Pentamethylcyclopentadienyltitanium-(III) and -(IV) Carboxylates. Crystal Structures of $[Ti(\eta\text{-}C_5Me_5)(O_2CPh)_3]$ and $[\{Ti(\eta\text{-}C_5Me_5)(O_2CPh)_2\}_2]$ *

Pilar Gómez-Sal,[a] Beatriz Royo,[a] Pascual Royo,[a] Ricardo Serrano,[a] Isabel Sáez[a] and Sagrario Martinez-Carreras[b]

[a] *Departamento de Química Inorgánica, Universidad de Alcalá, 28871 Alcalá de Henares, Spain*

[b] *Departamento de Rayos X, C.S.I.C., Madrid, Spain*

The compound $[Ti(\eta\text{-}C_5Me_5)Me_3]$ reacts with 3 equivalents of carboxylic acids HO_2CR (R = Me, Ph, or p-$MeOC_6H_4$) to give the corresponding tris(carboxylates) $[Ti(\eta\text{-}C_5Me_5)(O_2CR)_3]$. The X-ray structure of the complex with R = Ph shows the three benzoate ligands acting as chelates, the geometry around Ti is a distorted pentagonal bipyramid and the metal attains the 18-electron configuration. Methyl carboxylate complexes $[Ti(\eta\text{-}C_5Me_5)Me_{3-n}(O_2CR)_n]$ (n = 1 or 2) could not be isolated, but exposure of their solutions to sunlight gave the dimers $[\{Ti(\eta\text{-}C_5Me_5)(O_2CR)_2\}_2]$. The X-ray structure of the acetato complex reveals four O_2CMe groups bridging two $Ti(C_5Me_5)$ fragments.

We have been studying the chemistry of mono(pentamethylcyclopentadienyl)titanium(IV) derivatives $[Ti(\eta\text{-}C_5Me_5)X_3]$ which are formally 12-electron compounds if X is a one-electron ligand (*e.g.* halide or alkyl); this electronic deficiency of the metal atom has as a consequence, for example, the appearance of Ti ··· H–C and Ti ··· C–C interactions in alkyl derivatives [1,2] and makes this kind of compounds very reactive, often in an uncontrollable way. For this reason we have been searching for a way of introducing some potentially bidentate three-electron ligands which could relieve partially the electronic and co-ordinative unsaturation of the metal centre. Carboxylate ligands seemed well suited for this purpose, and although our initial goals could not be fully reached we have obtained and describe in this paper a series of carboxylate derivatives of (pentamethylcyclopentadienyl)titanium-(IV) and -(III) which are formally 18- and 15-electron species.

Results and Discussion

Preparations and General Characterization.—Some mono(pentamethylcyclopentadienyl)titanium carboxylates have been described in the literature, mainly by Australian and Russian groups,[3] but their characterization is in many cases limited to elemental analysis and IR spectroscopy. We have taken the readily available trimethyl(pentamethylcyclopentadienyl)-titanium as the starting compound by using protonolysis reactions. Thus, the reaction between $[Ti(\eta\text{-}C_5Me_5)Me_3]$ and carboxylic acids HO_2CR (R = Me, Ph, or p-$MeOC_6H_4$) leads to substitution of methyl by carboxylate groups with concomitant methane evolution; if the molar ratio of the starting compounds is 1:3, the yellow tris(carboxylates) **1**–**3** are obtained according to equation (1). They are air-stable substances in contrast to the (formally) 12-electron $[Ti(\eta\text{-}C_5Me_5)X_3]$ derivatives that are immediately (X = alkyl) or slowly (X = halide) hydrolysed.

$$[Ti(\eta\text{-}C_5Me_5)Me_3] + 3\,HO_2CR \longrightarrow [Ti(\eta\text{-}C_5Me_5)(O_2CR)_3] + 3\,CH_4 \quad (1)$$

1 R = Me
2 R = Ph
3 R = p-$MeOC_6H_4$

Infrared spectroscopy is generally taken as the quickest, although not unequivocal, method to ascertain the co-ordination mode of carboxylate groups according to the value of the separation $\Delta\nu$ between the symmetric and assymmetric OCO stretching bands relative to the value for the free (ionic) ligand.[4] Values of $\Delta\nu$ lower than the ionic may indicate bidentate co-ordination, and we observe for instance that $\Delta\nu$ = 110 cm^{-1} for compounds **1** and **2** while for the ionic carboxylates the respective differences are 164 for O_2CMe and 140 cm^{-1} for O_2CPh. Noteworthy also is the comparison with $[Ti(\eta\text{-}C_5Me_5)_2(O_2CPh)_2]$ ($\Delta\nu$ = 292 cm^{-1}) in which both benzoato groups are bonded in a unidentate fashion.[5] In complex **3** the asymmetric vibration cannot be assigned unequivocally but $\Delta\nu$ is not greater than 80 cm^{-1}. Thus, bidentate carboxylate groups are indicated by IR spectroscopy, as confirmed by the X-ray analysis discussed below. In solution the ^1H NMR spectra of compounds **1**–**3** show one C_5Me_5 peak along with the corresponding carboxylate R signals, shifted with respect to the free acid as expected (see Experimental section).

