Molecular Solids as Ligands in Organometallic Chemistry: $[\text{Cp}^*\text{Ti}_6\text{Na}_7\text{F}_{19} \cdot 2.5 \text{ thf}]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) and $[\text{Cp}^*\text{Ti}_4\text{Mg}_2\text{F}_{12} \cdot 7 \text{ thf}]$, Links Between Ionic Solids and Organometallic Compounds**

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We previously reported the isolation of inclusion complexes from the reaction of $[\text{Cp}^*\text{TiF}_3]$ (**1**) ($\text{Cp}^* = \text{C}_5\text{Me}_5$) with NaF in acetonitrile. These complexes can be considered as analogues of crown ethers;^[1] encapsulation of the Na^+ ion by two $[(\text{Cp}^*\text{TiF}_3)_2\text{F}]^-$ fragments corresponds to that in $[\text{Na}(\text{12crown-4})_2]^+$. Here, the nucleophilic host has a fluoride surface which surrounds the sodium ion. The reaction of $[\text{Cp}^*\text{TiF}_3]$ with sodium metal in THF in a 1:1 molar ratio results in the formation of NaF and the expected reduction of Ti^{IV} to Ti^{III} . Surprisingly, no NaF precipitates out during this synthesis. If the solution is left to stand for an extended period of time, green crystals of composition $[\text{Cp}^*\text{Ti}_6\text{Na}_7\text{F}_{19} \cdot 2.5 \text{ thf}]$ (**2**) are formed.

The structure of **2** has been determined by a single-crystal X-ray analysis,^[2] and its central inorganic structural unit is depicted in Figure 1. The structure has a noncrystallographic two-

Fig. 1. Structure of the central inorganic unit of **2** in the crystal. Selected bond lengths [pm]: Ti–F 204.6* (194.7–215.2), Ti– $\text{Cp}^*_{(\text{center})}$ 203.2*, Na–F 234.9* (215.3–275.1), Na4–O1 229.1(4), Na5–O2 231.9(4), Na7–O9 263(2). The values marked with a * are average values.

fold axis which runs through Na1 and F19. The six Cp^*TiF_2 groups almost completely enclose seven NaF molecules such that a “molecular NaF structure” is formed within the aggre-

gate. Here, however, a different coordination is found than that in crystalline NaF. Only F19 is octahedrally coordinated; all other fluorine atoms exhibit lower coordination. Thus, F9 and F15 have the coordination number five, F3 and F6 the coordination number four, and the remaining fluorides exhibit a coordination number of three. Although Na1, Na6, and Na7 are six-coordinate, their coordination polyhedra are distorted in such a way as to prohibit their description as octahedra. While Na2 and Na3 are seven-coordinate, the peripherally “naked” atoms Na4 and Na5 are each coordinated to four fluorine atoms and one oxygen atom (from a THF molecule). The average Na–F bond length (234.9 pm) is similar to that in solid NaF (231 pm),^[3] but significantly shorter than that in $[\text{tBu}_3\text{SiFNa}(\text{tBu})_2]$ (243.4 pm and 332.5 pm),^[4] $[\text{2,4,6-(CF}_3)_3\text{C}_6\text{H}_2\text{ONa} \cdot 2 \text{ thf}]_2$ (266.4 and 272.0 pm),^[5] or $[\text{2,4,6-(CF}_3)_3\text{C}_6\text{H}_2\text{SNa} \cdot 2 \text{ thf}]_x$ (243.4 to 257.1 pm).^[5] The Ti–F distances in **2** (204.6 pm) are similar to those in $[(\text{Cp}_2\text{TiF}_2)_3\text{Ti}]$ (209.4 pm; $\text{Cp} = \text{C}_5\text{H}_5$).^[6] In the crystal of **2**, a THF molecule is trapped between two $[\text{Cp}^*\text{Ti}_6\text{Na}_7\text{F}_{19} \cdot 2 \text{ thf}]$ units in such a way that the molecule is disordered with its oxygen atom directed towards one of the sodium atoms (Fig. 2). The Na–O bond to this molecule is about 30 pm longer than those to the rigidly coordinated THF molecules.

Fig. 2. Arrangement of two molecules of **2** about a trapped THF molecule.

We then investigated whether the coordination pattern found in **2** would also be exhibited by Group 2 elements. $[\text{Cp}^*\text{TiF}_3]$ (**1**) reacted with magnesium metal in THF to form **3** [Eq. a]. In this

reaction, two magnesium atoms are incorporated between four $[\text{Cp}^*\text{TiF}_3]$ units. The single-crystal X-ray structure analysis of **3**^[2] (Fig. 3) revealed a six-coordinate magnesium atom similar to that in solid MgF_2 .^[3] Two of the six coordination sites in **3**, however, are occupied by THF molecules. Whereas the THF molecules containing O1 and O2 are each bound to one magnesium atom as terminal ligands, the O3-containing THF molecule bridges the two Mg atoms. To our knowledge, such μ_2 -

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Fig. 3. Structure of **3** in the crystal. Selected bond lengths [pm]: Ti–F 202.5* (200.4–203.6), Ti–Cp*_{center} 204.6*, Mg–O(1,2) 206.0*, Mg1–O3 226.8(3), Mg2–O3 235.8(4), Mg1–F4 202.6(3), Mg2–F4 201.8(3), Mg–F 190.5* (190.0–190.9). The values marked with a * are average values.

bridging THF molecules in alkaline earth metal compounds are unknown to date. Although the Mg–F distances to the Mg bridging fluorine atom F4 (202.2 pm) correspond to the distances in the rutile lattice of MgF₂ (205 pm),^[7] the remaining Mg–F bond lengths in **3** (mean 190.5 pm) are significantly shorter. The central Ti₄Mg₂F₁₂ inorganic core is outwardly shielded by both the Cp* groups and the coordinated THF molecules. Four Ti, two Mg, and twelve F atoms build a cage-like framework whose cavity has a μ_2 -bridging fluorine atom (Mg1–F4–Mg2) projecting into it.

