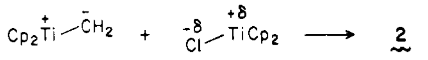
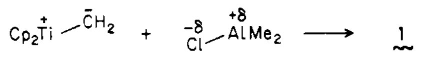
low value of the ^{47,49}Ti coupling in **2** (4.5 G) compared to that of $Cp_2TiCl(THF)$ (12.1 G) and of other Ti^{III} species (10–12 G) is also consistent with the unpaired electron being shared equally by two titanium centers.

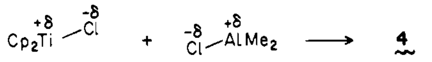
We consider that **2** is the result of the union of Cp_2TiCl with a transient mononuclear titanium methylene complex $Cp_2Ti{=}CH_2$, which may be represented by the ylide structure $Cp_2Ti^{+}{-}C^{-}H_2$ (eq 2). In this reaction the Cp_2TiCl plays the same role as the Me_2AlCl in the formation of **1** (eq 3). In both cases the polarizations of the Cl–Ti and Cl–Al bonds are the same, and the fourth coordination sites of the Ti atoms are filled by the appropriate donor ligand (chlorine or methylene). This type of reaction is evidently fairly general. Very recently the dimer **7** of Cp_2TiCH_2 (eq 5) has been reported.[15] It was formed in a reaction that most probably generates mononuclear Cp_2TiCH_2. As another example of such a coupling reaction, we found that the paramagnetic complex **4** and its dialkyl analogues are cleanly prepared by mixing equimolar toluene solutions of Cp_2TiCl and $ClAlR_2$ (eq 4).[16] Previously, complexes such as **4** were prepared in the much more complex reductions of Cp_2TiCl_2 with aluminum haloalkyls.[9]



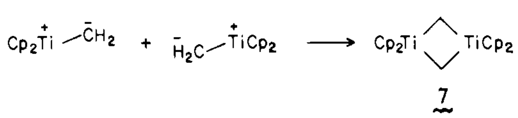
(2)



(3)



(4)



(5)

Isotopically labeled derivatives of **1**, treated as above with THF, yield the expected ESR spectra of the corresponding labeled analogues of **2**. The spectrum of Figure 2B is obtained on adding about 10 equiv of THF to a toluene solution of $Cp_2TiCD_2AlCl(CD_3)_2$.[4] The triplet spectrum is now replaced by a single broader line (marked d) since the expected 1:2:3:2:1 quintet for two deuterons ($I = 1$) cannot be resolved. This is because the deuteron splitting is smaller than the proton splitting by a factor of 6.5144, that is, the ratio of the proton and deuteron magnetic moments. Similarly, the spectrum of Figure 2C was obtained from $Cp_2Ti^{13}CH_2AlClMe_2$, about 45% enriched in ^{13}C.[17] Although the presence of the ^{47,49}Ti satellite lines of $Cp_2TiCl(THF)$ (labeled b) complicates somewhat the analysis, accurate ESR measurements show that the three lines marked a correspond to unlabeled $TiCH_2\cdot$ and the lines marked c belong to a doublet-of-triplets spectrum (see inset, Figure 2C) appropriate for $Ti^{13}CH_2\cdot$ ($a(^{13}C) = 7.3$ G, doublet).

Methylene exchange between the diamagnetic complex **1** and olefins of the type $CH_2{=}CR_2$ is activated by ethers.[18] Our ESR study now shows that the paramagnetic methylene complex **2** is also involved in this exchange process, although the mechanism of its participation is not known with certainty. A toluene solution 0.02 M in $Cp_2TiCD_2AlCl(CD_3)_2$, 0.08 M in methylenecyclohexane, $CH_2{=}C_6H_{10}$, and 0.04 M in THF was allowed to stir overnight at room temperature. When examined by ESR (Figure 2D), the exchange of the metal–CD_2 fragment with the olefin–CH_2 fragment was evident by the appearance of the triplet spectrum (marked a) appropriate for $TiCH_2\cdot$. A comparable result was obtained with mixtures prepared in the same fashion from $Cp_2TiCD_2AlCl(CD_3)_2$ and $^{13}CH_2{=}C_6H_{10}$. In this case, the appearance of the lines appropriate for $Ti^{13}CH_2$ (marked c, Figure 2E) indicates that the CD_2 fragment of the original methylene complex has been exchanged, albeit incompletely (note residual $TiCD_2\cdot$, line d), with the terminal $^{13}CH_2$ group of the labeled methylenecyclohexane. In a final experiment, **1** and $^{13}CH_2{=}C_6H_{10}$ were treated with THF as above to produce the spectrum of Figure 2F, which is clearly analogous to that of Figure 2C obtained from an authentic mixture of **1** and its $^{13}CH_2$-labeled derivative, once again demonstrating the occurrence of methylene exchange.

