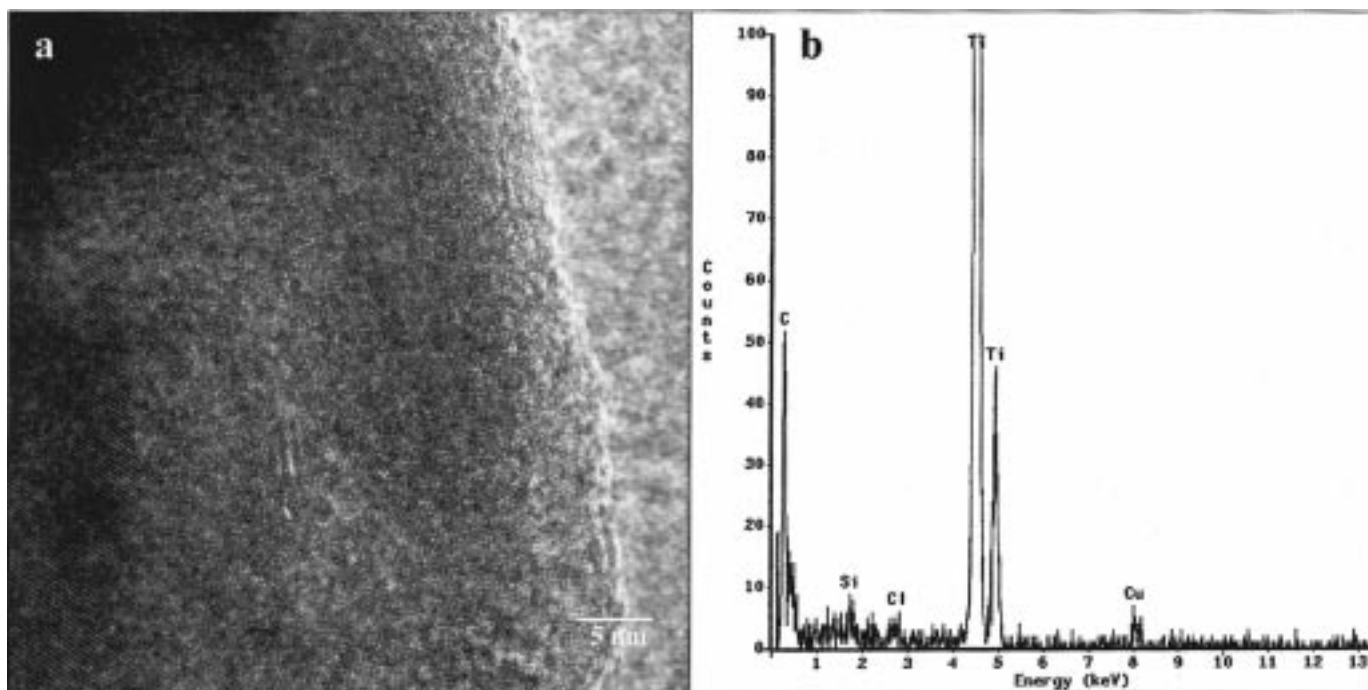
Figure 3. Electron microscopic investigation of commercial titanium powder activated with triethylchlorosilane: (a) HRTEM (high-resolution transmission electron microscopy) image of the subsurface area and (b) EDX spectrum of the sample area shown in panel a.
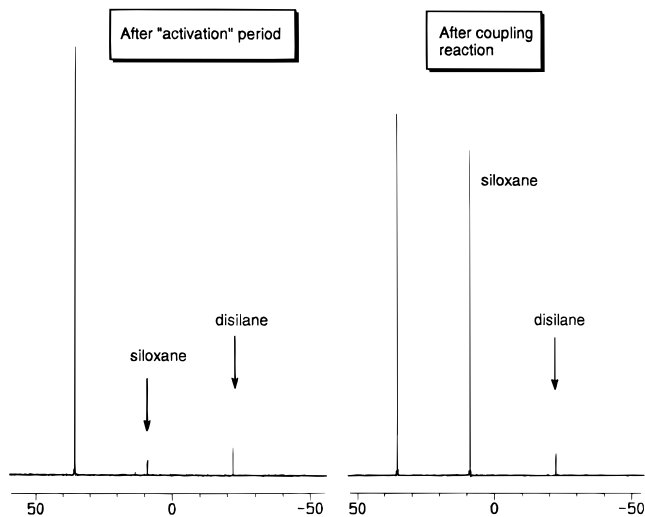
Figure 4. ^{29}Si NMR spectra (16 000 scans) of the reaction mixture after the activation of commercial titanium (Ti, Et$_3$-SiCl, THF-d_8, 70 h, reflux), and of the reaction mixture after effecting the conversion of oxo amide **5** into indole **6**. The signal at δ 35.4 ppm in both spectra is due to excess Et$_3$SiCl.

