



Synthesis and crystal structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-COR})\text{B}(\text{C}_6\text{H}_5)_3\text{CN}]$

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Abstract

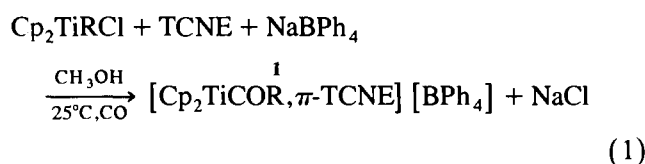
The synthesis, spectroscopic study and X-ray structure determination of η^2 acylcyclopentadienyl complexes of titanium are reported. These complexes, showing an η^2 acyl group, exhibit a zwitterionic character because the anionic $[\text{BPh}_3\text{CN}]$ group is intimately bound to the titanium atom.

Keywords: Titanium; Cyanide; Acyl; Cyclopentadienyl; Nitrile complexes; X-ray structure

1. Introduction

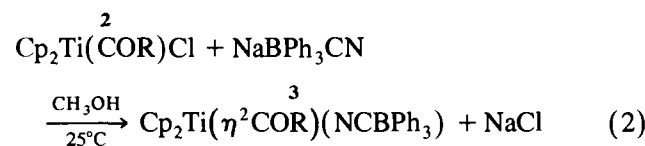
Haloalkyl and haloacyl complexes of titanium have been the subject of extensive research, since activation of the metal–halogen bond may produce species having catalytic activity, for example in the polymerisation of alkenes [1].

In this context [2], we have been interested in the coordination of cyanoalkenes such as tetracyanoethylene (TCNE) with a view to stabilizing the coordinated alkene using the reaction scheme



a: R = Me; b: R = ⁱPr

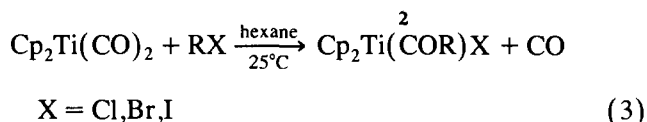
In attempting this reaction, however, we have isolated in quantitative yield an unexpected titanium complex **3** instead of **1**. Supposing that NaBPh_4 reacts with TCNE to give a BPh_3CN ligand (see Table 1), we have envisaged a rational synthesis of **3** using the method



Because of the insolubility of **3** in methanol, the role of this solvent is essential in this reaction.

Complexes such as **3** are air stable zwitterions in which the cationic and anionic fragments are intimately linked (see structure). We describe here their preparation as well as an X-ray structure determination of the CO^iPr derivative. The structure contains pentacoordinate titanium with the acyl group acting as a 3e donor. Though rare, this type of structure has been previously reported in the zirconium series [3,4].

The haloacyldicyclopentadienyl titanium complexes were prepared by oxidative addition of alkyl halide to $\text{Cp}_2\text{Ti}(\text{CO})_2$ [5] according to the reaction



Yields are quantitative. The method differs from that described by Fachinetti and Floriani [6] in which Cp_2TiCl_2 is treated with Grignard reagent, followed by carbonylation. Important spectral data for these complexes are contained in Table 1.

NaBPh_3CN , prepared following the literature process [7] by reaction of NaCN with commercial BPh_3 , was reacted with complex **2** in CH_3OH in equimolar amounts at room temperature for 6 h. After filtration, crystallisation of $\text{Cp}_2\text{Ti}(\text{COR})(\text{NCBPh}_3)$ **3** from CH_2Cl_2 gives clear yellow crystals which are suitable for X-ray structure determination. Important spectral data for these complexes **3** are contained in Tables 1 and 2.

A view [8] of compound **3b** is shown in Scheme 1.

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The nitrogen of the BPh_3CN is bound to titanium ($\text{Ti}-\text{N} = 2.131 \text{ \AA}$); this may be compared with a $\text{Ti}-\text{N}$ distance of 2.170 \AA in other nitrile complexes of titanium [9]. The NCB unit is almost linear ($\alpha = 173.13^\circ$), while the CN distance of 1.145 \AA may be compared with that of 1.124 \AA in the acetonitrile complex [9,10].

The zwitterionic character [11] of the molecule is compatible with the strong binding of the $[\text{BPh}_3\text{CN}]^-$ anion to titanium, and is in accord with the non-conductivity observed in CH_2Cl_2 ($\Lambda = 0.73 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) [12].

