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Bis(substituted benzoato) complexes of bis(η-cyclopentadienyl)titanium(IV). Synthesis and mass-, ^{1}H-, ^{13}C-NMR and IR-spectra

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Abstract

The syntheses of 32 complexes of the type $(\eta\text{-}C_5H_5)_2Ti(OOCC_6H_4X)_2$ are reported together with their mass, ^{1}H NMR, ^{13}C NMR, mid- and far-IR spectra. The data are consistent with a model in which the Ti–OOC bond strength (weaker than that of Ti–Cp and Ti–Hal) is stabilized by electron-withdrawing substituents X on the phenyl rings. The electronic influence of X also extends into the cyclopentadienyl rings.

Introduction

Titanium(IV) complexes of the type $(\eta\text{-}C_5H_5)_2TiL_2$, where L is a monodentate and/or a potentially bidentate ligand, have been associated with catalysis in organic synthesis [1], reductive fixation of small molecules, e.g. CO [2] and even with anti-tumor activity [3], and so the synthesis and structure of titanocene complexes have received much attention in recent years [4–7]. In the present study we report the synthesis and spectra of complexes $(\eta\text{-}C_5H_5)_2TiL_2$, where L is a substituted

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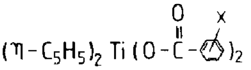
benzoic acid ligand. We include also some complexes, mostly with *ortho*-substituted benzoic acid ligands, which have been synthesized recently by Dang et al. [8].

We show that mass spectroscopy provides a new and useful tool for characterization of these compounds. Furthermore, we show that substitution in the benzoato ligands affects NMR chemical shifts in the cyclopentadienyl ligand as well as in the Ti–OC(O) moiety. This suggests that there is a variation in the Ti–O bond strength, and this is corroborated by IR results in the mid-IR region. Far-IR spectra (450–50 cm^{-1}) are also reported.

Synthesis

All complexes were synthesized by reaction of $(\eta\text{-}C_5H_5)_2TiCl_2$ with the sodium salt of the appropriately substituted benzoic acid in benzene [9]. $(\eta\text{-}C_5H_5)_2TiCl_2$ was purchased from Janssen Chimica and used without further purification. Sodium salts of the substituted benzoic acids were prepared from the acids and sodium hydroxide. Benzene was distilled from sodium-sand prior to use. All preparations were carried out under strictly anhydrous conditions. As a typical example we describe the preparation of $(\eta\text{-}C_5H_5)_2Ti(OOCC_6H_4CH_3\text{-}o)_2$.



$(\eta\text{-}C_5H_5)_2Ti(O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_4X)_2$

A mixture of $(\eta\text{-}C_5H_5)_2TiCl_2$ (1.25 g; 5 mmol) and $2\text{-}CH_3C_6H_4COONa$ (2.37 g; 15 mmol) in 100 ml of anhydrous benzene was stirred at 30 ° C for 4 h, during which it turned from blood red to orange. The orange solution was filtered and the filtrate concentrated by a rotary evaporation, then kept in a refrigerator until crystals separated. The product was recrystallized from benzene. Yield: 1.0 g (48%); m.p. 162–164 ° C (dec.).

Small variations were encountered with the $4\text{-}NH_2$ and $4\text{-}CH_3CONH$ substituted derivatives, which separated out during the stirring, and with the 2-Ph, $2\text{-}CH_3COO$ and $3\text{-}CH_3O$ derivatives, which were precipitated from the concentrated filtrate by addition of petroleum ether (60–80 ° C).

Table 1 gives the results for 32 complexes. Elemental analyses (Janssen Pharmaceutica, Beerse, Belgium) were satisfactory, with C, H and N percentages within 0.25% of the theoretical values. The complexes are orange-red to yellow solids, and are stable under dry conditions but susceptible to hydrolysis and alcoholysis. They are soluble in benzene, tetrahydrofuran, chloroform, and acetone, and insoluble in hexane and petroleum-ether.

Mass spectra

The mass spectrum of Cp_2TiCl_2 has been thoroughly investigated by use of electron impact (EI) at various electron energies [10–12], chemical ionization (CI) [13], and secondary ion (SI) methods [14]. In contrast, mass spectral data for $(\eta\text{-}C_5H_5)_2Ti(OCOR)_2$ compounds, where R is an aliphatic or aromatic residue, are rare [15,16]. Instead these compounds are normally studied by IR and NMR spectroscopy and X-ray diffraction [17,18]. The mass spectra of titanium-containing poly-α-amino acids did not show titanium-containing ions characteristic of the

Table 1

Yields and properties of phenyl substituted complexes of bis(cyclopentadienyl)bis(benzoato)titanium(IV), $(\eta\text{-}C_5H_5)_2Ti(OOCC_6H_4X)_2$

	X	Colour	Melting point (° C)	Yield (%)
1	H	yellow	190–191 (dec.)	86
2	$4\text{-}NH_2$	yellow	195 (dec.)	88
3	4-OMe	yellow	138–140	67
4	4-OEt	orange	149–151	61
5	4-Me	orange	174–176 (dec.)	40
6	4-Et	orange	157–159 (dec.)	30
7	4-t-Bu	orange	195–197 (dec.)	17
8	4-Ph	yellow	172–174	73
9	4-F	orange-red	185–187 (dec.)	81
10	4-Cl	orange	188–190 (dec.)	62
11	4-Br	orange-red	179–181 (dec.)	75
12	4-I	orange	168–172 (dec.)	35
13	4-CN	orange	203–205 (dec.)	66
14	$4\text{-}NO_2$	orange	227–230 (dec.)	77
15	$4\text{-}CH_3CONH$	yellow	205 (dec.)	78
16	3-OMe	orange	129–131	18
17	3-Me	orange	143–145 (dec.)	40
18	3-F	orange	185 (dec.)	81
19	3-Cl	orange-red	173–175	48
20	3-Br	orange-red	159–161	35
21	3-I	orange-red	153–154	7
22	3-CN	orange	199–201 (dec.)	55
23	$3\text{-}NO_2$	orange	215–217 (dec.)	44
24	2-Me	orange	162–164 (dec.)	48
25	2-Ph	yellow	169–171 (dec.)	4
26	2-F	orange-red	175–177 (dec.)	59
27	2-Cl	orange	164–166 (dec.)	48
28	2-I	yellow	183–185 (dec.)	65
29	$2\text{-}CH_3COO$	orange-brown	148–150 (dec.)	7
30	2,4-Cl,Cl	orange-red	201–203 (dec.)	80
31	3,4-Cl,Cl	orange-red	203–205 (dec.)	68
32	2-furyl [a]	orange	182–184 (dec.)	34

[a] Ligand in $Cp_2Ti(OOC\text{-furyl})_2$.

polymer ligand [19]. Our compounds, however, can be fully characterized from their mass spectra.