With these examples, we have shown for the first time that molecular solids can function as ligands in organometallic chemistry. Continuing investigations are aimed at determining how the size of the aggregates can be influenced by, for example, changes in the ligands, the solvent, or through template effects as well as whether corresponding oxide systems can be prepared.

Experimental Procedure

2: A solution of **1** (0.72 g, 3 mmol) in THF (40 mL) was added dropwise to a suspension of Na (0.07 g, 3 mmol) and mercury (10 g) in THF (20 mL) at 0 °C. The reaction must be carried out under careful exclusion of water and oxygen. The mixture was stirred for 12 h, filtered, and the solvent was then removed in vacuum. Crystalline **2** (0.52 g, 65% yield) was obtained by recrystallizing the green residue from THF/hexane (20 mL/40 mL). M.p. 204 °C (decomp). The decomposition temperature refers to the solvent-free compound, which is obtained by evacuation of **2** (10^{–2} mbar, 25 °C, 12 h). Correct elemental analyses. IR (Nujol): $\tilde{\nu}$ [cm^{–1}] = 1497(m), 1260(m), 1061(s), 1027(s), 815(s), 545(s), 507(s), 494(s), 471(s).

3: A solution of **1** (0.72 g, 3 mmol) in THF (40 mL) was added dropwise to Mg (0.35 g, 14 mmol) in THF (20 mL) under an inert atmosphere. The magnesium was first activated with HgCl₂ (5 mg). The mixture was stirred for 12 h at room temperature, filtered, and the solvent was then removed in vacuum. The residue was recrystallized from THF/hexane (40 mL/20 mL) which yielded 0.5 g of **3** (75%). M.p. 240 °C. Correct elemental analyses from the solvent-free compound (10^{–2} mbar, 25 °C, 12 h). IR (Nujol): $\tilde{\nu}$ [cm^{–1}] = 1498(m), 1260(m), 1031(s), 801(s), 519(s); MS(EI) *m/z*: 873 (M–Cp*, 1.2%), 135 (Cp*, 100%).

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[2] Crystal data for **2**: C₄₈H₁₀₆F₁₉Na₃O₂Ti₆ + 1/2 thf, *M*_r = 1800.91, triclinic, space group *P* $\bar{1}$, *a* = 1195.0(2), *b* = 1407.7(2), *c* = 2670.9(5) pm, α = 80.99(1), β = 77.67(1), γ = 72.46(1)°, *V* = 4.165(1) nm³, *Z* = 2, ρ_{calcd} = 1.436 g cm^{–3}, *F*(000) = 1860, λ = 71.073 pm, μ (MoK α) = 0.668 mm^{–1}. The data were collected on a Stoe-Siemens-Huber four-circle diffractometer. The intensities were determined at –120 °C from a rapidly cooled crystal in a drop of oil [8] having dimensions of 0.4 × 0.3 × 0.2 mm by the 2 θ / ω method over the range

8° ≤ 2 θ ≤ 45°. A semiempirical absorption correction method was applied to the 10922 independent reflections from the 18706 collected. 10920 of the independent reflections and 5683 restraints were used in the refinement of 1143 parameters. Largest minimum and maximum in the final difference-Fourier synthesis: 460 and –480 e nm^{–3}, respectively, *R*1(*F* > 4 σ (*F*)) = 0.046 and *wR*2 = 0.128 (for all data). **3**: C₃₂H₈₄F₁₂Mg₂O₃Ti₄ + 4 thf, *M*_r = 1513.83, monoclinic, space group *P*2₁/*m*, *a* = 1470.9(1), *b* = 1679.8(2), *c* = 1539.5(2) pm, β = 105.53(1)°, *V* = 3.6649(7) nm³, *Z* = 2, ρ_{calcd} = 1.372 g cm^{–3}, *F*(000) = 1600, λ = 71.073 pm, μ (MoK α) = 0.517 mm^{–1}. The data were collected on a Stoe-Siemens-AED four-circle diffractometer. The intensities were determined at –120 °C from a rapidly cooled crystal in a drop of oil [8] having dimensions of 0.2 × 0.2 × 0.1 mm by the 2 θ / ω method over the range 8° ≤ 2 θ ≤ 50°. From the 6666 independent reflections out of the 8199 collected, 6663 were used together with 1416 restraints in the refinement of 696 parameters. Largest minimum and maximum in the final difference-Fourier synthesis: 600 and –380 e nm^{–3}, respectively, *R*1(*F* > 4 σ (*F*)) = 0.048 and *wR*2 = 0.140 (for all data). The values for *R*1 and *wR*2 were defined as *R*1 = $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$; *wR*2 = $\{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_c^2)^2]\}^{1/2}$. The structures were solved by direct methods (SHELXS-90) [9] and refined by least-squares methods (SHELXL-93) [10]. The hydrogen positions were refined by a riding model in which CH₃ groups can rotate about their local threefold axes. Further details of the crystal structure investigations may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ on quoting the complete literature citation.

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Kinetic Resolution of the Acrolein Dimer by Asymmetric Horner–Wadsworth–Emmons Reactions**

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Dedicated to Professor Björn Åkermark on the occasion of his 60th birthday

The Diels–Alder dimer of acrolein **1**^[1] is available in bulk quantities and has great potential as a synthetic building block^[2] because of its aldehyde and enoether functionality.

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