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Reactions of molecular CaF_2 with $[(C_5Me_5)TiF_3]$ and $[(C_5Me_4Et)TiF_3]$: symbiosis between ionic solids and organometallic compounds

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The reaction between $[(C_5Me_5)TiF_3]$ or $[(C_5Me_4Et)TiF_3]$ respectively in the presence of CaF_2 (prepared *in situ*) resulted in the formation of $[\{(C_5Me_5)TiF_3\}_4CaF_2]$ **1** or $[\{(C_5Me_4Et)TiF_3\}_4CaF_2]$ **2**, an X-ray study of compound **2** showed it to possess a core analogous to a crown ether.

In recent years there has been considerable interest in self-organization processes for generating new compounds. This is due to the increasing realization that such compounds could serve as useful model compounds for many naturally occurring processes in addition to their possible use in understanding the mechanisms of many catalytic systems employing solid supported catalysts.[1–4]

Our group[5] has reported the synthesis of molecular solids incorporating NaF, KF, CaF_2, MgF_2, Li_2O and TiO_2 respectively in organometallic compounds and siloxanes.

Reactions of $[Cp^*TiF_3]$[6] with NaF or KF, respectively give inclusion compounds of the type $[(Cp^*{}_2Ti_2F_7)_2M_2]$ (M = Na or K, $Cp^* = C_5Me_5$). In the case of the sodium compound eight fluorine atoms of two $[Cp^*{}_2Ti_2F_7]^-$ units enclose one sodium ion. The geometry of the fluorine surface at the Na^+ ion is comparable to that found in the oxygen congener of $[Na(12\text{-crown-}4)_2]^+$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane).

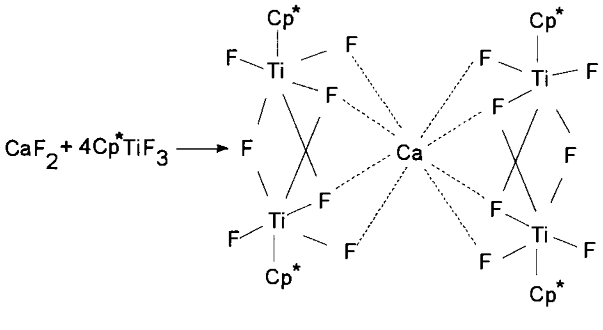
However, a similar reaction using $[Cp^*TiF_3]$ and CaF_2 is not observed due to the high lattice energy of CaF_2 and its insolubility in organic solvents. Furthermore, it was observed that sodium, magnesium and calcium metals are able to reduce $[Cp^*TiF_3]$ yielding paramagnetic complexes of $[Cp^*TiF_2]$, containing the corresponding metal fluorides.

In contrast, when calcium difluoride is formed *in situ*, according to the reaction shown in Scheme 1, in the presence of $[Cp^*TiF_3]$ or $[(C_5Me_4Et)TiF_3]$, the formation of $[(Cp^*TiF_3)_4CaF_2]$ **1** or $[\{(C_5Me_4Et)TiF_3\}_4CaF_2]$ **2** respectively is achieved. Moreover, under these conditions the precipitation of solid CaF_2 is not observed.†

Compounds **1** and **2** are soluble in thf, toluene, benzene and chloroform; furthermore, compound **2** is soluble in pentane and *n*-hexane, whilst **1** is only slightly soluble in *n*-hexane. These new compounds have been characterized by elemental analysis and IR, mass, and NMR spectroscopy.

In the gas phase the ions $[(C_5Me_5TiF_3)_2]^+$ and $[(C_5Me_4EtTiF_3)_2]^+$ respectively were observed by mass spectroscopy with 100% intensity. The ^{19}F NMR spectra of **1** and **2** in C_6D_6 give four resonances and the integration of the intensities (2 : 2 : 1 : 2) match well with their proposed structures as fluoro crown ether analogues of a metal bonded to two 12-crown-4 moieties in a sandwich fashion.‡,[9] Reactions of magnesium or strontium dichloride using trimethyltin fluoride as a fluorinating agent in solutions of $[Cp^*TiF_3]$ gave only insoluble MgF_2 or SrClF, respectively.

$$2\,Me_3SnF + CaCl_2 \longrightarrow CaF_2 + 2\,Me_3SnCl$$



$Cp^* = C_5Me_5$ **1** $Cp^* = C_5Me_4Et$ **2**

Scheme 1 Synthesis of CaF_2 inclusion compounds **1** and **2**, fluoro analogues of crown ethers

