when **4** is protonated directly in the presence of acetonitrile, is obtained in 46% yield with respect to the starting cot complex **1**!

Experimental Section

2a,b: A solution of sodium dimethyl malonate (286 mg, 1.8 mmol) in THF (20 mL) was added dropwise to a suspension of **1**-PF_6 (748 mg, 1.8 mmol) in THF (50 mL) at −78 °C. After warming to room temperature the solvent was removed under reduced pressure. The residue was extracted with diethyl ether, and the extract filtered through kieselguhr. After removal of the solvent the product was obtained as a pale yellow powder (yield: 561 mg, 78%). The haptomers **2a** and **2b** were, for the most part, separated by column chromatography (Al_2O_3/5% H_2O, toluene/diethyl ether 1/1). Elemental analysis calcd for $C_{18}H_{20}O_4Ru$ (401.41): C 53.86, H 5.02; found: C 54.12, H 5.18.

3a,b: A mixture of **2a** and **2b** (652 mg, 1.6 mmol) was dissolved in diethyl ether (50 mL) and allowed to react with $HBF_4 \cdot OEt_2$ (54%, 0.23 mL) at −78 °C. After warming to room temperature the mixture was filtered, and the residue washed several times with diethyl ether. The yellow filter residue was dissolved in CH_2Cl_2. The mixture of the products **3a** and **3b** was precipitated with diethyl ether and dried under vacuum (yield: 724 mg, 93%). The composition varied according to the duration of the reaction and the work-up. For the partial deuteration a corresponding amount of HBF_4/H_2O dissolved in D_2O was used instead of $HBF_4 \cdot OEt_2$. Elemental analysis calcd for $C_{18}H_{21}BF_4O_4Ru$ (489.23): C 44.19, H 4.33; found: C 43.49, H 4.38.

4: A solution of sodium dimethyl malonate (223 mg, 1.45 mmol) in THF (20 mL) was added to a suspension of **3a** and **3b** (645 mg, 1.3 mmol) in THF (50 mL) at room temperature. The work-up of the reaction mixture was analogous to that for the synthesis of **2**. Compound **4** was obtained as yellow crystals (yield: 558 mg, 80%). Elemental analysis calcd for $C_{23}H_{28}O_8Ru$ (533.52): C 51.78, H 5.29; found: C 51.63, H 5.60.

5: The protonation was carried out as for **2a,b** (see above). $HBF_4 \cdot OEt_2$ (54%, 0.22 mL) was added to a solution of **4** (613 mg, 1.15 mmol) in diethyl ether (40 mL) at −65 °C. Compound **5** (yield: 581 mg, 82%) was isolated as a yellow powder which slowly decomposed in solution. Elemental analysis calcd for $C_{23}H_{29}BF_4O_8Ru$ (621.34): C 44.46, H 4.70; found: C 44.13, H 4.69.

6: $HBF_4 \cdot OEt_2$ (54%, 0.16 mL, 1.16 mmol) was added to a solution of **4** (617 mg, 1.16 mmol) and acetonitrile (0.2 mL, 3.48 mmol) in diethyl ether (60 mL) at −78 °C. The suspension was warmed to room temperature and filtered. The yellow residue was washed with diethyl ether. After removal of the solvent **6** (yield: 287 mg, 67%) remained as an oil. The extraction residue was also dried under vacuum and identified by ^1H NMR spectroscopy as $[Ru(Cp)(CH_3CN)_3]BF_4$ (**7**). Elemental analysis calcd for $C_{18}H_{24}O_8$ (368.37): C 58.69, H 6.57; found: C 58.87, H 6.91.

Cleavage of **6** from **5**: Acetonitrile (2 mL) was added to a suspension of **5** (56 mg, 0.09 mmol) in diethyl ether (25 mL) at room temperature. The mixture was stirred for one hour, and worked up as in the preparation of **6** from **4**. **6**: 32 mg (97%), **7**: 33 mg (97%).