If the $[Ti(\eta\text{-}C_5Me_5)Me_3]$:$HO_2CR$ molar ratio is lowered to 1:2 or 1:1 the bis- and mono-carboxylates **4** and **5**, which could be formed according to equation (2), cannot be isolated in a pure state whichever of the three carboxylic acids tested is used. Instead, a mixture of the mono-, bis-and tris-carboxylates along with some unreacted starting product seems to be formed and it cannot be separated by fractional crystallization. Monitoring the addition of the acid by ^1H NMR spectroscopy shows how different C_5Me_5 and MeTi peaks appear immediately after the addition of the first amounts of acid. This would indicate that the Ti–Me bonds in the starting trimethyl derivative and in the di- and mono-methyl carboxylates are similarly reactive

$$[Ti(\eta\text{-}C_5Me_5)Me_3] + n\,HO_2CR \longrightarrow [Ti(\eta\text{-}C_5Me_5)Me_{3-n}(O_2CR)_n] + n\,CH_4 \quad (2)$$

4 n = 2
5 n = 1

* Tris(benzoato-κO,O')(η-pentamethylcyclopentadienyl)titanium(IV) and tetrakis(μ-benzoato-κO:κO')-bis[(η-pentamethylcyclopentadienyl)titanium(III)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

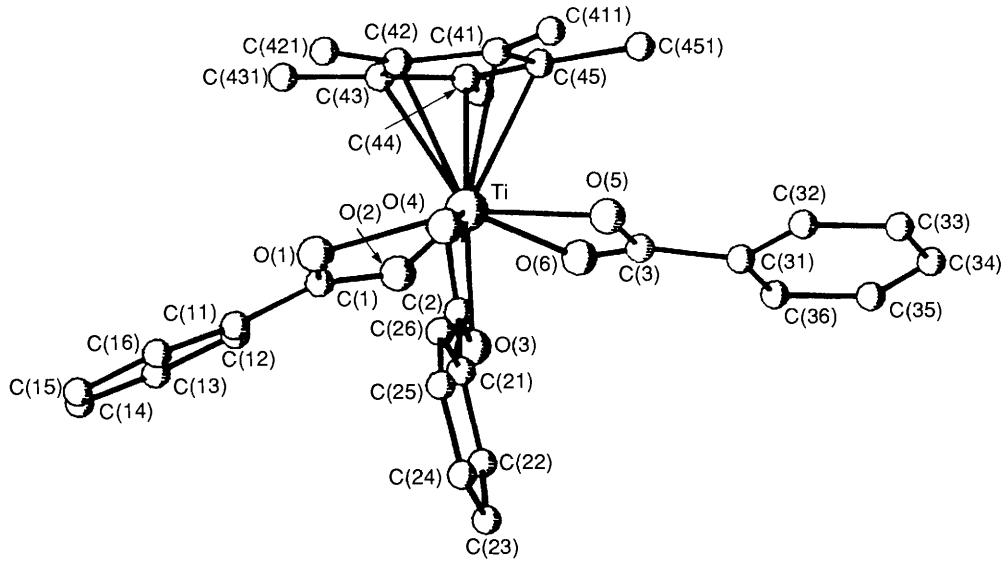

Fig. 1 The molecular structure of complex **2**, showing the crystallographic numbering scheme

