Organometallics **1996,** *15,* 809−813

Organometallic Selenides: Preparation of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ and $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ by Reduction of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ with $Bu^n{}_3SnH$ and Preparation of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ by Oxidation of $(\eta\text{-}C_5H_5)TiCl_2$ with H_2Se[†]

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A mixture of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ (**1**) and $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ (**2**) was formed on reduction of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ with $Bu^n{}_3SnH$. A structure with opposed capped octahedra of Ti and Se atoms is proposed for $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ (**1**) on the basis of spectroscopic data. Oxidation of $(\eta\text{-}C_5H_5)TiCl_2{\cdot}2thf$ with H_2Se in the presence of triethylamine gave $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ (**2**), which has a trigonal bipyramidal arrangement of Ti atoms (average $Ti_{ax}-Ti_{eq}$ 3.215(2) Å, average $Ti_{eq}-Ti_{eq}$ 3.374(3) Å) and is paramagnetic with one unpaired electron.

Introduction

We have been interested in the synthesis of (cyclopentadienyl)titanium clusters containing chalcogenide atoms.[1−4] This interest stems from the use of such compounds as models for industrially important catalysts[5] and their unusual electronic structure.[6] The cluster $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}S)_6$ was obtained by oxidation of $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ with H_2S.[1] However, only the noncluster compounds $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)_2Ti(\eta\text{-}C_5H_5)]_2(\mu\text{-}Se)$ were obtained when $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ was oxidized with H_2Se, although there was mass spectral evidence for $(C_5H_5)_4Ti_4Se$, $(C_5H_5)_5Ti_5Se_6$, and $(C_5H_5)_6Ti_6Se_8$.[2] The clusters $[(\eta\text{-}C_5H_4Me)Ti]_5(\mu_3\text{-}A)_6$ (A = Se, Te) were obtained in 60−70% yield from the reaction between $(\eta\text{-}C_5H_4Me)TiCl_3$ and $(Me_3Si)_2A$,[7] although the reducing agent in this reaction is unknown. We wished to find a rational synthesis for (cyclopentadienyl)titanium selenide clusters. A reasonable approach appeared to be reduction of $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ with zinc, since the analogous reduction of $(\eta\text{-}C_5H_5)_2Ti(SH)_2$ gave $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}S)_6$[3] and reduction of $[(\eta\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$ with zinc gave $[(\eta\text{-}C_5H_5)Ti]_6(\mu_3\text{-}Cl)_2(\mu_3\text{-}O)_6$.[8] The synthesis of $(\eta\text{-}C_5H_5)_2Ti(SH)_2$ was initially reported by Köpf[9] and later improved by Shaver.[10] Our attempt to apply that synthesis to the selenium analogue gave the cluster $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$.[4] We therefore reduced this cluster and obtained a mixture of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ and $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$. We also aggregated $(\eta\text{-}C_5H_5)TiCl_2{\cdot}2thf$, a (cyclopentadienyl)titanium compound that was already in a reduced oxidation state. Ligand exchange of Cl^- by Se^{2-} was accompanied by partial oxidation, giving $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$. Full details are reported here.

Results and Discussion

Reaction between $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ and $Bu^n{}_3SnH$ or $Bu^n{}_3P$: Formation of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ (1) and $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ (2). When $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ in tetrahydrofuran was reduced wth $Bu^n{}_3SnH$, a mixture of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ (**1**) (approximately 50% yield based on titanium) and $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ (**2**) (approximately 10% yield) was formed. There was no evidence of any unreacted $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. The cluster $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ was identified by NMR, mass spectrometry, and X-ray diffraction. The characterization of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ is given below.

When a solution of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ in tetrahydrofuran was stirred with $Bu^n{}_3P$ for 7 days, the product was a mixture of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ and the starting materials.

