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FIVE-COORDINATE ORGANOTITANIUM(IV) DITHIOCARBAMATES

R.S.P. COUTTS

Division of Chemical Technology, CSIRO, P.O. Box 310, South Melbourne (Australia)

P.C. WAILES

Division of Applied Organic Chemistry, CSIRO, P.O. Box 4331 G.P.O., Melbourne (Australia)

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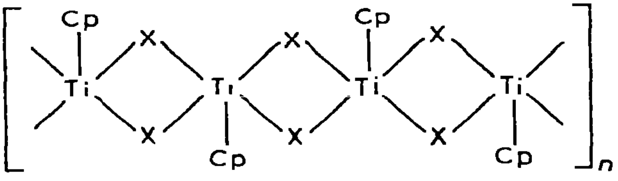
Summary

Monocyclopentadienyltitanium(III) halides, $CpTiX_2$ (X = Cl or Br) are oxidized by thiuram disulphides, $R_2NC(S)S{-}SC(S)NR_2$ [R = CH_3, C_2H_5, n-C_4H_9 or R_2 = $-(CH_2)_5-$] to monomeric dithiocarbamates, $CpTi(S_2CNR_2)X_2$, which contain five-coordinate titanium.

Introduction

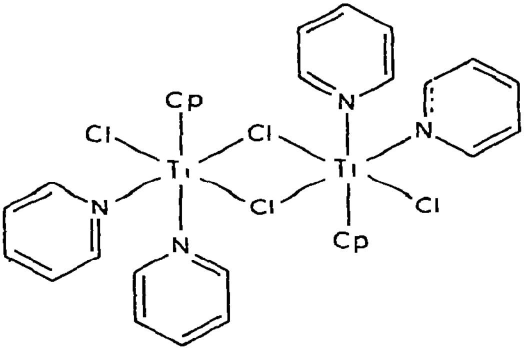
In recent years considerable interest has developed in five-coordinate titanium(III) and titanium(IV) derivatives. Five-coordinate stereochemistry in monomeric compounds has been confirmed by X-ray crystallographic analysis for $[TiOCl_4]^{2-}$ [1] and $TiBr_3 \cdot 2N(CH_3)_3$ [2] while the only organotitanium compound with this stereochemistry confirmed is the dimeric methyl derivative, $[(CH_3)_2Ti(C_6H_{12}O_2)]_2$, where $C_6H_{12}O_2$ = 2-methyl-2,4-pentanediolato [3]. Complexes of stoichiometry $TiX_4 \cdot L$ [4] and $TiX_3 \cdot 2L$ [5] are usually dimeric compounds of hexacoordinate titanium.

The halides $CpTiX_2$ are generally thought to be polymeric [6, 7], although a dimeric structure has been proposed [8]. $CpTiCl_2$ shows only one halide NQR signal (7.328 MHz at 298K or 7.412 MHz at 77K), which appears to correspond to equivalent bridging Cl groups [9] (cf. α-$TiCl_3$ [10]), so that five-coordinate titanium in a structure such as I seems likely.



(I)

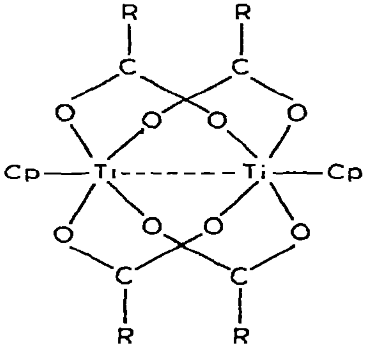
Complexes $CpTiX_2 \cdot 2L$ with various nitrogen [11] and oxygen [12] ligands (L) are mostly of unknown stereochemistry, except for $CpTiCl_2 \cdot 2$ py which shows bridging (7.370 MHz) and non-bridging (7.945 MHz) halide NQR signals. The compound therefore probably has six-coordinate titanium in a dimeric structure such as II.



(II)

Recently the complex $CpTiCl_2 \cdot 2$ (cyclohexyl isocyanide) has been reported as a five-coordinate monomer with either trigonal bipyramidal or square pyramidal stereochemistry [8].

