stirred further for 15 min at −45 °C and for 15 min at 0 °C, the reaction mixture was warmed to room temperature and the volatile components were distilled into a −197 °C trap until a yellow liquid and a white solid began to condense in the trap. Then, most of the solvent CH_2Cl_2 was pumped out from the cold trap at the temperatures below −60 °C. The remaining fraction was passed through −23 and −45 °C traps. The dichloroboryl compound was trapped in the −45 °C trap. Thus, treatment of 4.85 mmol of KB_5H_8 (estimated from the amount of hydrogen gas evolved in the reaction of KH with B_5H_9) with 14.6 mmol of BCl_3 in about 5 mL of dichloromethane yielded 3.04 mmol (0.437 g) of $(\mu\text{-}Cl_2B)B_5H_8$ (62.7% yield based on the $B_5H_8^-$ used). Anal. Calcd for $B_6H_8Cl_2$: Cl, 49.4%. Found: 49.1%. Infrared Spectrum (gas phase, 1 mm pressure, 100-mm path length cell, KBr windows, Beckman IR-20 spectrophotometer): 2608 (s), 2580 (m, sh), 1422 (m, br), 996 (w), 940 (w), 908 (s), 829 (m), 778 (m), 670 (w), 593 (w) cm^{-1}.

The product is extremely sensitive to moisture and air. The inner walls of the glassware need to be dried exhaustively before being brought into contact with the compound if the formation of a white solid deposit on the glass surface and the contamination of the compound with pentaborane(9) are to be avoided. Also, the compound is absorbed by Apiezon grease. The grease that is contaminated by the compound will catch fire when exposed to air. Extensive pumping is necessary before greased joints are disconnected.

Reactions of $(\mu\text{-}Cl_2B)B_5H_8$ with Ethers. When the dichloroboryl compound was treated with diethyl ether in dichloromethane at −80 °C a reaction occurred as evidenced by the appearance of a new set of ^{11}B NMR signals in the spectrum of the solution. The new signals were at +7.8 (br), −3.3 (br), −14.3 (d), and −52.3 (d) ppm in an approximately 1:1:3:1 intensity ratio. As long as the amount of the ether added was less than 1 mol/mol of the dichloroboryl compound, the signals of the dichloroboryl compound were still present in the spectrum even when the solution was warmed to room temperature. The product slowly decomposed at room temperature. The ^{11}B spectra of the products from the reactions with dimethyl ether and tetrahydrofuran were similar to that of the diethyl ether reaction product.

When a CH_2Cl_2 solution containing the ether addition compound was treated with excess boron trifluoride, the etherate of BF_3 and a compound that could be identified by a set of ^{11}B NMR signals were produced. The set of resonance signals was characterized by three doublets at −51, −12, and −8 ppm in an intensity ratio 1:~2:1 and a very broad signal centered at about +66 ppm and was independent of the kind of ethers in the orignal addition compound. It is noted that this set of signals could not be detected in the spectra of the room-temperature decomposition products of the $(\mu\text{-}Cl_2B)B_5H_8$ etherates.

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office. Thanks are due to Mr. Leonard H. Wojcik for undertaking the mass spectral measurements.

Registry No. $(\mu\text{-}Cl_2B)B_5H_8$, 81643-54-1; KB_5H_8, 56009-95-1; BCl_3, 10294-34-5; diethyl ether, 60-29-7.

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and Company, Wilmington, Delaware 19898

ESR Study of a Paramagnetic Titanium Methylene Complex and of Its Reactions with Olefins

Paul J. Krusic* and Fred N. Tebbe

Received July 13, 1981

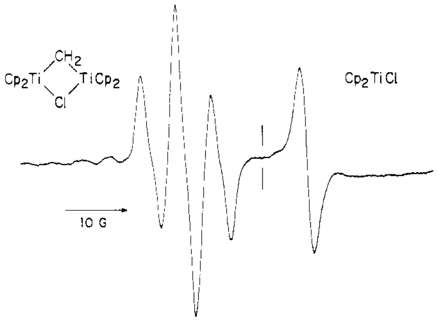

Figure 1. ESR spectrum (−50 °C) obtained by combining equal volumes of 0.02 M solutions of **1** and of THF in toluene at room temperature.