Characterization of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ (1). Total elemental analysis of the product of the reduction of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ with $Bu^n{}_3SnH$ showed that the empirical formula was $[(C_5H_5)TiSe]_n$. The average molecular weight, by osmometry, was 1381. For $n = 7$, $M_r = 1343$. The magnetic moment was 3.41 μ_B (0.49 μ_B per titanium atom), measured in solution[11−13] at 291 K. The EPR spectrum at 293 K showed no signal, indicating a diamagnetic cluster (which $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ cannot be), a cluster with more than one unpaired

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[†] Dedicated to Professor William A. G. Graham on the occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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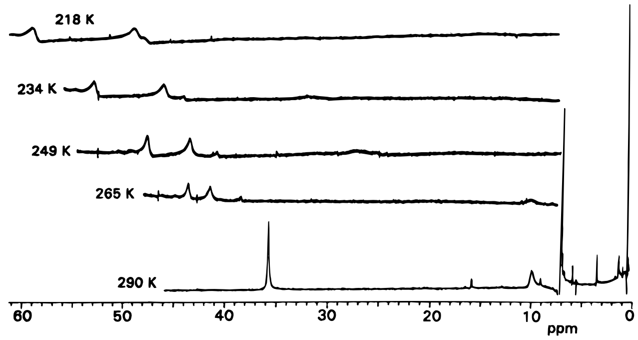

Figure 1. Variable-temperature ^{1}H NMR spectrum of [(η-C_5H_5)Ti(μ_3-Se)]$_7$.

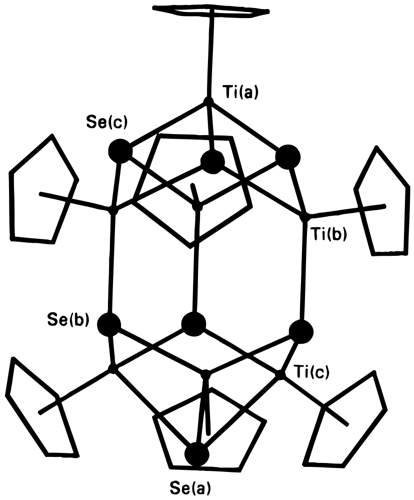

Figure 2. Structure of [(η-C_5H_5)Ti(μ_3-Se)]$_7$.

electron,[14] or a cluster with electrons in degenerate orbitals. The infrared spectrum showed absorptions for the C_5H_5 ligand only. The mass spectrum did not show any peak which could be assigned to a parent ion or a fragment of any (cyclopentadienyl)titanium selenide.

The ^{1}H NMR spectrum, at room temperature, showed two resonances, one at 35.44 ppm ($\Delta\nu_{1/2} = 28.9$ Hz) and one at 10.01 ppm ($\Delta\nu_{1/2} = 79.9$ Hz). The relative integration of the two resonances did not vary with concentration. As the temperature was lowered, the resonance at 35.44 ppm split into two (Figure 1). These two resonances continued to shift to lower field as the temperature was lowered, which indicated that the magnetic moment of the cluster was temperature dependent. The resonance at 10.01 ppm merged with the background as the temperature was lowered (see Figure 1).

Structure of [(η-C_5H_5)Ti(μ_3-Se)]$_7$. A structure for [(η-C_5H_5)Ti(μ_3-Se)]$_7$ which accounts for the above observations is shown in Figure 2. The cluster consists of two interpenetrating monocapped octahedra, one of titanium atoms and one of selenium atoms. Each selenium atom triply bridges three titanium atoms. This structure is similar to that of [Bu^{t}Ga(μ_3-S)]$_7$, which has been characterized by X-ray crystallography.[15] There are three environments for the titanium atoms and three for the selenium atoms, labeled a–c in Figure 2. The relative ratio of the environments is 1:3:3. Therefore there are three environments (in the ratio 1:3:3) for the η-C_5H_5 ligand.

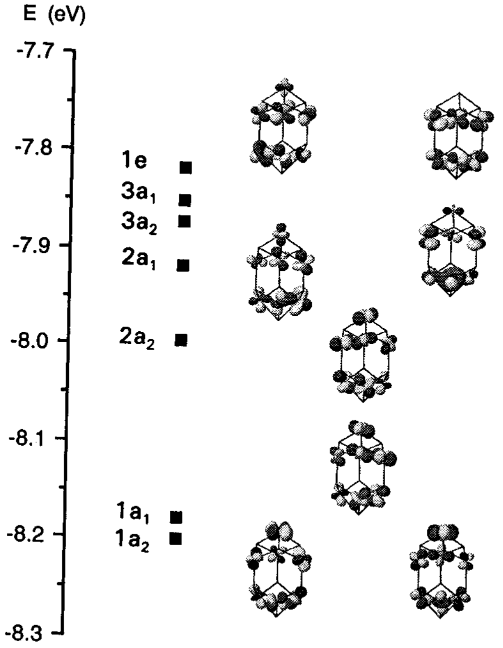

Figure 3. Energies, composition, and symmetries of the eight lowest energy cluster orbitals of [(η-C_5H_5)Ti(μ_3-Se)]$_7$.