Low resolution electron impact (EI) spectra were obtained with a Jeol OI-SG-II spectrometer connected to a Jeol JEC-6 computer system. The ionisation energy was maintained at 70 eV and the ionisation current was 300 μA. All compounds were introduced by means of a direct probe insertion system. Desorption chemical ionisation (DCI) mass spectra of compounds **6** and **13** were recorded on a Ribermag 10-10B (Nermag S.A.) quadrupole mass spectrometer equipped with a Sidar data system. Primary ionisation of the NH_3 reagent gas was performed with 70 eV electrons. The ionisation current was 0.08 mA, the source temperature 100 °C, and the pressure in the ionisation chamber 0.1 mmHg.

Fast atom bombardment (FAB) spectra and linked scans on compounds **1** and **14** were obtained with a VG70-SEQ hybrid mass spectrometer (VG Analytical Ltd., Manchester, U.K.), equipped with an Ion Tech saddle field ion gun. The instrument

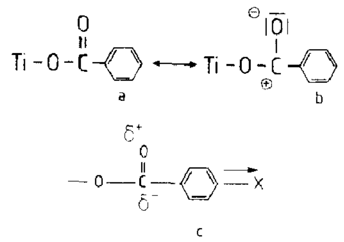


Fig. 1. Some resonance hybrids of Cp_2TiL_2, and the concept of localised polarisation [29].

consists of a high resolution double focussing mass spectrometer with EB configuration (MS-I) followed by an RF-only quadrupole collision gas cell and a high performance quadrupole mass analyzer (MS-II). Xenon atoms with energies of approximately 8 keV and a beam flux of 1 mA, were used as the ionizing beam. Positive and negative FAB spectra were recorded under the control of the VG 11-250J data system by repetitive scanning over the range 20–600 a.m.u., with a scan time of 2s/decade.

Standard EI spectra were taken of all compounds. In an effort to obtain high signal intensity and minimize fragmentation of the high mass ions the probe temperature was varied over a wide range (200–400 ° C), revealing an unexpected influence (Table 2) upon the fragmentation. Because of this and because of the low decomposition temperature (Table 1) of most of the compounds the question arises whether the EI spectra are really representative of the title compounds (Cp_2TiL_2) and not of thermolysis products. The presence of a molecular ion would be helpful, but none of the EI spectra shows such a signal. Unfortunately neither the CI spectra (with NH_3 as the reagent gas) of compounds **6** and **13**, nor the FAB spectra (using glycerol, *m*-nitrobenzyl alcohol mixed with dichloromethane, and 18-crown-6 mixed with 2% tetraglyme as matrices) of compounds **1** and **14** showed a molecular ion. Thus thermolysis cannot be rigorously excluded. Nevertheless, we believe that the spectra presented in Tables 3 and 4, are representative of the title compounds. The spectra are recorded at the lowest possible temperature (200–250 ° C). At still lower temperatures no EI spectrum could be recorded.

The data (Tables 2–4) show several interesting features. First, the spectra are in agreement with the structures proposed for the title products. Although they do not show the molecular ion (as in the case for the SIMS spectrum of Cp_2TiL_2 [14]), they do give peaks corresponding to structurally informative ions, e.g. (Cp_2TiL), ($CpTiL$), ($CpTiL_2 - CO_2$), (Cp_2Ti) and ($CpTi$) (see Table 3). Furthermore, numerous ions characteristic of the ligands L are present, including the molecular ion of the free substituted benzoic acid, HL (see Table 4).

Second, the loss of a benzoic acid ligand $L^{\cdot}$ radical seems to be preferred over the loss of a $Cp^{\cdot}$ radical from the unstable molecular ion $(Cp_2TiL_2)^{+\cdot}$. In fact at the lower temperatures (200–240 ° C) of the direct probe the $(Cp_2TiL)^+$ ion is often the base peak. It is necessary to raise the temperature to about 300 ° C to observe a $(CpTiL_2)^+$ ion, which then reaches intensities of up to 25% of the base peak, proving that the loss of the stable $Cp^{\cdot}$ radical is indeed a competitive process. The major loss of $L^{\cdot}$ is in accordance with the well-known preference for ejection of the heaviest radical and the most effective carrier of the excess of energy. It can also be regarded as reflecting a greater strength of the Ti–Cp bond than of the Ti–OOC

(*continued on p. 340*)

Table 2

Relationship between fragmentation and temperature of the direct probe in EIMS of Cp_2TiL_2 complexes $L = OOCC_6H_4X$, with X a substituent on the phenyl ring. Entries numbered as in Table 1

Nr.	X	Temperature (°C)	Base peak at *m/z*	$CpTiL_2$		Cp_2TiL		CpTiL		$CpTiL - CO_2$	
				m/z	int.	*m/z*	int.	*m/z*	Int.	*m/z*	int.
3	4-OMe	240	135			329	1	264	0	220	0
		205	135				70		40		23
		200	329				100		54		35
		190	329				100		39		20
4	4-OEt	400	121	443	2	343	10	278	6	234	3
		360	121		2		21		8		6
		280	343		4		100		44		23
		250	343		0		100		44		28
		200	343		0		100		49		21
5	4-Me	400	91	383	4	313	44	248	35	204	28
		300	119		26		66		42		29
		260	313		25		100		75		52
		250	313		7		100		75		57
		230	313		0		100		74		69
		220	313		0		100		79		57
17	3-Me	370	91	383	0	313	0	248	0	204	0
		280	66		10		18		9		9
		260	91		6		43		34		28
		200	313		0		100		76		73
24	2-Me	350	119	383	0	313	0	248	0	204	0
		300	119		7		14		13		13
		260	119		10		21		13		14
		230	119		10		57		34		39
		200	119		4		87		57		71
9	4-F	400	123	391	10	317	19	252	21	208	12
		200	123		0		63		86		48
26	2-F	400	123	391	0	317	4	252	4	208	14
		205	123		0		59		32		72
10	4-Cl	400	139	423	5	333	32	268	33	224	20
		380	139		2		59		55		22
		230	333		0		100		84		34
19	3-Cl	240	66	423	6	333	90	268	49	224	12
		210	333		10		100		48		13
		180	333		0		100		73		19
21	3-I	240	66			425	11	360	12	316	2
		230	66				41		29		3
		190	425				100		58		8
		160	425				100		69		12
28	2-I	250	66			425	48	360	4	316	8
		230	425				100		10		17
		210	425				100		8		13
30	2,4-Cl,Cl	380	173	493	4	367	0	302	0	258	0
		280	66		0		34		8		12
31	3,4-Cl,Cl	380	173			367	3	302	2	258	0
		270	66				70		47		4
32	2-furyl [a]	380	68	335	23	289	8	224	6	180	7
		220	289		0		100		12		56