Table 1 Atomic coordinates for compound **2**

Atom	*X/a*	*Y/b*	*Z/c*
Ti	0.638 10(12)	0.246 42(15)	0.539 61(9)
O(1)	0.815 02(52)	0.217 21(43)	0.591 21(39)
O(2)	0.712 98(57)	0.103 55(46)	0.534 77(39)
C(1)	0.806 93(81)	0.130 53(70)	0.570 21(50)
C(11)	0.902 72(77)	0.057 03(66)	0.587 22(50)
C(12)	0.877 63(90)	−0.042 00(75)	0.581 19(62)
C(13)	0.966 80(116)	−0.109 04(86)	0.597 86(69)
C(14)	1.078 13(130)	−0.078 10(109)	0.619 45(74)
C(15)	1.102 28(89)	0.020 13(102)	0.627 77(65)
C(16)	1.012 81(103)	0.088 55(88)	0.610 45(75)
O(3)	0.759 43(52)	0.283 29(44)	0.446 44(38)
O(4)	0.718 35(59)	0.384 40(46)	0.540 44(44)
C(2)	0.771 58(77)	0.366 93(75)	0.477 29(51)
C(21)	0.843 85(76)	0.444 02(71)	0.437 72(55)
C(22)	0.895 02(93)	0.427 27(85)	0.366 66(60)
C(23)	0.961 63(99)	0.499 75(114)	0.328 36(72)
C(24)	0.977 29(108)	0.587 69(103)	0.370 10(91)
C(25)	0.928 53(88)	0.604 12(77)	0.439 64(74)
C(26)	0.860 35(85)	0.532 82(73)	0.474 59(57)
O(5)	0.528 98(54)	0.332 85(48)	0.459 27(42)
O(6)	0.541 32(54)	0.176 37(48)	0.447 62(40)
C(3)	0.498 63(68)	0.257 50(86)	0.421 34(43)
C(31)	0.406 66(71)	0.259 57(85)	0.359 91(47)
C(32)	0.342 64(101)	0.344 91(73)	0.348 56(66)
C(33)	0.248 42(104)	0.345 48(89)	0.295 72(68)
C(34)	0.218 15(93)	0.263 24(107)	0.255 96(63)
C(35)	0.281 63(103)	0.179 12(87)	0.265 92(65)
C(36)	0.375 01(89)	0.177 28(75)	0.318 34(54)
C(41)	0.501 41(95)	0.327 69(74)	0.625 92(64)
C(42)	0.597 54(93)	0.293 96(81)	0.671 77(63)
C(43)	0.593 35(97)	0.190 68(81)	0.671 36(64)
C(44)	0.499 16(85)	0.159 88(72)	0.624 79(64)
C(45)	0.440 56(69)	0.243 72(85)	0.595 31(42)
C(411)	0.463 71(115)	0.431 68(77)	0.610 32(75)
C(421)	0.681 86(101)	0.357 86(97)	0.717 36(71)
C(431)	0.669 26(113)	0.127 08(99)	0.722 23(71)
C(441)	0.463 23(95)	0.056 20(80)	0.608 87(72)
C(451)	0.325 39(75)	0.243 93(98)	0.551 91(56)

towards acid, and even at low temperatures the selectivity cannot be improved.

A surprising result is observed when the reactions (2) are carried out in direct sunlight. Under these conditions, the orange to red solutions of the methyl carboxylate mixtures darken gradually and turn green (R = Me) or violet (R = Ph or *p*-$MeOC_6H_4$) at the same time as a crystalline precipitate of the same colour is formed. Methane is detected in the gas phase by gas chromatography–mass spectrometry (GC-MS), even if the CH_4 first produced in reaction (2) is evacuated. The crystalline deep green or violet products so formed are sparingly soluble in the common organic solvents and they are the dimeric titanium(III) carboxylates $[\{Ti(\eta\text{-}C_5Me_5)(O_2CR)_2\}_2]$ **6** (R = Me), **7** (R = Ph) and **8** (R = *p*-$MeOC_6H_4$) in which the four O_2CR groups bridge both $Ti(C_5Me_5)$ fragments. Their IR spectra show higher values of $\Delta\nu$ compared to **1**–**3**: 183, 170 and 180 cm^{-1} for **6**, **7** and **8** respectively. Although two titanium(III) centres are present in these molecules, a weak paramagnetism is observed; their molar susceptibilities are below 150 × 10^{-6} cm^3 mol^{-1} (0.6 BM) and the most soluble of them **8** gives a featureless ESR signal at 3404 G (0.3404 T) with g_{av} = 1.7744. This behaviour has been previously observed for related titanium(III) and vanadium(III) carboxylates $[\{M(\eta\text{-}C_5H_5)(O_2CR)_2\}_2]$ and has been attributed to a superexchange mechanism through the π system of the carboxylate bridging groups.[6,7] A metal–metal interaction must be excluded in our case because of the long Ti · · · Ti separation (see below).