There are seven cluster electrons in [(η-C_5H_5)Ti(μ_3-Se)]$_7$. These are accommodated in 21 cluster orbitals. An extended Hückel calculation was performed using the geometry shown in Figure 2, with the distances Ti(a)–Se(c) 2.21 Å, Ti(b)–Se(c) 2.36 Å, Ti(b)–Se(b) 2.30 Å, Ti(c)–Se(b) 2.28 Å, and Ti(c)–Se(a) 2.51 Å. The eight cluster orbitals of lowest energy are shown in Figure 3. In the ground state the configuration of [(η-C_5H_5)Ti(μ_3-Se)]$_7$ will be $1a_2^2\ 1a_1^2\ 2a_2^2\ 2a_1^1$. However, the six orbitals $2a_2$, $2a_1$, $3a_2$, $3a_1$, and 1e all lie within a span of 0.2 eV in energy. Thus the three electrons shown as occupying $2a_2$ and $2a_1$ may thermally occupy any of the six orbitals. It is predicted that [(η-C_5H_5)Ti(μ_3-Se)]$_7$ will be antiferromagnetic, with a magnetic moment appropriate to one unpaired electron at low temperature and appropriate to three unpaired electrons at high temperature. It was observed that the magnetic moment was temperature dependent and had a value of 3.41 μ_B at 291 K. This value lies between the spin-only value for two (2.84 μ_B) and three (3.87 μ_B) unpaired electrons.

The two resonances at 35.44 and 10.01 ppm in the ^{1}H NMR spectrum of [(η-C_5H_5)Ti(μ_3-Se)]$_7$ were broad because of the magnetism. The resonance at 35.44 ppm appeared to be more intense than that at 10.01 ppm, although because of the broadness integration was not possible. As the temperature was lowered, the resonance at 35.44 ppm split into two (Figure 1) and that at 10.01 ppm merged into the background. It is apparent from Figure 2 that the environment of Ti(a) is markedly different from Ti(b) and Ti(c), which have similar environments. We therefore assign the resonance at 10.01 ppm to the η-C_5H_5 attached to Ti(a) and the resonance at 35.44 ppm to the η-C_5H_5 attached to Ti(b) and Ti(c). At low temperture the inequivalency in the environment of Ti(b) and Ti(c) is manifested by the splitting in the resonance at 35.44 ppm. Thus the magnetic and spectroscopic results are in excellent

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[14] Hill, H. A. O.; Day, P. *Physical Methods in Advanced Inorganic Chemistry*; Interscience: London, 1969; p 302ff.

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Table 1. Crystal and Refinement Data for $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$[a]

molecular formula	$C_{25}H_{25}Ti_5Se_6$
M_r	1038.73
cryst system	orthorhombic
space group	*Pnab*
a, Å	16.9288(8)
b, Å	10.1226(11)
c, Å	17.2681(13)
V, Å^3	2959.1(4)
Z	8
D(calcd), Mg m^{-3}	4.663
μ(Mo *K*α), mm^{-1}	17.2
cryst size (mm)	0.3 × 0.3 × 0.25
temp, K	295
2θ limits, deg	2−50
scan type	$\theta-2\theta$
reflns collcd	7016
unique reflns	2606
obsd reflns ($I > 2.0\sigma(I)$)	1795
$R(F')$ $(\Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert)$	0.055
$R_w(F')$ $((\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o)^2)^{1/2}$; $w = 1/(\sigma(F^2) + 0.001F^2))$	0.064
GoF $(\Sigma w(F_o - F_c)^2/(\text{no. reflns} - \text{no. params}))$	1.55
max height in diff Fourier map, e Å^{-3}	1.030
N_o/N_v	11.1

[a] No correction for absorption.

agreement with the structure shown in Figure 2.

Reaction between $(\eta\text{-}C_5H_5)TiCl_2{\cdot}2thf$ and H_2Se in the Presence of Et_3N: Formation of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$ (2). The reaction between $(\eta\text{-}C_5H_5)TiCl_2{\cdot}2thf$ and H_2Se, in tetrahydrofuran as solvent and in the presence of triethylamine, produced $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$ in 71% yield (eq 1).

$$5[(\eta\text{-}C_5H_5)TiCl_2]_n{\cdot}2thf + 10Et_3N + 6H_2Se \rightarrow [(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6 + 10Et_3NHCl + H_2 \quad (1)$$

No other complex containing titanium was observed. We had expected that the reaction would produce the Ti(III) cluster $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-Se})]_4$, but eq 1 shows that two titanium atoms were oxidized to Ti(IV). Dihydrogen was not observed experimentally, but the only possible oxidizing agent is the H^+ of H_2Se.

Structure of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$. The structure of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$ was determined by X-ray diffraction (Table 1). All heavy atoms except the carbon of the disordered cyclopentadienyl ring (Cp(1), Figure 4) were refined anisotropically. Cp(1) was disordered over two sites, each refined with 50% occupancy. An ORTEP plot of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$ is shown in Figure 4, and important distances and angles are given in Table 2. There are three seven-coordinate equatorial titanium atoms (designated Ti_{eq}) and two six-coordinate axial titanium atoms (Ti_{ax}), which together form a trigonal bipyramid. The six selenide ligands triply bridge the triangular faces of the trigonal bipyramid. The equatorial titanium atoms form an equilateral triangle with an average Ti−Ti distance of 3.374(3, 3, 5)[16] Å. The $Ti_{ax}-Ti_{eq}$ distances are essentially equal, averaging 3.322(3, 2, 3) Å. The Ti_{ax}−Se distances average 2.421(2, 5, 10) Å while the Ti_{eq}−Se distances average 2.636(2, 10, 15) Å. The idealized D_{3h} symmetry of a trigonal bipyramid is reduced to C_1 by the short Ti(2)−Se(1) distance of 2.626(2) Å and the longer Ti(1)−Se(2) distance of 2.641(1) Å. The shorter average Ti_{ax}−Se distance, as compared to Ti_{eq}−Se, is due to the lower coordination number of the axial titanium atoms. The $Ti_{eq}-C_5$(ring centroid) distances range from 2.06(1) to 2.08(2) Å (including Cp(1)), and the average $Ti_{ax}-C_5$(ring centroid) distance is 2.04(1) Å.

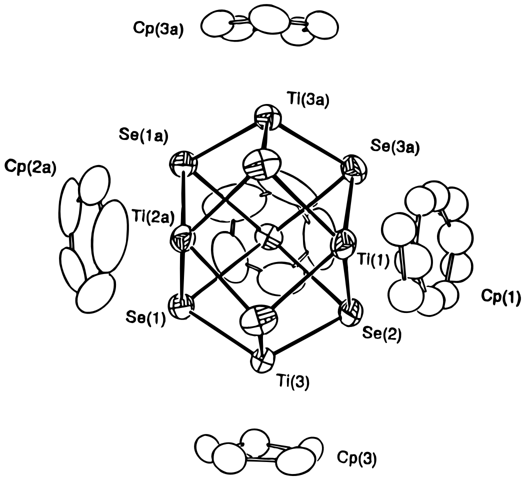

Figure 4. Numbering scheme for $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$. (Hydrogen atoms are omitted for clarity.)

Table 2. Distances (Å) and Angles (deg) in $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-Se})_6$

Ti(1)−Ti(2)	3.376(3)[a]	Ti(2)−Se(1a)	2.636(2)
Ti(1)−Ti(2a)	3.376(3)	Ti(2)−Se(2)	2.639(2)
Ti(1)−Ti(3)	3.323(2)	Ti(2)−Se(3a)	2.634(2)
Ti(1)−Ti(3a)	3.323(2)	Ti(3)−Ti(2a)	3.320(2)
Ti(1)−Se(2)	2.641(1)	Ti(3)−Se(1)	2.426(2)
Ti(1)−Se(2a)	2.641(1)	Ti(3)−Se(2)	2.417(2)
Ti(1)−Se(3)	2.634(1)	Ti(3)−Se(3)	2.419(2)
Ti(1)−Se(3a)	2.634(1)	Se(1)−Ti(2a)	2.636(2)
Ti(2)−Ti(2a)	3.371(3)	Se(3)−Ti(2a)	2.634(2)
Ti(2)−Ti(3)	3.322(2)	Ti(1)−Cp(1)[b]	2.08(2)
Ti(2)−Ti(3a)	3.320(2)	Ti(2)−Cp(2)	2.06(1)
Ti(2)−Se(1)	2.626(2)	Ti(3)−Cp(3)	2.04(1)

Se(2)−Ti(1)−Se(2a)	141.76(10)	Se(1)−Ti(3)−Se(2)	102.03(7)
Se(2)−Ti(1)−Se(3)	91.10(5)	Se(1)−Ti(3)−Se(3)	102.33(7)
Se(2)−Ti(1)−Se(3a)	76.47(4)	Se(2)−Ti(3)−Se(3)	102.29(7)
Se(2a)−Ti(1)−Se(3)	76.47(4)	Ti(2)−Se(1)−Ti(2a)	79.66(5)
Se(2a)−Ti(1)−Se(3a)	91.10(5)	Ti(2)−Se(1)−Ti(3)	82.12(6)
Se(3)−Ti(1)−Se(3a)	141.72(10)	Ti(2a)−Se(1)−Ti(3)	81.84(6)
Se(1)−Ti(2)−Se(1a)	76.14(5)	Ti(1)−Se(2)−Ti(2)	79.50(6)
Se(1)−Ti(2)−Se(2)	91.29(6)	Ti(1)−Se(2)−Ti(3)	82.03(6)
Se(1)−Ti(2)−Se(3a)	142.06(7)	Ti(2)−Se(2)−Ti(3)	82.02(6)
Se(1a)−Ti(2)−Se(2)	141.86(7)	Ti(1)−Se(3)−Ti(2a)	79.71(6)
Si(1a)−Ti(2)−Se(3a)	91.46(6)	Ti(1)−Se(3)−Ti(3)	82.13(6)
Se(2)−Ti(2)−Se(3a)	76.51(6)	Ti(2a)−Se(3)−Ti(3)	82.03(6)

[a] Estimated standard deviations in parentheses. [b] Cp denotes the centroid of the C_5H_5 ring.

Fenske and Grissinger found a significant distortion in the titanium core of $[(\eta\text{-}C_5H_4Me)Ti]_5(\mu_3\text{-Se})_6$, with the $Ti_{eq}-Ti_{eq}$ distances averaging 3.368(3, 37, 62) Å while the $Ti_{eq}-Ti_{ax}$ distance averaged 3.314(3, 32, 47) Å.[7] The average Ti_{eq}−Se distance was 2.618(3, 20, 37) Å and for Ti_{ax}−Se 2.405(3, 4, 7)Å.[7] The two $[(\eta\text{-}C_5R_5)Ti]_5(\mu_3\text{-Se})_6$ compounds are compared in Table 3. The difference between the two clusters can only be due to intermolecular packing forces, since the substitution of one Me for H has no electronic effect. As well, intramolecular steric interactions are unlikely since both $[(\eta\text{-}C_5H_5)Cr(\mu_3\text{-}O)]_4$[17] and $[(\eta\text{-}C_5Me_5)Cr(\mu_3\text{-}O)]_4$[18] have the same structure, as do $[(\eta\text{-}C_5H_5)Ti]_6(\mu_3\text{-}O)_6(\mu_3\text{-}Cl)_2$ and $[(\eta\text{-}C_5H_4Me)\text{-}$

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[16] The first figure in parentheses is the esd followed by the maximum deviation and the range.

[17] Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 5581.

Table 3. Comparison of Distances in Cyclopentadienyl−Transition Metal Trigonal Bipyramid Structures

	$\text{M}_{\text{eq}}-\text{M}_{\text{eq}}$[a]	$\text{M}_{\text{eq}}-\text{M}_{\text{ax}}$	$\text{M}_{\text{eq}}-\text{A}$	$\text{M}_{\text{ax}}-\text{A}$	ref
$[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$	3.371−3.376(3)[b]	3.320−3.323(2)	2.626−2.641(2)	2.416−2.426(2)	this work
$[(\eta\text{-C}_5\text{H}_4\text{Me})\text{Ti}]_5(\mu_3\text{-Se})_6$	3.331−3.393(3)	3.299−3.346(3)	2.601−2.638(3)	2.401−2.408(3)	7
$[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-S})_6$	3.148−3.214(5)	3.076−3.173(5)	2.443−2.506(7)	2.263−2.308(6)	1
$[(\eta\text{-C}_5\text{H}_5)\text{V}]_5(\mu_3\text{-O})_6$	2.737−2.744(6)	2.744−2.754(6)	1.983−2.003(6)	1.846−1.876(6)	19
$\{[(\eta\text{-C}_5\text{H}_4\text{Me})\text{V}]_5(\mu_3\text{-S})_6\}^+$	3.21−3.25	2.97−3.01	2.38	2.22	25
$[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_4(\mu_2\text{-Se})_3(\mu_3\text{-Se})_3$	3.270−3.306(4)	3.453−3.471(4)	2.665−2.729(4)	2.387−2.392(4)	4

[a] All distances in Å; M = transition metal, and A = O, S, or Se. [b] Estimated standard deviations in parentheses.

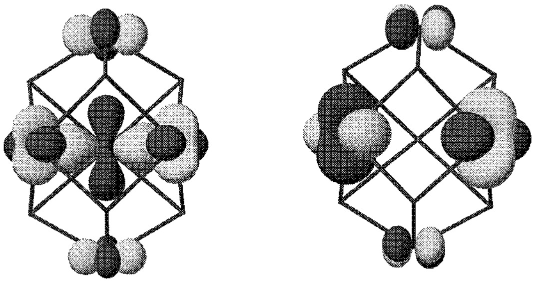

Figure 5. Energies, composition, and symmetries of the highest occupied molecular orbital of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}](\mu_3\text{-Se})_6$.

$\text{Ti}]_6(\mu_3\text{-O})_6(\mu_3\text{-Cl})_2$.[8] The titanium core of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$ was slightly more compact than the core of $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{Ti}]_5(\mu_3\text{-Se})_6$, as judged by the Ti−Ti distances. The $\text{Ti}_{\text{eq}}-\text{Se}-\text{Ti}_{\text{ax}}$ angles in $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$ range from 82.02(6) to 82.13(6)° and lie within the range quoted for Ti−Se−Ti in $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{Ti}]_5(\mu_3\text{-Se})_6$ of 78.80(6)−83.20(6)°.

A summary of important distances for related trigonal bipyramidal clusters is given in Table 3. The clusters containing S or Se are characterized by $\text{M}_{\text{eq}}-\text{M}_{\text{eq}}$ distances which are longer than the corresponding $\text{M}_{\text{eq}}-\text{M}_{\text{ax}}$ distances. In $[(\eta\text{-C}_5\text{H}_5)\text{V}]_5(\mu_3\text{-O})_6$ all M−M distances are equal.[19] The $\text{M}_{\text{eq}}-\text{A}$ distances are longer than the $\text{M}_{\text{ax}}-\text{A}$ distances by as much as 0.2 Å. These results are attributed to the higher coordination number for M_{eq}. The cluster $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$ can also be compared with $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_4(\mu_2\text{-Se})_3(\mu_3\text{-Se})_3$.[4] These are related by removing a $(\eta\text{-C}_5\text{H}_5)\text{Ti}$ fragment from an axial position in $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$. The $\text{M}_{\text{eq}}-\text{M}_{\text{eq}}$ distance in $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_4(\mu_2\text{-Se})_3(\mu_3\text{-Se})_3$ is significantly shorter than the $\text{M}_{\text{eq}}-\text{M}_{\text{ax}}$ distance. This is the reverse of the trend seen for the trigonal bipyramidal clusters and may be due to the strength of the $\text{Ti}-(\mu_2\text{-Se})$ bond compared to $\text{Ti}-(\mu_3\text{-Se})$, the decreased coordination number around Ti_{eq}, or the presence of three electrons in the cluster orbitals of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$. These three cluster electrons occupy the e orbitals, which are heavily localized on the equatorial titanium atoms but by symmetry are bonding to the axial titanium atoms (Figure 5).

NMR and EPR Spectra of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$. Two resonances were observed in the NMR spectrum of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$, one at 15.88 ppm assigned to the three cyclopentadienyl ligands attached to equatorial titanium atoms and one at 9.01 ppm assigned to the two cyclopentadienyl ligands attached to the axial titanium atoms. The position and intensities of the signals were similar to those observed for $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-S})_6$.[1] Fenske and Grissinger stated that the NMR spectrum of $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{Ti}]_5(\mu_3\text{-Se})_6$ showed broad resonances but reported no chemical shifts.[7] The EPR spectrum of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$ comprised a single line with $g = 1.979$. This is similar to $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-S})_6$ ($g = 1.993$).[1] The significant distortion of the titanium/selenium core of the cluster to C_1 symmetry allows the observation of an EPR spectrum even though the ground state in D_{3h} symmetry is orbitally degenerate.

Conclusion

A (cyclopentadienyl)titanium selenide, $[(\eta\text{-C}_5\text{H}_5)\text{Ti}(\mu_3\text{-Se})]_7$, with the novel septatitanium structure, shown in Figure 2, has been prepared.

Experimental Section

General Techniques and Reagents. All experiments were carried out under vacuum or argon using standard vacuum line techniques. Volumes of H_2Se were measured using a manometer and calibrated bulb. Solvents were predried by standard drying agents, stored over Bu^nLi, and distilled under vacuum. Literature methods were used to prepare $(\eta\text{-C}_5\text{H}_5)\text{TiCl}_2{\cdot}2\text{thf}$[20] and $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_4(\mu_3\text{-Se})_3(\mu_2\text{-Se})_3$.[4] Other chemicals were reagent grade. Microanalyses (C and H) were carried out by Beller Laboratorium, Göttingen, Germany. Titanium and selenium were determined by atomic absorption spectroscopy in the department of Geology, UNB. X-ray diffraction experiments were carried out on an Enraf-Nonius CAD4 diffractometer operating under the control of the NRCCAD software.[21] Refinement used the NRCVAX suite of programs.[22] Extended Hückel calculations made use of the CAChe system.

Reaction of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_4(\mu_2\text{-Se})_3(\mu_3\text{-Se})_3$ with $\text{Bu}^n{}_3\text{SnH}$: Formation of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}(\mu_3\text{-Se})]_7$. To an unstirred solution of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_4(\mu_2\text{-Se})_3(\mu_3\text{-Se})_3$ (1.54 g, 1.67 mmol) in tetrahydrofuran (100 cm^3) was added $\text{Bu}^n{}_3\text{SnH}$ (1.80 cm^3, 6.66 mmol) in tetrahydrofuran (50 cm^3) over a period of 2 h. The solution was set aside for 7 days. A gradual color change from dark green to olive green was observed. The solution was filtered, giving an olive green solid (0.837 g). The crude product was soluble in dichloromethane and chloroform and slightly soluble in tetrahydrofuran and toluene. The cluster $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$ was crystallized from the crude reaction mixture by layering a saturated dichloromethane solution (75 cm^3) with diethyl ether (75 cm^3). Crystals of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6{\cdot}\text{CH}_2\text{Cl}_2$ were removed by filtration. The filtrate was reduced in volume to 50 cm^3, and diethyl ether (75 cm^3) was layered onto it. The cluster $[(\eta\text{-C}_5\text{H}_5)\text{Ti}(\mu_3\text{-Se})]_7$ was isolated as microcrystals (0.650 g, 0.48 mmol, 50.7% yield based on titanium).

The structure of $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6{\cdot}\text{CH}_2\text{Cl}_2$ was determined by X-ray diffraction, and $[(\eta\text{-C}_5\text{H}_5)\text{Ti}]_5(\mu_3\text{-Se})_6$ was also characterized by comparison of the EPR spectrum (toluene solution, 293 K: single sharp resonance with $g = 1.980$) and NMR spectrum (C_6D_6 solution: 15.88 ppm, s, 15 H, and 9.11

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ppm, s, 10H) with spectra from a sample prepared by the original synthesis. $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ was formed in 10% yield as determined by NMR spectroscopy.

The cluster $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ was identified by spectroscopy and analysis. ^1H NMR (200 MHz): CD_2Cl_2 solution, 35.44 ppm, $\Delta\nu_{1/2} = 28.9$ Hz, and 10.01 ppm, $\Delta\nu_{1/2} = 79.9$ Hz; C_6D_6 solution, 35.39 and 9.98 ppm; variable-temperature spectrum (CD_2Cl_2 solution, Figure 1): between 290 K and 218 K the resonance at 35.44 ppm split into two signals of equal intensity while the resonance at 10.01 ppm merged into the background. Anal. Calcd for $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$: C, 31.29; H, 2.63; Ti, 24.92; Se, 40.63. Found: C, 31.28; H, 2.76, Ti, 25.38; Se, 41.16. Molecular weight (by osmometry, CH_2Cl_2 solution): 1290, 1471 (average = 1380). Magnetic moment (Evans' solution method,[11-13] $CDCl_3$ solution, 291 K, corrected): 3.41 μ_B. For the diamagnetic correction, values of -50.90×10^{-6} cm^{-3} M^{-1} per $C_5H_5^-$ ring, -9.0×10^{-6} cm^{-3} M^{-1} per Ti^{3+}, and -23×10^{-6} cm^{-3} M^{-1} per Se^{2-} were used.[23] Infrared spectrum (Nujol mull): 1009 cm^{-1}, π(C−H); 796 cm^{-1}, π(C−H).

Reaction between $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ and $Bu^n{}_3P$: Formation of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$. A solution of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ (0.499 g, 0.539 mmol) in tetrahydrofuran (100 cm^3) was stirred with $Bu^n{}_3P$ (0.268 cm^3, 1.08 mmol) for 7 days. The solution was evaporated to 75 cm^3 under vacuum and layered with diethyl ether (50 cm^3). An olive green solid, which was a mixture of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ was collected (0.293 g). ^1H NMR (200 MHz, C_6D_6 solution): 35.74 and 9.98 ppm, assigned to the C_5H_5 of $[(\eta\text{-}C_5H_5)Ti(\mu_3\text{-}Se)]_7$; 7.15 ppm, 15 H, and 6.55 ppm, 5 H, assigned to $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ by comparison with an original sample.

Reaction between $(\eta\text{-}C_5H_5)TiCl_2\cdot 2thf$ and H_2Se in the Presence of $(C_2H_5)_3N$: Formation of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$. To a solution of $(\eta\text{-}C_5H_5)TiCl_2\cdot 2thf$ (0.679 g, 2.07 mmol), in tetrahydrofuran (100 cm^3), was added triethylamine (0.6 cm^3, 4.3 mmol), and the mixture was incubated with H_2Se (4.0 mmol), with stirring, for 24 h. The initial color of the solution changed from turquoise to deep purple and eventally to olive green. Filtration of the mixture gave a green filtrate and a light brown precipitate (0.709 g). The precipitate was dissolved in chloroform (30 cm^3), and the solution was layered with hexane (40 cm^3), giving Et_3NHCl (0.25 g, 1.82 mmol, 44% based on eq 1). This was identified by comparison of its infrared spectrum (2605, 2525, 2500 cm^{-1}) with the literature (2620, 2530, 2510 cm^{-1}).[24] The mass spectrum showed *m/e* 101 ($\{Et_3N\}^+$) and 86 ($\{Et_2NCH_2\}^+$). The green filtrate was reduced in volume to 50 cm^3, and diethyl ether (50 cm^3) was layered onto it. On being set aside for 3 days, the solution deposited olive green crystals of $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}Se)_6$ (0.304 g, 0.29 mmol, 71% yield based on eq 1). The crystals were identified by X-ray diffraction and the following data. ^1H NMR (200 MHz, C_6D_6 solution): 15.88 ppm ($\Delta\nu_{1/2} = 13.73$ Hz, 15 H, 3 C_5H_5); 9.01 ppm ($\Delta\nu_{1/2} = 11.05$ Hz, 10 H, 2 C_5H_5). EPR (293 K, toluene solution): $g = 1.979$ as a single narrow line. Mass spectrum (El): *m/e* 1038 ($\{[(C_5H_5)Ti]_5(^{80}Se)_6\}^+$), 973 ($\{(C_5H_5)_4Ti_5(^{80}Se)_6\}^+$), 908 ($\{(C_5H_5)_3Ti_5(^{80}Se)_6\}^+$), 843 ($\{(C_5H_5)_2Ti_5(^{80}Se)_6\}^+$), 778 ($\{(C_5H_5)Ti_5(^{80}Se)_6\}^+$), 713 ($\{Ti_5(^{80}Se)_6\}^+$). Infrared (KBr pellet): 3090, ν(C−H); 1475, ν(C−C); 1170 cm^{-1}, π(C−H).

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Supporting Information Available: Tables of complete atomic positional and thermal parameters and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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