C16 angle in II which is 118°. The conformation about the C–S bonds was found to be gauche in all cases.

Ferrocenophane II contains two carbon atoms, namely, C11 and C20, which are asymmetric centers. The priority sequence of the ligands around these carbons is S > C(Cp ring) > C(methyl) > H.[27] As can be seen from Figure 2, both asymmetric centers have identical *S* conformations. Thus, II packs as a racemic compound containing *SS* and *RR* molecules. This confirms the conjecture[7] made by analogy of thin-layer chromatographic behavior, that the crystalline diastereomer of II is the racemic compound. Thus II is shown to be different from V in which the two asymmetric centers are enantiomeric which gives the meso molecule.

Electrochemical Studies. The cyclic voltammogram of I in acetonitrile solution (0.10 M in tetrabutylammonium perchlorate), with initial anodic sweep, was as expected for a reversible, one-electron oxidation of the ferrocenophane to the corresponding ferricenium cation.[12] The reduction potential (vs SHE) of the ferricenium cation derived from I is +416 mV. Reduction potentials for previously studied ferrocenophanes III and IV were found to be +405 and +419 mV, respectively. Thus the reduction potentials for the ferricenium cations derived from I and IV are essentially the same, and both Fe (II) species are slightly weaker reductants than III, which has the shortest bridging chain of the series.

Acknowledgment. We thank the Robert A. Welch Foundation [Grants E-594 (I.B.), D-735 (R.A.H.), and D-775 (R.A.B.)] and the National Science Foundation (I.B.) for support of this research.

Registry No. I, 80973-98-4; II, 71840-04-5.

Supplementary Material Available: Tables of anisotropic temperature factors and least-square planes for I and II (5 pages); listings of observed and calculated structure factors for I and II (23 pages). Ordering information is given on any current masthead page.

---

(27) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, 385.

A Dinuclear Bis(1,3-diene) Complex of Titanium: Crystal and Molecular Structure of μ-[o-$(CH_2)_2C_6H_4$](μ-Cl)$_2$[(η^5-C_5Me_5)Ti]$_2$, Containing an Unprecedented "*o*-Xylidene" Bridging Group

Miguel Mena, Pascual Royo,* and Ricardo Serrano

Departamento de Química Inorgânica, Universidad de Alcalá de Henares, Campus Universitario, Alcalá de Henares, Madrid, Spain

Maria Angela Pellinghelli and Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Received January 5, 1987

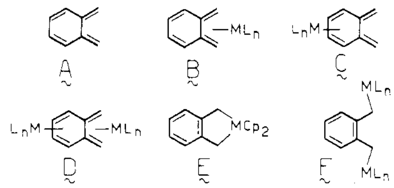
(η^5-C_5Me_5)$TiCl_3$ reacts with [o-$(CH_2)_2C_6H_4$]Mg$(THF)_2$ to give (η^5-C_5Me_5)TiCl[o-$(CH_2)_2C_6H_4$] (**3**) or μ-[o-$(CH_2)_2C_6H_4$](μ-Cl)$_2$[(η^5-C_5Me_5)Ti]$_2$ (**4**) depending on the solvent. The crystal structure of **4** has been determined by X-ray diffraction methods. Crystals of **4** are monoclinic of space group $C2/c$ with $Z = 8$ in a unit cell of dimensions $a = 26.746$ (4) Å, $b = 11.832$ (3) Å, $c = 16.781$ (3) Å, and $\beta = 90.44$ (1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.080$ and $R_w = 0.095$ for 1089 observed reflections. The complex shows an o-xylidene ligand bridging two Ti(η^5-C_5Me_5) fragments through its exo- and endocyclic conjugated diene systems which are bonded in different (σ^2 and π^2) modes to the titanium atoms.

Introduction

1,3-Diene complexes of the early transition group 4 and 5 metals (especially Zr, Hf, and Ta) are being actively investigated because of their particular bonding features and chemical reactivity.[1] In this context the lack of similar titanium derivatives is surprising, and just a few titanium diene compounds have been so far reported,[2] although no crystallographic characterization is available.

The "*o*-xylidene"[6b] group (A) coordinates to transition metals usually as a 1,3-diene through its exocyclic π system, as in B,[3] and less frequently through its endocyclic π system (C)[4] or both of them (D).[5] With the early transition metallocenes the bonding is more adequately described as a metallobenzocyclopentane (E)[6a] where the σ

Chart I



---

(1) For leading references see: (a) Erker, A.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

(2) (a) Zwijnenburg, A.; van Oven, H. O.; Groenenboom, C. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *94*, 23. (b) Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71. (c) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353. (d) Blenkers, J.; Hesse, B.; van Bolhuis, F.; Wagner, A. J.; Teuben, J. *Organometallics* **1987**, *6*, 459.