a low range ($\leq$6 nm) and the local ordering at the very surface is believed to be close to that of TiO$_2$ (rutile),[16] although substoichiometric compositions at the Ti/TiO$_2$ interface may complicate matters. In view of the paucity of secured information on the "parent" titanium samples, the reasons for the severe damage caused by

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Table 1. Solvent Effects in the Reductive Indole Formation Induced by Commercial Titanium Powder Activated by Chlorosilanes[a]
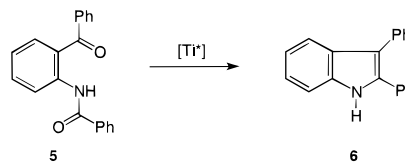
entry	solvent	R$_3$SiCl	time (h)	GC yield (%)	isolated yield (%)
1	THF	Me$_3$SiCl	21	99	
2	THF	Et$_3$SiCl	25	95	
3	DME	Me$_3$SiCl	19	>99	92
4	DME	Et$_3$SiCl	25	>99	90
5	EtOAc	Me$_3$SiCl	25	>99	
6	pyridine	Me$_3$SiCl	42	98	94
7	MeCN	Me$_3$SiCl	48	1[b]	
8	DME/MeCN (100/1)	Me$_3$SiCl	39	1[b]	

[a] All reactions were carried out at reflux in the given solvent under Ar using 3−5 mol of Ti powder and 3−5 mol of R$_3$SiCl/mol of substrate. [b] Starting material recovered unchanged.

R$_3$SiCl in a rather moderate temperature regime (60−90 °C) must remain somewhat speculative, and the following discussion trying to rationalize our experimental results is therefore necessarily tentative.
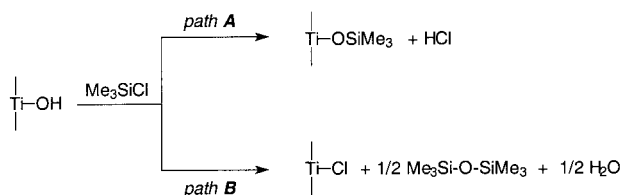
It is well-established that terminal OH groups of oxidic surfaces can react with chlorosilanes in two different ways, either by simple silanization (Scheme 2, path A) or by substitution of the OH for Cl (Scheme 2, path B).[16−19]

Path A will hardly lead to a low-valent titanium species as required for McMurry couplings. However, if OH groups on the surface are replaced by Cl, a subsequent conproportionation of the titanium (oxy)-halide initially formed with the bulk Ti(0) underneath may lead to an ensemble of "low valent" titanium (oxy)-

Scheme 2

halide species exposed to the substrate at the solid/liquid interphase. This process creates initiation sites for pitting and crevice corrosion and communicates the structural changes occurring at the boundary to the interior of the particle, thus effecting the severe perturbation of the core structure, as visible in TEM and HRTEM.[20] It is important to note that Ti^{n+} ($0 \leq n < 3$) species rather than Ti(0) are the active principles in "classical" McMurry reactions, as has been proved by Bogdanovic et al.[2,21] Moreover, model studies of Barteau et al. have shown that TiO_2 single crystals—after sputtering off the terminal oxygen atoms by bombardement with Ar^+—expose defect sites containing Ti^{n+} ($0 < n \leq 3$) cations which were also found to induce reductive C−C-bond formations.[22]