Transition-metal complexes of the simplest carbene, methylene, are of current interest because of their probable involvement in processes such as olefin metathesis[1] and Fischer–Tropsch[2] synthesis. The mononuclear complexes of this type, with one notable exception, $Cp_2(Me)Ta{=}CH_2$,[3] have all proven to be too reactive to be isolated as stable compounds. In several cases, however, the metal methylene complex could be stabilized by association with a suitable organometallic entity. This resulted in methylene groups that bridge two metal centers. Examples of such stabilization are found in the titanium methylene complex $Cp_2TiCH_2AlClMe_2$ (**1**),[4] which can be viewed as the union of Cp_2TiCH_2 and the diphilic $ClAlMe_2$, and the iron methylene complex $(\mu\text{-}CH_2)Fe_2(CO)_8$,[5] which can be viewed as $(CO)_4FeCH_2$ associated with the coordinatively unsaturated $Fe(CO)_4$ fragment. These complexes are diamagnetic as are the other known methylene complexes.[6] We wish to report now ESR evidence for a paramagnetic transition-metal methylene complex,[7] as well as ESR evidence that demonstrates, with the aid of appropriate isotopically labeled reagents, the facile exchange of the metal-bound CH_2 fragment with the CH_2 group of a terminal olefin, a step considered essential to the so-called degenerate metathesis reaction,[1] which exchanges methylene groups between terminal olefins of the type $CR_2{=}CH_2$ (eq 1).

$$CR_2{=}CH_2 \;+\; CR'_2{=}{}^*CH_2 \;\rightleftharpoons\; CR_2{=}{}^*CH_2 \;+\; CR'_2{=}CH_2 \qquad (1)$$

Experimental Section

General Considerations. All chemical manipulations were carried out in a glovebox (Vacuum Atmospheres Co.) under pure nitrogen. Toluene and THF were distilled from Na/benzophenone under nitrogen. The titanium methylene complex **1** was prepared according to a published procedure.[4] Careful recrystallizations from toluene are necessary to obtain **1** free of the paramagnetic impurity $Cp_2Ti(\mu\text{-}Cl)_2AlMe_2$ (**4**) (for ESR parameters see ref 16). Cp_2TiCl was obtained by degradative treatment of **1** with pyridine. The purified product was indistinguishable from Cp_2TiCl obtained by a more conventional method.[8] [^{13}C]Methylenecyclohexane, $^{13}CH_2{=}C_6H_{10}$, was purchased from Merck Sharp and Dohme Canada Ltd.

ESR spectra were obtained with a Bruker ER-420 spectrometer equipped with a field-tracking proton NMR gauss meter (B-NM 12) and a direct-reading microwave frequency counter. A field-frequency marking system interacting with a BNC 12 computer and a Teletype terminal allowed the precise measurement by computer of ESR splitting and *g* values with Bruker software.

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[1] For a review on olefin metathesis chemistry see: Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1.

[2] See: Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. Olivé, G. H.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136. Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

[3] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[4] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

[5] Summer, C. E., Jr.; Riley, P. E.; David, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

[6] For a recent review, see: Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[7] Relatively few paramagnetic transition-metal carbene complexes are known: Lappert, M. F.; MacQuitty, J. J.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 411. Lappert, M. F.; McCabe, R. W.; MacQuitty, J. J.; Pye, P. L.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* **1980**, 90. Krusic, P. J.; Klabunde, U.; Casey, C. P.; Block, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 2015.

[8] Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *47*, 375.

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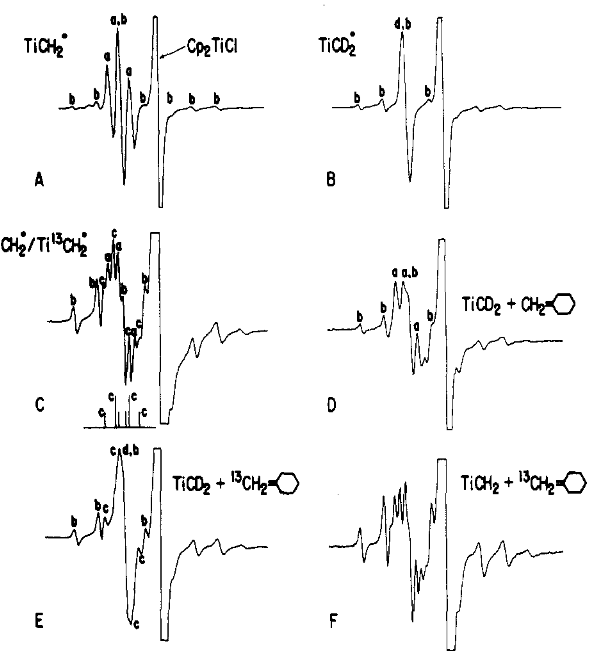


Figure 2. ESR spectra (−50 °C) of $TiCH_2$· and its labeled derivatives with the Cp_2TiCl byproduct. Spectra A, B, and C were obtained by treating 0.02 M toluene solutions of authentic **1**, $Cp_2TiCD_2AlCl(CD_3)_2$, and $Cp_2Ti^{13}CH_2AlClMe_2$ (about 45% ^{13}C enriched) with THF. Spectrum D is from a mixture of $Cp_2TiCD_2AlCl(CD_3)_2$, $CH_2{=}C_6H_{10}$, and THF in toluene. Spectrum E is from $Cp_2TiCD_2AlCl(CD_3)_2$, $^{13}CH_2{=}C_6H_{10}$, and THF, and spectrum F is from **1**, $^{13}CH_2{=}C_6H_{10}$, and THF, each in toluene.