X-Ray Structure of $[Ti(\eta\text{-}C_5Me_5)(O_2CPh)_3]$ **2**.—Fig. 1 shows a perspective of the molecular structure of **2**, Table 1 the atomic coordinates and Table 2 the most relevant distances and angles. The three carboxylate groups bind in a bidentate fashion to the metal atom and the Ti–O bond distances range from 2.095(6) to 2.206(6) Å with a mean value of 2.152 Å. The geometry around the metal atom can be described as a distorted pentagonal bipyramid, oxygen atoms O(1), O(2), O(4), O(5) and O(6) forming the equatorial plane with a maximum deviation of 0.09 Å; the Ti atom is 0.50 Å from that best plane. The oxygen pentagon is not regular as two O–Ti–O angles are smaller because of the OCO bites, but otherwise the pairs O(1)–O(2), belonging to the same benzoate group, and O(5)–O(6) from a second benzoate, are rather symmetrically disposed in relation to O(4) (Fig. 2). The centroid of the C_5Me_5 ring and the O(3) atom, which together with O(4) corresponds to the third benzoate, define the axial positions of the pentagonal bipyramid; the chelate nature of the benzoate ligand again imposes asymmetry at the axial sites and O(3) is not on the centroid (Cp)–titanium axis, the angle Cp–Ti–O being 167.2(2)°. The cyclopentadienyl C–Ti distances range between 2.39(1) and 2.44(1) Å with a mean value of 2.42 Å, the Ti–Cp distance is 2.103 Å and all these data reveal that the C_5Me_5 ring is situated slightly farther from the metal atom than in the

Table 2 Selected bond distances (Å) and angles (°) for compound **2**

Ti–O(1)	2.206(6)	O(1)–C(1)	1.244(11)
Ti–O(2)	2.133(6)	O(1)–C(1)	1.268(11)
Ti–O(3)	2.158(6)	O(1)–C(11)	1.501(12)
Ti–O(4)	2.095(6)	O(3)–C(2)	1.269(11)
Ti–O(5)	2.185(6)	O(4)–C(2)	1.258(11)
Ti–O(6)	2.135(6)	C(2)–C(21)	1.495(13)
Ti–C(41)	2.405(10)	O(5)–C(3)	1.265(12)
Ti–C(42)	2.395(10)	O(6)–C(3)	1.291(12)
Ti–C(43)	2.430(11)	C(3)–C(31)	1.469(10)
Ti–C(44)	2.444(10)	Ti(1)–Cp	2.103
Ti–C(45)	2.416(7)		
O(1)–Ti–O(2)	59.6(2)	O(1)–C(1)–O(2)	118.3(8)
O(3)–Ti–O(4)	61.4(2)	O(3)–C(2)–O(4)	118.5(8)
O(5)–Ti–O(6)	59.9(2)	O(5)–C(3)–O(6)	115.2(7)
O(1)–Ti–O(4)	77.0(2)	Cp–Ti–O(1)	102.5(2)
O(4)–Ti–O(5)	75.7(2)	Cp–Ti–O(2)	104.3(2)
O(6)–Ti–O(2)	75.9(2)	Cp–Ti–O(4)	105.8(2)
Cp–Ti–O(3)	167.2(2)	Cp–Ti–O(5)	100.3(2)
Cp–Ti–O(6)	105.9(2)		

Cp is the centroid of the cyclopentadienyl ring.

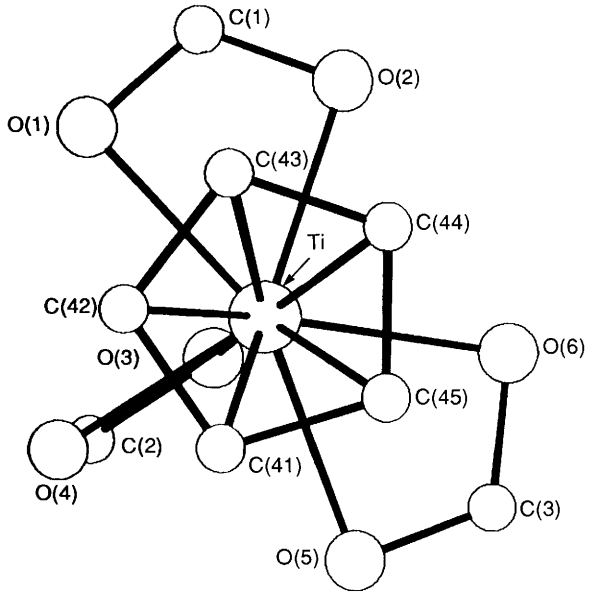

Fig. 2 Projection of complex **2** on the equatorial co-ordination plane

more electron-deficient mono(pentamethylcyclopentadienyl)-titanium(IV) alkyls, halides and oxides in which, for instance, the Ti–Cp distances are found between 2.04 and 2.07 Å,[8–10] with the exception of the crowded $[\{Ti(\eta\text{-}C_5Me_5)(CH_2SiMe_3)_2\}_2O]$ in which it amounts to 2.159 Å.[11] The angles between the C_5Me_5 centroid, the Ti atom and the equatorial oxygens are between 100.3(2) and 105.9(2)°, and this makes also a difference with respect to the unsaturated derivatives referred to above, in which the centroid–titanium–substituent angles are wider (110–120°). The internal lengths and angles within the pentamethylcyclopentadienyl and benzoate ligands deserve no special comments; the C–O distances in the latter are all rather similar, being between 1.24(1) and 1.29(1) Å.

