(22) Although the incident photon energy is high, the total number of photons absorbed is very small compared to the number of molecules present. Under typical conditions, at 7 KeV the flux is on the order of 10^8 photons/s with a bandwidth of about 1 eV.

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Crystal Structure, Raman Spectrum, and Nuclear Magnetic Resonance Spectrum of Methoxythionyl μ-Fluoro-bis(pentafluoroantimonate(V)), $CH_3OSO^+Sb_2F_{11}^-$

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Abstract: The compound $CH_3OSO^+Sb_2F_{11}^-$ has been prepared by the reaction of methyl fluoride with antimony pentafluoride in liquid sulfur dioxide. Its structure has been investigated by ^{19}F spectroscopy of its solutions in SO_2, by Raman spectroscopy of the polycrystalline solid, and by an x-ray crystallographic examination of a single crystal. The crystals are triclinic with $a = 5.391$ (5), $b = 8.059$ (3), $c = 13.932$ (4) Å, $\alpha = 90.63$ (4), $\beta = 102.12$ (5), $\gamma = 102.62$ (2)°. The structure was refined in the space group $P\bar{1}$ to a final agreement index of 0.0420 for 1405 independent reflections. The structure is made up of discrete CH_3OSO^+ cations and linear $Sb_2F_{11}^-$ anions.

Solutions of CH_3F and SbF_5 in sulfur dioxide and in sulfuryl chlorofluoride have long been thought to contain one or more CH_3F–SbF_5 complexes for which various formulations have been given.[1,2] However, the absence of H–F coupling in the ^1H and ^{19}F NMR spectra of these solutions has long remained an unexplained difficulty. Very recently Peterson et al.[3] reported the preparation of a white crystalline compound from the reaction of a 1:1 mixture of SbF_5 and CH_3F with SO_2 in solution in SO_2ClF. Because the compound reacted with methanol and ethanol to give dimethyl sulfite and methyl ethyl sulfite, respectively, rather than dimethyl ether and methyl ethyl ether, as reported previously,[1] Peterson proposed that the compound was $CH_3OSO^+SbF_6^-$ (or $Sb_2F_{11}^-$), in which, of course, no H–F coupling is expected.

At the same time Olah et al.[4] reinterpreted their earlier NMR data in terms of the formation of CH_3OSO^+ in SO_2 solution and $CH_3OSOClF^+$ in SO_2ClF solution. He has also shown by the observation of the expected H–F coupling in the ^1H NMR spectrum in SO_2F_2 as solvent, that the CH_3F–SbF_5 complex is formed in this solvent which, unlike SO_2 and SO_2ClF, is not methylated.

In this paper we report the isolation of a white crystalline compound from a solution of CH_3F and SbF_5 in SO_2, which is presumably the same compound as was reported by Peterson et al.[3] and also mentioned briefly by Olah et al.[4] Investigation of this compound by x-ray crystallography, Raman spectroscopy, and ^1H and ^{19}F NMR spectroscopy has shown that it is indeed not a CH_3F–SbF_5 complex but is the compound $CH_3OSO^+Sb_2F_{11}^-$.

Experimental Section

Antimony pentafluoride (Ozark-Mahoning) was purified by a double distillation in an all glass apparatus and sulfur dioxide (Matheson) was repeatedly distilled from, and kept over, phosphorus pentoxide before use. Methyl fluoride (Peninsular Chemical Research) was not further purified.

In a typical experiment, SbF_5 (5×10^{-3} mol) was syringed into one arm of a rigorously dried Pyrex glass double ampule inside a drybox. The apparatus was connected to the vacuum line and methyl fluoride (2.5×10^{-3} mol) and sulfur dioxide (2×10^{-2} mol) were condensed onto the SbF_5 at −196 °C. The mixture was allowed to warm to −78 °C and was stirred at this temperature for about 30 min. The mixture was allowed to warm up to −7 °C and the solvent was then removed by cooling the other ampule to −30 °C. White crystals were left behind and were pumped to dryness. Suitable crystals for x-ray studies were mounted in thin-walled quartz capillaries inside a drybox equipped with a microscope.