Table I. ESR Parameters for $TiCH_2$· (**2**) and $Cp_2TiCl(THF)$[a]

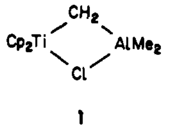
	$TiCH_2$·[b]	$Cp_2TiCl(THF)$[b]	$Cp_2TiCl(THF)$[c]
g	1.9888 (1.9894)	1.9774 (1.9783)	1.9776 (1.9785)
a(Ti), G	4.5 (4.5)	12.2 (12.4)	12.1 (12.4)
a(H), G	5.5 (5.5)		
$a(^{13}C)$, G	(7.3)		
ΔH_{ptp},[d] G	3.2 (3.2)	3.8 (2.3)	3.8 (2.2)

[a] At room temperature. Values in parentheses are those parameters at −50 °C. [b] From addition of THF to **1** in toluene. [c] From addition of THF to authentic samples of Cp_2TiCl in toluene. [d] Peak-to-peak field separation.

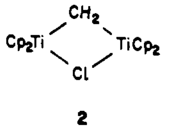
Synthesis of Cp_2TiCl. A 5-g quantity of **1** in 15 mL of toluene was treated with 1 equiv of pyridine. After the solution stood over a weekend, a precipitate formed, which was isolated (2.69 g) and crystallized twice from warm THF to yield 0.9 g (24%) of $(Cp_2TiCl)_2$. Anal. Calcd for $C_{10}H_{10}TiCl$: C, 56.25; H, 4.72; Ti, 22.43; Cl, 16.60. Found: C, 56.59; H, 4.60; Ti, 22.75; Cl, 16.32. The mass spectrum showed $C_{10}H_{10}ClTi$ (calculated 212.9950, found 212.9950) and $C_{20}H_{20}Cl_2Ti_2$ (calculated 425.9900, found 425.9886).

Results and Discussion

When dilute toluene solutions (0.02 M) of $Cp_2TiCH_2AlClMe_2$ (**1**) are reacted at room temperature with an equivalent of tetrahydrofuran (THF), two paramagnetic species are detected by ESR. Their spectra are unchanged for many hours at room temperature, and optimum line widths are observed at −50 °C (Figure 1). The intensities of both spectra are enhanced when excesses of THF are used, but the single line at high field (g = 1.9783) grows faster than the triplet spectrum at lower field (g = 1.9894) (Figure 2A). Under these conditions ^{47}Ti ($I = {}^5/_2$) and ^{49}Ti ($I = {}^7/_2$) satellites for each spectrum are easily discerned ($a(^{47,49}Ti)$ = 4.5 G for the three-line spectrum and $a(^{47,49}Ti)$ = 12.1 G for the single-line spectrum). The singlet at high field is indistinguishable in all its characteristics (Table I) from the ESR spectrum obtained when a slight molar excess of THF is added to a dilute toluene solution of authentic Cp_2TiCl.[9] In pure toluene or benzene, as in the solid state, the latter exists as the diamagnetic dimer **3**.[10] Addition of THF breaks up these dimers and produces mononuclear paramagnetic $Cp_2TiCl(THF)$ with a THF molecule in the fourth position of a distorted tetrahedral environment around Ti.[11] The achievement of such an environment governs much of the chemistry of cyclopentadienyltitanium compounds.



1



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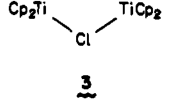

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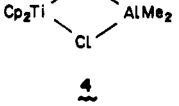
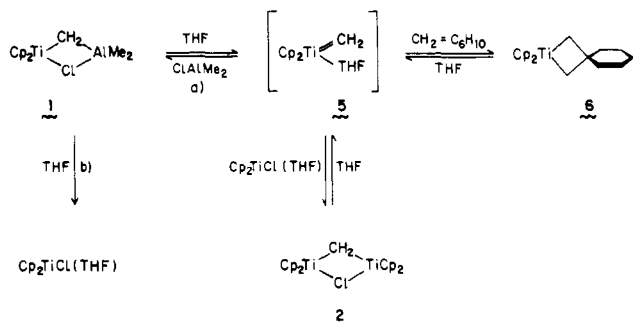