Complex **2** is one of the few 18-electron titanium monocyclopentadienyls structurally characterized; the tris(dithiocarbamate) $[Ti(\eta\text{-}C_5H_5)(S_2CNMe_2)_3]$, with a similar structure to **2**, is another high-valance example[12] and some low-valence carbonylate anions such as $[Ti(\eta\text{-}C_5H_5)(CO)_4]^-$ and $[Ti(\eta\text{-}C_5H_5)H(CO)_2(dmpe)]^-$ (dmpe = $Me_2PCH_2CH_2PMe_2$) have recently been reported.[13,14]

X-Ray Structure of $[\{Ti(\eta\text{-}C_5Me_5)(O_2CMe)_2\}_2]$ **6**.—A view of the structure appears in Fig. 3, Table 3 lists the atomic coordinates and Table 4 some relevant bond lengths and angles. Although the crystals gave some problems at the refinement stage the data obtained allow some conclusions to be drawn. The molecule has a symmetry centre and consists of two $Ti(C_5Me_5)$ fragments bonded through four acetato groups which are situated in two mutually perpendicular planes [90(1)°] which in turn are also nearly perpendicular to the C_5Me_5 best planes: 89(1) and 86(1)°. The Ti • • • Ti separation is 3.660(7) Å, very similar to that of the related $[\{Ti(\eta\text{-}C_5H_5)(O_2CCPh)_2\}_2]$,[15] and any metal–metal interaction should be excluded. The geometry about each Ti atom is of the four-legged piano-stool type and the Ti–O distances vary from 2.03(2) to 2.05(3) Å with a mean value of 2.04 Å, slightly lower than in **2**; the four oxygen atoms bonded to the metal lie in a plane which is almost parallel to the C_5Me_5 best plane. The mean ring C–Ti distance of 2.31 Å is also *ca.* 0.1 Å shorter than in **2** and these shorter lengths might be related to the electronic unsaturation of **6** relative to **2**. The centroid–titanium–oxygen angles have values between 109 and 112°.

The internal parameters of the C_5Me_5 ring deserve no special mention. The wider O–C–O angles of the acetato groups in comparison with the benzoate group of **2** should be mentioned: the mean values are 126° in **6** and 119.6° in **2** and this difference is undoubtedly related to the bridging *vs.* chelate nature.

Table 3 Atomic coordinates for compound **6**

Atom	*x*	*y*	*z*
Ti(1)	0.9629(8)	0.1515(7)	0.8352(6)
O(1)	0.8048(32)	−0.0576(35)	0.8395(29)
O(2)	1.1604(33)	0.2420(31)	0.9686(29)
O(3)	0.8172(33)	0.1718(33)	0.9265(30)
O(4)	1.1405(29)	0.0101(31)	0.8758(24)
C(6)	0.7699(56)	−0.1922(57)	0.9126(48)
C(7)	0.7931(56)	0.1013(56)	1.0340(47)
C(1)	1.0163(79)	0.2625(69)	0.6331(52)
C(2)	1.0433(77)	0.3773(66)	0.6807(53)
C(3)	0.9023(75)	0.4065(63)	0.6862(50)
C(4)	0.7760(65)	0.2871(58)	0.6379(45)
C(5)	0.8571(70)	0.2098(61)	0.6166(48)
C(11)	1.1643(135)	0.2429(118)	0.6172(97)
C(21)	1.1878(148)	0.4882(137)	0.7234(108)
C(31)	0.7881(139)	0.4818(133)	0.7092(106)
C(41)	0.5927(104)	0.2206(90)	0.6039(73)
C(51)	0.8136(105)	0.0726(104)	0.5566(80)
C(61)	0.6307(46)	−0.3006(43)	0.8501(34)
C(71)	0.6669(60)	0.1715(54)	1.0523(44)