Crystal Data. $CH_3OSO^+Sb_2F_{11}^-$ is triclinic with $a = 5.391$ (5), $b = 8.059$ (3), $c = 13.932$ (4) Å, $\alpha = 90.63$ (4), $\beta = 102.12$ (3), $\gamma = 102.62$ (1)°, $V = 576$ Å^3, $Z = 2$, $D_c = 3.06$, fw = 531.4, $F(0,0,0) = 488$, $\lambda(\text{Mo K}\bar{\alpha}) = 0.71069$ Å, and $\mu(\text{Mo K}\alpha) = 51$ cm^{-1}. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the region $20° < 2\theta \leqslant 25°$. The structure was successfully refined in the centrosymmetric space group $P\bar{1}$. (C_i,[5]No. 2).

X-Ray Intensity Measurements. The crystal, which was an irregular block of approximate dimensions $0.28 \times 0.16 \times 0.09$ mm, was sealed in a thin-walled quartz capillary and mounted on a Syntex $P\bar{1}$ diffractometer with its 0.28-mm edge, which was approximately perpendicular to the (1,0,0) face, almost coincident with the ϕ axis of the diffractometer. Intensities were measured using graphite monochromated Mo K$\bar{\alpha}$ radiation, with a θ–2θ scan and a scan rate varying from 8.0 to 24.0°/min in 2θ so that weaker reflections were examined more slowly to minimize counting errors. Stationary background counts, with a time equal to half the scan time for each reflection, were made at each end of the scan range. The scan width varied from 2° at low 2θ to 2.5° for high-angle reflections. One standard reflection was regularly checked to monitor the stability of the crystal and its alignment, but no significant variation was observed. Independent reflections (1405) within the range $2\theta < 50°$ were measured resulting in 1331 reflections with intensities greater than three times their

Table I. Positional and Anisotropic[a] Temperature Parameters (×10⁴)

	x/a	y/b	z/c	$u(1,1)$	$u(2,2)$	$u(3,3)$	$u(1,2)$	$u(1,3)$	$u(2,3)$
Sb(1)	−237 (2)	2158 (1)	634 (1)	517 (6)	346 (5)	282 (5)	157 (4)	40 (3)	−17 (3)
Sb(2)	2537 (1)	2788 (1)	4448 (1)	409 (5)	348 (5)	247 (5)	9 (3)	25 (3)	−41 (3)
F(1)	−422 (23)	4155 (12)	1229 (7)	1345 (88)	706 (57)	864 (64)	504 (58)	109 (60)	−325 (40)
F(2)	2286 (27)	1736 (16)	1640 (8)	1366 (107)	1254 (87)	734 (73)	834 (82)	−448 (73)	−142 (64)
F(3)	−2756 (22)	827 (15)	1172 (9)	1178 (80)	1090 (87)	1110 (83)	207 (65)	748 (69)	405 (69)
F(4)	2339 (18)	3179 (16)	32 (9)	691 (56)	1335 (94)	1478 (98)	259 (57)	604 (62)	561 (79)
F(5)	−2728 (20)	2288 (14)	−468 (6)	862 (66)	1038 (72)	540 (51)	330 (55)	−163 (47)	77 (48)
F(6)	0000	0000	0000	1576 (138)	798 (87)	760 (91)	606 (90)	101 (91)	−320 (71)
F(7)	328 (18)	764 (11)	3929 (7)	833 (60)	547 (50)	767 (57)	−194 (43)	41 (48)	−253 (43)
F(8)	538 (18)	3272 (11)	5287 (6)	799 (59)	711 (53)	592 (50)	218 (44)	401 (45)	53 (40)
F(9)	1124 (18)	4078 (10)	3493 (6)	949 (63)	719 (56)	507 (47)	356 (48)	66 (43)	154 (41)
F(10)	4351 (15)	1825 (11)	5486 (5)	620 (44)	761 (55)	448 (41)	227 (40)	−23 (35)	147 (38)
F(11)	4953 (15)	2543 (12)	3732 (6)	615 (47)	952 (65)	535 (45)	182 (44)	273 (38)	−84 (42)
F(12)	5000	5000	5000	991 (99)	587 (79)	753 (81)	−266 (70)	50 (74)	−216 (64)
S	4978 (7)	954 (4)	7373 (2)	553 (20)	520 (20)	455 (19)	192 (15)	111 (15)	−1 (15)
O(1)	7540 (18)	1797 (14)	7459 (14)	470 (54)	1001 (79)	534 (53)	294 (53)	125 (42)	45 (51)
O(2)	3199 (15)	2065 (11)	7536 (6)	390 (43)	484 (50)	567 (51)	95 (37)	92 (39)	18 (39)
C	3949 (31)	3952 (19)	7721 (11)	742 (98)	537 (87)	562 (93)	185 (73)	127 (77)	−29 (71)

[a] The anisotropic temperature parameters are given in the expression $\exp[-2\pi^2(h^2a^{*2}u(1,1) + k^2b^{*2}u(2,2) + l^2c^{*2}u(3,3) + 2hka^*b^*u(1,2) + 2hla^*c^*u(1,3) + 2klb^*c^*u(2,3))]$.