(3) (a) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053. (b) Grosselin, J.-M.; Le Bozec, H.; Moinet, C.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1985**, *107*, 2809. (c) Chappel, S. D.; Cole-Hamilton, D. J.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1982**, 1867. (d) Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834.

(4) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 1716.

(5) Victor, R., Ben-Shoshan, R.; *J. Organomet. Chem.* **1974**, *80*, C1.

0276-7333/88/2307-0258$01.50/0

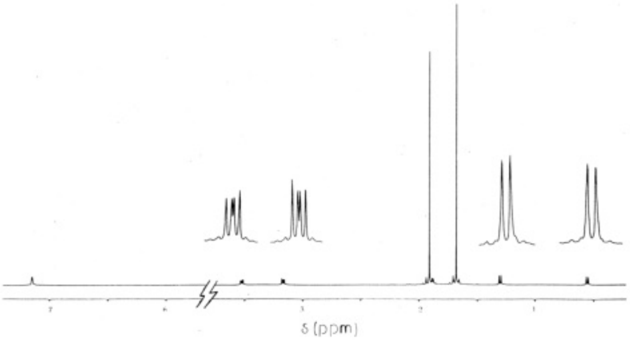


Figure 1. ^1H NMR spectrum (360 MHz) of 4 in C_6D_6.

character of the metal–carbon bond predominates. An intermediate situation is found in the tris(*o*-xylidene) derivative of tungsten.[6b] The *o*-$(CH_2)_2C_6H_4$ group can also act as a bridging ligand (F), as found in its magnesium salt[7] and in a cobalt complex[3d] (see Chart I).

We have recently described the isolation and characterization of (η^5-pentamethylcyclopentadienyl)titanium trialkyls and their oxo derivatives, which show distinct structural features,[8] and in this paper we report the synthesis and X-ray structure of an unusual dinuclear bis(diene)titanium complex containing the Cp*Ti (Cp* = η^5-C_5Me_5) moiety and an unprecedented *o*-xylidene bridging group.

Results and Discussion

The reaction of Cp^*TiCl_3 (**1**) and [*o*-$(CH_2)_2C_6H_4$]Mg-$(THF)_2$ (**2**) in toluene overnight leads to a red solution whose workup affords in moderate yield red crystals of Cp*TiCl[*o*-$(CH_2)_2C_6H_4$] (**3**), the expected product according to our previous results on the facile alkylation of **1** with magnesium or lithium alkyls.[8a] The spectroscopic features of **3**, especially those associated with the methylene unit of the *o*-xylidene group, are characteristic of an alkyl derivative: the ^1H NMR spectrum shows two doublets (AB spin system) centered at 1.30 and 2.63 ppm with a $^2J_{HH}$ coupling constant of 10.5 Hz, the same value found in $Cp^*TiCl(CH_2Ph)_2$.[9] The $^1J_{CH}$ coupling constant is somewhat high: 144 Hz. The solutions of **3** in benzene-d_6 or THF-d_8 are stable for several days in the absence of air.

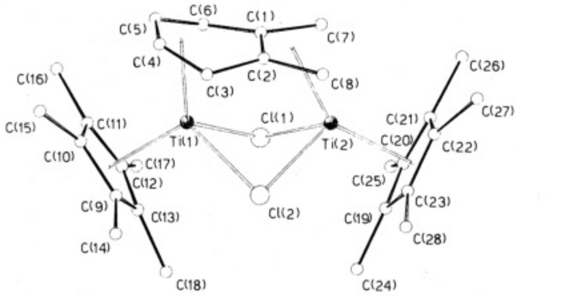


Figure 2. View of the structure of **4** with the atomic numbering scheme.

Table I. Important Interatomic Distances (Å) for 4[a]