[a] Ligand in $Cp_2Ti(OOC\text{-}furyl)_2$.

Table 3

Ti-containing ions in mass spectra of Cp_2TiL_2 complexes (L = ligand, and X = substituent on phenyl ring). m/z values with intensities (% of the base peak) in parentheses. Entries numbered as in Table 1. Direct probe temperature in column 1

Entry	X	Temp. (°C)	Mol weight	Base peak at	Cp_2TiL	CpTiL	CpTiL − CO_2	Cp_2Ti	CpTi	CpTiL − CO_2 − HX
1	H	205	420	299	299(100)	234(80)	190(79)	178(6)	113(18)	
2	4-NH_2	200	450	66	314(5)	249(2)	205(2)			
3	4-OMe	200	480	329	329(100)	264(54)	220(35)	178(5)	113(4)	188(2)
16	3-OMe	320	480	66	329(7)	264(4)	220(1)			
4	4-OEt	200	508	343	343(100)	278(49)	234(21)	178(7)	113(4)	188(2)
5	4-Me	220	448	313	313(100)	248(79)	204(57)	178(13)	113(8)	
17	3-Me	200	448	313	313(100)	248(76)	204(74)	178(7)	113(14)	
24	2-Me	200	448	119	313(87)	248(57)	204(71)	178(18)	113(14)	
6	4-Et	240	476	327	327(100)	262(26)	218(23)			
7	4-t-Bu	220	532	163	355(4)	290(1)	246(2)	178(19)		
8	4-Ph	280	572	66	375(28)	310(8)	266(8)		113(3)	
25	2-Ph	200	572	375	375(100)	310(6)	266(32)	178(6)	113(4)	188(5)
9	4-F	200	456	123	317(63)	252(86)	208(48)	178(11)	113(14)	188(7)
18	3-F	200	456	317	317(100)	252(85)	208(64)	178(11)	113(13)	188(10)
26	2-F	205	456	123	317(59)	252(32)	208(72)	178(8)	113(9)	188(27)
10	4-Cl	230	488	333	333(100)	268(84)	224(34)	178(17)	113(24)	188(7)
19	3-Cl	210	488	333	333(100)	268(48)	224(13)	178(14)	113(27)	188(8)
27	2-Cl	210	488	333	333(100)	268(10)	224(25)	178(8)	113(21)	188(36)
11	4-Br	210	576	66	377(64)	312(48)	268(23)	178(8)	113(15)	
20	3-Br	200	576	377	377(100)	312(56)	268(7)	178(14)	113(12)	188(6)
12	4-I	200	672	425	425(100)	360(45)	316(8)	178(7)	113(11)	
21	3-I	190	672	425	425(100)	360(58)	316(8)	178(26)	113(21)	188(9)
28	2-I	230	672	425	425(100)	360(10)	316(17)	178(21)	113(34)	188(40)
14	4-NO_2	205	510	445	344(9)	279(4)			113(1)	
23	3-NO_2	180	510	314	344(26)	279(7)		178(13)	113(11)	
13	4-CN	230	470	324	324(100)	259(39)	215(34)	178(3)	113(17)	188(10)
22	3-CN	220	470	66	324(18)	259(18)	215(13)	178(1)	113(3)	188(5)
30	2,4-Cl,Cl	280	556	66	367(34)	302(8)	258(12)	178(3)		222(29)
31	3,4-Cl,Cl	270	556	66	367(70)	302(47)	258(4)	178(6)	113(5)	222(47)
32	2-furyl [a]	220	400	289	289(100)	224(12)	180(56)	178(20)	113(12)	