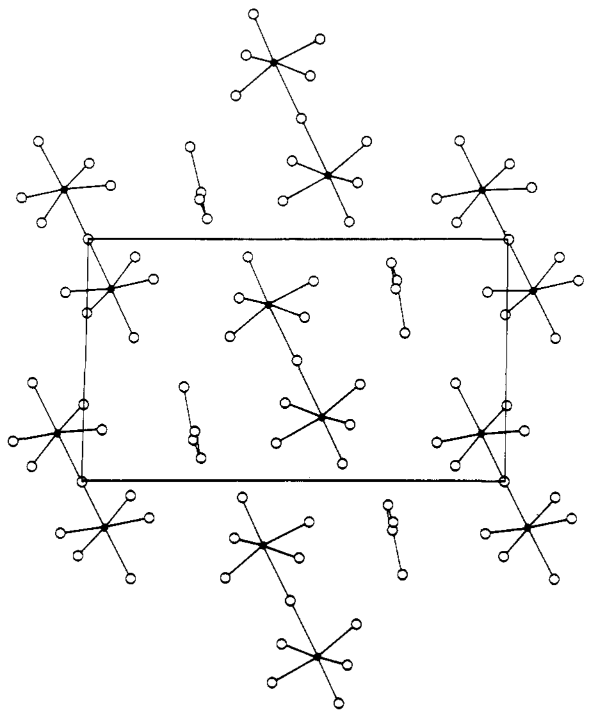

Figure 1. A projection of the structure down the a axis.

Table II. Bond Lengths (Å) and Angles (deg)

Sb(1)-F(1)	1.834 (10)	Sb(2)-F(7)	1.835 (8)
F(2)	1.828 (12)	F(8)	1.839 (9)
F(3)	1.835 (12)	F(9)	1.839 (9)
F(4)	1.820 (12)	F(10)	1.847 (10)
F(5)	1.836 (9)	F(11)	1.839 (9)
F(6)	1.983 (1)	F(12)	2.009 (1)
O(2)-C	1.492 (17)	S-O(1)	1.379 (10)
		O(2)	1.491 (10)
F(1)-Sb(1)-F(2)	94.1 (5)	F(7)-Sb(2)-F(8)	95.6 (4)
F(3)	94.6 (5)	F(9)	94.9 (4)
F(4)	94.0 (5)	F(10)	94.5 (4)
F(5)	94.5 (5)	F(11)	92.8 (4)
F(6)	179.4 (3)	F(12)	178.9 (4)
F(2)-Sb(1)-F(3)	90.1 (6)	F(8)-Sb(2)-F(9)	92.4 (4)
F(4)	88.2 (6)	F(10)	87.4 (4)
F(5)	171.4 (5)	F(11)	171.1 (3)
F(6)	85.4 (4)	F(12)	85.5 (3)
F(3)-Sb(1)-F(4)	171.4 (6)	F(9)-Sb(2)-F(10)	170.5 (3)
F(5)	89.5 (5)	F(11)	89.8 (4)
F(6)	85.6 (4)	F(12)	85.0 (2)
F(4)-Sb(1)-F(5)	90.9 (5)	F(10)-Sb(2)-F(11)	89.1 (4)
F(6)	85.8 (4)	F(12)	85.6 (2)
F(5)-Sb(1)-F(6)	86.0 (4)	F(11-Sb(2)-F(12)	86.1 (3)
		O(1)-S-O(2)	114.7 (6)
		S-O(2)-C	125.8 (8)

standard error based on counting statistics. Lorentz, polarization, and absorption corrections were applied to the observed intensities.