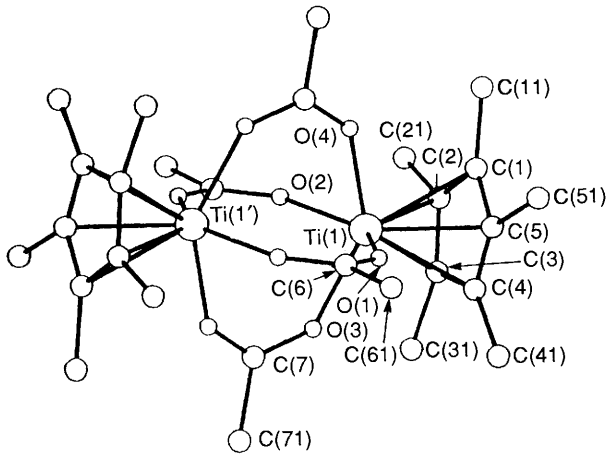

Fig. 3 The molecular structure of complex **6**, showing the crystallographic numbering scheme

Table 4 Selected bond distances (Å) and angles (°) for compound **6**

Ti(1)–O(1)	2.03(2)	O(3)–C(7)	1.24(6)
Ti(1)–O(2)	2.05(2)	C(6)–C(61)	1.49(5)
Ti(1)–O(3)	2.04(4)	C(7)–C(71)	1.52(9)
Ti(1)–O(4)	2.05(3)	Ti(1)–Cp	2.00
O(1)–C(6)	1.23(5)	Ti(1)···Ti(1′)	3.660(7)
O(1)–Ti(1)–O(2)	136(1)	Cp–Ti(1)–O(1)	111
O(1)–Ti(1)–O(3)	81(1)	Cp–Ti(1)–O(2)	111
O(1)–Ti(1)–O(4)	81(1)	Cp–Ti(1)–O(3)	112
O(2)–Ti(1)–O(4)	82(1)	Cp–Ti(1)–O(4)	109
O(3)–Ti(1)–O(4)	138(1)	O(4)–C(7)–O(4′)	128(5)
O(2)–Ti(1)–O(3)	83(1)	O(1)–C(6)–O(2′)	124(4)

Primed atoms are at $-x + 2, -y, -z + 2$.

Experimental

All manipulations were carried out under nitrogen using conventional Schlenk techniques. The solvents were refluxed over the following drying agents and distilled in a nitrogen atmosphere: toluene, Na; hexane, Na/K amalgam; tetrahydrofuran (thf) and diethyl ether, sodium–benzophenone. The carboxylic acids were purified as follows: HO_2CPh, sublimation; $HO_2CC_6H_4OMe$-*p*, recrystallization in toluene; HO_2CMe, refluxing with acetic anhydride over CrO_3 and distillation. The compound [Ti(η-C_5Me_5)Me_3] was prepared by a literature method.[1] Carbon and hydrogen analysis were done in a Perkin-Elmer 240B microanalyser. Infrared spectra were recorded as Nujol and Florolube mulls in a Perkin-Elmer 883 spectrometer, ^{1}H NMR spectra on a Varian FT80A spectrometer and ESR measurements were done in thf solution at room temperature in a Bruker ESP 200 spectrometer.

Preparations.—[Ti(η-C_5Me_5)(O_2CMe)$_3$] **1**. To an ice-cooled solution of [Ti(η-C_5Me_5)Me_3] (1.8 g, 7.98 mmol) in hexane (150 cm^3) was added dropwise acetic acid (1.35 cm^3, 23.69 mmol) in diethyl ether (5 cm^3). The mixture was warmed to room temperature and left to stir for 1 h, then slightly concentrated *in vacuo* to eliminate the ether. The yellow precipitate was then collected by filtration and recrystallized from toluene–hexane. Yield 77% (Found: C, 53.3; H, 6.9. Calc. for $C_{16}H_{24}O_6Ti$: C, 53.4; H, 6.7%). IR: ν_{asym}(OCO) 1540, ν_{sym}(OCO) 1430 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.99 (15 H, C_5Me_5) and 1.83 (3 H, O_2CMe).

[Ti(η-C_5Me_5)(O_2CPh)$_3$] **2**. This was obtained as above from HO_2CPh (3.2 g, 26.32 mmol) in diethyl ether (75 cm^3) and [Ti(η-C_5Me_5)Me_3] (2 g, 8.77 mmol) in hexane (100 cm^3). Yield 80% (Found: C, 68.0; H, 5.2. Calc. for $C_{31}H_{30}O_6Ti$: C, 68.1; H, 5.5%). IR: ν_{asym}(OCO) 1530, ν_{sym}(OCO) 1420 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.12 (C_5Me_5), 6.96 and 8.10 (m, Ph).