Entry	X	CpTiX	$C_3H_3TiL-CO_2$	HTiL	Other Ti-containing fragments > 5% of base peak	
1	H		164(5)			
2	4-NH_2	129(3)				
3	4-OMe	144(4)	194(2)	200(3)		
16	3-OMe			200(2)	415(1)	$CpTiL_2$
4	4-OEt	158(2)		214(2)	314(5)	$Cp_2TiL-C_2H_5$; 249(5) $CpTiL-C_2H_5$; 204(5)
5	4-Me	128(20)	178(13)	184(3)	267(5)	$Cp_2TiL-CO_2-2H$
17	3-Me	128(3)	178(7)	184(3)		
24	2-Me	128(9)	178(18)		383(5)	$CpTiL_2$
6	4-Et					
7	4-t-Bu				202(8)	"246" $-CH_3)_2CH_2$; 185(6)
8	4-Ph					
25	2-Ph					
9	4-F	132(40)	182(27)	188(7)	271(5)	CpTi(L)(F); 206(18) Ti(L)(F); 187(7) TiL; 151(5) $CpTiF_2$
18	3-F	132(61)	182(52)	187(10)	271(5)	CpTi(L)(F); 206(12) Ti(L)(F); 187(6) TiL; 151(6) $CpTiF_2$
26	2-F	132(51)	182(7)	188(27)	271(7)	CpTi(L)(F); 206(14) Ti(L)(F); 187(10) TiL; 151(16) $CpTiF_2$ 197(7) Cp_2TiF
10	4-Cl	148(40)	198(14)	204(4)	371(24)	Cp_2TiL-O; 252(25) $CpTiL-O$; 208(16)
					182(7)	$CpTiCl_2-H$
19	3-Cl	148(36)	198(50)		423(7)	$CpTiL_2$; 375(9); 287(7); 181(10); $CpTiCl_2-2H$
27	2-Cl	148(19)		204(18)	232(8)	$CpTiL-HCl$
11	4-Br	192(34)	242(3)		189(5)	"268" − Br
20	3-Br	192(18)	242(31)	248(4)	513(8)	$CpTiL_2$
12	4-I	240(14)	290(3)	296(11)	298(6)	Cp_2TiL-I; 233(5) $CpTiL-I$; 189(10) "316" − I; 163(7) "290" − I
21	3-I	240(20)	290(58)	296(4)	379(9)	$Cp_2TiL-CO_2-2H$; 332(16) $CpTiL-CO$
					298(11)	Cp_2TiL-I: 233(6) $CpTiL-I$; 163(9) "290" − I
28	2-I	240(6)			379(4)	$Cp_2TiL-CO_2-2H$; 342(7); 332(16)$CpTiL-CO$
					298(11)	Cp_2TiL-I; 280(9); 233(11)$CpTiL-I$
14	4-NO_2				445(100)	$CpTiL_2$; 399(2) $CpTiL_2-NO_2$; 298(5) $Cp_2TiL-NO_2$
23	3-NO_2				445(92)	$CpTiL_2$; 415(6) $CpTiL_2-NO$; 399(2) $CpTiL_2-NO_2$
					314(100)	$Cp_2TiL-NO$; 298(11) $Cp_2TiL-NO_2$
13	4-CN			195(5)		
22	3-CN		189(2)	195(2)		
30	2,4-Cl,Cl	148(6)		238(6)	266(5)	$CpTiL-HCl$
31	3,4-Cl,Cl	148(10)				
32	2-furyl [a]				245(7)	$Cp_2TiL-CO_2$; 152(10) "180" − CO

[a] Ligand in $Cp_2Ti(OOC\text{-}furyl)_2$.

Table 4

Ligand ions in the mass spectra of Cp_2TiL_2 complexes $L = OOCC_6H_4X$, with X a substituent on the phenyl ring. Other conditions as in Table 3.

	X	HL				Other fragments
		XC_6H_4COOH	XC_6H_4CO	XC_6H_4	Phenyl	
1	H	122(32)	105(73)		77(91)	
2	4-NH_2		120(4)		78(9)	
3	4-OMe	152(11)	135(67)	107(9)	77(16)	92(12) C_6H_4O
16	3-OMe	152(50)	135(27)	107(14)	77(13)	105(7) C_6H_5CO; 92(6) C_6H_4O
4	4-OEt	166(11)	149(37)	121(54)	77(2)	138(17) HOC_6H_4COOH; 121(54) HOC_6H_4CO; 93(13) C_6H_4OH
5	4-Me	136(33)	119(51)	91(59)	78(10)	
17	3-Me	136(44)	119(69)		77(10)	
24	2-Me	136(30)	119(100)	91(90)	77(8)	
6	4-Et	150(20)	133(16)	105(25)	77(15)	
7	4-t-Bu	178(17)	161(35)	133(3)	77(12)	163(100) "178" − CH_3, 147(5) "163" − CH_3, 135(27) "163" − CO 119(10) "147" − CO, 105(10) C_6H_5CO, 91(25) C_7H_7
8	4-Ph	198(40)	181(39)	153(36)	76(12)	
25	2-Ph	198(11)	181(51)	153(20)	76(4)	
9	4-F	140(39)	123(100)	95(81)	75(38)	104(6) C_6H_4CO
18	3-F	140(25)	123(75)	95(100)	75(44)	
26	2-F	140(22)	123(100)	95(46)	75(26)	106(8) C_6H_6CO
10	4-Cl	156(21)	139(44)	111(39)	75(26)	104(14) C_6H_4CO
19	3-Cl	156(33)	139(48)	111(50)	75(24)	
27	2-Cl		139(55)	111(36)	75(34)	
11	4-Br	200(17)	183(27)	155(25)	76(28)	104(14) C_6H_4CO
20	3-Br	200(90)	183(89)	155(44)	76(30)	104(7) C_6H_4CO
12	4-I	248(40)	231(36)	203(12)	76(23)	121(9) C_6H_4COOH, 104(9) C_6H_4CO
21	3-I	248(64)	231(46)	203(39)	76(63)	121(39) C_6H_4COOH, 104(12) C_6H_4CO
28	2-I	248(88)	231(76)	203(32)	76(78)	122(35) C_6H_5COOH, 105(58) C_6H_5CO
14	4-NO_2	167(7)	150(83)		76(12)	135(6) HL − NO − 2H, 104(28) C_6H_4CO
13	4-CN	147(21)	130(39)	102(35)	76(11)	
22	3-CN	147(17)	130(35)	102(19)	76(8)	
30	2,4-Cl,Cl	190(21)	173(48)	145(11)	75(16)	
31	3,4-Cl,Cl	190(21)	173(39)	145(19)	75(19)	
32	2-furyl [a]	112(46)	95(39)	67(74)		39(35) C_3H_3

[a] Ligand in $Cp_2Ti(OOC\text{-}2\text{-}furyl)_2$.

bond. The interpretation in terms of bond strengths is in our opinion an attractive working model, because it simultaneously rationalizes aspects of the MS, NMR, IR and X-ray data (see below).