Ti(1)–Ti(2)	3.187 (5)	Ti(2)–C(22)	2.34 (2)
Ti(1)–Cl(1)	2.487 (7)	Ti(2)–C(23)	2.35 (2)
Ti(1)–Cl(2)	2.510 (7)	Ti(2)–CE(2)	2.05 (2)
Ti(2)–Cl(1)	2.435 (7)	C(1)–C(2)	1.49 (3)
Ti(2)–Cl(2)	2.473 (6)	C(2)–C(3)	1.47 (4)
Ti(1)–C(3)	2.37 (2)	C(3)–C(4)	1.36 (4)
Ti(1)–C(4)	2.38 (3)	C(4)–C(5)	1.53 (5)
Ti(1)–C(5)	2.39 (3)	C(5)–C(6)	1.31 (4)
Ti(1)–C(6)	2.28 (2)	C(1)–C(6)	1.46 (3)
Ti(1)–C(9)	2.32 (2)	C(1)–C(7)	1.47 (3)
Ti(1)–C(10)	2.43 (2)	C(2)–C(8)	1.47 (3)
Ti(1)–C(11)	2.41 (2)	C(9)–C(10)	1.44 (3)
Ti(1)–C(12)	2.41 (2)	C(9)–C(13)	1.35 (3)
Ti(1)–C(13)	2.33 (2)	C(10)–C(11)	1.34 (3)
Ti(1)–CE(1)	2.07 (2)	C(11)–C(12)	1.42 (3)
Ti(2)–C(1)	2.53 (2)	C(12)–C(13)	1.38 (3)
Ti(2)–C(2)	2.49 (2)	C(19)–C(20)	1.36 (3)
Ti(2)–C(7)	2.26 (3)	C(19)–C(23)	1.44 (3)
Ti(2)–C(8)	2.24 (2)	C(20)–C(21)	1.35 (3)
Ti(2)–C(19)	2.34 (2)	C(21)–C(22)	1.32 (3)
Ti(2)–C(20)	2.40 (2)	C(22)–C(23)	1.39 (3)
Ti(2)–C(21)	2.36 (2)		

[a] Estimated standard deviations are given in parentheses. CE(1) and CE(2) are the centroids of the C(9)···C(13) and C(19)···C(23) rings, respectively.

Table II. Important Interatomic Angles (deg) for 4[a]

Cl(1)–Ti(1–)Cl(2)	78.6 (2)	Cl(2)–Ti(2)–C(7)	131.7 (7)
CE(1)–Ti(1)–Cl(1)	107.9 (7)	Cl(2)–Ti(2)–C(8)	83.2 (6)
CE(1)–Ti(1)–Cl(2)	109.7 (7)	Cl(2)–Ti(2)–C(1)	96.5 (6)
CE(1)–Ti(1)–C(3)	125.7 (9)	Cl(2)–Ti(2)–C(2)	75.4 (6)
CE(1)–Ti(1)–C(4)	106.7 (10)	Ti(1)–Cl(1)–Ti(2)	80.7 (2)
CE(1)–Ti(1)–C(5)	102.8 (10)	Ti(1)–Cl(2)–Ti(2)	79.5 (2)
CE(1)–Ti(1)–C(6)	121.2 (9)	C(6)–C(1)–C(7)	126 (2)
Cl(1)–Ti(1)–C(3)	126.0 (7)	C(2)–C(1)–C(7)	112 (2)
Cl(1)–Ti(1)–C(4)	138.0 (8)	C(2)–C(1)–C(6)	121 (2)
Cl(1)–Ti(1)–C(5)	111.0 (8)	C(1)–C(2)–C(8)	119 (2)
Cl(1)–Ti(1)–C(6)	79.4 (6)	C(1)–C(2)–C(3)	119 (2)
Cl(2)–Ti(1)–C(3)	78.2 (7)	C(3)–C(2)–C(8)	122 (2)
Cl(2)–Ti(1)–C(4)	110.9 (8)	C(2)–C(3)–C(4)	111 (2)
Cl(2)–Ti(1)–C(5)	141.3 (9)	C(3)–C(4)–C(5)	127 (3)
Cl(2)–Ti(1)–C(6)	128.6 (6)	C(4)–C(5)–C(6)	117 (3)
Cl(1)–Ti(2)–Cl(2)	80.3 (2)	C(1)–C(6)–C(5)	117 (2)
CE(2)–Ti(2)–Cl(1)	110.5 (7)	C(10)–C(9)–C(13)	106 (2)
CE(2)–Ti(2)–Cl(2)	111.7 (7)	C(9)–C(10)–C(11)	108 (2)
CE(2)–Ti(2)–C(7)	116.6 (9)	C(10)–C(11)–C(12)	109 (2)
CE(2)–Ti(2)–C(8)	116.9 (9)	C(11)–C(12)–C(13)	105 (2)
CE(2)–Ti(2)–C(1)	151.8 (9)	C(9)–C(13)–C(12)	111 (2)
CE(2)–Ti(2)–C(2)	152.4 (9)	C(20)–C(19)–C(23)	106 (2)
Cl(1)–Ti(2)–C(7)	82.9 (7)	C(19)–C(20)–C(21)	111 (2)
Cl(1)–Ti(2)–C(8)	132.6 (7)	C(20)–C(21)–C(22)	107 (2)
Cl(1)–Ti(2)–C(1)	73.9 (6)	C(21)–C(22)–C(23)	111 (2)
Cl(1)–Ti(2)–C(2)	96.9 (6)	C(19)–C(23)–C(22)	104 (2)

[a] Estimated standard deviations are given in parentheses. CE(1) and CE(2) are the centroids of the C(9)···C(13) and C(19)···C(23) rings, respectively.

