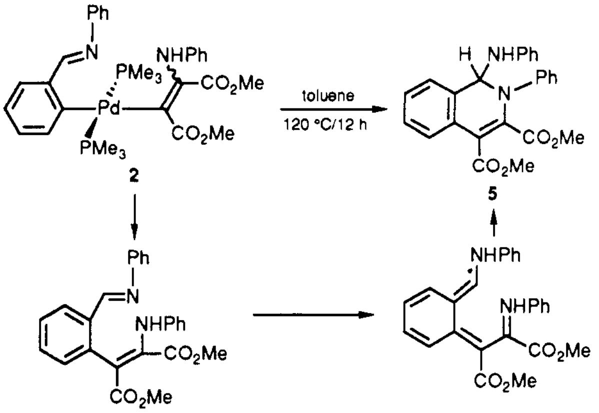
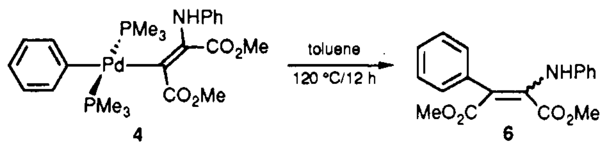


(3)

Structure elucidation of **5** was assisted by 2D COSY ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. A mechanism that is consistent with the formation of **5** involves thermally induced reductive elimination of the two organic substituents followed by a formal [1,7]-sigmatropic shift and rearrangement to regain aromaticity. Although sigmatropic shifts of this nature involving heteroatoms are not common,[13] they are symmetry-allowed rearrangements.[14] Both isomers of **2** lead to the formation of **5**; however, it is not known if reductive elimination occurs first, followed by generation of the *Z* isomer of the styrene intermediate or if only the *Z* isomer of **2** reductively eliminates and cyclizes. Thermolysis of **4** under the same conditions as **2** afforded the substituted styrene **6** (eq 4).[15] A broad singlet at 11.07 ppm and two singlets at 3.31 and 2.91 ppm in the ^{1}H NMR spectrum of **6** are assigned to the amine and methoxy protons, respectively.

The potential of these palladium–amido complexes to facilitate carbon–nitrogen bond formation has been demonstrated by the thermal generation of the trisubstituted



(4)

dihydroisoquinoline **5** from compound **2**. Although the synthesis of dihydroisoquinolines can be achieved by conventional organic methods, they can be limited by reaction conditions and availability of starting materials.[16] The synthesis of *N*-alkylisoquinolinium salts via the reaction between *cationic* palladium complexes and acetylenes is known.[17] The formation of other heterocycles by the reaction of metallated palladium complexes with acetylenes is also known;[18] however, these reactions proceed by insertion of the acetylene into the metal–carbon bond rather than the metal–nitrogen bond. Research involving the reaction of **1** and **3** with other substituted acetylenes is currently in progress in order to determine whether less electrophilic substrates will undergo similar reactions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Text giving experimental details of the synthesis of compounds **1**–**6**, tables of NMR data for **1**–**6**, and X-ray crystal structure details and tables of fractional coordinates, thermal parameters, and bond distances and angles for **4** (25 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of an Organotitanium Hydroxide Containing an O–H–O Bond

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Summary: The preparation of the first binuclear titanium hydroxide containing an O–H–O bond is described. The X-ray structural analysis indicates that steric factors prevent the elimination of water.

Organotitanium compounds are the most widely used reagents for the synthesis of basic organic compounds and polymers.[1] To the best of our knowledge there are no reports on multinuclear Ti(IV) hydroxides.[2,3] Compounds of this type might play an important role in condensation and epoxidation reactions.

According to Parshall[4] Re, Cr, Mo, V, Zr, and Ti are active catalysts in this field. Our interest in model compounds for metal oxides on silica surfaces[5] prompted us

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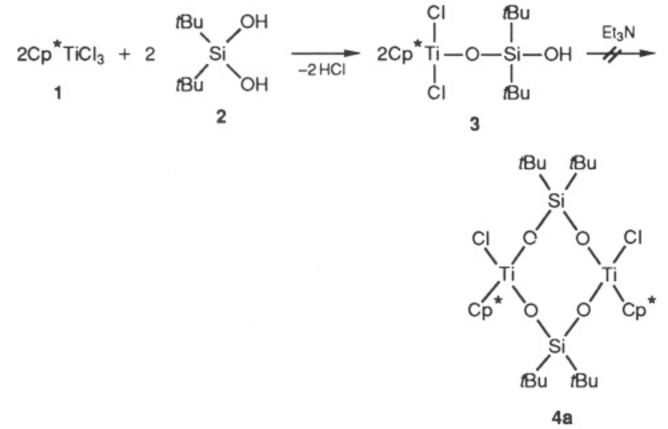
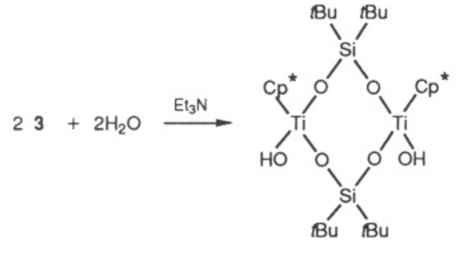
to study hydrolysis reactions of titanium compounds.