Third, in the low temperature spectra exceptions are observed for the 4-NO_2 and 3-NO_2 complexes (**14** and **23**), where the intensity of the $(Cp_2TiL)^+$ ion is low (~ 5%) and that of the $(CpTiL_2)^+$ ion is high (~ 100%). The following rationaliza-

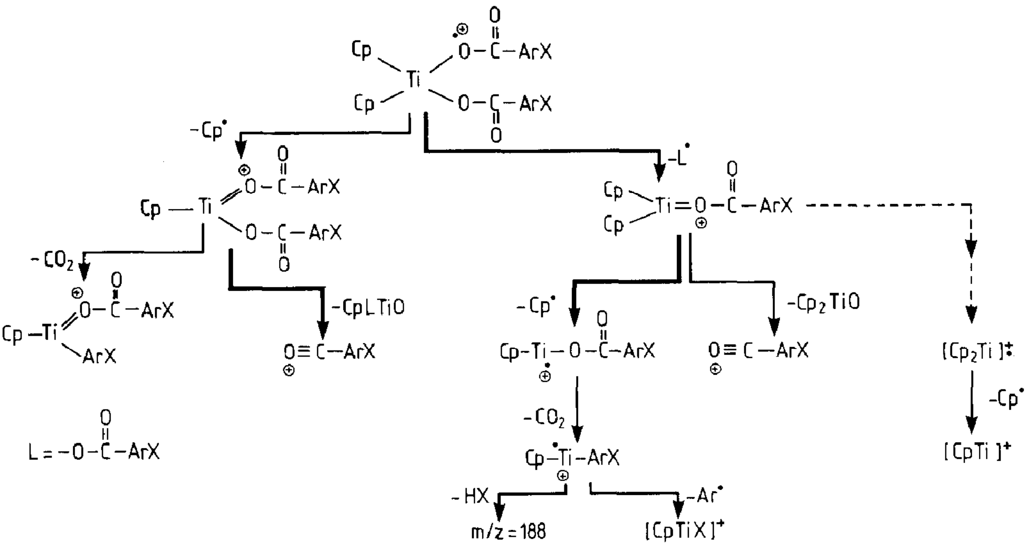


Fig. 2. Major fragmentation paths in EIMS of Cp_2TiL_2 complexes with $L = OOCC_6H_4X$ and X = substituent on phenyl.

tion may be given. Part of the Ti–O bonding is due to interaction of lone pairs at oxygen with low-lying Ti orbitals. The more readily these lone pairs are available, the stronger the Ti–O bond will be. This availability is greater the more resonance the hybrid **a** (Fig. 1) describes the actual electron density in the complex. In other words the influence of hybrid **b** (Fig. 1) interferes with this part of the Ti–O bond and the better hybrid **b** portrays the electron density the weaker the Ti–O bond will be. Substitution on the phenyl ring by a strong electron-withdrawing group such as NO_2 polarizes the π-electrons locally in the C=O bond [29] as shown in Fig. 1c. Such polarisation could also be regarded as a decrease of importance of hybrid **b** and an increase of **a**, with concomitant strengthening of the Ti–O bond. If so, then *meta* substituents with $+M$; $-I$ effect will also exercise a stabilizing influence on the Ti–O bond. In keeping with this, the $(CpTiL_2)^+$ ion is observed in such compounds in the 200–250 °C range.

Fourth, linked scan experiments proved that the high intensity ion $(CpTiL)^{+\cdot}$ originates from $(Cp_2TiL)^+$ and not from $(CpTiL_2)^{+\cdot}$. Furthermore $(Cp_2Ti)^{+\cdot}$ was shown not to be a direct daughter of $(Cp_2TiL)^+$. Thus, whereas $(Cp_2TiL)_2$ loses $Cp^\cdot$ with difficulty, (Cp_2TiL) easily loses $Cp^\cdot$ and not its second $L^\cdot$ ligand. The latter behaviour can be explained in terms of a combination of an entropy effect (twice the chance of losing the stable Cp radical) and an increasing bond strength of Ti–O upon Cp_2TiL formation (see Fig. 2). We also mention yet another possibility, namely that the phenomenon could be a reflection of a difference in Ti–O bond strength between the two benzoic acid ligands in the neutral Cp_2TiL_2 molecule. Support for such a difference stems from single crystal X-ray diffraction study of $Cp_2Ti(OOCC_6H_5)_2$ [7,18c,20]; in the orthorhombic form (β-modification) two quite different monodentate carboxylates were observed [7,20].

Fifth, the (Cp_2TiL) ion is found by linked scan to fragment into $(XArCO)^+$ by ejection of the neutral molecule Cp_2TiO. This fragmentation, however, is only a minor path. In contrast, the similar reaction of $(CpTiL_2)^+$, with ejection of CpLTiO to yield $(XArCO)^+$, is a major fragmentation pathway. A minor route here is the loss of CO_2.

Sixth, fragmentation of CpTiL may follow several paths. It may lose CO or CO_2, and Table 3 shows that the loss of CO_2 is the preferred process, giving rise to a stable ion in which Ti is directly bonded to aryl type ligands. The latter ion $CpTi(C_6H_4X)$ may then (i) lose HX or (ii) rearrange to CpTiX. The rearrangement is prominent when X = Hal, with fluorine showing the strongest tendency to coordinate titanium. In fact the fluorine-containing complexes exhibit a series of such rearrangements, leading to characteristic ions including $[Ti(L)(F)]^+$; they lose both their Cp ligands. This confirms reports by other researchers [16,21] that fluorine migrates readily from a phenyl ring to titanium in these complexes.

Finally, Fig. 2 summarizes the major fragmentation pattern for the title compounds.

Table 5

Proton chemical shifts (in ppm, relative to TMS) of $(\eta\text{-}C_5H_5)_2Ti(OOCC_6H_4X)_2$ complexes in $CDCl_3$ solution

