Preparation and Characterization of Alkane– and Arene–Chalcogenolate Complexes of η^5-Cyclopentadienyltitanium(IV): First Synthesis of $[Ti(\eta^5-C_5H_5)(SeCH_3)_3]$

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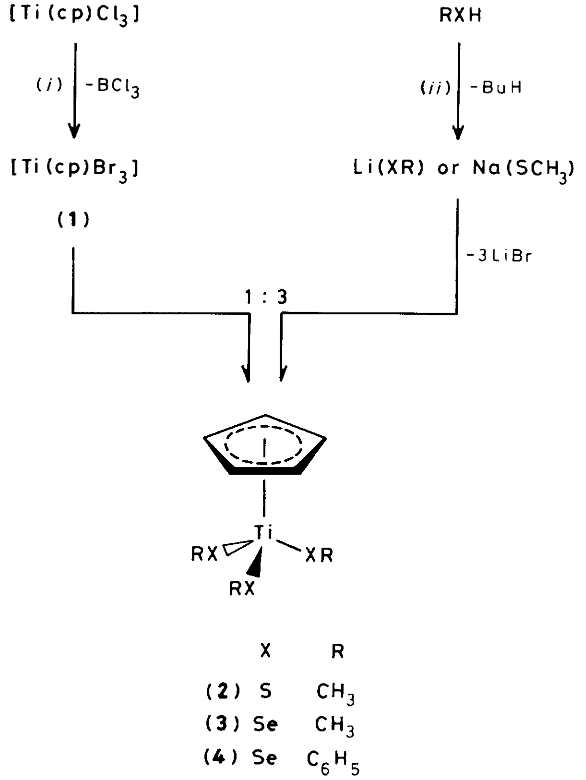
A simple synthesis of $[Ti(cp)Br_3]$ (**1**) (cp = η^5-C_5H_5) from $[Ti(cp)Cl_3]$ and BBr_3 is described. Reaction of complex (**1**) with $Na(SCH_3)$ or Li(SeR) (R = CH_3 or C_6H_5) afforded the derivatives $[Ti(cp)(SCH_3)_3]$ (**2**), $[Ti(cp)(SeCH_3)_3]$ (**3**), or $[Ti(cp)(SeC_6H_5)_3]$ (**4**), respectively. Complexes (**2**)—(**4**) were characterized by ^1H n.m.r., i.r., and mass spectroscopy; (**3**), the first example of a cyclopentadienyltris(selenolato)titanium compound, was also studied by ^{77}Se n.m.r. spectroscopy. The oxidation and hydrolysis behaviour of (**2**) and (**3**) in solution is discussed on the basis of their ^1H n.m.r. spectra.

Although numerous reactions of the thiolate complexes of the bis(cyclopentadienyl)titanium(IV) system are well known and several compounds $[Ti(cp)_2(SR)_2]$ (cp = η^5-C_5H_5, R = alkyl or aryl) have been prepared,[1–4] only a few thiolate complexes of the corresponding mono(cyclopentadienyl) species have been described.[5,6] We recently reported the preparation of a thiophenol derivative;[7] the methanethiolate complex was mentioned once in a patent but without any details.[8] Analogous selenium and tellurium complexes are not yet known. In this paper we describe the synthesis, characterization, and reactivity of $[Ti(cp)(XCH_3)_3]$ [X = S (**2**) or Se (**3**)] and $[Ti(cp)(SeC_6H_5)_3]$ (**4**).



Scheme. Preparation of complexes (**1**)—(**4**). (*i*) BBr_3, (*ii*) LiBu

Results and Discussion

Complexes (**2**)—(**4**) were prepared by modification of the synthesis of $[Ti(cp)(SC_6H_5)_3]$ (**5**) (Scheme).[7] The salts $Na(SCH_3)$ and $Li(SeCH_3)$ spontaneously react with $[Ti(cp)Br_3]$ (**1**) (*cf.* ref. 9); $Na(TeCH_3)$ was prepared too,[10,11] but cyclopentadienyltris(methanetellurolato)titanium(IV) could not be isolated. Instead $Te_2(CH_3)_2$ was found to be the only Te-containing product.