When the same reaction between **1** and **2** is carried out in THF overnight, a green instead of red solution is obtained from which dark green crystals of compound **4**, having the stoichiometry $(Cp^*Ti)_2[o\text{-}CH_2)_2C_6H_4Cl_2$, can be isolated. If shorter reaction times (1–2 h) are employed, a mixture of **1**, **3**, and **4** is obtained. The ^1H NMR spectrum of **4** (Figure 1) shows two Cp* signals at 1.67 and 1.90 ppm, indicating a dinuclear structure, an AB system centered at 1.19 and 0.55 ppm with a low value of $^2J_{HH}$ (5.3 Hz) which is ascribable to the methylene protons of the *o*-xylidene ligand and two multiplets (AA′XX′ spin system) centered at 3.16 and 3.52 ppm which must originate from the endocyclic protons of the *o*-xylidene group even though they resonate at an unusual high field. The gated decoupled ^{13}C NMR spectrum also shows unusual features in line with the ^1H NMR data: the methylene C atoms originate a triplet centered at 63.0 ppm with a value of $^1J_{CH}$ intermediate between that of sp^2 and sp^3-hybridized car-

---

[6] (a) Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. F. *J. Chem. Soc., Dalton Trans.* **1984**, 399. (b) Lappert, M. F.; Raston, C. L.; Rowbotton, G. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 883.

[7] Lappert, M. F.; Martin, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1959.

[8] (a) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118. (b) Garcia Blanco, S.; Gómez Sal, M. P.; Martinez Carreras, S.; Mena, M.; Royo, P.; Serrano, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1572.

[9] Mena, M.; Royo, P.; Serrano, R., unpublished results.

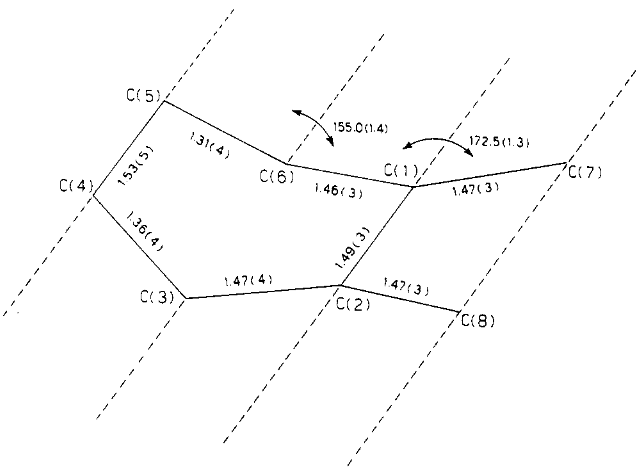


Figure 3. Selected bond lengths (Å) and angles (deg) in the *o*-xylidene ring in 4.

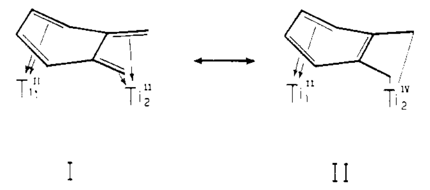
bons (149 Hz) while the $^1J_{CH}$ coupling constant of the endocyclic carbons (166 Hz) are typical for a sp^2-C atom.[10]

In view of the unusual features disclosed by the ^{1}H and ^{13}C NMR spectra an X-ray study of 4 was undertaken. The structure is shown in Figure 2 together with the atom numbering system; important bond distances and angles are given in Tables I and II, respectively. In the complex two Cp*Ti fragments are nearly symmetrically bridged by two chlorine atoms; an *o*-xylidene group also acts as a bridge between the two Ti atoms. The most striking feature is probably the distortion of the *o*-xylidene ring that has lost its aromatic character and planarity. The dihedral angle between the two C(3)C(4)C(5)C(6) and C(1)C(2)C(3)C(6) planes is 155.0 (1.4)° with the two C(3)–C(4) and C(5)–C(6) bonds (typical of carbon–carbon double bonds) longer than the C(4)–C(5) bond (typical of a single carbon–carbon bond) (see Figure 3), even if the very high standard deviations prevent any discussion of them. The C(3)C(4)C(5)C(6) endocyclic diene system is bonded in a η^4 fashion to the Ti(1) atom which is nearly equidistant from the C(3), C(4), C(5), and C(6) atoms [the distances are 2.37 (2), 2.38 (3), 2.39 (3), and 2.28 (2) Å, respectively, shorter than those with C(1) and C(2) which are 2.57 (2) and 2.61(2) Å, respectively]. The Ti(1)–endocyclic C distances are of the same order as the Ti(1)–cyclopentadienyl C distances [in the range 2.32 (2)–2.43 (2) Å].