X	C_5H_5	H(2)	H(3)	H(4)	H(5)	H(6)	Other protons
H	6.64	8.10	7.50	7.50	7.50	8.10	
4-NH_2	6.59	7.84	6.66		6.66	7.84	
4-OMe	6.64	8.03	6.96		6.96	8.03	3.88(OCH_3)
4-OEt	6.65	8.04	6.97		6.97	8.04	1.47(OCH_2CH_3), 4.17(OCH_2CH_3)
4-Me	6.65	7.99	7.28		7.28	7.99	2.44(CH_3)
4-Et	6.69	8.08	7.36		7.36	8.08	1.31(CH_2CH_3), 2.77(CH_2CH_3)
4-t-Bu	6.63	8.04	7.48		7.48	8.04	1.31[$C(CH_3)_3$]
4-Ph	6.70	8.16	7.71		7.71	8.16	7.71, 7.48, 7.26 (H on 4-Ph)
4-F	6.66	8.04	7.14		7.14	8.04	
4-Cl	6.63	7.95	7.41		7.41	7.95	
4-Br	6.63	7.91	7.59		7.59	7.91	
4-I	6.64	7.80	7.80		7.80	7.80	
4-CN	6.69	8.14	7.77		7.77	8.14	
4-NO_2	6.68	8.10	8.42		8.42	8.10	
3-OMe	6.67	7.64		7.10	7.38	7.70	3.86(OCH_3)
3-Me	6.63	7.84		7.32	7.34	7.84	2.42(CH_3)
3-F	6.64	7.80		7.28	7.46	7.80	
3-Cl	6.64	7.95		7.44	7.44	7.95	
3-Br	6.69	8.26		7.74	7.46	8.08	
3-I	6.64	8.42		7.93	7.26	8.03	
3-CN	6.76	8.40		7.84	7.84	7.84	
3-NO_2	6.72	8.84		7.78	7.78	8.43	
2-Me	6.63		7.44	7.44	7.44	7.82	2.62(CH_3)
2-Ph	6.12		7.26	7.26	7.26	7.90	7.26(H on 2-Ph)
2-F	6.59		7.12	7.36	7.12	7.87	
2-Cl	6.67		7.28	7.28	7.28	7.74	
2-I	6.66		7.70	7.30	7.09	7.93	
2,4-Cl,Cl	6.66		7.46		7.26	7.76	
3,4-Cl,Cl	6.69	8.10			7.61	7.92	
2-furyl [a]	6.64		7.12	6.52	7.59		
2-CH_3COO	6.68		7.43	6.99	6.99	7.86	6.43(CH_3COO)

[a] Ligand in $Cp_2Ti(OOC\text{-}furyl)_2$.

Table 6. ^{13}C chemical shifts (in ppm, relative to TMS) of $(\eta\text{-}C_5H_5)_2Ti(OOC_6H_4X)_2$ complexes in $CDCl_3$ solution

X	C_5H_5	C=O	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other carbons
H	118.49	172.04	133.78	129.88	128.18	131.71			
4-NH_2	118.25								
4-OMe	118.49	172.16	126.41	131.95	113.49	162.66			55.44(OCH_3)
4-OEt	118.43	172.16	126.23	131.89	113.98	161.99			63.72(OCH_2), 14.74(CH_3)
4-Me	118.43	172.22	130.98	130.06	128.98	142.19			21.57(CH_3)
4-Et	118.49	172.28	131.34	130.19	127.75	148.46			28.94(CH_2), 15.47(CH_3)
4-t-Bu	118.37	172.16	131.04	129.88	125.13	155.22			34.91(C), 31.19(CH_3)
4-Ph	118.61	172.16	132.56	130.49	127.02	144.62			1a: 140.42, 2a: 127.26, 3a: 128.91, 4a: 127.87
4-F	118.67	171.00	130.06	132.20	115.14	165.12			
4-Cl	118.73	171.06	132.26	131.22	128.48	138.17			
4-Br	118.73	171.12	132.68	131.47	131.47	126.77			
4-I	118.73			131.47	137.62	96.01			
4-CN	119.10	169.97	137.62	130.25	132.20	115.38			118.06(CN)
4-NO_2	119.22	168.44	141.46	130.73	123.55				
3-OMe	118.61	171.86	135.18	114.47	159.67	118.19	129.15	122.39	55.32(OCH_3)
3-Me	118.49	172.16	133.72	130.49	137.80	132.50	128.12	127.08	21.32(CH_3)
3-F	118.86	170.88	136.12	116.71	163.28	118.40	129.82	125.56	
3-Cl	118.79	170.64	135.55	129.94	134.39	131.77	129.64	127.93	
3-Br	118.73	170.33	135.67	132.81	122.39	134.63	129.94	128.36	
3-I	118.73	170.21	135.61	138.77	94.00	140.54	130.12	128.96	
3-CN	119.10	169.66	134.94	133.54	112.64	129.46	128.30	133.78	118.37(CN)
3-NO_2	119.22	169.48	135.61	124.76	148.40	126.41	129.70	135.61	
2-Me	118.25	173.01	133.29	139.08	130.61	131.40	125.37	130.86	21.87(CH_3), 1a: 140.97, 2a: 127.99, 3a: 128.66, 4a: 127.99
2-Ph	118.06	174.84	135.91	142.31	127.02	130.43	127.02	129.45	
2-F	118.73	166.92	122.42	162.91	116.66	132.99	123.67	132.50	
2-Cl	118.67	170.58	132.44	133.96	130.49	131.10	126.35	130.98	
2-I	118.86	171.67	139.14	93.88	140.79	131.28	127.75	130.80	
2,4-Cl,Cl	118.98	169.91	132.32	133.90	130.61	136.77	126.84	132.32	
3,4-Cl,Cl	118.98	169.91	132.74	131.83	133.66	136.40	130.49	128.91	
2-furyl [a]	118.79	164.12		147.79	116.54	111.61	145.23		
2-CH_3COO	119.22								

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[a] Ligand in $Cp_2Ti(OOC\text{-}furyl)_2$.

Nuclear magnetic resonance spectra

Proton and carbon nuclear magnetic resonance spectra were recorded on a Jeol NMR PS-100 and a Jeol NMR FX100 spectrometer, respectively. All spectra were recorded at room temperature, with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Signals of the phenyl protons and carbons are readily assigned by applying standard increments for the substituents [22] to the known chemical shifts of the unsubstituted bis-benzoato complex [7,8,18]. In the ^1H spectra normal H–H coupling constants (J_o 8 Hz and J_m 2 Hz) are observed. The ^1H and ^{13}C chemical shifts are given in Tables 5 and 6, respectively.

The 10 protons of the two cyclopentadienyl rings are chemically equivalent and give rise to one sharp singlet. In the case of the *ortho*-phenylbenzoato complex these protons give the singlet at δ 6.12 ppm, probably because of the shielding effect of the phenyl ring. For all other complexes the signals appear in the range δ 6.59 to 6.76 ppm. Although at an accuracy of ± 0.02 ppm for $\delta(C_5H_5)$ no statistically significant conclusion can be drawn, there are clear indications that electron-withdrawing substituents on the phenyl ring cause an increase in the chemical shift of the cyclopentadienyl protons and electron-releasing substituents cause a decrease.