The diamagnetic carboxylates, $CpTi(O_2CR)_2$, are dimeric with bridging OCO groups [13] (structure III). The existence of a Ti—Ti bond and hence the final coordination number of the metal (5 or 6) is in doubt.



(III)

The possibility of forming a five-coordinate titanium derivative of type $CpTiBX_2$, where B is a uninegative bidentate ligand, seemed feasible from preliminary oxidative addition reactions [14]. We now report fully on the compounds $CpTi(S_2CNR_2)X_2$, which have proved to be monomeric compounds of five-coordinate titanium. The known dithiocarbamates of titanium are $Ti(S_2CNR_2)_4$ [15] and $Ti(S_2CNR_2)_3X$ [16] in which titanium(IV) shows the coordination numbers of 8 and 7 respectively, and the titanium(III) derivatives, $Cp_2Ti(S_2CNR_2)$, reported earlier by the present authors [17].

Results and discussion

The dithiocarbamates were prepared by reaction of $CpTiX_2$ with slightly more than one-half mole of thiuram disulphide.

$$2\,CpTiX_2 + R_2NC(S)SSC(S)NR_2 \xrightarrow[RT]{THF} 2\,CpTi(S_2CNR_2)X_2$$

$R = CH_3, C_2H_5, n\text{-}C_4H_9$ and $R_2 = -(CH_2)_5-$; $X = Cl$ or Br

The products, obtained in > 60% yield, showed surprising hydrolytic stability and freedom from disagreeable odour. They are all monomeric and non-ionic. Table 1 lists the compounds and summarizes their properties.

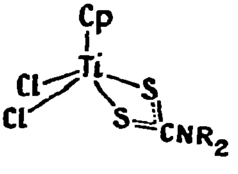
Table 2 shows the important infrared bands recorded between 4000 and 240 cm^{-1} in KBr discs. The assignments of bands due to the dithiocarbamato ligand follows those in recent reports [18]. The "thioureide" band near 1500 cm^{-1} implies considerable double bond character in the $S_2C{-}NR_2$ bond. The presence of only one band in the region 1050-950 cm^{-1} substantiates the bidentate nature of the dithiocarbamato ligand [19].

The assignment of the Ti—Cp vibration is in keeping with recent reports which show it to occur near 430 ± 20 cm^{-1} and 330 ± 10 cm^{-1} in compounds of the type $CpTiX_2OR$, where X = Cl or Br and OR = alkoxide [20, 21]. On exchanging Cl for Br a shift to lower frequency occurs.

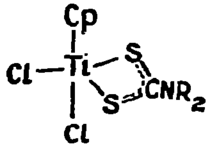
When chloride is present in the compound, the Ti—S band at 364 ± 6 cm^{-1} is intensified and a shoulder appears at 373 cm^{-1}, which is assigned to a Ti—Cl stretching mode [22].

In $CDCl_3$ the PMR spectra of the dithiocarbamates, $CpTi(S_2CNR_2)X_2$, showed a sharp cyclopentadienyl proton signal at δ 6.83-6.94 ppm together with a weaker signal some δ 0.1 ppm upfield. If the solutions were heated to 90° and cooled, the weaker signal disappeared and minor signals in the aliphatic proton region were removed to give the δ values shown in Table 3.

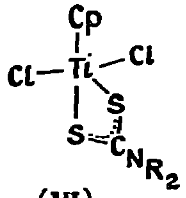
Several isomeric forms of these compounds are possible (structures IV, V and VI) and the PMR behaviour can be explained if two or more of these isomers are formed and slowly converted to the final stable form, the identification of which must await a crystal structure determination.



(IV)



(V)



(VI)

Experimental

All handling of, and measurements on, these compounds were carried out under inert atmosphere as described in earlier papers [11, 17]. $CpTiX_2$ (X = Cl or Br) was prepared by published methods [6], while the thiuram disulphides were gifts from Robinson Bros. Ltd., West Bromwich, England.