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$Ti_2Nb_6Cl_{14}O_4$: A Unique 2D–1D Network Combination in Niobium Cluster Chemistry**

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The formation of clusters by metal–metal bonding is characteristic of many compounds with early transition metals in low oxidation states.[1] The most common structural motif in reduced niobium halides and oxides is the cluster unit $[(Nb_6L^i_{12})L^a_6]^{n-}$ (L = F, Cl, Br, O).[2, 3] It is based on an octahedron of Nb atoms surrounded by twelve inner (L^i) and six outer ligands (L^a). In compounds obtained through solid-state synthesis, these units can be present as discrete anions (as in $KLuNb_6Cl_{18}$,[4] $In_2Li_2Nb_6Cl_{18}$,[5] and $Rb_4Al_2Nb_{35}O_{70}$[6]) or link to each other by sharing outer and/or inner ligands to form various polymeric structures (as in

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Nb_6Cl_{14},[7] $NaNb_6Cl_{15}$,[8] $InNb_6Cl_{15}$,[9] and $LaNb_7O_{12}$[10]). Experimental and theoretical investigations have shown that valence electrons that are available for metal–metal interactions in these compounds are distributed among a_{1g}, t_{1u}, t_{2g}, and a_{2u} energy states.[3, 11] The energy of the a_{2u} state is determined by the balance between its Nb–Nb bonding character and Nb–L antibonding character. In niobium oxides, the a_{2u} state is overall antibonding, leading to compounds with a valence-electron concentration (VEC) that ranges from 13 to 15 (with 14 being preferred). In niobium halides, however, the a_{2u} state is overall nonbonding and is partially or fully occupied, leading to compounds with a VEC of 15 or 16 (with 16 being preferred). Modification of these cluster units by introduction of both halogen and oxygen as ligands can lead to changes in electronic configuration, charge, and symmetry, and is, therefore, conducive to formation of new structural types. Indeed, the recently reported oxohalides $ScNb_6Cl_{13}O_3$ and $Cs_2LaTa_6Br_{15}O_3$ crystallize in structure types that have no analogues among halide or oxide clusters.[12]

To explore correlations that exist between stoichiometry, structure types, and VEC in the niobium oxohalide clusters, we are investigating the system $Nb/NbCl_5/Nb_2O_5/Ti$. We recently obtained and structurally characterized the oxochloride $Ti_2Nb_6Cl_{14}O_4$, which crystallizes in an original structure type. In this compound niobium clusters form layers linked to each other through zigzag chains of edge-sharing $[TiCl_4O_2]$ octahedra (Figure 1).[13]

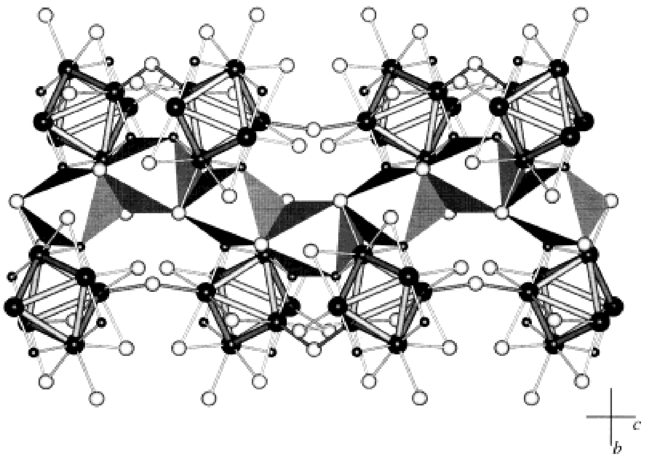

Figure 1. View of the structure of $Ti_2Nb_6Cl_{14}O_4$ in approximately the $\vec{a}$ direction. Large dark spheres, small dark spheres, and light spheres represent Nb, O, and Cl atoms, respectively. $[TiCl_4O_2]$ octahedra are highlighted.