The exocyclic C(7)C(1)C(2)C(8) system shows C–C distances of 1.47 (3), 1.49 (3), and 1.47 (3) Å, intermediate between those of single and double bonds. The Ti(2)–C(7) and Ti(2)–C(8) distances [2.26 (3) and 2.24 (2) Å] are somewhat longer than those in Cp*Ti(CH$_2$Ph)$_3$ [2.14 (1) and 2.16 (1) Å for the "non-agostic" benzyls][8a] and very close to that [2.204 (4) Å] found in Cp$_2$Ti[*o*-(CH$_2$)$_2$C$_6$H$_4$] in which predominantly Ti–C σ bonds were proposed;[6a] on the other hand, the distances Ti(2)–C(1) and Ti(2)–C(2) [2.53 (2) and 2.49 (2) Å, respectively] are significantly longer. The fold angle between the planes defined by C(7))C(1)C(2)C(8) and C(7)C(8)Ti(2) [100 (1)°] supports the σ character of the C(7)–Ti(2) and C(8)–Ti(2) bonds.[1]

All the above data suggest the description of the *o*-xylidene–dititanium bond as a resonance hybrid between the forms depicted in Scheme I in which II corresponds to a formally mixed valence Ti^{II}–Ti^{IV} complex; the well-separated Cp* signals in the ^{1}H NMR spectrum and the shorter (μ-Cl)–Ti(2) bonds [2.435 (7) and 2.473 (6) Å] compared to the (μ-Cl)–Ti(1) bonds [2.487 (7) and 2.510 (7) Å] might be related to the unequal electron density around the titanium atoms.

Scheme I



Both cyclopentadienyl rings are planar, and all the methyl groups are bent out of these planes away from the titanium with a maximum deviation of 0.30 (3) Å in Cp*(1) and 0.29 (3) Å in Cp*(2). The ring C–methyl C distances are in the range 1.48 (3)–1.59 (4) Å in Cp*(1) and 1.52 (3)–1.64 (4) Å in Cp*(2). All these figures are in line with those reported for other bis(pentamethylcyclopentadienyls) of titanium.[11-14] The ring C–titanium distances vary from 2.32 (2) to 2.43 (2) Å for Ti(1) and from 2.34 (2) to 2.40 (2) Å for Ti(2), so both Cp* rings are bonded in a true η^5 fashion.

The geometry around Ti(2) atom can be viewed as a four-legged piano stool. The angles between the legs [C(7), C(8) Cl(1), and Cl(2)] vary from 75.7 (9) to 83.2 (6)° and those formed between the legs and the Ti(2)–centroid(2) axis vary from 110.5 (7) to 116.9 (9)°. Taking into account the midpoints of the two olefinic C(3)–C(4) and C(5)–C(6) bonds, Ti(1) also can be viewed as a four-legged piano stool, even if more distorted than for Ti(2), the other two legs being the Cl(1) and Cl(2) atoms. The angles between these legs range from 59.2 (11) to 95.6 (8)° and those formed by the legs and the Ti(1)–centroid(1) axis range from 107.9 (7) to 117.0 (10)°.

There is still another aspect that warrants mention, the short Ti(1)–Ti(2) length [3.187 (5) Å], which might indicate a dative Ti^{II}(1)$\rightarrow$Ti^{IV}(2) metal–metal interaction if we compare it with the distance found in [(η^5-C$_5$H$_5$)$_2$Ti{μ-(η^1:η^5-C$_5$H$_4$)}Ti(η^5-C$_5$H$_5$)(THF)] [3.336 (4) Å][15] in which a Ti–Ti bond was proposed. Nevertheless, still shorter distances have been reported in cases where a Ti–Ti interaction is not possible although the chelating substituents held both metal atoms very close one to another {2.724 (1) Å in [(η^5-C$_5$Me$_5$)Ti]$_2$[μ-(η^1:η^5-C$_5$Me$_4$CH$_2$)](μ-O)$_2$}.[16] As a result of the short Ti–Ti distance the angles Ti(1)–(μ-Cl)–Ti(2) [79.5 (2) and 80.7 (2)°] are rather acute compared with values reported for other dinuclear Ti$_2$(μ-Cl) systems: 101.5 (3)° in [Cp$_2$Ti(μ-Cl)]$_2$[17] or 99.6 (2)° in [(η^7-C$_7$H$_7$)-Ti(THF)(μ-Cl)]$_2$.[18]

Experimental Section

All manipulations were carried out under dry argon in a Vacuum Atmospheres drybox. Solvents were distilled from drying

---

(10) Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy*; Verlag Chemie: Weinheim, 1974.

(11) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265.

(12) Sanner, R. D.; Duggan, M. D.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358.

(13) Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51.

(14) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457.

(15) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072.

(16) Bottomley, F.; Egharevba, G. O.; Lin, J. B. I.; White, P. S. *Organometallics* **1985**, *4*, 550.

(17) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

(18) Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 356.