The ^{29}Si NMR results summarized above are very well in line with the assumed OH for Cl exchange process as an elementary step of the activation process. It may be possible to favor this pathway over the competing silanization[16−19] of the surface hydroxyl groups by the proper choice of the reaction medium. Therefore, we carried out several coupling experiments in different solvent systems (Table 1). While THF, DME, EtOAc, and even pyridine lead to active titanium samples, the use of MeCN does not entail any reactivity. Even minor amounts of MeCN admixed to DME suffice to suppress a subsequent McMurry-type reaction (Table 1, entries

7 and 8). It is not yet possible to fully rationalize this somewhat unexpected but very pronounced solvent effect. However, MeCN is known to be a particularly effective medium for surface modifications of TiO_2, for example, by O-acylation of its superficial hydroxyl groups.[23] Therefore, one may speculate that a rapid silanization of the superficial OH groups according to Scheme 2, path A, takes place in this particular solvent,[24] leading to a titanium sample that does not react any more even if the MeCN is filtered off and replaced by fresh DME/Me_3SiCl. This is in fact the case (cf. the Experimental Section). However, the initial activity can be restored on addition of catalytic amounts of, for example, $ZnCl_2$ due to the known lability of silyl ethers toward Lewis acids.[25]

Although further investigations are required in order to probe the elementary steps leading to the activation of commercial titanium in more detail, the data summarized above indicate that the reactivity of commercial titanium simply activated by chlorosilanes stems *from altered surface and from altered bulk properties*. In view of the fact that Me_3SiCl is widely used as an initiating agent for various kinds of metal-induced reactions,[26,27] our study suggests the re-evaluation of its mode of action in other relevant cases as well. Studies along these lines are currently in progress.

Experimental Section

General. Commercial titanium powder (Alfa, Johnson Matthey, 325 mesh, 99.4%) was carefully rinsed with hexane and then dried in vacuo (10^{-4} Torr) at 50 °C for 8 h prior to use. Me_3SiCl (Aldrich, 99+%) and Et_3SiCl (Aldrich, 99%) were redistilled under Ar. The solvents used were distilled over the following drying agents and transferred under Ar: THF-d_8 ($LiAlH_4$), THF (Mg−anthracene), DME (Na/K alloy), pyridine (KOH), and MeCN (P_4O_{10}). All manipulations were carried out under Ar using Schlenk techniques.

Instrumentation. ^{29}Si NMR spectra were recorded on a Bruker AMX-400 spectrometer (79.5 MHz); shifts (δ) are given in ppm relative to TMS. MS were recorded with a Finnigan MAT 8200. The SEM micrographs were taken by means of an ISI 60 operated at 15 kV acceleration voltage. The transmission electron microscopy (TEM) was carried out on a Hitachi HF 2000 operated at 200 kV, which is equipped with a cold field emitter gun and a VOYAGER EDX-system with a

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(20) Eventual mobility of the titanium oxy chlorides formed may also contribute to transmit the chemical reactions at the surface to the interior of the particle; for a discussion of related effects of FeO_x-Cl_y species on oxide surfaces, see: Klabunde, K. J.; Stark, J.; Koper, O.; Mohs, C.; Park, D. G.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. *J. Phys. Chem.* **1996**, *100*, 12142−12153.

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(23) Wada, Y.; Tomita, K.; Murakoshi, K.; Yanagida, S. *J. Chem. Res. (M)* **1996**, 1801−1816 and ref cited.

(24) This interpretation is supported by IR studies on Ti powder treated with Me_3SiCl in MeCN, which show weak bands ascribed to −O−Si bonds.

(25) We cannot rigorously exclude that MeCN simply "poisons" the active sites on the surface, because nitriles bind to low-valent titanium with rather high affinity. However, the fact that MeCN was found to be a suitable solvent for indole syntheses induced by $TiCl_3$ cat./TMSCl/Zn renders this scenario rather unlikely. For selected references on low-valent titanium−nitrile complexes, see: (a) Fowles, G. W. A.; Lester, T. E. *Chem. Commun.* **1967**, 47−48. (b) Clark, R. J. H.; Machin, D. J.; Nyholm, R. S. *J. Chem. Soc.* **1963**, 379−387. (c) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem.* **1985**, *97*, 425−426.