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† Compound **1**: $[Cp^*TiF_3]$ (0.480 g, 2 mmol), $CaCl_2{\cdot}1.5thf$ (prepared from CaH_2 by the procedure described for the chlorides of lanthanides)[7] (0.110 g, 0.5 mmol) and Me_3SnF (0.183 g, 1 mmol) were stirred for 18 h at room temperature in toluene (60 cm^3). The clear yellow solution was evaporated to dryness *in vacuo*. The solid residue was washed with pentane and recrystallized from thf–hexane (40 : 20 cm^3) and dried *in vacuo*. Yield 0.26 g (50%), m.p. 250 °C; ^1H NMR (C_6D_6): δ 2.09 (s); ^{19}F NMR (C_6D_6): δ 194.5 (s, 2 F), 14.8 (s, 2 F), −52.2 (s, 1 F), −63.5 (s, 2 F); mass spectrum (APCI), *m/z* 480 ($C_{20}H_{30}F_6Ti_2$, 100%); IR (Nujol) $\tilde{\nu}/cm^{-1}$, 634vs, 616vs, 533vs, 458s (Found: C, 45.6; H, 5.95. $C_{40}H_{60}CaF_{12}Ti_4$ requires C, 46.26; H, 5.82%).

Compound **2**: $[(C_5Me_4Et)TiF_3]$ (0.254 g, 1 mmol), $CaCl_2{\cdot}1.5thf$[7] (0.055 g, 0.25 mmol) and Me_3SnF (0.094 g, 0.5 mmol) were stirred for 18 h at room temperature in toluene (30 cm^3). The clear yellow solution was evaporated to dryness *in vacuo*. The solid residue was recrystallized from pentane. Yield 0.21 g (77%), m.p. 190 °C; ^1H NMR (C_6D_6): δ 0.86 (t, 3 H), 2.07 (s, 6 H), 2.13 (s, 6 H), 2.73 (q, 2 H); ^{19}F NMR (C_6D_6): δ 195.6 (s, 2 F), 15.0 (s, 2 F), −52.8 (s, 1 F), −62.7 (s, 2 F); mass spectrum (APCI), *m/z* 508 ($C_{22}H_{34}F_6Ti_2$, 100%); IR (Nujol) $\tilde{\nu}/cm^{-1}$, 637s, 620vs, 533s, 453s (Found: C, 47.43; H, 6.18. $C_{44}H_{68}CaF_{14}Ti_4$ requires C, 48.28; H, 6.26%).

‡ The resonances at δ 194.5 (**1**) and 195.6 (**2**) have been assigned to the terminal fluorine atoms, those at δ 14.8 (**1**) and 15.0 (**2**) to the terminal fluorine atoms bonded to the calcium atom, δ −52.2 (**1**) and −52.8 (**2**) to the bridging fluorine atom and δ −63.5 (**1**) and −62.7 (**2**) to the bridging fluorine atoms bonded to the calcium atom. The resonances of the terminal fluorine atoms giving positive shifts and the bridging ones giving negative shifts were also observed in the spectra of organozirconium fluorides.[8]

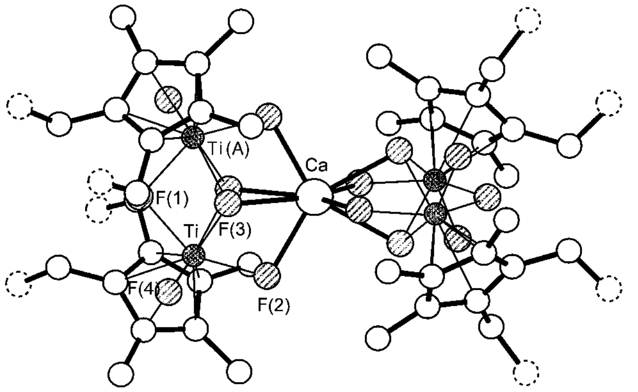

Fig. 1 Molecular structure of compound **2** (point-group symmetry S_4); C empty, C with 50% occupancy dashed, Ti filled, F shaded circles. Selected bond distances (pm) and angles (°): Ca–F(2) 231.2(2), Ca–F(3), 239.6(2), Ti–F(1), 201.7(2), Ti–F(2) 190.8(2), Ti–F(3) 202.3(2), Ti–F(4) 181.4(2), Ti(A)–F(3) 224.1(2), Ti–C 235.9(4) to 240.6(4), Ti–Ca 332.3(2), Ti–Ti(A) 311.5(2); Ti–F(1)–Ti(A) 101.06(13), Ti–F(3)–Ti(A) 93.71(9), F(2)–Ti–F(4) 97.09(12), F(2)–Ti–F(1) 142.90(10), F(2)–Ti–F(3) 80.71(10)