[Ti(η-C_5Me_5)($O_2CC_6H_4OMe$-*p*)$_3$] **3**. This can also be obtained in a similar way from $HO_2CC_6H_4OMe$-*p* (4.4 g, 28.96 mmol) in ether (75 cm^3) and [Ti(η-C_5Me_5)Me_3] (2.2 g, 9.65 mmol) in hexane (150 cm^3). Yield 82% (Found: C, 63.9; H, 5.5. Calc. for $C_{34}H_{36}O_9Ti$: C, 64.2; H, 5.7%) IR ν_{asym}(OCO) overlapped, ν_{sym}(OCO) 1430 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.22 (15 H, C_5Me_5), 3.10 (3 H, OMe), 6.56 [d, ^2J(HH) = 9, C_6H_4], and 8.13 [d, ^2J(HH) = 9 Hz, C_6H_4].

[{Ti(η-C_5Me_5)(O_2CMe)$_2$}$_2$] **6**. Acetic acid (0.77 cm^3, 13.16 mmol) in ether (5 cm^3) was added dropwise to a solution of [Ti(η-C_5Me_5)Me_3] (2 g, 8.77 mmol) in hexane (150 cm^3) and the resulting orange solution was then water-cooled and exposed to direct sunlight for 5–6 h. The green crystalline solid precipitated was filtered off and recrystallized from toluene–hexane. Yield 45% (Found: C, 55.3; H, 7.1. Calc. for $C_{28}H_{42}O_8Ti_2$: C, 55.8; H, 7.0%). IR: ν_{asym}(OCO) 1613, ν_{sym}(OCO) 1430 cm^{-1}.

[{Ti(η-C_5Me_5)(O_2CPh)$_2$}$_2$] **7**. This can be obtained as above from benzoic acid (0.8 g, 6.58 mmol) in ether (30 cm^3) and [Ti(η-C_5Me_5)Me_3] (1 g, 4.38 mmol) in hexane (60 cm^3) and recrystallized from toluene. Yield 40% (Found: C, 67.3; H, 6.0. Calc. for $C_{48}H_{50}O_8Ti_2$: C, 67.8; H, 5.6%). IR: ν_{asym}(OCO) 1555, ν_{sym}(OCO) 1385 cm^{-1}.

[{Ti(η-C_5Me_5)($O_2CC_6H_4OMe$-*p*)$_2$}$_2$] **8**. This was obtained by the same procedure from *p*-methoxybenzoic acid (1 g, 6.58 mmol) in ether (40 cm^3) and [Ti(η-C_5Me_5)Me_3] (1 g, 4.38 mmol) in hexane (60 cm^3) and recrystallized from toluene–hexane. Yield 40% (Found: C, 64.4; H, 6.1. Calc. for $C_{52}H_{53}O_{12}Ti_2$: C, 64.3; H, 6.0%). IR ν_{asym}(OCO) 1560, ν_{sym}(OCO) 1380 cm^{-1}.

Table 5 Crystal and experimental data for the X-ray structure determinations *

	2	**6**
Formula	$C_{31}H_{30}O_6Ti$	$C_{28}H_{42}O_8Ti_2$
M	546.47	602.43
Symmetry	Monoclinic	Triclinic
Crystal dimensions/mm	0.4 × 0.3 × 0.25	0.28 × 0.20 × 0.20
Space group	$P2_1/c$	$P\bar{1}$
a/Å	11.221(1)	8.612(9)
b/Å	13.710(1)	9.201(8)
c/Å	17.080(1)	11.818(9)
α/°		65.86(1)
β/°	90.21(2)°	114.04(2)
γ/°		105.59(2)
U/Å^3	2627.6(3)	774(1)
Z	4	1
D_c/g cm^{-3}	1.38	1.29
F(000)	1144	318
μ/cm^{-1}	3.62	5.50
Number of reflections:		
Independent	6523	4510
observed [$I > 3\sigma(I)$]	2276	662
Range of *hkl*	−14 0 0 to 14 18 22	−13 −14 0 to 13 14 18

* Details in common: prismatic crystal; unit-cell parameters determined by least-squares fit from 25 reflections with $\theta < 25°$; Enraf-Nonius CAD-4 four-circle diffractometer, bisecting geometry, graphite-oriented monochromator; Mo-Kα radiation; ω–2θ scans; two standard reflections every 100, no variation.

Crystal Structure determinations.—The crystallographic and experimental data for the X-ray crystal structure determinations of compounds **2** and **6** are collected in Table 5. For both compounds data were collected at room temperature with the crystals sealed in Lindemann tubes under a nitrogen atmosphere. Intensities were corrected for Lorentz and polarization effects in the usual manner. No extinction corrections were made. The structures were solved by a combination of direct methods and Fourier synthesis.

