Molecular Solids as Ligands in Organometallic Chemistry: \([\text{Cp}^*\text{Ti}_6\text{Na}_7\text{F}_{10} \cdot 2.5\text{thf}] \quad \text{(Cp}^* = \text{C}_5\text{Me}_5)\) and \([\text{Cp}^*\text{Ti}_6\text{Mg}_2\text{F}_{12} \cdot 7\text{thf}]\), Links Between Ionic Solids and Organometallic Compounds**

Feng-Quan Liu, Annja Kuhn, Regine Herbst-Irmer, Dietmar Stalke, and Herbert W. Roesky

We previously reported the isolation of inclusion complexes from the reaction of \([\text{Cp}^*\text{TiF}_4]\) (1) (\(\text{Cp}^* = \text{C}_5\text{Me}_5\)) with NaF in acetonitrile. These complexes can be considered as analogues of crown ethers;** encapsulation of the Na\(^+\) ion by two \([\text{Cp}^*\text{TiF}_4]^2\) fragments corresponds to that in \([\text{Na}(\text{l2crown-4})]^+\). Here, the nucleophilic host has a fluoride surface which surrounds the sodium ion. The reaction of \([\text{Cp}^*\text{TiF}_4]\) 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\(^{II}\). 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 \([\text{Cp}^*\text{Ti}_6\text{Na}_7\text{F}_{10} \cdot 2.5\text{thf}] \quad \text{(2)}\) are formed.

The structure of 2 has been determined by a single-crystal X-ray analysis, and its central inorganic structural unit is depicted in Figure 1. The structure has a noncrystallographic two-fold axis which runs through Na1 and F19. The six \(\text{Cp}^*\text{TiF}_4\) groups almost completely enclose seven NaF molecules such that a "molecular NaF structure" is formed within the aggregate. 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), but significantly shorter than that in \([\text{tBu}_3\text{SiFNaNtBu}]_2\) (243.4 pm and 332.5 pm), \([2,4,6-(\text{CF}_3)_2\text{C}_6\text{H}_4\text{ONa} \cdot \text{2thf}]_2\) (266.4 and 272.0 pm), or \([2,4,6-(\text{CF}_3)_2\text{C}_6\text{H}_4\text{SNa} \cdot \text{2thf}]_2\) (243.4 to 257.1 pm). The Ti-F distances in 2 (204.6 pm) are similar to those in \([\text{Cp}^*\text{TiF}_4\text{Mg}_2]\) (209.4 pm; \(\text{Cp} = \text{C}_5\text{H}_5\)).

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–Cp\(_{\text{Cp}^*}\) 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 * are average values.

We then investigated whether the coordination pattern found in 2 would also be exhibited by Group 2 elements. \([\text{Cp}^*\text{TiF}_4]\) (1) reacted with magnesium metal in THF to form 3 [Eq. a]. In this reaction, two magnesium atoms are incorporated between four \([\text{Cp}^*\text{TiF}_4]\) 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\(_2\). 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 \(\mu_2\)-

![Diagram](https://via.placeholder.com/150)

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

![Diagram](https://via.placeholder.com/150)

We then investigated whether the coordination pattern found in 2 would also be exhibited by Group 2 elements. \([\text{Cp}^*\text{TiF}_4]\) (1) reacted with magnesium metal in THF to form 3 [Eq. a]. In this reaction, two magnesium atoms are incorporated between four \([\text{Cp}^*\text{TiF}_4]\) 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\(_2\). 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 \(\mu_2\)-
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),[1] the remaining Mg–F bond lengths in 3 (mean 190.5 pm) are significantly shorter. The central Ti3MgF12 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 μ2-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 mixture was stirred under an inert atmosphere. 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 evaporation of 2 (100 °C, 24 hr) over the range 0.4 x 0.2 x 0.1 mm by the 2θ(ω) method over the range 8° < 2θ < 45°. A semiempirical absorption correction method was applied to the 10922 independent reflections from the 18706 collected. 10920 of the independent reflections and 5863 restraints were used in the refinement of 1143 parameters. Largest minimum and maximum in the final difference-Fourier synthesis: 460 and 530 eÅ⁻³, respectively. RI(F > 4σ(F)) = 0.046 and wR2 = 0.128 (for all data). 3, C12H8F2; Mg3O7Ti3; M = 1513.83; monoclinic, space group P2₁/m, a = 1479.0(1), b = 1679.9(2), c = 1539.5(2) pm, β = 105.5(1) °, V = 3.6649(7) nm³, Z = 2, ρcalcd = 1.372 g cm⁻³, F(000) = 1600, θ = 71.073 pm, μ(MoKα) = 0.117 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 0.2 x 0.2 x 0.1 mm by the 2θ(ω) method over the range of 8° < 2θ < 45°.

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

Tobias Rein,* Nina Kann, Reinhard Kreuder, Benoit Gangloff, and Oliver Reiser*
Dedicated to Professor Björn Åkermark on the occasion of his 60th birthday


[*] Dr. T. Rein, Dipl.-Chem. N. Kann
Organic Chemistry, Royal Institute of Technology
S-100 44 Stockholm (Sweden)
Telefax: Int. code +46 (8) 796 23 33
Dr. O. Reiser, R. Kreuder**
Institut für Organische Chemie der Universität
Tammannstraße 2, D-70776 Stuttgart (FRG)
Telefax: Int. code +49 (0) 711 394 47 52
B. Gangloff
Univ. de Marseille, Marseille (France)

[1] Erasmus exchange students at the Royal Institute of Technology, Stockholm.

[**] We thank the Swedish Natural Sciences Research Council, the Deutsche Forschungsgemeinschaft (Re 548/1-2), Carl Trygger Foundation for Scientific Research, the Foundation Bengt Lundqvists Minne, Hjalmar Ax:son Johnsons Foundation, and the Foundation of Technology for financial support. Dr. D. Yu. Degussa AG, Germany, is acknowledged for a generous sample of aldehyde I. Travel grants from the Erasmus program for student exchange (B. G.) and the Bundesamt für Ausbildungsförderung (B. K.) are gratefully acknowledged. We also thank Professors B. Åkermark, Royal Institute of Technology, Stockholm, A. de Meijere, Göttingen, and P. Helquist, University of Notre Dame IN, USA, for their continued interest and support, and Ms. Guri Hamborg for assistance with spectroscopic analyses.

Fig. 3. Structure of 3 in the crystal. Selected bond lengths [Å]: Ti–F = 202.5 (200.4–203.6), Mg–O(1) = 206.0 (203.6–209.3), Mg–O(2) = 226.8 (223.4–233.0), Mg–F = 202.6 (201.3–203.8), Mg–F = 190.5 (189.0–190.9). The values marked with an * are average values.