Table III. Experimental Data for the X-ray Diffraction Study on 4 ($C_{28}H_{38}Cl_2Ti_2$)

cryst system	monoclinic
space group	$C2/c$
a, Å	26.746 (4)
b, Å	11.832 (3)
c, Å	16.781 (3)
β, deg	90.44 (1)
V, Å^3	5310 (2)
Z	8
$F(000)$	2272
D_{calcd}, g cm^{-3}	1.354
mol wt	541.31
cryst dimens, mm	0.27 × 0.28 × 0.50
linear absorptn, cm^{-1}	71.47
diffractometer	Siemens AED
scan type	$\theta/2\theta$
scan speed, θ	3–12°/min
scan width	$(\theta - 0.6) - [\theta + (0.6 + \Delta\theta)]$ $\{\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda] \tan \theta\}$
radiatn	Ni-filtered Cu Kα (λ = 1.541 84 Å)
2θ range, deg	6–120
reflcns measd	$\pm h,+k,l$
std reflcn	1 measured after every 50 reflections
unique total data	4084
unique obsd data [$I \geq 3\sigma(I)$]	1089
no. of variables	149
R	0.080
R_w	0.095

Table IV. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms

	x/a	y/b	z/c
Ti(1)	3452 (2)	784 (3)	3636 (3)
Ti(2)	3777 (2)	3327 (3)	3991 (2)
Cl(1)	4276 (2)	1742 (5)	3524 (3)
Cl(2)	3494 (2)	1850 (4)	4928 (3)
C(1)	3327 (8)	2560 (21)	2774 (13)
C(2)	2963 (8)	2673 (21)	3434 (14)
C(3)	2662 (9)	1685 (24)	3657 (15)
C(4)	2640 (11)	922 (27)	3049 (20)
C(5)	3020 (13)	772 (30)	2382 (20)
C(6)	3396 (8)	1483 (20)	2371 (13)
C(7)	3634 (9)	3580 (21)	2674 (15)
C(8)	2958 (9)	3718 (21)	3907 (15)
C(9)	3357 (8)	−789 (17)	4445 (13)
C(10)	3164 (9)	−1162 (18)	3685 (14)
C(11)	3542 (9)	−1131 (18)	3162 (15)
C(12)	3993 (9)	−841 (20)	3570 (14)
C(13)	3853 (9)	−650 (18)	4351 (14)
C(14)	3073 (9)	−819 (22)	5195 (15)
C(15)	2612 (10)	−1570 (22)	3516 (15)
C(16)	3533 (11)	−1495 (25)	2282 (20)
C(17)	4539 (10)	−812 (22)	3198 (16)
C(18)	4219 (10)	−519 (21)	5063 (17)
C(19)	4393 (9)	3763 (17)	4943 (14)
C(20)	4575 (9)	4177 (21)	4248 (15)
C(21)	4270 (8)	4982 (20)	3944 (14)
C(22)	3912 (9)	5156 (20)	4471 (14)
C(23)	3959 (8)	4430 (19)	5122 (14)
C(24)	4630 (9)	2890 (22)	5496 (16)
C(25)	5076 (10)	3717 (21)	3849 (15)
C(26)	4365 (11)	5764 (24)	3152 (17)
C(27)	3534 (11)	6249 (23)	4437 (17)
C(28)	3629 (10)	4403 (22)	5873 (17)

agents as follows and stored in the drybox: sodium benzophenone ketyl for diethyl ether and tetrahydrofuran, sodium for toluene, and sodium–potassium amalgam for hexane. [*o*-$(CH_2)_2C_6H_4$]Mg$(THF)_2$ was prepared by a literature method.[7] ^1H NMR spectra were recorded on a Varian FT-80A or a Bruker WH 360 spectrometer. ^{13}C NMR spectra were recorded at 20 MHz on a Varian FT-80A instrument. C, H analysis were done with a Perkin-Elmer 240B microanalyzer.

Cp*TiCl[*o*-$(CH_2)_2C_6H_4$] (3). [*o*-$(CH_2)_2C_6H_4$]Mg$(THF)_2$ (0.73 g, 2.67 mmol) was added to a suspension of 0.77 g (2.67 mmol) of Cp*$TiCl_3$ in 50 mL of toluene at −40 °C; the temperature was raised to the ambient and the mixture stirred overnight. The solvent was evaporated under reduced pressure, and the residue was extracted with 40 mL of hexane; the red solution so obtained was concentrated to ca. 20 mL and cooled to −40 °C affording small crystalline aggregates of **3**. From the mother liquor a second crop can be obtained upon further concentration and cooling. The combined yield was 45–50%. Anal. Calcd for $C_{18}H_{23}ClTi$: C, 67.00; H, 7.14. Found: C, 67.31; H, 7.17. ^1H NMR (ppm in C_6D_6): 7.17 (m, overlapped, C_6H_4), 2.66 (2 H, d, $^2J_{HH}$ = 10.5 Hz, CH_2 syn), 1.84 (15 H, s, C_5Me_5), 1.32 (2 H, d, $^2J_{HH}$ = 10.5, CH_2 anti). ^{13}C NMR (gated decoupled) (ppm in C_6D_6): 135–125 (complex and overlapped signals, C_6H_4), 124 (s, C_5Me_5), 79.1 (t, $^1J_{CH}$ = 144 Hz, CH_2), 12.1 (q, $^1J_{CH}$ = 127 Hz, $C_5\mathit{Me}_5$).