An attractive scheme describing both the formation of **2** and the observed CH_2 exchange in the presence of THF is shown in Scheme I. We consider that THF has a dual role: one leading to the activated mononuclear $TiCH_2$ complex **5** (path a), which is responsible for the methylene scrambling reaction via the titanacyclobutane **6**, and another, degradative in nature, leading to the observed $Cp_2TiCl(THF)$ (path b).[19] The latter is then converted to **2** by interaction with the activated complex **5**. Direct evidence for a pyridine-assisted conversion of **1** to a diamagnetic titanacyclobutane is now available in a report by Grubbs and co-workers, who found that an isolable titanacyclobutane analogous to **6** is formed in high yield from **1** and $CH_2{=}CHCMe_3$.[20]

Acknowledgment. We thank B. F. Gordon and D. J. Jones for skillful and dedicated technical assistance.

Registry No. **1**, 97719-69-1; **2**, 81642-85-5; **3**, 1271-18-7; **4**, 81554-28-1; Cp_2TiCl, 60955-54-6; $Cp_2TiCl(THF)$, 65466-17-3; $CH_2{=}C_6H_{10}$, 1192-37-6.

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(14) Natta, G.; Corradini, P.; Bassi, I. W. *J. Am. Chem. Soc.* **1958**, *80*, 755. See also ref 9, p 176.

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(16) The ESR parameters of **4** are as follows: $g = 1.9770$, $\Delta H_{ptp} = 13.9$ G, a(Al) = 2.3 G (partially resolved), a(Ti) = 11.7 G, $T = -50$ °C. For the methyl analogue of **4**, prepared in the same fashion, the Al hyperfine structure can no longer be resolved, and the spectrum consists of a single line with a very pronounced inflection of the kind discussed above. The smaller Al coupling is reflected by a smaller distance between the maximum and the minimum of the inflected line shape (peak-to-peak line width, $\Delta H_{ptp} = 11.0$ G, $g = 1.9770$, $T = -50$ °C). An analogous reaction with Et_2AlH gave blue $Cp_2Ti(\mu\text{-}H)(\mu\text{-}Cl)AlEt_2$ ($g = 1.9857$, a(H) = 5.6 G (doublet), a(Ti) = 10.0 G, $T = -50$ °C).

(17) Prepared from **1** and $^{13}CH_2{=}CMe_2$ in C_6D_6 solution (Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074).

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(19) A similar degradation evidently occurs when **1** is treated with pyridine, a stronger Lewis base than THF. Indeed, $(Cp_2TiCl)_2$ has been isolated in substantial yields from the reaction of **1** with pyridine (see Experimental Section).

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Contribution from the Facultad de Farmacia, Universidad de Navarra, Pamplona, Spain, and the Instituto de Quimica Inorgânica "Elhúyar", Serrano 113, Madrid-6, Spain

Preparation and Crystal Data of Cerium Antimony(III) Trioxide

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In addition to the Ln_3SbO_7 compounds[2] and four stoichiometrically undefined oxides of Sb(III) and lanthanides,[2a,3] the first reported $LnSbO_3$ compounds (Ln = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) were prepared[4] by Nasanova

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(1) (a) University of Navarre. (b) Elhuyar Institute.

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Table I. X-ray Powder Diffraction Data for $CeSbO_3$

hkl	d_{obsd}, Å	d_{calcd}, Å	I_{obsd}	I_{calcd}
111	6.18	6.25	14	12
222	3.127	3.125	970	1000
400	2.709	2.706	263	328
440	1.913	1.914	520	488
622	1.631	1.632	408	418
444	1.5622	1.5624	76	87
800	1.3530	1.3531	69	70
662	1.2416	1.2417	165	162
840	1.2102	1.2102	106	114
844	1.1048	1.1048	157	142
10,2,2, 666	1.0415	1.0416	140	133
880	0.9567	0.9568	59	55
10,6,2	0.9148	0.9148	215	183
12,0,0, 884	0.90203	0.90205	96	94
12,4,0	0.85578	0.85576	152	125
10,6,6	0.82538	0.82537	135	124
12,4,4	0.81595	0.81593	110	110
888	0.78120	0.78120	104	104

et al. from Sb_2O_3 and Ln_2O_3 under vacuum at 929 K. Six of them (Ln = Nd, Sm, Dy, Y, Ho, Er) are cubic, with *a* in the range 5.52–5.36 Å and smallest observed *d* spacings of ca. 1.20 Å. The purpose of this paper is to report the preparation of polycrystalline $CeSbO_3$ and to establish powder diffraction data of this new compound.

