Detecting Labile Acid–Base Interactions at Low Temperature: Synthesis and *X*-Ray Structure of the Ternary Titanium Tetrachloride–Sulphur Dioxide–Arene Systems

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Reaction of SO_2 solutions of $TiCl_4$ with benzene and durene led to the isolation at −60 °C of structurally defined very labile complexes, $[(TiCl_4)_2(\sigma\text{-}OSO)_2(C_6R_6)_2]$ containing a biphilic SO_2.

The acid–base interaction between the strong Lewis acid $TiCl_4$[1] and SO_2[2] is assumed to exist in the absence of any competing solvent interaction, *i.e.* in liquid SO_2. The structure of the resulting very labile system seems almost impossible to determine. We found, however, that the addition of arenes to an SO_2 solution of $TiCl_4$ caused a significant change of the colour from very pale yellow to yellow (benzene) and deep red (durene). By cooling the solution to −60 °C compounds (**1**) and (**2**) crystallized in significant amounts.

$$2\,TiCl_4 + 2\,C_6R_6 \xrightarrow[-60\,^{\circ}C]{\text{liquid }SO_2} [(TiCl_4)_2(SO_2)_2(C_6H_2R_4)_2]$$

$$(\mathbf{1})\,R = H$$
$$(\mathbf{2})\,R_4 = 1,2,4,6\text{-}Me_4$$

Complexes (**1**) and (**2**) can be handled only in liquid SO_2 at −60 °C. On increasing the temperature to −30 °C they dissolve. We were able to transfer crystals of (**1**) and (**2**) at −60 °C from the liquid SO_2 to a diffractometer and to collect *X*-ray data at −103 °C. We expected from the *X*-ray analysis an answer to the question of the nature of the labile and weak interactions in these crystals, which are a sort of frozen solution. A picture of (**1**) is given in Figure 1.† The structure is a centrosymmetric dimer containing six-co-ordinate titanium atoms bridged by two chlorine atoms. Similar dimeric adducts have been observed between $TiCl_4$ and oxygen donor monodentate ligands.[1] Sulphur dioxide is σ-O bonded, as expected for an oxophilic metal, with a rather long Ti–O bond distance [2.179(3) Å].[1,3] The σ-O bonding mode is rare in transition metal chemistry, an example being $[trans\text{-}\{(SO_2)_2Mn(OPPh_3)_4\}I_2]$.[4] More examples are, however, known in main group chemistry, *e.g.* $[F_5Sb(OSO)]$.[5]

The structural parameters of SO_2 are only slightly affected by the interaction with the metal. The S–O bond distances [S–O(1), 1.459(4), S–O(2), 1.403(5) Å] and the O–S–O angle [117.0(2)°] are very close to those in free SO_2 (S–O, 1.43 Å; O–S–O, 119.5°).[6] We believe, however, that a significant stabilization to the system comes from the interaction between SO_2 and the arene ring. Sulphur interacts with the arene ring which is almost perpendicular to the SO_2 plane (81°) but at a rather long distance [3.20(1) Å]. The shortest S–C observed

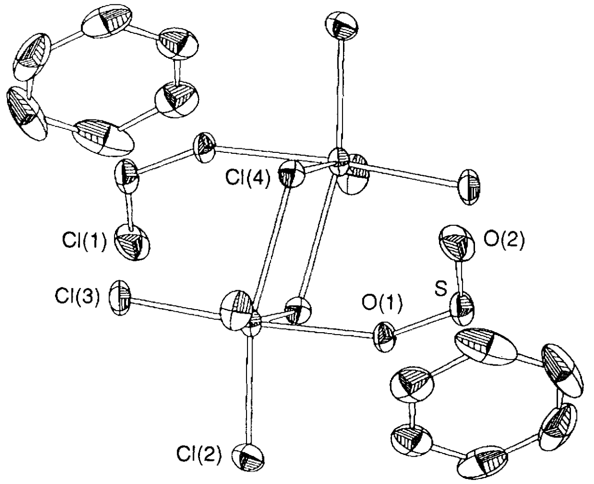

Figure 1. An ORTEP drawing of complex (**1**). Bond lengths (Å) and angles (°): Ti–Cl(1) 2.217(1), Ti–Cl(2) 2.195(2), Ti–Cl(3) 2.200(2), Ti–Cl(4) 2.462(2), Ti–Cl(4*) 2.460(2), Ti–O(1) 2.179(3), S–O(1) 1.459(4), S–O(2) 1.403(5), O(1)–S–O(2) 117.0(2). The shortest S–C distance is 3.06(1) Å, while the perpendicular distance from S to the C_6H_6 ring is 3.20(1) Å. Symmetry operation: * corresponds to $1 - x, -y, -z$.

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† *Crystal data* for (**1**): $C_6H_6Cl_4O_2STi$, $M = 331.9$, monoclinic, space group $P2_1/c$, $a = 8.9628(8)$, $b = 10.411(1)$, $c = 13.300(1)$ Å, $\beta = 104.355(7)°$, $U = 1202.6(2)$ Å^3, $Z = 4$, $D_c = 1.83$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.71069$ Å), $\mu(Mo\text{-}K_\alpha) = 17.4$ cm^{-1}; 1436 unique observed structure amplitudes $[I > 3\sigma(I)]$ collected at 170 K on a Nicolet R3m diffractometer in the range $6 < 2\theta < 57°$. The structure was solved using direct methods; the model converged to $R = R_w = 0.047$. No attempt to locate hydrogen atoms was made. All calculations were carried out using SHELX 76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

interactions are at 3.06(1) [S ··· C(2)] and 3.07(1) Å [S ··· C(3)]. The S ··· arene interaction is very significant and the benzene is not present as a lattice solvent. In order to prove this we used a substituted benzene, durene. Reaction (1) led to the same kind of compound, as proved by a preliminary *X*-ray analysis on (**2**).[7] If this is a case of an authentic sulphur–arene interaction, complexes (**1**) and (**2**) should be considered as charge-transfer complexes formed between the electrophilic activated SO_2 and the electron-rich arene. A reasonable number of 1 : 1 charge transfer complexes between amines and sulphur dioxide have been characterized adequately both in gas and in condensed phases.[8] Sulphur dioxide in complexes (**1**) and (**2**) experiences a sort of bifunctional interaction sitting in the middle of an acidic and a basic site. In addition, the Ti–SO_2–arene fragment may represent a structural model for the metal-assisted addition of an electrophile to benzene.

Other small molecules like carbon dioxide may undergo the same sort of electrophile activation. *X*-Ray analysis of complexes (**1**) and (**2**) has allowed us to inspect precisely the first and second co-ordination sphere in solution of a very labile species like the Lewis acid $TiCl_4$. Being able to freeze such weak interactions we have recently been able to identify $TiCl_4$–arene complexes.[9] In the presence of SO_2 as a solvent, $TiCl_4$ prefers to interact with the oxygen. In addition, attempted reaction of $TiCl_4$ solutions in benzene with SO_2 did not give any results.

We thank the Office of Naval Research (Grant No. N00014-89-J-1810) and the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-26245-89) for financial support.

Received, 9th April 1990; Com. 0/01590C

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