Structure Determination. The positions of two independent heavy atoms were located from the three-dimensional Patterson function, assuming the space group to be $P\bar{1}$. These atoms were assumed to be antimony. The scattering factors for neutral antimony were corrected for anomalous dispersion using the values for the real and imaginary parts given in the International Crystallographic Tables.[5] Full-matrix least-squares refinement of positional and isotropic temperature parameters produced a conventional agreement index, R_1, of 0.27. Subsequent difference electron density maps yielded the positions of 16 light atoms. Each antimony was surrounded by an octahedral arrangement of light atoms, assumed to be fluorine. Ten of these atoms lay on twofold general positions, while the other two lay on the special positions (0,0,0) and (½,½,½). Since the electron density map showed the presence of four additional light atoms (excluding hydrogen) it was evident that the compound under investigation was not $CH_3Sb_2F_{11}$. In view of the fact that SO_2 had been used as a solvent, that the Raman spectrum showed the probable presence of an SO bond, and that the NMR spectrum showed the presence of a CH_n group, it was assumed that the light atoms were sulfur, two oxygens, and a carbon with the arrangement OSOC, in other words that the cation was CH_3OSO^+. When the appropriate scattering curves were applied and anisotropic temperature factors were introduced, a final agreement index, $R_2 = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma wF_o^2]^{1/2}$ of 0.0600, where $w = (11.59 + 0.28F_o + 0.0062F_o^2)^{-1/2}$, was obtained for reflections. The final R_1 index for observed reflections was 0.0420 and the final difference synthesis showed no significant peaks. The largest shift Δ/σ in the final cycle was 0.1. The atomic parameters are given in Table I, and a set of structure factor tables is available.[6]

Description of the Structure

The interatomic distances and bond angles are given in Table II and the atomic arrangement is shown in Figure 1. The asymmetric unit contains the CH_3OSO^+ cation, shown in Figure 2, and two halves of two $Sb_2F_{11}^-$ anions.

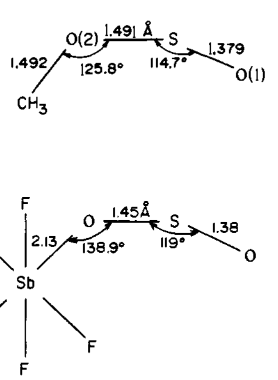

Figure 2. The CH_3OSO^+ cation and the SbF_5SO_2 molecule.

The CH_3OSO^+ ion has a bent cis structure with bond angles of 125.8° at oxygen and 114.7° at sulfur. The S-O(1) bond length, 1.379 Å, is shorter than those found in SO_2 (1.432 Å)[7] and in SOF_2 (1.412 Å),[8] but similar to that found in the SOF_3^+ cation (1.37 Å),[9] which is the shortest known S-O bond length. It has been estimated that this bond length corresponds to an S-O bond order of 2.3[10] and it seems reasonable to conclude that structure 2 shown in Figure 3 is of some importance. The S-O(2) bond length, 1.491 Å, is longer than that found in SO_2, but much shorter than the length of an S-O single bond, which is expected to be about 1.70 Å.[10]

The length of the S-O(2) bond is indicative of a bond order of about 1.5,[10] hence structure 3 must also be considered to be an important resonance form. The bond lengths indicate that structures 2 and 3 are considerably more important than 1. The geometry of the sulfur atom is of the type AX_2E and therefore, to a first approximation, a bond angle of 120° is expected, as is found in SO_2.[7] It is noteworthy that the observed bond angle is close to the angle of 116° in the closely related $F{-}\ddot{S}{\equiv}N$.[11]

The fourth atom in the cation cannot be identified with certainty from the x-ray data; it could be C, O, or F; however, neither of the corresponding cations, $OSOF^+$ or $OSOOH^+$, seem very probable and in any case the spectroscopic data strongly supports the presence of a methyl group. The bond length of 1.492 Å between this atom and the neighboring oxygen is also in agreement with it being a carbon atom. This bond length is, in fact, slightly longer than the sum of the covalent radii of carbon and oxygen (1.43 Å), which is indeed the CO bond length in a number of molecules.[12] The COS angle, 125.8°, is quite large and again suggests a strong contribution from structure 3, for which the ideal bond angle is 120°. The rather long bond length and the rather large bond angle can both be plausibly attributed to the formal charge on the oxygen increasing the polarity of the C-O bond in the sense $C^{\delta+}\text{-}^{\delta-}O$ and thus increasing the bond length and at the same time increasing the bond-bond repulsions in the valency shell of the oxygen atom and thus increasing the bond angle.