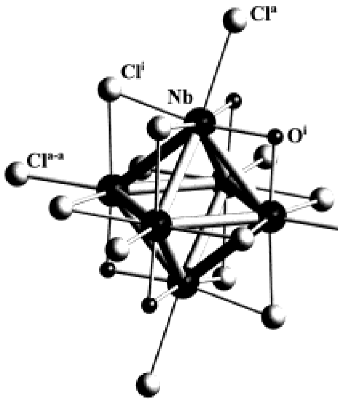

Figure 2. View of the $[(Nb_6Cl^i_8O^i_4)Cl^a_6]^{6-}$ cluster in $Ti_2Nb_6Cl_{14}O_4$.

The basic cluster unit $[(Nb_6Cl^i_8O^i_4)Cl^a_6]^{6-}$ has four oxygen and eight chlorine atoms as inner ligands and six chlorine atoms as outer ligands, and exhibits $\bar{1}$ symmetry (Figure 2). The Nb_6 octahedra are distorted owing to the difference in size and charge of the oxide and chloride ligands. The Nb–Nb bond distances range from 2.8174(7) to 2.8350(7) Å for oxygen-bridged niobium atoms, and from 2.9469(7) to 2.9916(7) Å for chlorine-bridged ones. These distances compare well with those in $ScNb_6Cl_{13}O_3$ (2.805(1)–3.007(1) Å).[12a] The average niobium–ligand distances ($\bar{d}$(Nb–O^i) = 2.026 Å, $\bar{d}$(Nb–Cl^i) = 2.4536 Å, $\bar{d}$(Nb–Cl^a) = 2.6067 Å) are in good agreement with typical values in niobium oxide and chloride clusters.[3, 12c]

Each cluster shares four outer chlorine atoms with four neighboring clusters, leading to the formation of pseudo-square layers $^2_\infty[(Nb_6Cl^i_8O^i_4)Cl^a_2Cl^{a-a}_{4/2}]^{4-}$ parallel to the *ac* plane (Figure 3). Adjacent layers are shifted with respect to each other by $1/2\vec{c}$. The layers have a buckled appearance resulting from about ±28° canting of the clusters from the normal to the layers and bent Nb-Cl^{a-a}-Nb bridges (Nb-Cl(1)$^{a-a}$-Nb 165, Nb-Cl(2)$^{a-a}$-Nb 131°). These layers are similar to those present in the binary compound Nb_6Cl_{14}, in which they are bridged through outer–inner chlorine atoms to form a three-dimensional framework. In contrast to Nb_6Cl_{14}, the layers in $Ti_2Nb_6Cl_{14}O_4$ are connected to each other through zigzag chains (parallel to the $\vec{c}$ direction) of edge-sharing $[TiCl_4O_2]$ octahedra.

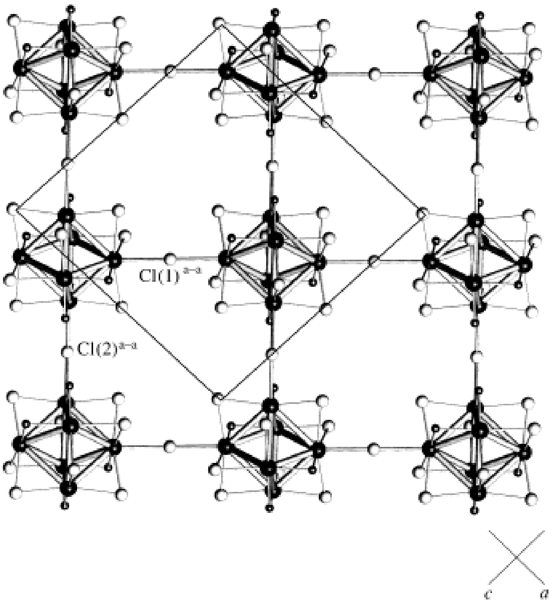

Figure 3. View of a $^2_\infty[(Nb_6Cl^i_8O^i_4)Cl^a_2Cl^{a-a}_{4/2}]^{4-}$ cluster layer in $Ti_2Nb_6Cl_{14}O_4$. Large dark spheres, small dark spheres, and light spheres represent Nb, O, and Cl atoms, respectively.