4

Scheme I



The three-line spectrum at low field is the result of a hyperfine interaction with two equivalent protons (a(H) = 5.5 G). Under conditions of high resolution, each of the three lines displays an inflection at the point where the first-derivative signal crosses the base line. Line shapes of this sort are the result of unresolved hyperfine interaction with an additional nucleus with $I \geq {}^1/_2$ when the line width of each of the $2I + 1$ hyperfine components is slightly greater than the hyperfine splitting.[12] Since a hyperfine interaction with a single proton is highly unlikely in this case, the observed line shape is most readily accounted for by a hyperfine interaction with a chlorine nucleus of 0.8 G ($I(^{35}Cl,^{37}Cl) = {}^3/_2$). We assign this spectrum to the paramagnetic methylene complex **2** (abbreviated $TiCH_2$·) with a structure similar to that of **1** and of several other bridged titanium species such as $(Cp_2TiCl)_2$ (**3**) and the paramagnetic $Cp_2Ti(\mu\text{-}Cl)_2AlMe_2$ (**4**).[14] The exceptionally

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(9) For a review of the chemistry and properties of Cp_2TiCl and other Ti^{III} complexes see: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974.

(10) Martin, R. L.; Winter, G. *J. Chem. Soc.* **1965**, 4709. Nöth, H.; Hartwimmer, R. *Chem. Ber.* **1960**, *93*, 2246. Natta, G. *Angew. Chem.* **1959**, *71*, 205.

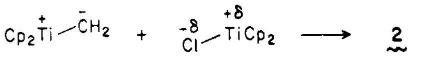
(11) A similar cleavage was observed for the closely related diamagnetic $Cp_2Ti(\mu\text{-}H)_2TiCp_2$, which can be thought of as the dimer of two Ti(III) paramagnetic Cp_2TiH units (Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301). Cleavage promoted by THF gave $Cp_2TiH(THF)$ while cleavage with triphenylphosphine gave $Cp_2TiH(PPh_3)$; both were well characterized by ESR spectra of high quality. The related paramagnetic Cp_2TiR complexes also exist in solution with a donor molecule in the fourth coordination site of the Ti(III) center, e.g., $Cp_2TiCH_3(THF)$ and $Cp_2TiCH_3(PPh_3)$ (Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *188*, 97).

(12) Cf.: Lebedev, Ya. S.; Chernikova, D. M.; Tikhomirova, N. N.; Voevodskii, V. V. "Atlas of Electron Spin Resonance Spectra"; Consultants Bureau: New York, 1963.

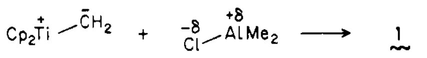
(13) The X-ray crystal structure of a dineopentyl derivative of **1**, $Cp_2TiCH_2AlCl(CH_2CMe_3)_2$, is reported. See: Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37.

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.

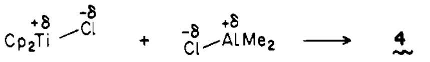
We consider that **2** is the result of the union of Cp_2TiCl with a transient mononuclear titanium methylene complex $Cp_2Ti{=}CH_2$, which may be represented by the ylide structure $Cp_2Ti^+{-}C^-H_2$ (eq 2). In this reaction the Cp_2TiCl plays the same role as the Me_2AlCl in the formation of **1** (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]



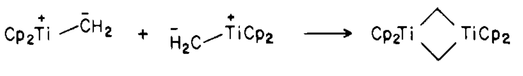
$$Cp_2\overset{+}{Ti}{-}\overset{-}{C}H_2 + \overset{-\delta}{Cl}{-}\overset{+\delta}{Ti}Cp_2 \longrightarrow \mathbf{2} \quad (2)$$



$$Cp_2\overset{+}{Ti}{-}\overset{-}{C}H_2 + \overset{-\delta}{Cl}{-}\overset{+\delta}{Al}Me_2 \longrightarrow \mathbf{1} \quad (3)$$



$$Cp_2\overset{+\delta}{Ti}{-}\overset{-\delta}{Cl} + \overset{-\delta}{Cl}{-}\overset{+\delta}{Al}Me_2 \longrightarrow \mathbf{4} \quad (4)$$



(5)

7

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.

(15) Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922.

(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).

(18) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

(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).

(20) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358.

Contribution from the Facultad de Farmacia, Universidad de
Navarra, Pamplona, Spain, and the Instituto de Quimica
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Preparation and Crystal Data of Cerium Antimony(III) Trioxide

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Received November 19, 1981

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.

(2) (a) Adachi, G; Kawahito, T.; Matsumoto, H.; Shiokawa, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 681; **1971**, *33*, 1520. (b) Nath, D. K. *Inorg. Chem.* **1970**, *9*, 2714.

(3) Adachi, G.; Ishihara, M.; Shiokawa, J. *J. Less Common Met.* **1973**, *32*, 175.