The identity of complexes (**1**)—(**4**) was established by elemental analysis, ^1H n.m.r, and mass spectra (Table). The i.r. spectra of (**2**) and (**3**) show the typical absorptions of the cyclopentadienyl ring and those of the methyl group (see Experimental section). The cyclopentadienyl range of the ^1H n.m.r. spectra of (**2**)—(**4**) shows in each case one sharp singlet, shifted to high field in comparison with that of complex (**1**). In addition the intense signal of the CH_3X protons appears in the range 3—3.5 p.p.m. (Table). The ^{77}Se n.m.r. spectrum of (**3**) in C_6D_6 shows a sharp singlet at +226 p.p.m., relative to dimethyl selenide in $C_6D_5CD_3$, indicating three equivalent Se atoms. The low-field shift (compared with CH_3SeH, −130 p.p.m.) is in accord with the donor ability of the chalcogen atom. This is, as far as we know, the first ^{77}Se n.m.r. spectrum of a monocyclopentadienyltitanium(IV) selenolate complex.[12]

The mass spectra of complexes (**2**)—(**4**) show an intense peak for the molecular ion with highest *m*/*z* value. For the selenium derivatives the base peak is the fragment ion $M^+ - 3SeR$ [= $Ti(cp)^+$], which points to an easy breaking of the titanium–chalcogen bond under the experimental conditions. While (**2**) and (**3**) are stable up to 230 and 130 °C, (**2**) shows a base peak corresponding to the cluster ion $[Ti_5(cp)_5(\mu_3-S)_6]$ ($m/z = 757$) at 300 °C and (**3**) decomposes to the diselenide $Se_2(CH_3)_2$ ($m/z = 190$) at 160 °C. The analogous disulphide ($m/z = 90$) of (**2**) however only occurs with low intensity. These results are in accord with the spontaneous decomposition of $[Ti(cp)(TeCH_3)_3]$ to the ditelluride $Te_2(CH_3)_2$.

The oxidation and hydrolysis behaviour of complexes (**2**) and (**3**) in solution under ambient conditions was investigated by ^1H n.m.r. spectroscopy. While the decomposition products CH_3SH and $S_2(CH_3)_2$ of (**2**) appear in nearly the same amounts, (**3**) shows the diselenide as the main product but also the selenol, which could be oxidized quantitatively with hydrogen peroxide to $Se_2(CH_3)_2$ (Figure). The time-dependent decrease of the cp

Table. Analytical and spectroscopic data for complexes (1)—(4)

		Analysis (%)[a]			^{1}H N.m.r.[b]	
Complex	Colour	C	H	*M*	δ_{cp}	δ_R
(1)	Orange	17.00	1.50	352	7.11 (s)	
		(17.00)	(1.45)	(352.69)		
(2)	Red	37.60	5.60	254	6.66 (5 H, s)	3.18 (9 H, s)
		(37.80)	(5.55)	(254.28)		
(3)	Deep red	24.20	3.40	396	6.57 (5 H, s)	3.22 (9 H, s)
		(24.35)	(3.55)	(394.96)		
(4)	Deep red	47.35	3.60	582	6.52 (5 H, s)	7.75—6.99
		(47.55)	(3.45)	(581.17)		(15 H, m)

[a] Required values are given in parentheses. [b] Solvent: CD_2Cl_2.

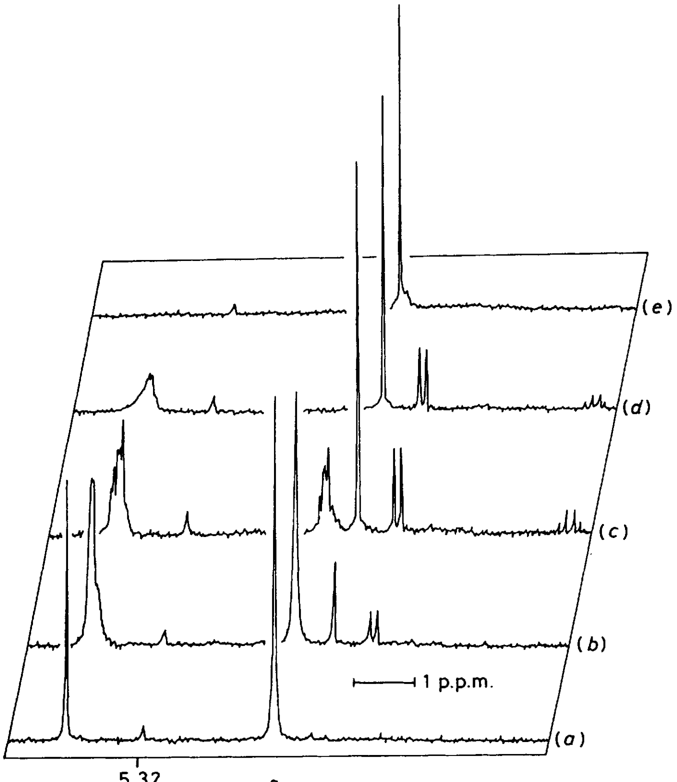


Figure. Time-dependent decomposition of complex (**3**). Proton n.m.r. spectra, in CD_2Cl_2, δ with reference to $CHDCl_2$ as internal standard (5.32): (*a*) under argon; (*b*) under ambient conditions after 12 h; (*c*) after 48 h; (*d*) after 72 h; and (*e*) after 72 h and treatment with H_2O_2

and methyl resonances indicates a preferred cleavage of the labile titanium–chalcogen bonds instead of those of the Ti–cp ring system. The remaining yellow residue gave a peak at m/z = 904 in the mass spectrum consistent with its formulation as polymeric Ti(cp).