This paper describes the preparation and characterization of the first titanium hydroxide containing an O–H–O bond.

The reaction of Cp^*TiCl_3 (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$)[6] with $(tBu)_2Si(OH)_2$[7] (**2**) in a molar ratio of 1:1 gives $Cp^*TiCl_2OSi(tBu)_2OH$[8] (**3**). The hydrolysis of **3** leads to the target molecule $[Cp^*Ti(OH)OSi(tBu)_2O]_2$[9] (**4**). Regarding the reaction pathway, it is interesting to mention that **3** is not converted to **4a** with elimination of HCl in the presence of Et_3N.





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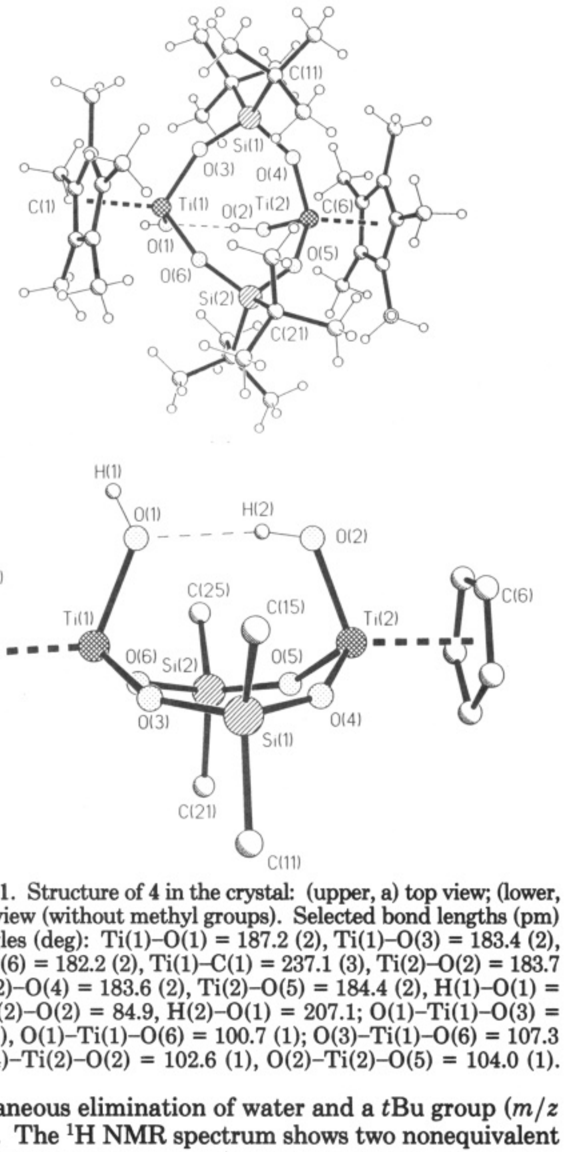

Figure 1. Structure of **4** in the crystal: (upper, a) top view; (lower, b) side view (without methyl groups). Selected bond lengths (pm) and angles (deg): Ti(1)–O(1) = 187.2 (2), Ti(1)–O(3) = 183.4 (2), Ti(1)–O(6) = 182.2 (2), Ti(1)–C(1) = 237.1 (3), Ti(2)–O(2) = 183.7 (2), Ti(2)–O(4) = 183.6 (2), Ti(2)–O(5) = 184.4 (2), H(1)–O(1) = 83.7, H(2)–O(2) = 84.9, H(2)–O(1) = 207.1; O(1)–Ti(1)–O(3) = 103.0 (1), O(1)–Ti(1)–O(6) = 100.7 (1); O(3)–Ti(1)–O(6) = 107.3 (1), O(4)–Ti(2)–O(2) = 102.6 (1), O(2)–Ti(2)–O(5) = 104.0 (1).