The structure of compound **2** was refined (on *F*) by full-matrix least-squares calculations. Before refining all the non-hydrogen atoms anisotropically, an empirical absorption correction was made by the Walker and Stuart method.[16] All the non-hydrogen atoms were refined anisotropically. In the later stages of refinement the hydrogen atoms were included in geometric calculations with fixed positions and thermal parameters.

Final values of $R = 0.075$ and $R' = 0.069$ (weighting scheme: empirical fit so as to give no trends in $< w\Delta^2F >$ *vs.* $< F_o >$ and *vs.* $< \sin\theta/\lambda >$ were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from ref. 17. Calculations were performed with the system X-RAY 80[18] and the programs MULTAN,[19] DIRDIF,[20] PARST[21] and PESOS[22] on a VAX-11750 computer.

The refinement of the structure of compound **6** presented serious problems because of the scarce number of data obtained

from the only poor quality single crystal available after several attempts at crystallization. The high values of the thermal parameters indicate disorder; the structure was also refined in the space group $P1$ in an attempt to avoid these problems, but the final results were not improved. We decided finally to refine anisotropically only the Ti and O atoms and left the C atoms with isotropic thermal parameters; the H atoms were fixed. The final values of $R = 0.14$ and $R' = 0.16$ are not good, but allowed us to ascertain the dimeric nature of the compound. The programs used were as above for the structure of **2**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Financial support from Comisión Interministerial de Ciencia y Tecnologia (PB87-0756) and the EEC[SCI/0137-C(AM)] is gratefully acknowledged.

References

1 M. Mena, M. A. Pellinghelli, P. Royo, R. Serrano and A. Tiripicchio, *J. Chem. Soc., Chem. Commun.*, 1986, 1118.
2 M. Mena, P. Royo, R. Serrano, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1989, **8**, 476.
3 *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, 1982, vol. 3, pp. 300, 348.
4 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
5 D. M. Hoffman, N. D. Chester and R. C. Fay, *Organometallics*, 1983, **2**, 48.
6 R. P. S. Coutts, R. L. Martin and P. C. Wailes, *Aust. J. Chem.*, 1973, **26**, 941.
7 G. M. Larin, V. T. Kalinnikov, G. G. Aleksandrov, Y. T. Struchkov, A. A. Panskii and N. E. Kolobova, *J. Organomet. Chem.*, 1971, **27**, 53.
8 M. P. Gómez Sal, M. Mena, P. Royo, and R. Serrano, *J. Organomet. Chem.*, 1988, **358**, 147 and refs. therein.
9 R. Serrano, J. C. Flores, P. Royo, M. Mena, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1989, **8**, 1404.
10 F. Palacios, P. Royo, R. Serrano, J. L. Balcázar, I. Fonseca and F. Florencio, *J. Organomet. Chem.*, 1989, **375**, 51.
11 M. P. Gómez-Sal, M. Mena, F. Palacios, P. Royo, R. Serrano and S. Martinez-Carreras, *J. Organomet. Chem. 1989*, **375**, 59.
12 W. L. Steffen, H. K. Chun and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 3493.
13 B. E. Kelsey and J. E. Ellis *J. Am. Chem. Soc.*, 1986, **108**, 1344.
14 S. R. Frerichs, B. K. Stein and J. E. Ellis, *J. Am. Chem. Soc.*, 1987, **109**, 5558.
15 T. N. Tarkhova, E. A. Gladkikh, I. A. Grishim, A. N. Linera and W. Khalmanov, *Zh. Strukt. Khim.*, 1976, **17**, 1052.
16 A. Walker and J. Stuart, DIFABS, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
18 J. M. Stewart, F. A. Kundell and J. C. Baldwin, The X-Ray 80 system, Computer Science Center, University of Maryland, 1980.
19 P. Main, S. E. Fiske, S. L. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, MULTAN, Universities of York and Louvain, 1980.
20 P. T. Beurskens, W. P. Bossman, H. M. Doesburg, R. O. Gould, T. E. M. van der Hark, P. A. J. Prick, J. H. Noordick, G. Beurskens and V. Parthasarathi, DIRDIF, Manual 81, Tech. Rep. 1981/82, University of Nijmegen, 1981.
21 M. Nardelli, *Comput. Chem.*, 1983, **7**, 96.
22 M. Martínez Ripoll and F. H. Cano, PESOS, Instituto Rocasolano, C.S.I.C. Madrid, 1975.

Received 3rd *October* 1990; *Paper* 0/04461J