Experimental

The complexes $[Ti(cp)_2Cl_2]$ and $[Ti(cp)Cl_3]$ were prepared as described.[13,14] All reactions were carried out under argon using the Schlenk technique with dried and argon-saturated solvents. Infrared spectra were recorded on a Perkin-Elmer 580 B, ^{1}H n.m.r. spectra on a Bruker WP 80, and ^{77}Se n.m.r. on a Varian XL 100 spectrometer. Mass spectra (electron-impact) were measured with a Varian MAT 311 A instrument; the values given relate to ^{32}S, ^{48}Ti, and ^{80}Se.

Syntheses.—*Tribromo*(η^5-*cyclopentadienyl*)*titanium*(IV), (**1**). Boron tribromide (13.00 g, 51.89 mmol) in CH_2Cl_2 (50 cm^3) was slowly added with stirring to $[Ti(cp)Cl_3]$ (6.60 g, 30.07 mmol) in the same solvent (100 cm^3). The mixture was stirred for 4 h and then refluxed for another 2 h. The volatile compounds were removed *in vacuo* and the residue dried for 24 h *in vacuo* to give analytically pure orange (**1**) (10.05 g, 94.8%), m.p. 180 °C; $\nu_{max.}$(cp) 3 095w, 1 425m, 1 010m, and 820vs cm^{-1} (KBr); m/z 350 (M^+), 285 (M – cp), 271 (M – Br), 206 (M – cp – Br), 192 (M – 2Br), 127 (M – cp – 2Br), and 113 (M – 3Br).

(η^5-*Cyclopentadienyl*)*tris*(*methanethiolato*)*titanium*(IV), (**2**). Complex (**1**) (6.05 g, 17.15 mmol) in toluene (50 cm^3) was added with stirring to $Na(SCH_3)$ (3.61 g, 51.46 mmol) in the same solvent (250 cm^3) at –90 °C. After warming to 25 °C during 12 h the deep red solution was filtered and evaporated to dryness. The residue was recrystallized from chloroform–pentane (1:1) to yield compound (**2**) (2.56 g, 58.6%); $\nu_{max.}$(cp) 3 095m, 1 430s, 1 015vs, 845(sh), 815vs, and (CH_3) 2 910m cm^{-1} (KBr); m/z 254 (M^+), 206 (M – CH_3SH), 174 (M – cp – CH_3), 159 (M – CH_3SH – CH_3S), 145 (M – $2CH_3S$ – CH_3), 113 (M – $3CH_3S$), and 80 (M – cp – $2CH_3S$ – CH_3).

(η^5-*Cyclopentadienyl*)*tris*(*methaneselenolato*)*titanium*(IV), (**3**). Methaneselenol (5.05 g, 53.16 mmol) was treated with butyllithium (53.16 mmol) to yield $Li(SeCH_3)$ and then with complex (**1**) (6.25 g, 17.72 mmol) as described for the preparation of (**2**). The product was recrystallized from chloroform–pentane (1:1), resulting in deep red analytically pure (**3**) (5.56 g, 79.4%); $\nu_{max.}$(cp) 3 080w, 1 015m, 810s, and (CH_3) 2 960(sh) cm^{-1} (Nujol); m/z 398 (M^+), 383 (M – CH_3), 368 (M – $2CH_3$), 353 (M – $3CH_3$), 303 (M – $SeCH_3$), 288 (M – $SeCH_3$ – CH_3), 287 (M – $SeCH_3$ – CH_4), 273 (M – $SeCH_3$ – $2CH_3$), 208 (M – $2SeCH_3$), 207 (M – $SeCH_3$ – Se – CH_4), 193 (M – $2SeCH_3$ – CH_3), 128 (M – cp – $2SeCH_3$ – CH_3), and 113 (M – $3SeCH_3$).

(η^5-*Cyclopentadienyl*)*tris*(*phenylselenolato*)*titanium*(IV), (**4**). The synthesis was carried out as for (**3**). Complex (**1**) (2.16 g, 6.13 mmol) was treated in toluene with freshly prepared $Li(SeC_6H_5)$ (2.99 g, 18.37 mmol) and recrystallized twice from chloroform–pentane (1:1) and toluene to yield the desired (**4**) (1.73 g, 48.6%); $\nu_{max.}$(cp) 3 090w, 1 015m, and 815s cm^{-1} (Nujol); m/z 584 (M^+), 427 (M – SeC_6H_5), 270 (M – $2SeC_6H_5$), 193 (M – $2SeC_6H_5$ – C_6H_5), 128 (M – cp – $2SeC_6H_5$ – C_6H_5), and 113 (M – $3SeC_6H_5$).

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