Compound **4** is a yellow, crystalline solid showing characteristic OH absorptions (3665 and 3220 cm^{-1}) in the IR spectrum. FD mass spectroscopy of **4** indicates $M^+ - OH$ ($m/z = 731$) and $M^+ - tBu$ ($m/z = 691$) as well as the simultaneous elimination of water and a *t*Bu group ($m/z = 693$). The ^1H NMR spectrum shows two nonequivalent signals for the *t*Bu groups (intensity ratio 1:1, δ 0.95, 0.96 ppm) and one for each of the methyl (δ 2.06 ppm) and OH protons (δ 7.9 ppm, broad). The ^1H NMR spectrum in solution is consistent with the X-ray crystal structure. The Cp* groups are both on the same side of the molecule, resulting in nonequivalent *t*Bu groups. The protons of the OH group in **4** show rapid exchange, when D_2O is added to a sample in an NMR tube. The OH signals (δ 7.9 ppm) disappear, while the water signals (δ 4.8 ppm) are increased. Compound **4** is completely decomposed in water after several days; however, in the solid state in open air decomposition is not observed. Compound **4** has been completely characterized by a single-crystal X-ray analysis[10] (Figure 1).

The side view in Figure 1 shows an eight-membered ring in a boat form where one hydrogen atom (H(2)) of the OH groups forms a transannular bridge while the other hy-

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(8) Compound **3**: A solution (0.87 g, 3 mmol) of **1** in toluene (50 mL) is added dropwise to a mixture of **2** (0.43 g, 3 mmol) and Et_3N (0.31 g, 3 mmol) in toluene (30 mL) at −30 °C. After the addition is complete, the solution is stirred at room temperature for 4 h and finally for 0.5 h at 70 °C. The solution is filtered and concentrated (7 mL). After addition of hexane (10 mL) and a cooling process (−34 °C), 1.2 g (95%) of orange colored crystals is obtained; mp 125 °C. Anal. Calcd for $C_{18}H_{34}Cl_2O_2SiTi$ (M_r 429.3): C, 50.36; H, 7.98; Cl, 16.52. Found: C, 50.1; H, 7.7; Cl, 16.3. ^1H NMR ($CDCl_3$, TMS): δ 1.04 (s, 18 H), 2.24 (s, 15 H), 2.25 (s, 1H). ^{29}Si NMR ($CDCl_3$, TMS): δ −6.7. MS (EI): m/z 371 ($M^+ - Bu$). IR (KBr): 3608 s, 2961 s, 2931 s, 1471 s, 975 vs, 825 s, 799 s, 647 s, 450 s, 391 s cm^{-1}.

(9) Compound **4**: A solution of H_2O (0.072 g, 4 mmol) and of Et_3N (1.01 g, 10 mmol) in THF (5 mL) is added dropwise at 0 °C to a solution of **3** (1.72 g, 4 mmol) in toluene (60 mL). During the addition a white solid is formed. The color of the solution changed from orange to yellow. After 2 h the white solid is recovered by filtration and washed with toluene (20 mL). The filtrate is evaporated to dryness in vacuo and the residue recrystallized from THF/hexane (1:1) to give a yellow crystalline solid (1.39 g, 93%) of **4**, mp 223 °C. Anal. Calcd for $C_{36}H_{68}O_6Si_2Ti_2$ (M_r 748.9): C, 57.74; H, 9.15; Si, 7.50; Ti, 12.79. Found: C, 58.0; H, 9.1; Si, 7.5; Ti, 12.3. IR (Nujol) 3666 m, 3210 br m, 931 s, 913 s, 826 m, 821 m, 682 m, 647 m, 426 m cm^{-1}. ^{29}Si NMR ($CDCl_3$, TMS): δ −19.3 (s).

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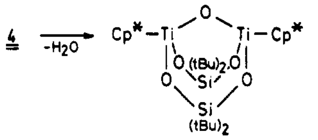
(10) (a) Crystallographic data for **4** (−150 °C): monoclinic, $a = 1208.3$ (2) pm, $b = 2113.6$ (2) pm, $c = 3195.9$ (10) pm, $\beta = 90.54$ (2)°, $V = 8.162$ (3) nm^3, space group $C2/c$, $Z = 8$, $\rho_{calcd} = 1.22$ Mg m^{-3}, 7177 independent reflections ($F_o > 4\sigma(F_o)$), $2\theta = 7\text{–}50°$, weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$, refinement $R = 4.94\%$, R_w 5.48, for all data. (b) Further details of the structure determination (atomic coordinates, complete bond lengths and angles, structure factors, and displacement parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote the full literature citation and the reference number (CSD 56398).

drogen atom is end-on bonded. The hydrogen bridge (H(2)–O(1)) gives an increase of the coordination number at O(1), resulting in an increase of the Ti(1)–O(1) bond length (187.2 (2) pm). Normally a water molecule would result and then be eliminated. In this case, however, steric factors prevent the reaction of the OH groups. A frozen situation results. We have not been able to eliminate water from 4 on a preparative scale to yield 5.[11] However, 5 has



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been prepared in 45% yield by reacting Cp*Li, $TiCl_3$·3THF, $(tBu)_2Si(OLi)_2$, and oxygen.[12]

The titanium atoms in 4 have a tetrahedral coordination, forming the well-known piano-stool structure. The distances within the eight-membered ring are comparable with those in known examples.[5] To demonstrate that the OH group in 3 does not migrate from the silicon to the titanium atom, an X-ray investigation was undertaken. The single-crystal structure shows clearly that in 3 the OH group is bonded to silicon.[13]

A few multinuclear hydroxide derivatives of zirconium have been reported;[14] however, none contain O–H–O bonds.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung. F.L. is thankful to the Alexander von Humboldt Foundation for a fellowship.