Titanium atoms occupy two inequivalent positions, Ti(1) and Ti(2), that alternate throughout the chain (Figure 4). In

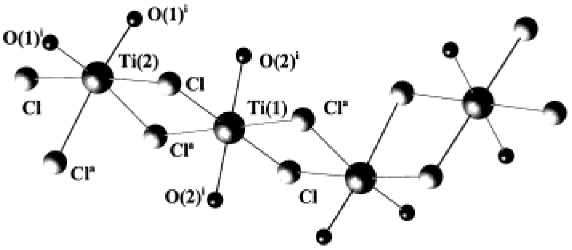

Figure 4. Section of an infinite chain of $[TiCl_4O_2]$ octahedra. Bond lengths [Å]: Ti(1)–O(2) 2.001(2), Ti(1)–Cl 2.4243(10), Ti(1)–Cl^a 2.4569(10), Ti(2)–O(1) 1.913(2), Ti(2)–Cl 2.4305(11), Ti(2)–Cl^a 2.5438(11).

the $[Ti(1)Cl_4O_2]$ octahedron, oxygen atoms are located in *trans* positions with respect to each other, whereas the oxygen atoms in $[Ti(2)Cl_4O_2]$ are in *cis* positions. Each *trans*-$[TiCl_4O_2]$ octahedron shares two opposite edges with two adjacent *cis*-$[TiCl_4O_2]$ octahedra, which in turn share their skew edges with adjacent *trans*-$[TiCl_4O_2]$ octahedra. This results in a zigzag *cis – trans* chain. To our knowledge, this is the first example of this type of linkage of octahedra into chains in titanium compounds. Titanium octahedra usually form rutile-like (*trans*) or brookite-like (*cis*) chains. Among other transition metal compounds, *cis – trans* chains were found in $AM_3(P_2O_7)_2$ (A = Sr, Ba; M = Co, Ni).[14] Two of the four chlorine atoms and both oxygen atoms coordinating to titanium also serve as outer and inner ligands for the clusters, respectively. Each *trans*-$[TiCl_4O_2]$ octahedron connects two clusters from adjacent layers, whereas each *cis*-$[TiCl_4O_2]$ octahedron bridges two clusters within the same layer. The remaining two chlorine atoms coordinate only to titanium atoms. The chains are separated from each other by empty channels running between the layers in the $\vec{c}$ direction (Figure 5). The minimum distance from the center of the channel to chlorine atoms is 2.350 Å.

The oxidation state of both Ti(1) and Ti(2) estimated from bond-valence sums is +3.[15] This implies that the number of valence electrons per niobium cluster in $Ti_2Nb_6Cl_{14}O_4$ is 14, as in $ScNb_6Cl_{13}O_3$ and $Cs_2LaTa_6Br_{15}O_3$. Although this conclusion needs to be experimentally verified, other oxidation states of titanium such as +2 or +4 seem to be less plausible. The former suggests an unstable electronic configuration for the cluster (VEC of 12), and the latter (implying a VEC of 16) does not agree with observed intracluster bond distances.[12c]

The combination of one- and two-dimensional sublattices in this new oxochloride is unprecedented for compounds with octahedral clusters. The novelty of the structural features in $Ti_2Nb_6Cl_{14}O_4$ indicates that further investigations into the chemistry of niobium oxohalides will undoubtedly lead to the discovery of many compounds with original structure types.