(26) For recent studies on $Cr(II)/Me_3SiCl$, see: (a) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 2533−2534. (b) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349−12357. (c) Fürstner, A. *Chem. Eur. J.* **1998**, *4*, 567−570.

(27) See the following for leading references: (a) Lautens, M.; Ren, Y. *J. Org. Chem.* **1996**, *61*, 2210−2214. (b) Ohno, T.; Ishino, Y.; Tsumagari, Y.; Nishiguchi, I. *J. Org. Chem.* **1995**, *60*, 458−460. (c) Picotin, G.; Miginiac, P. *J. Org. Chem.* **1987**, *52*, 4796−4798. (d) Takai, K.; Kakiuchi, T.; Utimoto, K. *J. Org. Chem.* **1994**, *59*, 2671−2673. (e) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390−2392. (f) Takai, K.; Ueda, T.; Hayashi, T.; Moriwake, T. *Tetrahedron Lett.* **1996**, 7049−7052.

Si detector (NORAN) cooled with liquid nitrogen. For thin section preparations, the Ti powder was embedded in a spurr medium and cut by means of an ultramicrotome (ULTRACUT FC4, Reichert). The thickness of the sections thus prepared is 50−70 nm.

Sample Preparation. A Schlenk tube (15 mL) was flame dried and cooled to ambient temperature in vacuo (10^{-4} Torr) before it was flushed with Ar. It was then charged with commercial titanium powder (0.50 g, 10.4 mmol), THF-d_8 (5 mL), and Et$_3$SiCl (2 mL, 11.9 mmol), and the suspension was refluxed for 70 h. The mixture was filtered off under Ar, and the particles were thoroughly washed with THF-d_8 (2 mL in several portions) and dried in vacuo (10^{-2} Torr, 2 h) prior to electron microscopic analysis. An aliquot of the filtrate was transferred via cannula into a thoroughly dried NMR tube for ^{29}Si NMR inspection (16 000 scans).

Control Experiment Concerning the Siloxane Formation. A flame-dried Schlenk tube (15 mL) was charged with THF-d_8 (5 mL) and Et$_3$SiCl (2 mL) and the mixture was refluxed for 70 h. Samples were taken as described above. ^{29}Si NMR inspection (16 000 scans) showed unchanged Et$_3$SiCl, but no disiloxane peak could be detected.

Control Experiment Concerning the Activity of the Filtrate. A flame-dried Schlenk tube (50 mL) was charged with commercial titanium powder (2.0 g, 41.8 mmol), THF (20 mL), and Me$_3$SiCl (5 mL, 39.4 mmol). The suspension was refluxed for 70 h, the titanium particles were filtered off, oxo amide **5** (250 mg, 0.83 mmol) was added to the greenish filtrate, and the resulting homogeneous mixture was refluxed for 20 h. After this reaction time, however, no indole **6** could be detected (GC, TLC), and substrate **5** was found to be unchanged.

Passivation/Depassivation of Titanium in MeCN. A flame-dried Schlenk tube (100 mL) was charged with commercial titanium powder (4.86 g, 101.5 mmol), MeCN (50 mL), and Me$_3$SiCl (15 mL, 118 mmol), and the mixture was stirred at 90 °C for 120 h. The titanium was filtered off, rinsed with MeCN (ca. 10 mL in several portions), and thoroughly dried in vacuo (10^{-2} Torr, 2 h).

A suspension of this pretreated Ti (116 mg, 2.42 mmol), oxo amide **5** (244 mg, 0.81 mmol), and Me$_3$SiCl (0.4 mL, 3.15 mmol) in DME (10 mL) was refluxed for 23 h. After that time no indole **6** could be detected by GC and TLC, whereas substrate **5** was found to be unchanged (GC 98.7%).

ZnCl$_2$ (11 mg, 0.08 mmol, 10 mol %) was then introduced and reflux continued for another 21 h. GC control indicated a complete conversion of substrate **5** into indole **6** (97.5%). This product was isolated by filtration, evaporation of the solvent, and flash chromatography (hexane/ethyl acetate 2/1) as colorless crystals (196 mg, 90%), the analytical and spectroscopic data of which are in full accordance with those previously reported.[7e]