Supplementary Material Available: Tables of crystallographic details, positional parameters, isotropic and anisotropic parameters, and all bond distances and angles and a figure showing the structure for 3 (8 pages). Ordering information is given on any current masthead page.

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(11) Heating 4 in the presence of a molecular sieve forms compound 5 in moderate yield.

(12) Compound 5: A solution of Cp*Li (0.71 g, 5 mmol) and $TiCl_3$·3THF (1.85 g, 5 mmol) in THF (60 mL) is stirred for 2 days. A second solution of $(tBu)_2Si(OLi)_2$ (0.94 g, 5 mmol) in THF (40 mL) is added dropwise at −78 °C. The solution turns deep green. After the solution is stirred for 24 h, the solvent is removed in vacuo. The residue is treated with hexane (70 mL) and finally filtered. A small amount of O_2 is passed through the solution until it turns yellow. After the solution is concentrated (30 mL) and cooled in a refrigerator, 0.83 g (45%) of yellow crystals separated; mp 142–144 °C. MS (EI): m/z 673 ($M^+ - Bu$). IR: 1392 m, 1261 m, 1096 m, 1018 m, 903 s, 863 s, 824 s, 641 s, 572 m cm^{-1}.

(13) Crystallographic data for 3: monoclinic, $a = 877.6$ (1) pm, $b = 1309.5$ (3) pm, $c = 1067.4$ (1) pm, $\beta = 109.52$ (1) °, $V = 1.1561$ (3) nm^3, space group $P2_1$, $Z = 2$, $\rho_{calcd} = 1.23$ Mg m^{-3}, 1822 independent reflections $[F_o > 3\sigma(F_o)]$, $2\theta = 2–45°$, weighting scheme $w^{-1} = \sigma^2(F) + 0.0004F^2$, refinement $R = 4.18\%$, $R_w = 5.42\%$ for all data.[10b]

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Mono(amido–diphosphine) Complexes of Yttrium: Synthesis and X-ray Crystal Structure of $\{Y(\eta^3\text{-}C_3H_5)[N(SiMe_2CH_2PMe_2)_2]\}_2(\mu\text{-}Cl)_2$

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Summary: The reaction of allylmagnesium chloride with the bis(amido–phosphine) complex $YCl[N(SiMe_2CH_2PMe_2)_2]_2$ (1) results in displacement of one of the tridentate ligands rather than simple metathesis of the chloride to generate the new complex $\{Y(\eta^3\text{-}C_3H_5)[N(SiMe_2CH_2PMe_2)_2]\}_2(\mu\text{-}Cl)_2$. Careful product analysis showed that the identity of the magnesium byproduct was in fact the bis(amide) derivative $Mg[N(SiMe_2CH_2PMe_2)_2]_2$; improved procedures utilize the diallylmagnesium compound $Mg(C_3H_5)_2$·(dioxane), which obviates the production of $MgCl_2$. Attempts to introduce hydrocarbyl groups on the mono(ligand) derivative $YCl_2[N(SiMe_2CH_2PMe_2)_2]$ by control of stoichiometry have so far failed, with the exception of the formation of the bis(allyl) derivative $[Y(\eta^3\text{-}C_3H_5)_2[N(SiMe_2CH_2PMe_2)_2]$ by the reaction with $Mg(C_3H_5)_2$·(dioxane); this bis(allyl) derivative acts as a catalyst precursor for the polymerization of ethylene.

Phosphine ligands are still found infrequently in complexes in the group 3[1-6] and lanthanide metals.[1] We have recently described derivatives of yttrium(III) containing two hybrid ligands that incorporate an amide ligand flanked by two phosphine donors into a potentially tridentate chelate array; complexes of the formula $YCl[N(SiMe_2CH_2PMe_2)_2]_2$ (1) have been shown to be seven-coordinate and fluxional.[5] Although the hydrocarbyl derivatives $YR[N(SiMe_2CH_2PMe_2)_2]_2$ (2; R = Ph, $PhCH_2$) could be prepared by metathesis of the chloride of 1 with organolithium or potassium reagents,[5] the chemistry of these complexes was dominated by hydrocarbon elimination and

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[‡] Experimental Officer: UBC Crystallographic Service.

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