(continued on p. 52)

TABLE 1

ANALYTICAL DATA

$CpTi(S_2CNR_2)X_2$		M.p. (°C)	Colour	Analysis found (calcd.) (%)						Mol. wt.
R	X			C	H	N	S	Hal	Ti	Found (calcd.)
CH_3	Cl	252-256 (dec.)	Orange-red	31.8 (31.6)	3.9 (3.6)	5.3 (4.6)	21.3 (21.1)	23.8 (23.3)	15.6 (15.8)	320[a] (304)
CH_3	Br	244-247	Orange	24.7 (24.4)	2.9 (2.8)	3.6 (3.6)	16.9 (16.3)	41.4 (40.7)	12.5 (12.2)	407[a] (393)
C_2H_5	Cl	181-184	Red	35.7 (36.2)	4.3 (4.6)	4.6 (4.2)	19.3 (19.3)	21.8 (21.3)	14.5 (14.4)	323[b] (332)
C_2H_5	Br	189-190	Red-brown	28.5 (28.5)	3.7 (3.6)	4.9 (3.3)	15.2 (15.2)	38.6 (38.0)	11.9 (11.4)	428[b] (421)
$n\text{-}C_4H_9$	Cl	76-78	Orange-red	43.6 (43.2)	6.1 (6.0)	4.2 (3.0)	16.7 (16.5)	18.4 (18.3)	12.1 (12.3)	399[b] (388)
$-(CH_2)_5-$[c]	Cl	170 (dec.)	Orange	37.9 (38.4)	4.4 (4.4)	4.0 (4.1)	18.4 (18.6)	20.7 (20.6)	14.1 (13.9)	

[a] Ebulliometric molecular weight determination in chloroform solvent. [b] Ebulliometric molecular weight determination in benzene solvent. [c] R_2.

TABLE 2

CHARACTERISTIC INFRARED BANDS

$CpTi(S_2CNR_2)X_2$		ν(C—N)	π-Cp(C—H deformation)	ν(C—S)	ν(Ti—Cp)	ν(Ti—X)	ν(Ti—S)	Other bands[a]
R	X							
CH_3	Cl	1531 vs	1014 mw	986 ms	422 m 339 w	373 (sh)	368 s	280 (sh) 270 (sh)
C_2H_5	Cl	1505 vs	1024 mw	1006 ms	418 s 340 (sh)	374 (sh)	363 vs	280 (sh) 270 m
$-(CH_2)_5-$[b]	Cl	1508 vs	1020 mw	984 ms	422 m	373 (sh)	358 vs	290 (sh) 280 (sh) 270 s
CH_3	Br	1530 vs	1015 mw	985 ms	412 m 342 m		368 s	320 w 270 (sh) 255 (sh)
C_2H_5	Br	1508 vs	1026 mw	1010 ms	411 m 342		370 vs	280 (sh) 260 (sh)

[a] 400-250 cm^{-1} region. [b] R_2.

TABLE 3

PMR DATA

$CpTi(S_2CNR_2)X_2$		Chemical Shifts[a]
R	X	
CH_3	Cl	6.84 s (Cp), 3.40 s (CH_3)
CH_3	Br	6.94 s (Cp), 3.39 s (CH_3)
C_2H_5	Cl	6.85 s (Cp), 3.83 q (CH_2), 1.31 t (CH_3)
C_2H_5	Br	6.92 s (Cp), 3.81 q (CH_2), 1.31 t (CH_3)
n-C_4H_9	Cl	6.83 s (Cp), 3.75 m (NCH_2), 1.54 m (CH_2CH_2), 0.94 t (CH_3)
—$(CH_2)_5$—[b]	Cl	6.85 s (Cp), 3.90 m (NCH_2), 1.74 m ($CH_2CH_2CH_2$)

[a] In $CDCl_3$, δ values relative to TMS (ppm). [b] R_2.

Reactions

After addition of thiuram disulphide to $CpTiX_2$ in THF, the colour changed from blue-green to orange and an orange-red precipitate formed at room temperature. This was collected by filtration under argon and was washed with diethyl ether to remove excess disulphide, then pumped dry.

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