μ-[*o*-$(CH_2)_2C_6H_4$](μ-Cl)$_2$(Cp*Ti)$_2$ (4). To a stirred solution of 0.28 g (0.95 mmol) of Cp*$TiCl_3$ in 40 mL of THF at −40 ° was added 0.26 g (0.95 mmol) of solid [*o*-$(CH_2)_2C_6H_4$]Mg$(THF)_2$; the temperature was slowly raised, and the mixture was left under stirring overnight, turning dark green. After filtration, the solvent was evaporated under reduced pressure and the residue was extracted with 20 mL of toluene. The filtrate was concentrated to ca. 5 mL, and 10 mL of hexane was added. Cooling to −40 °C gave dark green crystals of **4** in 60% yield. Anal. Calcd for $C_{14}H_{19}ClTi$: C, 62.13; H, 7.08. Found: C, 62.74, H, 7.23. ^1H NMR (ppm in C_6D_6): 3.52 (2 H, m, C3–H and C6–H), 3.16 (2 H, m, C4–H and C5–H), 1.90 (15 H, s, Ti2–Cp*), 1.67 (15 H, s, Ti1–Cp*), 1.29 (2 H, d, $^2J_{HH}$ = 5.3 Hz, C7–H_{syn} and C8–H_{syn}), and 0.55 (2 H, d, $^2J_{HH}$ = 5.3 Hz, C7–H_{anti} and C8–H_{anti}). ^{13}C NMR (gated decoupled) (ppm in C_6D_6): 123.5 (s, Ti2–C_5Me_5), 123.1 (s, Ti1–C_5Me_5), 117.5 (s, C1 and C2), 112.9 (dd, $^1J_{CH}$ = 166 Hz, $^2J_{CH}$ = 8 Hz, C6 and C3), 88.2 (dm, $^1J_{CH}$ = 166 Hz, C4 and C5), 63.0 (t, $^1J_{CH}$ = 149 Hz, C7 and C8), 13.1 (q, $^1J_{CH}$ = 126 Hz, Ti2–$C_5\mathit{Me}_5$), 12.7 (q, $^1J_{CH}$ = 126 Hz, Ti1–$C_5\mathit{Me}_5$).

X-ray Data Collection, Structure Determination, and Refinement for μ-[*o*-$(CH_2)_2C_6H_4$](μ-Cl)$_2$[(η^5-C_5Me_5)Ti]$_2$ (4). Crystals of **4** were of very poor quality; one was sealed in a Lindemann glass capillary under dry argon and used for data collection. The crystallographic data are summarized in Table III. Unit-cell parameters were determined from the setting angles of 29 carefully centered reflections, having 20 < θ < 37°. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[19] The structure amplitudes were obtained after usual Lorentz and polarization reduction.[20] A correction for absorption was applied (maximum and minimum applied absorption correction factors were 1.194 and 0.813, respectively).[21] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares. The crystal diffracted very weakly, so only a limited number of observed reflections could be collected. This prevented an accurate structure determination. Only the Ti and Cl atoms could be refined anisotropically in the last least-squares cycles. All efforts to localize the hydrogen atoms in the final difference Fourier map were unsuccessful. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence the values of K and g were 1.374 and 0.001, respectively. The scattering factors were taken from ref 22 with the exceptions of those of the hydrogen atoms that were taken from ref 23. Corrections for the real and immaginary components of the anomalous dispersion were made for the Ti and Cl atoms. Final atomic coordinates for the non-hydrogen atoms are listed in Table IV; thermal pa-

---

(19) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(20) Data reduction, structure solution, and refinement were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, using the SHELX-76 system of crystallographic computer programs (Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Cambridge; Cambridge, England, 1976).

(21) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A.: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1983**, *A39*, 158. The program ABSORB was used (Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109).

(22) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

rameters are given in Table SI.

Acknowledgment. We gratefully thank the Comisión Asesora de Investigación Científica y Técnica (ref 2001/83) and Italian Ministero della Pubblica Istruzione for financial support.

Registry No. 1, 12129-06-5; 2, 110825-75-7; 3, 110825-76-8; 4, 110850-66-3.