The situation for the 10 carbon atoms of the two cyclopentadienyl rings is quite similar. They also show one sharp singlet, with the signals for the *ortho*-phenylbenzoato complex appearing at the lowest δ value, namely 118.06 ppm. For the other complexes the signals fall in the range 118.25–119.22. The ^{13}C chemical shifts of the cyclopentadienyl carbons can be correlated with the electronic properties of the substituents on the phenyl rings. As expected electron-donating groups shield the cyclopentadienyl carbons, causing an up-field shift, while electron-withdrawing groups cause a down-field shift.

On the other hand the carboxylato carbons, giving signals between 164.12 and 174.84 ppm, show the opposite trend; that is there is a decrease in chemical shift with electron-withdrawing substituents and an increase with electron-donating substituents on the phenyl ring. Such a reversed shift effect has been observed for many other compounds [23,24]. It has been shown by Brownlee and others [29] to arise predominantly from local polarisation of the C=O bond by the inductive field of the substituent (Fig. 1c). As such it reflects the greater impact of resonance hybrid **a** (Fig. 1) in the presence of an electron-withdrawing substituent and of hybrid **b** in the presence of a donating one.

Infrared spectra

Infrared spectra were recorded on a Bruker 113v FT spectrometer. Samples were recorded under vacuum, as KBr pellets in the mid-IR (4000–400 cm^{-1}), and as polyethylene pellets in the far-IR (500–100 cm^{-1}). For the mid-IR spectra a KBr/Ge beam-splitter and a KBr-window DTGS detector were used, and for the far-IR a mylar beam-splitter and a PE-window DTGS detector. In both regions a globar source was used. Either 32 scans (mid-IR) or 64 scans (far-IR) were co-added to give spectra with 1 cm^{-1} resolution.

In the mid-IR, C–H stretching bands appear near 3100 and 3080 cm^{-1}, characteristic of cyclopentadienyl and phenyl rings, respectively. In the ring breathing range, characteristic bands of the phenyl ring appear near 1580 and 1500 cm^{-1},

Table 7

IR frequencies (cm^{-1}) of the vibrations in the COO group

X	ν_{asym}	ν_{sym}
H	1650m, 1635vs	1336s, 1311s, 1290s
4-NH_2	1635ms, 1618ms	1337ms, 1321vs, 1288s
4-OMe	1634ms, 1616s	1339s, 1301s, 1290s
4-OEt	1638ms, 1627s	1338s, 1294s
4-Me	1625m	1335s, 1304vs
4-Et	1644m, 1625s	1339vs, 1311s, 1292s
4-t-Bu	1639ms, 1627s, 1622s	1347s, 1314s, 1292s
4-Ph	1629vs	1337s, 1307s, 1287s
4-F	1645s, 1635s, 1630s	1339s, 1305ms, 1289s
4-Cl	1642s, 1629vs	1336vs, 1289vs
4-Br	1646s, 1635s	1341vs, 1292vs
4-I	1637vs	1336vs, 1311s, 1289s
4-CN	1638s	1332vs, 1314s, 1293vs
4-NO_2	1666ms, 1635s	1336vs, 1295vs
4-CH_3CONH	1644ms, 1621s	1325s, 1288s
3-OMe	1648ms, 1627s	1338s, 1300s, 1285m
3-Me	1644m, 1624s	1337s, 1305vs, 1285m
3-F	1637vs	1342s, 1300s
3-Cl	1650ms, 1627s	1341s, 1305vs
3-Br	1633s	1335s, 1306s
3-I	1626vs	1347s, 1318s
3-CN	1640vs	1342s, 1297s, 1279ms
3-NO_2	1657m, 1638s	1348s, 1332s, 1296vs
2-Me	1629s	1333vs, 1303s, 1280ms
2-Ph	1641s, 1619s	1344s, 1310s, 1285m
2-F	1646s, 1634s	1329s, 1306s
2-Cl	1652vs, 1631ms	1332s, 1295s
2-I	1655m, 1639vs	1343s, 1300s
2-CH_3COO	1636m	1340s, 1306s
2,4-Cl,Cl	1645vs	1335vs, 1287s
3,4-Cl,Cl	1635vs	1337s, 1303s
2-furyl [a]	1646s	1332s, 1309s

[a] Ligand in $Cp_2Ti(OOC\text{-}furyl)_2$.

whereas those of the cyclopentadienyl rings are near 1450 and 1370 cm^{-1}. Strong bands indicative of *para*-substitution are observed near 840 cm^{-1} for compounds **2–15**, medium to strong bands reflecting *meta* substitution occur at 750–780 cm^{-1} and 860–900 cm^{-1} for compounds **16–23**, and medium to strong bands characteristic for *ortho*-substitution at 740–760 cm^{-1} for compounds **24–29**. This again confirms the proposed structures. The positions of the bands assigned to asymmetric and symmetric COO stretching frequencies are listed in Table 7. Although in some cases the bands are split, possibly owing to crystal packing effects, the difference $\Delta\nu$ (defined as ν(asymmetric, COO) minus ν(symmetric, COO)) is in the range 300 to 370 cm^{-1} for all the compounds. This large difference is clear evidence of monodentate coordination of the benzoato ligands [25]. The actual value of $\Delta\nu$ depends upon the substituent on the phenyl ring. A qualitative analysis of the *meta*- and *para*-substituted complexes, including those reported by Dang et al. [8], indicates there is an increase in $\Delta\nu$ with the electron-withdrawing ability of

Table 8. Far-infrared spectra of $(\eta\text{-}C_5H_5)_2Ti(OOC\text{-}C_6H_4X)_2$ (cm^{-1})