Since CH_3OSO^+ may be regarded as a complex of the Lewis acid CH_3^+ and the base SO_2, it is interesting to compare its structure with that of another Lewis acid-base complex of SO_2, namely SbF_5SO_2. It may be seen in Figure 2 that the SO_2 molecule is similarly bound through an oxygen atom to the antimony and that the bond lengths and the angle of the SO_2 part of the molecule are remarkably similar to those of the CH_3OSO^+ ion.[13] The SOSb angle is appreciably larger than the SOC angle and the ideal value of 120°; however, large bond angles at oxygen are frequently encountered when oxygen is bonded to a heavy element such as antimony.[14]

The two crystallographically independent $Sb_2F_{11}^-$ ions have linear Sb-F-Sb bridges, the bridging fluorine atoms lying on centers of symmetry. In all the previously determined structures containing the $Sb_2F_{11}^-$ ion the bridge angle was in the range 141-173°. The mean Sb-F (bridge) and Sb-F (terminal) distances, 1.996 and 1.835 Å, respectively, are similar to those found for the $Sb_2F_{11}^-$ ion in other structures, e.g., $ClO_2^+Sb_2F_{11}^-$.[15] The equatorial plane of fluorine atoms in both $Sb_2F_{11}^-$ ions is displaced toward the bridging atoms as is observed in other structures.[15]

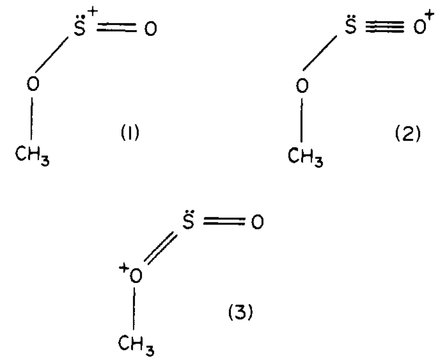

Figure 3. The three resonance forms of the CH_3OSO^+ cation.

Table III. Raman Spectrum of $CH_3OSO^+Sb_2F_{11}^-$

$\Delta\nu$, cm^{-1}	$\Delta\nu$, cm^{-1}
229 (mw)	677 (s)
295 (mw)	689 (m)
548 (w)	728 (mw)
591 (mw)	995 (m)
642 (s, sh)	1315 (m)
649 (s)	2985 (m)

The structure has an approximately cubic close-packed arrangement of light atoms. Edwards[15] has pointed out that, in structures containing the $Sb_2F_{11}^-$ ion and having an approximately close-packed arrangement of light atoms, the $Sb_2F_{11}^-$ bridge angle is expected to approach 132° if the close packing is hexagonal and 180° if it is cubic. Our results are clearly consistent with Edwards' suggestion. The efficiency of the close packing is reflected in the low volume per light atom (20.6 Å^3 neglecting hydrogens).

The ionic description of the structure is essentially correct, since the shortest interionic contact, S-F(7),[1] is 2.70 Å. Although this is shorter than the sum of the van der Waals radii of sulfur and fluorine, 3.20 Å,[9] it is only a little shorter than the shortest contact in $SOF_3^+AsF_6^-$ (2.89 Å),[9] which was described as being essentially ionic. There may be hydrogen bonding between the hydrogen atoms of the methyl group and the fluorine atoms of the $Sb_2F_{11}^-$ ions.

The proton NMR spectrum of a solution of $CH_3OSO^+Sb_2F_{11}^-$ in SO_2 has a single sharp peak at 5.33 ppm below external Me_4Si as found previously.[2] This is attributed to the CH_3OSO^+ cation. The deshielding of the protons with respect to methyl fluoride can be reasonably attributed to the greater electronegativity of O^+ than fluorine. The absence of H-F coupling, for which the previous explanations were not entirely satisfactory,[1,2] is now clearly understandable. The ^{19}F spectrum was that of an $Sb_2F_{11}^-$ ion as previously observed. There was no evidence for F on O or F on S.

A list of the peaks observed in the Raman spectrum is given in Table III. The sharp peak at 2985 cm^{-1} must be assigned as a C-H stretching vibration. The frequency is somewhat greater than that generally found for a methoxy group (~2900 cm^{-1}), but that is not surprising in view of the positive charge. The peak is 1315 cm^{-1} must be assigned as the S=O(1) stretch. This frequency is greater than that of the mean of the symmetric and antisymmetric vibrations in SO_2 (1363 and 1151 cm^{-1}, mean 1256 cm^{-1} [16]) and similar to that found in $SbF_5{\cdot}SO_2$ (1323 cm^{-1} [17]). This is consistent with a contribution from structure 2. The peak at 995 cm^{-1} is probably the S-O(2) stretch. This frequency is consistent with the bond length of 1.49 Å and appears to be the same as that found previously at 1010 cm^{-1}, which was assigned as a C-F vibration.[1] If the C-H vibrations are ignored, then there should be $3n - 6 = 6$ vibrations. The C—O stretch was not observed, but it may well be weak. The three bending vibrations are expected to have lower frequencies and it is difficult to make any certain assignments because of the large number of $Sb_2F_{11}^-$ bands.