Supplementary Material Available: Table SI, thermal parameters (1 page); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Sn–S and Sn–Se Bonding in Some Tin(IV) Compounds Studied by UV Photoelectron and NMR Spectroscopy and Pseudopotential ab Initio Calculations

Carla Cauletti* and Felice Grandinetti

Dipartimento di Chimica, Università "La Sapienza" di Roma, Q0185 Roma, Italy

Gaetano Granozzi

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padova, Italy

Angelika Sebald and Bernd Wrackmeyer

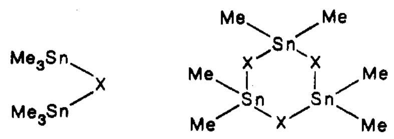
Laboratorium für Anorganische Chemie, Universität Bayreuth, Bayreuth, FRG

Received March 11, 1987

Tin–sulfur and tin–selenium bonding has been studied in the monomeric and trimeric units $(Me_3Sn)_2X$ and $(Me_2SnX)_3$ (X = S, Se) by means of ultraviolet photoelectron and NMR spectroscopy. The UPS results, supported by ab initio pseudopotential calculations, indicate that in $(Me_3Sn)_2X$ the HOMO is predominantly localized on the chalcogen p lone pair orbital, although a nonnegligible hyperconjugation with the orbitals of the CH_3 groups does occur. In $(Me_2SnX)_3$ the interactions between the three p lone pairs are not very strong. In contrast, both in the monomeric and in the trimeric molecules extensive delocalization of σ-electron density is suggested by the experimental and theoretical data. The NMR results show that the ^{119}Sn nuclei are remarkably deshielded in these molecules. This may be attributed not only to the presence of electronegative ligands but also to the high degree of delocalization of σ-electron density as indicated by the ultraviolet photoelectron spectra. The smaller electronegativity of selenium compared to sulfur results in a shift of the ionization energies to lower values and in an increase in ^{119}Sn nuclear shielding. The pseudopotential "ab initio" calculations confirmed their utility in the description of the electronic structure of molecules containing heavy atoms.

Introduction

In the framework of an extensive investigation on the electronic structure of organometallic compounds of group XIV (14[32]) elements containing M–S bonds (M = C, Si, Ge, Sn, and Pb),[1-3] we studied by gas-phase UV photoelectron spectroscopy (UPS) some Tin(IV) compounds, hexamethyldistannathiane, hexamethyldistannaselenane, hexamethylcyclotristannathiane, and hexamethylcyclotristannaselenane, whose schematic structures are shown below:



X = S, Se

The joint study of cyclic compounds and smaller open units, which can be considered in some way precursors of the former, provides an opportunity for verifying the changes in the tin–chalcogen bonding on passing from open to cyclic molecules, also in light of previous experience on some group XIV (14) thiospiranes.[3] In particular, we wanted to ascertain the importance of interactions between the various tin–chalcogen bonds, which in principle are allowed but not extremely favored by the geometry of the molecule, a twisted boat of C_2 symmetry in the solid state, as demonstrated by an X-ray structural analysis.[4-6] In the following discussion we will assume the same geometry also in gas phase, where the mass spectra[7,8] indicate retention of the trimeric structure. The availability of selenium-containing compounds allowed an evaluation of the influence of the substitution of chalcogen atoms on the electronic distribution. The present study is the first UPS investigation of tin–selenium containing compounds.

The UPS results were interpreted on the basis of experimental evidence (for example, He I/He II intensity variations), the comparison within the series and with parent molecules, and quantum mechanical calculations,

---

[1] Cauletti, C.; Nicotra, G.; Piancastelli, M. N. *J. Organomet. Chem.* **1980**, *190*, 147.

[2] Andoni, E.; Cauletti, C.; Furlani, C. *Inorg. Chim. Acta* **1983**, *76*, L35.

[3] Andoni, E.; Bossa, M.; Cauletti, C.; Furlani, C.; Palma, A. *J. Organomet. Chem.* **1983**, *244*, 343.

[4] Menzeloach, B.; Bleckman, P. *J. Organomet. Chem.* **1975**, *91*, 291.

[5] Dräger, M.; Blecher, A.; Jacobsen, H. J.; Krebs, B. *J. Organomet. Chem.* **1978**, *161*, 319.

[6] Jacobsen, H. J.; Krebs, B. *J. Organomet. Chem.* **1977**, *136*, 333.

[7] (a) Harrison, P. G.; Stobart, S. R. *J. Organomet. Chem.* **1973**, *47*, 89. (b) Mathiasch, B. *J. Organomet. Chem.* **1976**, *122*, 345.

[8] Mathiasch, B.; Blecher, A. *Bull. Soc. Chim. Belg.* **1975**, *84*, 1045.