X	Ligand band(s)	$\nu_{as}(Ti{-}C_5H_5)$	Ti–O	$\nu_s(Ti{-}C_5H_5)$	Cp–Ti–Cp	O–Ti–O
H	448m	426s, 414vs		352m, 294w	256m, 239m	130m
4-NH_2		443m, 417s	380m	345w, 285w	251m	125m
4-OMe		418s	404ms, 389m	337w, 306w	265w, 245m	128m, 123w
4-OEt	468m, 438m	433vs, 418s	383m	364m, 324w, 290w	250w, 236m	142m, 118w
4-Me	468s	423s		285vw	251m	129w
4-Et	452vw	420vs	376w	366w, 281vw	256m, 243m	125m, 120m
4-t-Bu	467vs, 447s	419s	396s, 379s	364m, 324w, 290w	241m	122m, 118m
4-Ph	488vs, 463s	416m	402m, 392m, 379w	366m, 298w	244m	134w, 119m
4-F	464w, 438m	428vs	393m, 376w	337w, 293w	250m, 236m	134m, 129m, 118w
4-Cl	477m, 471s	433m, 414s	406m, 392s	312w	253m, 244m, 224w	134m, 122m
4-Br	482vs, 476s, 467m, 458m	418m	396m, 376m	322w	264w, 248w, 231m	117m
4-I	458s	414m	390vw	368m, 315w	243m	115w
4-CN		418s	401s, 386s	351w, 329vw	249m, 238w	153s, 131w, 125w, 116w
4-NO_2		424s, 409m	401s, 381s	335w, 286w	265w, 246m, 228m	125m, 121m
4-CH_3CONH	451vs	417m	403w, 385m	370w, 357w, 320w	245m	119m
3-OMe	469ms, 441m	425s, 417s	383m	363m, 349m	251w, 232m	151w, 126m
3-Me	490m, 441s	433s, 415s		289w	232m	125m
3-F	453ms, 443vs, 434m	429m, 422m	402m, 379w	350w, 293w	243m	125m, 118m
3-Cl	495ms, 449vs, 442vs	427m, 417ms	390m, 375w	344w, 321vw	237m, 204m	125m, 110m
3-Br	485ms, 445vs, 438vs	423s, 415s	375w	345w, 294vw	239m, 187m	121m, 93m
3-I	483ms, 475m, 441m	433s, 415m			230m, 176m	126w, 120w, 115w
3-CN	460vs	419vs	405m, 376w	348w	243m	156m, 138m, 125w
3-NO_2	453w, 436s	427vs, 413s		335w, 300w, 275w	240m	137m, 125m
2-Me	488m, 461s, 438s	422s		347w, 298vw	251m	128m
2-Ph	465s, 452vs	424ms	398m, 393m	367w, 306w, 292m	259w, 235m, 199w	136m
2-F	473m, 444s	418m	391m	334w, 293w	244m	126m
2-Cl	489s, 459m	426ms	396m, 376w	356w, 275w	243m	126m
2-I	482m, 465ms	431s, 420ms	377w	352w, 301w	245m	143w
2-CH_3COO	473m, 463vs	413s		292w	234m	149m, 124m
2,4-Cl,Cl	484w, 463w, 448m	433vs	404m, 376w	352w	250m, 205w	134m, 123m, 117w
3,4-Cl,Cl	452m, 436s	429vs	396s	337w, 324w, 296w	250m, 235m	117m, 110m
2-furyl [a]	462s, 455vs	419s	387m	352m, 291w, 278w	262m, 223m, 163ms	139w

[a] Ligand in $Cp_2Ti(OOC\text{-}furyl)_2$.

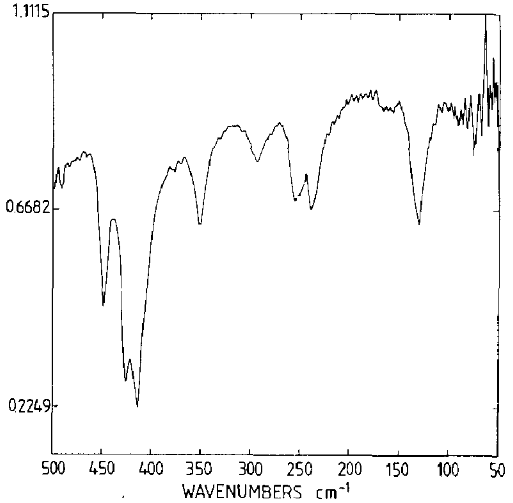

Fig. 3. Far infrared spectrum (50–450 cm^{-1}) of bis(benzoato)bis(η-cyclopentadienyl)titanium(IV).

substituents as measured by Hammett σ_m and σ_p values. The values of $\Delta\nu$ also correlate with carbon chemical shifts of cyclopentadienyl and carboxylato groups; we interpret this as another reflection of the growing importance of resonance hybrid **a** relative to **b** (Fig. 1) when electron-withdrawing substituents are present.

The far-infrared frequencies are listed in Table 8. In accord with previous reports [26–28] we assign the strong band appearing for all complexes at 420 ± 10 cm^{-1} to the asymmetric Ti–Cp stretching vibration. The corresponding symmetric stretching band appears in the region 335–370 cm^{-1} [26–28]. Its intensity is rather weak and it can consequently not be detected in some compounds. The ν_{as}(Ti–Cp) and ν_s(Ti–Cp) bands can be regarded as arising from pure vibrations because substituents influence their position, profile and intensity only very slightly. However, it should be noted that electronic substituent effects are negligable, while mass effects can be seen.

The bands in the range 375 to 405 cm^{-1} (see e.g. Fig. 3) are attributed to asymmetric and symmetric titanium-oxygen vibrations. The assignment is supported by the presence of very similar bands in the sodium salts of substituted benzoic acids. Since the Ti–Cl stretching bands for Cp_2TiCl_2 also appear near 400 cm^{-1}, and the reduced mass of Ti–Cl is larger than of Ti–O, the Ti–O force constant must be smaller than of Ti–Cl. To the best of our knowledge data below 350 cm^{-1} are not yet available for these complexes. The bands around 300 cm^{-1} are assumed to arise from titanium–cyclopentadienyl stretching and those near 240 cm^{-1} from Cp–Ti–Cp deformation modes. The O–Ti–O deformations probably appear in the range 140–110 cm^{-1}. Interestingly the band is observed at 125 ± 1 cm^{-1} for *ortho*- and *meta*-substituted complexes, but near 120 cm^{-1} for most *para*-substituted derivatives.

The ν(Ti–O) as well as δ(O–Ti–O) and δ(Cp–Ti–Cp) modes appear over a broad range with different profiles and intensities.This means that they are probably coupled with other modes (from the substituents). Thus the assignments shown in Table 8 must be regarded as approximate descriptions for these vibrations.

Finally, bands appearing above 440 cm^{-1} are believed to arise from benzoato ligand vibrations, because they are absent from the spectrum of Cp_2TiCl_2.

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