Supplementary Material Available: a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Chemistry of μ-(η^1:η^5-Cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti-Ti*). 1. Synthesis and Structural Studies

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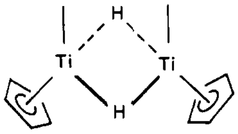
Abstract: The preparation of μ-(η^1:η^5-cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti-Ti*), $(\eta\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)\text{-}Ti}(\eta\text{-}C_5H_5)$, by the low-temperature reduction of $(\eta\text{-}C_5H_5)_2TiCl_2$ with potassium naphthalene is described. Treatment of the compound with tetrahydrofuran (C_4H_8O) leads to the formation of the crystalline adduct: $(\eta\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)\text{-}Ti}(\eta\text{-}C_5H_5)(C_4H_8O)\cdot C_4H_8O$. The structure of this material has been determined by single-crystal x-ray diffraction methods. The molecule may be considered as two bis(η-cyclopentadienyl)titanium units, held together by a metal-metal linkage. One of the cyclopentadienyl ligands, however, contains only four hydrogen atoms and serves to bridge the two titanium centers, in a monohapto pentahapto bonding arrangement. The Ti-Ti distance is 3.336 (4) Å. The most significant structural feature of the molecule is the high degree of coordinative unsaturation about the metal-metal bond. The tetrahydrofuran may readily be removed from the adduct by treatment with *n*-octane under vacuum to yield very pure samples of $(\eta\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)\text{-}Ti}(\eta\text{-}C_5H_5)$. Infrared spectra of the two titanium compounds are consistent with their molecular structure, but give no indication of the unusual μ-(η^1:η^5-C_5H_4) bonding arrangement. The 100-MHz ^1H NMR spectrum of $(\eta\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)\text{-}Ti}(\eta\text{-}C_5H_5)$ in toluene consists of a single temperature-dependent broad resonance which at 32 °C appears at δ_{Me_4Si} 15.0 and is typical of a paramagnetic species.

The discovery of ferrocene,[1] $(\eta\text{-}C_5H_5)_2Fe$, in 1951 was quickly followed by attempts to prepare so-called metallocenes of the other transition metals. Dicyclopentadienyl compounds of V, Cr, Mn, Co, Ni in the first transition series and of Ru, Rh, Os, and Ir in the group 8 family of elements are now well known.[2] It has only recently been recognized, however, that simple $(\eta\text{-}C_5H_5)_2M$ compounds of the earlier transition metals and of the lanthanide and actinide elements are not readily obtainable. Attempts to prepare such metallocenes invariably lead to complex organometallic molecules. For instance, a material commonly referred to as "niobocene" has proved to be the bridging bis(η^1:η^5-cyclopentadienyl)-bis(η-cyclopentadienyl)niobium hydride dimer: $(\eta\text{-}C_5H_5)HNb\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)_2\text{-}NbH(\eta\text{-}C_5H_5)$.[3] The same bridging cyclopentadienyl feature is seen in the thorium compound: $(\eta\text{-}C_5H_5)_2Th\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)_2\text{-}Th(\eta\text{-}C_5H_5)_2$.[4]

Many attempts have been made to synthesize discrete dicyclopentadienyltitanium(II) species. These efforts have recently been stimulated by the discovery that cyclopentadienyl compounds of low-valent titanium are able to reduce molecular nitrogen. Titanocene, $(\eta\text{-}C_5H_5)_2Ti$ or $[(\eta\text{-}C_5H_5)_2Ti]_2$, has been said to result from reaction of $TiCl_2$ with cyclopentadienylsodium,[5] from the hydrogenolysis of $(\eta\text{-}C_5H_5)_2Ti(CH_3)_2$,[6] and from reaction of $(\eta\text{-}C_5H_5)_2TiCl_2$ with various reducing agents.[7-9] The main product in these syntheses is now known[10,11] to be μ-(η^5:η^5-fulvalene)-di-μ-hydrido-bis(η-cyclopentadienyltitanium) (I).



I

The synthesis of a "metastable titanocene", $[(C_5H_5)_2Ti]_2$ (II), that is active towards N_2 was eported by Brintzinger and co-workers in 1971.[12,13] It was obtained by the decomposition of a dicyclopentadienyltitanium hydride, $[(C_5H_5)_2TiH]_n$: