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Preparation and Properties of $(\eta\text{-}C_5H_5)_2TiCl(SeH)$, $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$, $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$, and Related Cyclopentadienyl Selenides of Titanium

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The reaction between $(\eta\text{-}C_5H_5)_2TiCl_2$ and H_2Se in tetrahydrofuran as solvent and in the presence of $(C_2H_5)_3N$ gave $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. The structure of the product was determined by X-ray diffraction (crystal data for $(C_5H_5)_4Ti_4Se_6\cdot(C_2H_5)_3N$: $P\bar{1}$; $a = 10.971$ (1), $b = 11.148$ (2), $c = 13.943$ (1) Å; $\alpha = 88.38$ (1), $\beta = 78.29$ (7), $\gamma = 81.17$ (1)°; $Z = 2$; $R = 0.070$ for 335 variables and 2961 observed reflections). The cluster has one six-coordinate Ti atom linked to three μ_3-Se's (average Ti–Se = 2.389 (3) Å) and three seven-coordinate Ti atoms linked to three μ_3-Se's (average Ti–Se = 2.700 (3) Å) and to three μ_2-Se's (average Ti–Se = 2.508 (3) Å). The cluster is diamagnetic, since it contains four Ti(IV) centers. The reaction between $(\eta\text{-}C_5H_5)_2TiCl_2$ and H_2Se in tetrahydrofuran and in the presence of pyridine gave a mixture of $(\eta\text{-}C_5H_5)_2TiCl(SeH)$ and $(\eta\text{-}C_5H_5)Ti(SeH)_2$. When the reaction was conducted in the presence of O_2, the product was $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}Se_2)$. The reactions are compared to those between $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ and H_2Se.

Introduction

We have previously reported the preparation of $[(\eta\text{-}C_5H_5)Ti]_6(\mu_3\text{-}O)_8$ and $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}S)_6$ from the reactions between $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ and H_2O[1] and H_2S,[1,2] respectively. Extension of these reactions to H_2Se showed that clusters of the type $[(\eta\text{-}C_5H_5)Ti]_m(\mu_3\text{-}Se)_n$ (m, n = 6, 8; 5, 6; and 4, 4) were formed, but the yields were low. The major products were $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)_2Ti(\eta\text{-}C_5H_5)]_2(\mu\text{-}Se)$.[3] We therefore turned to other methods in order to prepare $[(\eta\text{-}C_5H_5)Ti]_m(\mu_3\text{-}Se)_n$. Floriani and co-workers showed that $[(\eta\text{-}C_5H_5)Ti]_6(\mu_3\text{-}O)_8$ could be obtained by reduction of $[(\eta\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$ or $[(\eta\text{-}C_5H_5)TiCl_2]_2(\mu\text{-}O)$ with zinc, followed by hydrolysis of the $[(\eta\text{-}C_5H_5)Ti]_6(\mu_3\text{-}Cl)_n(\mu_3\text{-}O)_{8-n}$ (n = 0, 2, 4) product.[4] We have used a similar reaction to obtain $[(\eta\text{-}C_5H_5)Ti]_5(\mu_3\text{-}S)_6$ and related clusters by reduction of $(\eta\text{-}C_5H_5)_2Ti(SH)_2$ with zinc.[5] In order to obtain $[(\eta\text{-}C_5H_5)Ti]_m(\mu_3\text{-}Se)_n$ by a similar route, we required reproducible, high-yield syntheses of $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ or other suitable starting materials. The results of our attempts at such syntheses have been the preparation of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$, $(\eta\text{-}C_5H_5)_2TiCl(SeH)$, $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$, and $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}Se_2)$, which are reported here. Recently, Fenske and Grissinger obtained $[(\eta\text{-}C_5H_4Me)Ti]_5(\mu_3\text{-}Se)_6$ from the reaction between $(\eta\text{-}C_5H_4Me)_2TiCl_2$ or $(\eta\text{-}C_5H_4Me)TiCl_3$ and $(Me_3Si)_2Se$.[6]

Results and Discussion

Reaction between $(\eta\text{-}C_5H_5)_2TiCl_2$ and H_2Se. Köpf and Schmidt first showed that $(\eta\text{-}C_5H_5)_2Ti(SH)_2$ could be prepared from the reaction between $(\eta\text{-}C_5H_5)_2TiCl_2$, H_2S, and $(C_2H_5)_3N$ in ethanol,[7] according to eq 1. They also

$$(\eta\text{-}C_5H_5)_2TiCl_2 + 2H_2S + 2(C_2H_5)_3N \rightarrow (\eta\text{-}C_5H_5)_2Ti(SH)_2 + 2(C_2H_5)_3N\cdot HCl \quad (1)$$

noted that the analogous reaction with H_2Se did not proceed.[8] Shaver found that reaction 1 gave a higher yield of $(\eta\text{-}C_5H_5)_2Ti(SH)_2$ when it was conducted in tetrahydrofuran (thf).[9] We observed a smooth reaction between $(\eta\text{-}C_5H_5)_2TiCl_2$, H_2Se, and $(C_2H_5)_3N$ in thf. The product was not $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ but $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ (Figure 1), according to eq 2. There was no evidence for $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ or $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$, nor for any intermediates in the reaction.

$$4(\eta\text{-}C_5H_5)_2TiCl_2 + 6H_2Se + 8(C_2H_5)_3N \rightarrow 4C_5H_6 + 8(C_2H_5)_3N\cdot HCl + [(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3 \quad (2)$$

Because of the unexpected reaction 2, we decided to change the base to pyridine, retaining thf as the solvent. In this case a mixture of products was obtained. These were derived from the equilibria (3) and (4). Even with

$$(\eta\text{-}C_5H_5)_2TiCl_2 + H_2Se + C_5H_5N \rightleftharpoons (\eta\text{-}C_5H_5)_2TiCl(SeH) + C_5H_5N\cdot HCl \quad (3)$$

$$(\eta\text{-}C_5H_5)_2TiCl(SeH) + H_2Se + C_5H_5N \rightleftharpoons (\eta\text{-}C_5H_5)_2Ti(SeH)_2 + C_5H_5N\cdot HCl \quad (4)$$

high concentrations of H_2Se a mixture of $(\eta\text{-}C_5H_5)_2TiCl(SeH)$ and $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ was obtained, and small quantities of $(\eta\text{-}C_5H_5)_2TiCl_2$ were also present. The different base strengths of $(C_2H_5)_3N$ and C_5H_5N may be responsible for the different products, but it is also possible that the different solubilities of $(C_2H_5)_3N\cdot HCl$ and $C_5H_5N\cdot HCl$ in thf influence the course of reactions 2–4. The constituents of the equilibria could be conveniently detected by using the ^1H NMR spectra of the various complexes.

It would be expected that $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ would be in equilibrium with $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$, according to eq 5.[10] In fact $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ was obtained from the reaction between $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ and H_2Se (eq 6).

$$2(\eta\text{-}C_5H_5)_2Ti(SeH)_2 \rightleftharpoons [(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2 + 2H_2Se \quad (5)$$

$$2(\eta\text{-}C_5H_5)_2Ti(CO)_2 + 2H_2Se \rightarrow [(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2 + 2H_2 + 4CO \quad (6)$$

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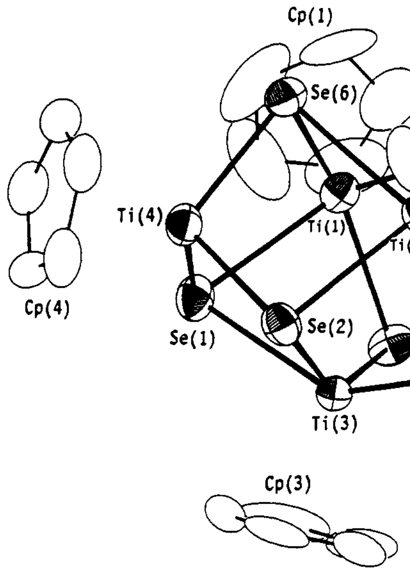

Figure 1. ORTEP plot of the structure of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$.

There was no evidence for $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ in that case.[3] It was suggested that $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ was formed via reactions 7–9 rather than via reactions 7, 10, and 5.[3,11]

$$(\eta\text{-}C_5H_5)_2Ti(CO)_2 + H_2Se \rightarrow (\eta\text{-}C_5H_5)_2Ti(SeH)(H) + 2CO \quad (7)$$

$$(\eta\text{-}C_5H_5)_2Ti(SeH)(H) + (\eta\text{-}C_5H_5)_2Ti(CO)_2 \rightarrow [(\eta\text{-}C_5H_5)_2Ti(H)]_2(\mu\text{-}Se) + 2CO \quad (8)$$

$$[(\eta\text{-}C_5H_5)_2Ti(H)]_2(\mu\text{-}Se) + H_2Se \rightarrow [(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2 + 2H_2 \quad (9)$$

$$(\eta\text{-}C_5H_5)_2Ti(SeH)(H) + H_2Se \rightarrow (\eta\text{-}C_5H_5)_2Ti(SeH)_2 + H_2 \quad (10)$$

This conclusion is strengthened by the present work, since no $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ was observed in the reaction between $(\eta\text{-}C_5H_5)_2TiCl_2$, H_2Se, and C_5H_5N. This may be because the equilibria (3) and (4) lie to the left and reasonable quantities of $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ are only formed under conditions of high H_2Se concentration, which in turn prevents formation of $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$. Because high-yield syntheses of $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)]_2$ have not been found, we have been unable to further investigate the formation of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$.

The reactions between $(\eta\text{-}C_5H_5)_2TiCl_2$, H_2Se, and C_5H_5N, or between $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ and H_2Se, must be conducted in the rigorous absence of air. In the presence of traces of O_2, the first reaction gave $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}Se_2)$ (Figure 2) as single crystals. This compound is the selenium analogue of $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}S_2)$ prepared by Maué and Fenske[12] and is related to $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se_2)]_2$ described by Rauchfuss.[13] Traces of O_2 in the reaction between $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ and H_2Se lead to the formation of $(\eta\text{-}C_5H_5)_2Ti(\eta^2\text{-}Se_5)$,[4,8] which was identified by comparison of the cell dimensions and space group with the published values.[14] Large-scale syntheses of $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}Se_2)$ and $(\eta\text{-}C_5H_5)_2Ti(\eta^2\text{-}Se_5)$ were not attempted. It has been shown previously that oxidation of S^{2-} ligands on titanium leads to S_2^{2-} derivatives.[15]

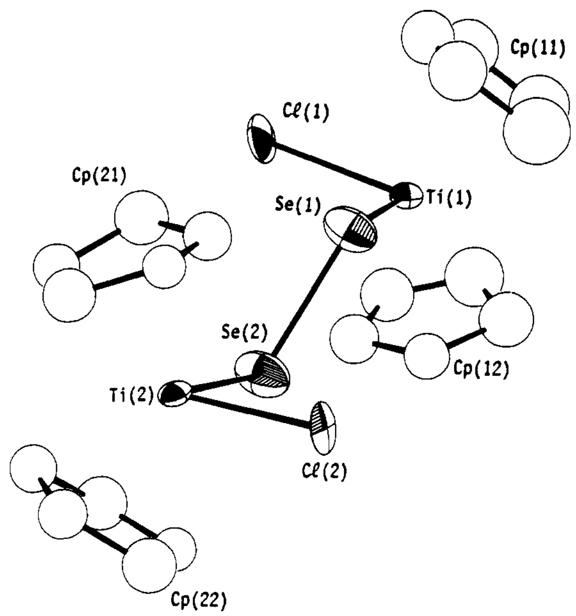

Figure 2. Structure of $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu_2\text{-}Se_2)$.

Table I. Distances (Å) and Angles (deg) in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$

Ti(1)–Se(1)	2.672 (3)[a]	Ti(4)–Se(2)	2.392 (4)
Ti(1)–Se(3)	2.521 (4)	Ti(4)–Se(6)	2.389 (3)
Ti(1)–Se(5)	2.498 (3)	Ti(1)–Ti(2)	3.306 (4)
Ti(1)–Se(6)	2.722 (3)	Ti(1)–Ti(3)	3.270 (4)
Ti(2)–Se(2)	2.711 (4)	Ti(1)–Ti(4)	3.453 (4)
Ti(2)–Se(3)	2.523 (4)	Ti(2)–Ti(3)	3.289 (4)
Ti(2)–Se(4)	2.504 (3)	Ti(2)–Ti(4)	3.461 (4)
Ti(2)–Se(6)	2.703 (4)	Ti(3)–Ti(4)	3.471 (4)
Ti(3)–Se(1)	2.665 (4)	Ti(1)–Cp(1)[b]	2.084 (21)
Ti(3)–Se(2)	2.729 (3)	Ti(2)–Cp(2)[b]	2.085 (21)
Ti(3)–Se(4)	2.494 (4)	Ti(3)–Cp(3)[b]	2.073 (17)
Ti(3)–Se(5)	2.510 (3)	Ti(4)–Cp(4)[b]	2.073 (19)
Ti(4)–Se(1)	2.387 (3)		
Se(1)–Ti(1)–Se(3)	141.7 (1)	Se(4)–Ti(3)–Se(5)	93.7 (1)
Se(1)–Ti(1)–Se(5)	78.9 (1)	Se(1)–Ti(4)–Se(2)	99.8 (1)
Se(1)–Ti(1)–Se(6)	86.1 (1)	Se(1)–Ti(4)–Se(6)	100.9 (1)
Se(3)–Ti(1)–Se(5)	93.8 (1)	Se(2)–Ti(4)–Se(6)	100.7 (1)
Se(3)–Ti(1)–Se(6)	76.9 (1)	Ti(1)–Se(1)–Ti(3)	75.6 (1)
Se(5)–Ti(1)–Se(6)	142.2 (1)	Ti(1)–Se(1)–Ti(4)	85.9 (1)
Se(2)–Ti(2)–Se(3)	142.1 (1)	Ti(3)–Se(1)–Ti(4)	86.6 (1)
Se(2)–Ti(2)–Se(4)	78.3 (1)	Ti(2)–Se(2)–Ti(3)	74.4 (1)
Se(2)–Ti(2)–Se(6)	85.6 (1)	Ti(2)–Se(2)–Ti(4)	85.1 (1)
Se(3)–Ti(2)–Se(3)	94.6 (1)	Ti(3)–Se(2)–Ti(4)	85.1 (1)
Se(3)–Ti(2)–Se(6)	77.2 (1)	Ti(1)–Se(3)–Ti(2)	81.9 (1)
Se(4)–Ti(2)–Se(6)	141.9 (1)	Ti(2)–Se(4)–Ti(3)	82.3 (1)
Se(1)–Ti(3)–Se(2)	85.3 (1)	Ti(1)–Se(5)–Ti(3)	81.5 (1)
Se(1)–Ti(3)–Se(4)	142.1 (1)	Ti(1)–Se(6)–Ti(2)	75.1 (1)
Se(1)–Ti(3)–Se(5)	78.8 (1)	Ti(1)–Se(6)–Ti(4)	84.7 (1)
Se(2)–Ti(3)–Se(4)	78.1 (1)	Ti(2)–Se(6)–Ti(4)	85.4 (1)
Se(2)–Ti(3)–Se(5)	142.1 (1)		

[a] Estimated standard deviations in parentheses. [b] Cp denotes the centroid of the C_5 ring of $\eta\text{-}C_5H_5$.

Structure of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. An ORTEP[16] plot of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ is shown in Figure 1, and important distances and angles are given in Table I. The $Ti_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ core can be regarded as a combination of a $[Ti(\mu_3\text{-}Se)]_4$ cubane with a $[Ti_4(\mu_2\text{-}Se)_6]$ adamantane. In $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ one titanium (Ti(4) in Figure 1) is six-coordinate, the other three being seven-coordinate. The average distance between Ti(4) and the μ_3-Se atoms is 2.389 (3, 3) Å.[17] The average distance

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between the seven-coordinate Ti(2)–(4) atoms and the μ_3-Se atoms is 2.700 (3, 35) Å, and that between Ti(2)–(4) and the μ_2-Se atoms 2.508 (3, 15) Å. The effective symmetry of the $[Ti_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3]$ core is C_{3v}. The Ti–C_5 ring-centroid distances average 2.081 (20) Å to the three seven-coordinate Ti atoms and 2.054 (19) Å to the six-coordinate Ti(4) atom. The Ti–Se and Ti–C_5 ring-centroid distances are in the range generally observed for cyclopentadienyl selenides of titanium(IV).[3,6,12,15,18,19]

The NMR spectra of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ are in accord with the structure shown in Figure 1. Both the ^1H and ^{13}C spectra show two singlets, one for the η-C_5H_5 rings attached to the three seven-coordinate titanium atoms and one for the η-C_5H_5 ring attached to the single six-coordinate titanium. The ^{77}Se spectrum showed resonances at 1162 and 2066 ppm relative to Me_2Se. The former is assigned to the μ_2-selenium by comparison with the literature.[20] Spectra of μ_3-selenium coordinated to titanium do not appear to have been reported.

There appears to be only one other example of a $[M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3]$ core (A = group 16 element), this being $[Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3]$ in $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$.[21] However, $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ will probably prove to be the first of many such molecular species. It has nine cluster orbitals, which are unoccupied since the formal oxidation state of titanium is IV. Since the nine orbitals may be occupied by up to 18 electrons, we may anticipate $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ clusters for metals, M, from groups 4 to 8.

Experimental Section

General Techniques and Reagents. All experiments were carried out under argon or vacuum by using standard vacuum-line techniques. Volumes of gaseous reactants were measured by using a manometer and calibrated bulb. Solvents were predried, stored over MeLi, and distilled under vacuum. The starting material $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ was prepared by the literature method;[22] $(\eta\text{-}C_5H_5)_2TiCl_2$ was purchased from Strem Chemicals and H_2Se from Matheson, Toronto, Canada. Triethylamine (Sigma) and pyridine (Anachemia) were refluxed over and distilled from KOH under argon. All other chemicals were reagent grade and used as received. Instruments used in this work were a Perkin-Elmer 683 infrared spectrophotometer (spectra measured as KBr disks), a Varian XL-200 NMR spectrometer, and a Kratos MS50 mass spectrometer. Microanalyses were by Beller Laboratorium, Göttingen, Germany.

Reaction of $(\eta\text{-}C_5H_5)_2TiCl_2$ with H_2Se in the Presence of $(C_2H_5)_3N$: Formation of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. To a solution of $(\eta\text{-}C_5H_5)_2TiCl_2$ (1.5 g, 6.0 mmol) in thf (125 cm^3) was added $(C_2H_5)_3N$ (1.17 cm^3, 6.0 mmol). The solution was incubated with H_2Se (12.0 mmol), with stirring, for 48 h. The initial red color of the solution rapidly turned to deep purple and eventually to dark green. Filtration of the mixture gave a green filtrate and a pale red solid. The residue was washed with $CHCl_3$ (25 cm^3), giving a red residue that contained selenium and was insoluble in thf, and a colorless filtrate. Addition of hexane (25 cm^3) to the filtrate precipitated white $(C_2H_5)_3N{\cdot}HCl$ (yield 1.37 g, 9.95 mmol, 83% based on eq 2). The product was identified by infrared and mass spectrometry.

To the green filtrate was added $(C_2H_5)_2O$ (50 cm^3), and the mixture was set aside for 12 h. After this time, filtration gave green, crystalline $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ (0.85 g, 0.90 mmol, 60%, based on eq 2). The crystals were identified as $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3{\cdot}(C_2H_5)_3N$ by X-ray diffraction (see below) and by the following data. Anal. Found: C, 30.5; H, 3.5; Ti (as TiO_2), 18.6. Calcd for $C_{26}H_{29}NSe_6Ti_4$: C, 30.4; H, 3.4; Ti, 18.8. Infrared: 1300 cm^{-1} (ν(C–N)); 405, 370 cm^{-1} (ν(Ti–Se)). ^1H NMR: (200 MHz, $^2H_1$ $CHCl_3$ solution): 6.23 ppm, s, 15 H; 6.00 ppm, s, 5 H. ^{13}C NMR (50 MHz, $^2H_1$ $CHCl_3$ solution): 110.56 ppm, s; 105.16 ppm, s. ^{77}Se NMR (38 MHz, $^2H_1$ $CHCl_3$ solution, relative to $(CH_3)_2Se$): 1162 ppm, s ($\Delta\nu_{1/2}$ 17 Hz), 3 μ_2-Se; 2006 ppm, s ($\Delta\nu_{1/2}$ 103 Hz), 3 μ_3-Se.

Table II. Atomic Parameters x, y, z and B_{iso} for $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3 \bullet (C_2H_5)_3N$[a]

	x	y	z	B_{iso}, Å^2
Se(1)	0.60419 (18)	0.06687 (15)	0.41278 (13)	2.84 (8)
Se(2)	0.92545 (18)	0.13285 (15)	0.33178 (14)	2.98 (9)
Se(3)	0.61951 (18)	0.39714 (16)	0.17243 (14)	3.24 (9)
Se(4)	0.88198 (18)	0.14483 (16)	0.10439 (13)	3.14 (9)
Se(5)	0.56042 (17)	0.08162 (15)	0.18609 (13)	2.84 (8)
Se(6)	0.66328 (19)	0.38385 (15)	0.39746 (14)	3.31 (9)
Ti(1)	0.5322 (3)	0.25428 (25)	0.30285 (22)	2.43 (14)
Ti(2)	0.8220 (3)	0.3148 (3)	0.22663 (23)	2.74 (14)
Ti(3)	0.7660 (3)	0.03263 (24)	0.24184 (21)	2.24 (13)
Ti(4)	0.7432 (3)	0.1909 (3)	0.45719 (23)	2.84 (15)
C(11)	0.3292 (22)	0.337 (3)	0.2772 (19)	7.0 (16)
C(12)	0.3174 (18)	0.2293 (20)	0.3185 (20)	4.8 (11)
C(13)	0.3345 (18)	0.234 (3)	0.4083 (17)	5.6 (12)
C(14)	0.3620 (22)	0.345 (4)	0.4252 (22)	8.0 (18)
C(15)	0.3587 (25)	0.4096 (21)	0.340 (4)	8.5 (22)
C(21)	0.981 (3)	0.415 (3)	0.2652 (24)	7.7 (20)
C(22)	0.884 (3)	0.5074 (23)	0.247 (3)	8.0 (18)
C(23)	0.883 (3)	0.497 (3)	0.147 (3)	7.7 (19)
C(24)	0.975 (3)	0.403 (3)	0.1110 (18)	6.2 (15)
C(25)	1.0347 (20)	0.3549 (20)	0.179 (3)	6.1 (16)
C(31)	0.7679 (22)	−0.1545 (17)	0.1640 (19)	5.3 (13)
C(32)	0.7252 (21)	−0.1728 (15)	0.2624 (19)	4.9 (12)
C(33)	0.8166 (24)	−0.1595 (16)	0.3117 (14)	4.4 (12)
C(34)	0.9217 (17)	−0.1411 (15)	0.2454 (14)	3.1 (8)
C(35)	0.8938 (19)	−0.1366 (15)	0.1538 (14)	3.8 (9)
C(41)	0.8024 (23)	0.0817 (18)	0.5924 (13)	4.3 (11)
C(42)	0.6766 (22)	0.1261 (19)	0.6216 (14)	4.4 (12)
C(43)	0.6700 (18)	0.2503 (19)	0.6212 (14)	4.1 (10)
C(44)	0.7862 (22)	0.2831 (17)	0.5944 (15)	4.5 (11)
C(45)	0.8704 (19)	0.1792 (22)	0.5759 (14)	4.7 (11)
N(1)	0.6555 (15)	0.2268 (12)	0.9387 (11)	4.1 (8)
C(1)	0.525 (3)	0.205 (3)	0.9388 (19)	8.6 (19)
C(2)	0.4184 (19)	0.2944 (19)	0.9947 (17)	4.8 (11)
C(3)	0.673 (3)	0.3450 (23)	0.8944 (20)	8.1 (17)
C(4)	0.7990 (24)	0.3842 (21)	0.8902 (19)	6.9 (15)
C(5)	0.743 (3)	0.132 (3)	0.8777 (17)	9.2 (20)
C(6)	0.7365 (24)	0.0047 (21)	0.9080 (19)	6.6 (14)

[a] Esd's refer to the last digit printed. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Reaction of $(\eta\text{-}C_5H_5)_2TiCl_2$ with H_2Se in the Presence of Pyridine: Formation of $(\eta\text{-}C_5H_5)_2TiCl(SeH)$ and $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$. $(\eta\text{-}C_5H_5)_2TiCl_2$ (1.14 g, 4.6 mmol) was dissolved in thf (125 cm^3) and pyridine (2.22 cm^3, 27.5 mmol) added. The mixture was incubated with H_2Se (41 mmol) while being stirred for 4 days. The initial red color slowly changed to purple, and a white precipitate of $C_5H_5N{\cdot}HCl$ (0.716 g, 6.2 mmol) was deposited. The $C_5H_5N{\cdot}HCl$ was removed by filtration and the solution evaporated to dryness. The purple residue was extracted with toluene (100 cm^3), giving a purple solution and a purple precipitate (0.64 g) that was a mixture of $(\eta\text{-}C_5H_5)_2TiCl(SeH)$ (55%) and $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ (45%), with a trace of $(\eta\text{-}C_5H_5)_2TiCl_2$, as judged by ^1H NMR spectroscopy. Hexane (50 cm^3) was layered onto the toluene solution, giving a purple precipitate (0.36 g) of $(\eta\text{-}C_5H_5)_2TiCl(SeH)$ (60%) and $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$ (40%). Total yield: 83%. Infrared: 2280 cm^{-1} (ν(SeH)); 415, 380, 353 cm^{-1} (ν(Ti–Se)) (all weak). ^1H NMR (C_6D_6): 5.78 ppm, s, 10 H, $(\eta\text{-}C_5H_5)_2TiCl(SeH)$; 2.68 ppm, s, 1 H, $(\eta\text{-}C_5H_5)_2TiCl(SeH)$); 5.65 ppm, s, 10 H, $N(C_2H_5)_3$); 1.06 ppm, s, 2 H, $(\eta\text{-}C_5H_5)_2Ti(SeH)_2$. Mass spectrum: (EI): *m/e* 341 ($[(C_5H_5)_2Ti(^{80}SeH)_2H]^+$), 248 ($[(C_5H_5)_2Ti^{35}Cl_2]^+$), 213 ($[(C_5H_5)_2Ti^{35}Cl]^+$).

Determination of the Structure of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ by X-ray Diffraction. Crystal data for $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$: $M_r(C_{26}H_{35}NSe_6Ti_4)$ = 1026.98; triclinic, $P\bar{1}$;

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[17] The first figure is the average esd. The second figure is the maximum deviation from the average.

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$a = 10.971$ (1), $b = 11.148$ (2), $c = 13.943$ (1) Å; $\alpha = 88.38$ (1), $\beta = 78.29$ (7), $\gamma = 81.17$ (1)°; $V = 1650.0$ (4) Å^3; cell dimensions determined from 25 reflections with $35 < 2\theta < 45$; $Z = 2$; $D_c = 2.07$ Mg m^{-3}; $\lambda = 0.70930$ Å; μ(Mo Kα) = 7.50 mm^{-1}; $F(000) = 980$ electrons. Crystal dimensions were 0.25 × 0.20 × 0.10 mm.

The intensities of a total of 6112 reflections were measured by the $\theta/2\theta$ method to $2\theta_{max} = 47.5°$. These were reduced and averaged to yield 5061 unique reflections, of which 2961 were judged observed ($I > 2.0\sigma(I)$). An empirical absorption correction (DIFABS[23]) was applied. Final refinement (by full-matrix methods) used 335 parameters (including an extinction coefficient) and a weighting scheme of the form $w = 1/(\sigma F^2 + 0.001F^2)$. The final R $(=\sum|\Delta F|/\sum|F_o|) = 0.070$, R_w $(=((\sum(w(F_o - F_c)^2)/\sum(wF_o)^2)^{1/2}) = 0.073$, and GoF $(=\sum w(F_o - F_c)^2/$(number of reflections − number of parameters)) = 1.474. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included as fixed contributions (r(C–H) = 0.96 Å, and sp^2 (C_5H_5) or sp^3 ($N(C_2H_5)_3$) geometry), with fixed isotropic thermal parameters equal to that of the C atom to which they were attached. A final difference Fourier had a highest peak of 0.44 e Å^{-3} (located in the Ti_4Se_6 core) and a deepest valley of −0.31 e Å^{-3}. Table II gives the atomic positions for the non-hydrogen atoms; Table I gives important distances and angles. The hydrogen atom positions, the thermal parameters, a comprehensive list of distances and angles, some mean planes, and a list of $|F_o|$ and $|F_c|$ are available in the supplementary material.

X-ray diffraction experiments were made on an Enraf-Nonius CAD4 diffractometer operating under the control of the NRCCAD software.[24] The structure was solved and refined by using the NRCVAX program package.[25] Scattering factors, corrected for anomalous dispersion except in the case of hydrogen, were taken from ref 26.

Determination of the Structure of $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu_2\text{-}Se_2)$. Crystal data for $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu_2\text{-}Se_2)$: $M_r = 585.02$; orthorhombic, *Pbca*; $a = 13.3242$ (7), $b = 13.9334$ (12), $c = 22.5441$ (18) Å; $V = 4185.3$ (5) Å^3 (from 24 reflections with $30 < 2\theta < 40°$); $Z = 8$; $D_c = 1.86$ Mg m^{-3}; μ(Mo Kα) = 4.46 mm^{-1}; $F(000) = 2287.6$ electrons. Crystal dimensions were 0.35 × 0.35 × 0.15 mm.

The intensities of a total of 5019 reflections were measured to $2\theta_{max} = 50°$. These were reduced and averaged to yield 3675 unique reflections, of which only 1734 could be judged as observed by the criteria that $I > 2.0\sigma(I)$. The structure was readily solved in the space group *Pbca* but could not be refined below $R = 0.17$. A difference Fourier map showed peaks of up to 2.65 e Å^{-3} in the region of the Se and Cl atoms. No better solution was found in the space groups *Pbcm* or *Pbma*. It should be noted that the cell dimensions, space group, and atomic positions found for $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu_2\text{-}Se_2)$ are very similar to those of the analogous sulfur compound, the structure of which was refined to $R = 0.081$ with no apparent difficulty.[12] The poor quality of the crystal and the low number of observed reflections (47%) is the probable reason for the inability to refine the structure. It is considered that the diffraction experiments clearly define the major constituent of the crystal as $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}Se_2)$, but further conclusions are not warranted. Accordingly, a list of atomic parameters and other details are given in the supplementary material only.

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Supplementary Material Available: Tables of hydrogen atom positions, thermal parameters for Ti, Se, and C atoms, comprehensive bond distances and angles, and relevant mean planes and atom-numbering diagrams for $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3\text{-}(\mu_3\text{-}Se)_3\cdot(C_2H_5)_3N$ and tables of atomic parameters and thermal parameters and an atom-numbering diagram for $[(\eta\text{-}C_5H_5)_2TiCl]_2(\mu\text{-}Se_2)$ (13 pages); tables of $|F_o|$ and $|F_c|$ for both structures (24 pages). Ordering information is given on any current masthead page.

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Effect of Molecular Shapes on Crystal Building and Dynamic Behavior in the Solid State: From Crystalline Arenes to Crystalline Metal-Arene Complexes

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The molecular organization and dynamic behavior in crystals of C_6H_6 and C_6Me_6 and of the mononuclear complexes $(C_6H_6)_2Cr$, $(C_6H_6)Cr(CO)_3$, $(C_6Me_6)Cr(CO)_3$, and $(1,3,5\text{-}C_6H_3Me_3)Mo(CO)_3$ are investigated by means of packing potential energy calculations and computer graphic analysis, showing that analogies and differences can be rationalized in terms of the shape of the molecules or constituent molecular fragments. Precise relationships are found not only between the crystal packings of these species but also between the shape of the arene fragments and the occurrence of dynamic behavior in the solid state.

Introduction

In spite of the wealth of information contained in the thousands of crystal structures of organometallic compounds characterized up to date, very little is known about the factors that control the organization of organometallic molecules in their crystals and their solid-state properties. While solid-state properties of organic materials have been studied for more than 30 years[1,2] (and are a matter of continuing investigation), no systematic study of organometallic crystal structures has, until now, appeared in the scientific literature.

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