The structure of **2** was determined by X-ray single-crystal analysis (Fig. 1) § and shows the calcium atom to be co-ordinated to eight fluorine atoms from two $[(C_5Me_4Et)_2Ti_2F_7]^-$ units. As is evident from Fig. 1 the four fluorine atoms in each $[(C_5Me_4Et)_2Ti_2F_7]^-$ unit which are co-ordinating to the calcium atom form a concave surface with a sphere radius of 223 pm. The calcium atom is located 20 pm from the centre of the sphere having Ca–F distances of 231.2(2) pm and 239.6(2) pm, which are comparable to those found in CaF_2[11] (236.6 pm) and $CaZnF_4$ (233.6 and 237.7 pm).[12]

The Ti–F distances of the fluorine atoms bonded to calcium in compound **2** are on average 4 pm longer than the Ti–F bonds of fluorine atoms bonded to sodium in $[(Cp^*{}_2Ti_2F_7)_2Na]^-$.[5] The Ti–Ti axes of both $[(C_5Me_4Et)_2Ti_2F_7]^-$ units are perpendicular to each other. The eight fluorine atoms co-ordinated to the calcium atom form an elongated dodecahedron with triangular faces. A similar co-ordination around calcium was found in $CaZnF_4$.[12]

Moreover, in $[(Cp^*TiF_2)_6CaF_2]$[5] eight fluorine atoms are bonded to calcium with Ca–F bond lengths in the range 225.2–266.3 pm. Although the Ca–F distances in **2**, CaF_2 and $CaZnF_4$ are similar, the closest F–F contacts between two $[(C_5Me_4Et)_2Ti_2F_7]^-$ units in **2** are 329.1 pm and they are somewhat longer than these distances in CaF_2 (273 pm) or $CaZnF_4$ (276 pm).

It was found that compound **1** crystallizes from thf–*n*-hexane solution with one thf molecule very loosely co-ordinated to calcium. (The poor quality of the crystals did not allow structure refinement.) This indicates that the calcium atom in **1**, although co-ordinated to eight fluorine atoms, is susceptible to additional co-ordination.

In summary, compounds **1** and **2** are the first CaF_2 inclusion compounds of fluoro analogues of crown ethers. The great difference in reactivity of bulk and *in situ* prepared CaF_2 is demonstrated. The easy accessability of reactive CaF_2 using the metathesis reaction of $CaCl_2$ and trimethyltin fluoride in the presence of an organometallic compound opens up an interesting new field of chemistry. Moreover, this type of reaction is far superior to that using metals for the reduction of organometallic fluorides. The resulting compounds reported in this paper are diamagnetic instead of paramagnetic (as obtained using metals) and have allowed the elucidation of their structures in solution using ^{19}F NMR investigations.

Acknowledgements

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§ Crystal data for **2**: $C_{44}H_{68}CaF_{14}Ti_4$, $M_r = 1094.66$, tetragonal, space group $P4/n$, $a = 1345.1(4)$, $c = 1473.4(8)$ pm, $U = 2.666(2)$ nm^3, $Z = 2$, $\rho_{calc} = 1.364$ Mg m^{-3}, $F(000) = 1132$, μ(Mo-Kα) = 0.750 mm^{-1}, face-indexed numerical absorption correction (0.716/0.839 min./max. transmission), red prismatic crystal of size 0.5 × 0.4 × 0.3 mm, Syntex P21 four-circle diffractometer, ω scan mode, 1246 independent reflections of $2\theta = 3.0$–$40.0°$ (293 K, Mo-Kα $\lambda = 71.073$ pm), and 996 with [$F > 4.0\,\sigma(F)$] for the refinement of 152 parameters by full-matrix least squares on F^2 [Siemens SHELXTL PLUS (VMS)/SHELXL 93];[10] $R1 = 0.037$, $wR2 = 0.110$, Et/Me disorder at two positions, hydrogen atoms: rigid model, fixed isotropic U; maximal residual electron density 306 and -224 e nm^{-3}. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/545.