Experimental Section

$CeSbO_3$ was prepared from a mixture of cerium dioxide and antimony(III) oxide of molar ratio Ce:Sb = 1:1, heated at 963 K for 7 days in a quartz ampule at 10^{-3} mmHg, and quenched in liquid nitrogen. Analytical grade reagents and a Heraeus KS-120 furnace were employed. The temperature was read with calibrated Pt—Pt-10% Rh thermocouples and is reliable to ±10 K. Powder data were recorded with W (99.99%) as internal standard, a = 3.16524 Å (JCPDS, 1976), nickel-filtered copper radiation (λ_1 = 1.540 598 Å), a Siemens Kristalloflex 810, and a D-500 goniometer provided with a graphite monochromator, at a scanning rate of 0.100° 2θ min^{-1}. The setting of the sample and the determination of interplanar spacings and lattice constant were made according to the method followed by the JCPDS Associateship at the NBS.[5] The unit-cell parameter was refined from the 2θ values of the last seven reflections. The integrated intensities were measured with a Hewlett-Packard 9830A computer with a 9864A digitizer. The intensities were calculated with the computer program LAZY-PULVERIX[6] and scattering factors for neutral atoms, including Lorentz and polarization factors and correction for anomalous dispersion. The discrepancy factor $R = (\sum|I_o^{1/2} - I_c^{1/2}|)/\sum I_o^{1/2}$ was computed after making $\sum I_o = \sum I_c$ with a Hewlett-Packard HP-85 computer.

Table II. Atomic Positions and Occupation Factors Assumed for $CeSbO_3$

Ce-1	(c)	0, 0, 0	1	0	0.5	1	1	0.5
Ce-2	(d)	$^1/_2$, $^1/_2$, $^1/_2$	0	1	0.5	0	1	0.5
Sb-1	(c)	0, 0, 0	0	1	0.5	0	1	0.5
Sb-2	(d)	$^1/_2$, $^1/_2$, $^1/_2$	1	0	0.5	1	0	0.5
O-1	(a)	$^1/_8$, $^1/_8$, $^1/_8$	$^6/_7$	$^6/_7$	$^6/_7$	0	0	0
O-2	(f)	x,[a] $^1/_8$, $^1/_8$	$^6/_7$	$^6/_7$	$^6/_7$	1	1	1

[a] x = 0.300, 0.3125, 0.325, 0.350, 0.375, 0.400, 0.425, 0.4375, 0.450.

Results

$CeSbO_3$ was obtained as a greenish white powder, which gave satisfactory chemical analyses (Ce, $45._1$%; Sb, $39._2$%) and a good X-ray diffraction pattern, as can be seen in Table I, which includes the observed and calculated *d* values. Systematic extinctions suggested the space group as $Fd3m$ (No. 227). Thus $CeSbO_3$ is a defect cubic pyrochlore with a = 10.8246 (3) Å, V = 1268.3 (1) $Å^3$, Z = 16, and D_c = 6.49 Mg m^{-3}, although all the reflections, except the weak one 111, could be indexed on the basis of a cubic cell of the fluorite type whose cell edge is half of the pyrochlore cell edge. On the basis of the origin as the center ($\bar{3}m$) in the space group $Fd3m$, the intensities were calculated for the sets of positions and occupation factors of the asymmetric cell atoms that are shown in Table II. The best agreement (R = 0.037) between observed and calculated intensities of the reflections with $I_c \geq 5$ was obtained for x = 0.375, Ce and Sb being at (c) and (d) positions, respectively, and O atoms randomly distributed at six of every seven (a) and (f) positions. Thus the average Ce–O and Sb–O distances are 2.3436 Å.

The cell volume per anion of $CeSbO_3$, 26.4 $Å^3$, is approximately equal to those calculated from the unit-cell parameters[7] for orthorhombic and cubic Sb_2O_3, 27.6, and 28.9 $Å^3$, respectively. If the volume of the Sb(III) lone pair and cation is computed as that of an anion[8] and the volume of Ce is ignored, the mentioned cell volume per *anion* is lowered to 19.8 $Å^3$, this magnitude being slightly higher than the figures 16.6 and 17.3 $Å^3$ for orthorhombic and cubic Sb_2O_3, respectively.

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Registry No. $CeSbO_3$, 81642-86-6.

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