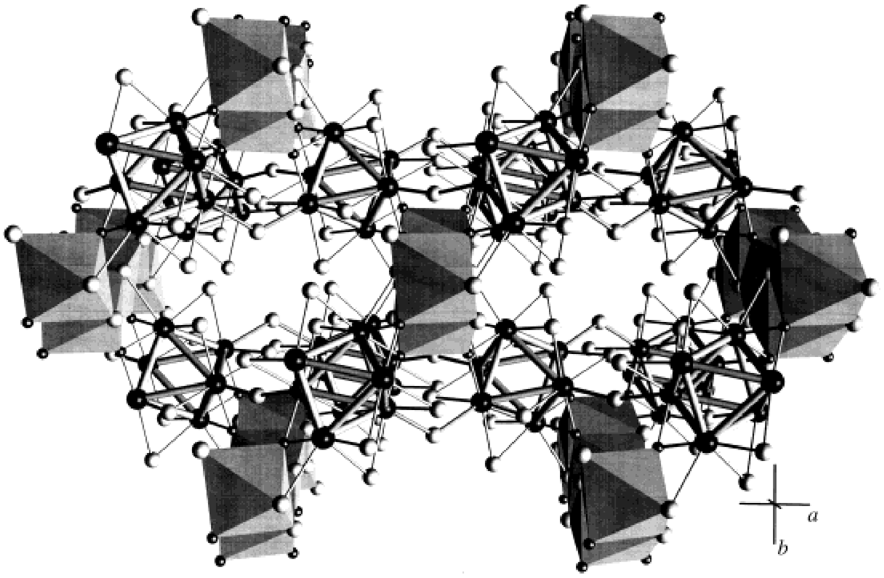

Figure 5. Perspective view of the structure of $Ti_2Nb_6Cl_{14}O_4$ in the $\vec{c}$ direction showing channels. Large dark spheres, small dark spheres, and light spheres represent Nb, O, and Cl atoms, respectively. $[TiCl_4O_2]$ octahedra are highlighted.

Experimental Section

A few crystals of the title compound were initially obtained by a reaction designed to yield $TiNb_6Cl_{18}$ in which contaminated $NbCl_5$ (probably containing $NbOCl_3$) was used. Subsequently, $Ti_2Nb_6Cl_{14}O_4$ was synthesized in high yield (>90%) from stoichiometric amounts of Nb powder, Ti foil, $NbCl_5$, and Nb_2O_5. The mixture (handled under a dry atmosphere) was placed in a quartz tube, sealed under vacuum, heated at 720 °C for 60 h, and cooled to room temperature within 3 h. The compound was obtained as black (dark brown when ground) columnlike crystals. The product was identified by comparing its X-ray powder diffraction pattern to that calculated based on crystal structure data for $Ti_2Nb_6Cl_{14}O_4$. The crystals did not undergo any noticeable decomposition in air.

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[13] Crystal structure data for $Ti_2Nb_6Cl_{14}O_4$: monoclinic, space group *C*2/*c* (no. 15), a = 12.729(3), b = 14.570(3), c = 12.586(3) Å,

$\beta = 95.38(3)^\circ$, $V = 2323.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.469$ Mg m^{-3}, $F(000) = 2240$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu(\mathrm{Mo_{K\alpha}}) = 5.116$ mm^{-1}, $T = 298$ K. Of 11197 reflections collected in the range $2.1 \leq 2\theta \leq 53.1^\circ$ using the $\theta-2\theta$ scan mode, 5132 were independent. Lorentzian polarization and empirical absorption corrections ($T_{min} = 0.252$, $T_{max} = 0.317$) were applied, and the structure solved and refined against F^2 using SHELX86 and SHELXL93 (G. M. Sheldrick, Universität Göttingen) with 5131 reflections (all unique reflections except for one with very negative F^2). All atoms were refined anisotropically. $R_1 = 0.058$, $wR_2 = 0.063$ for 121 parameters; max./min. residual electron density: 1.444/ – 0.924 e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-406839.

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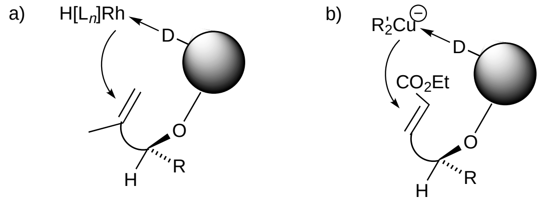
ortho-Diphenylphosphanylbenzoyl-Directed Cuprate Addition to Acyclic Enoates**

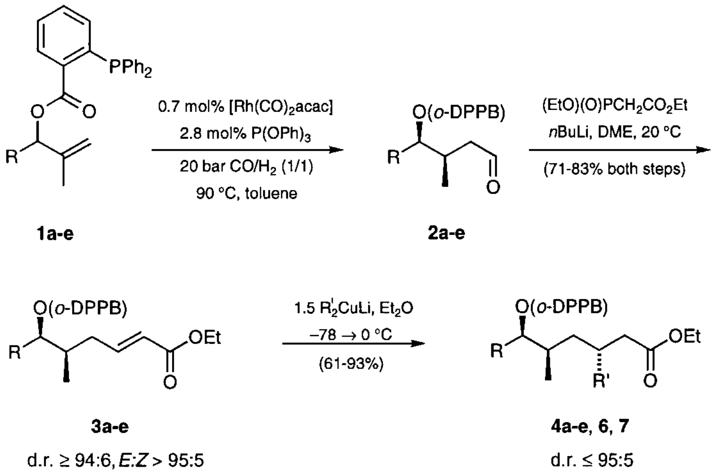
Bernhard Breit*

Reactions for constructing carbon skeletons, which lead to the formation of new stereogenic centers, are efficient transformations in organic synthesis. The control of stereoselectivity in such a process can be effected by either the reagent or the substrate. However, the latter is particularly difficult to achieve for acyclic substrates because of their structural flexibility. To overcome this problem, one has to make more efficient use of the chirality information inherent in the substrate. This can be achieved with the aid of a catalyst-directing group, which has been used successfully to control stereoselectivity in the rhodium-catalyzed hydroformylation of acyclic olefins (Scheme 1).[1] We report here that *ortho*-diphenylphosphanylbenzoyl (*o*-DPPB), the catalyst-directing group succesfully used in the hydroformylation reactions, can be employed in a subsequent step as a reagent-directing group for the diastereoselective addition of Gilman cuprates to α,β-unsaturated enoates (Scheme 1).



Scheme 1. Working hypothesis for the *o*-DPPB group (shown schematically as a sphere; D = donor) a) as a catalyst-directing group and b) as a reagent-directing group with the examples of hydroformylation and conjugated addition of cuprates.

Enoates **3** were chosen as the test substrates, because a stereoselective 1,4-addition of an organometallic reagent that transfers a methyl group would provide the structural building blocks found in biologically important natural products of the polyketide class (e.g. the antitumor agent dictyostatin 1 and the ionophor calcimycin).[2, 3] Enoates **3** were obtained by *o*-DPPB-directed diastereoselective hydroformylation followed by Horner–Wadsworth–Emmons (HWE) olefination of the crude hydroformylation products (**2**→**3**) in good yields (71–83%), diastereoselectivities (*syn*:*anti* ≥ 94:6), and *E*/*Z* selectivities (> 95:5).



Treatment of **3a** with 1.5 equivalents of lithium dimethyl cuprate provided the 1,4-addition product **4a** (93%) in a diastereomer ratio of 95:5 (Table 1, entry 1).[4] To determine the relative configuration, **4a** was transformed into the δ-lactone **5** by standard reactions (Scheme 2). A 2D NOESY NMR experiment with **5** confirmed the axial position of the proton at C3 as well as the methyl group at C5, that is, an *anti* relationship between the two 1,3-positioned methyl groups of the acyclic 1,4-addition product **4a**.

This reaction is not restricted to the transfer of a methyl group. Therefore, the addition of lithium di-*n*-butyl cuprate also proceeded with excellent diastereoselectivity (→*anti*-**6**, d.r. > 95:5, entry 2). In the case of lithium divinyl cuprate the diastereoselectivity was lower (→*anti*-**7**, d.r. = 80:20, entry 3).

With regard to the preparation of important building blocks of polyketide natural products, the addition of dimethyl cuprate is the most important reaction. Combining stereoselective *o*-DPPB-directed hydroformylation, HWE olefination, and stereoselective *o*-DPPB-directed cuprate addition provided access to acyclic building blocks with up to four stereogenic centers (→**4b**–**e**, entries 4–7). The 1,4-addition product **4b** is a potential C13–C20 building block of the ionophor calcimycin, since it has the correct relative configuration at the four stereogenic centers. In addition, **4e** possesses the correct absolute configuration of this polyketide (entries 4 and 7).[3]

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