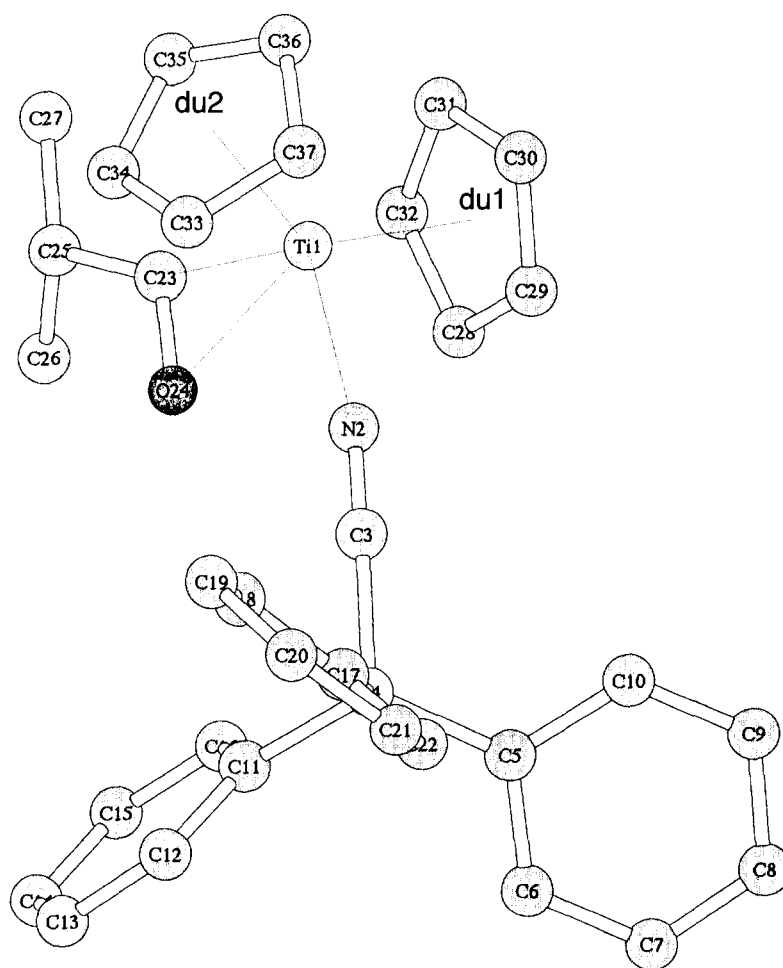
The IR spectrum of complex **3b** in $\text{Py}(d_5)$ is almost identical with the spectrum of the same complex in CH_2Cl_2 (Table 1). As a proof that the compound does not react with pyridine, ether addition to the solution precipitates **3b** unchanged.

With regard to $\eta^2\text{CO}^1\text{Pr}$ ligand [4], the “ η^2 acyl O-inside” geometry may be noted, in total agreement with the work of Hoffmann and coworkers [13]. The $\text{Ti}-\text{C}$ (2.040 \AA), $\text{Ti}-\text{O}$ (2.167 \AA) and $\text{C}-\text{O}$ (1.233 \AA) distances are in accord with a $3e^-$ acyl ligand. The

geometry is tetrahedral, consisting of two Cp ligands, the nitrogen of CN and the acyl carbon. The oxygen is oriented along the $\text{C}_{23}-\text{N}_2$ edge.

2. Spectroscopic properties

The IR spectra of **3a** and **3b** show characteristic absorptions of acyl and nitrile groups. The $\nu_{\text{C}=\text{O}}$ vibration is observed at $1627(\text{s}) \text{ cm}^{-1}$ **3a** and $1613(\text{s}) \text{ cm}^{-1}$ **3b**. The value of $\nu_{\text{C}=\text{O}}$ ($\text{CO}-\text{R}$ group) depends on several factors: (a) the character of R, (b) the charge on the metal atom ($\nu_{\text{CO}/\text{Me}}$ decreases in the series of $\text{Mn}-\eta^1(\text{CO} \cdot \text{CH}_3)(\text{CO})_{5-n}\text{L}_n$ from 1650 to 1550 cm^{-1} (IR hexane solution $\text{L} = \text{PMe}_3$, $\nu_{\text{C}=\text{O}}$ (acetyl group); $n = 0$, 1650 cm^{-1} ; $n = 1$, 1620 cm^{-1} ; $n = 2$, 1590 cm^{-1} , unpublished data of this laboratory)) and (c) the mode of coordination of the acyl group, η^1 or η^2 . Values of 1627 **3a** and 1613 **3b** lie in the characteristic region indicating η^2 coordination of the acyl group in all known cyclopentadienyl Ti^{IV} complexes [13,14].



Scheme 1.

Table 1
Selected IR data

	IR (cm ⁻¹)	
	$\nu_{C=N}$	$\nu_{C=O}$
Cp ₂ Ti(η^2 COMe)I 2a	—	1619(s)
Cp ₂ Ti(η^2 COMe)(NCBPh ₃) 3a	2207(s) ^a	1627(s) ^a
	2203(s) ^b	1627(s) ^b
Cp ₂ Ti(η^2 CO ⁱ Pr)I 2b	—	1605
Cp ₂ Ti(η^2 Co ⁱ Pr)(NCBPh ₃) 3b	2206(s) ^a	1613(s) ^a
	2206(s) ^b	1613(s) ^b
	2203(s) ^c	1613(s) ^c
NCBPh ₃	2168(s) ^c	

^a Fluorolube mulls.^b CH₂Cl₂ solution.^c Py(d₅) solution.

The only η^1 acyl Ti complexes [15] (C₅Me₅)₂TiCO · CH₂ · CH₂ · CHRO R = Me, Et, ⁱPr have $\nu_{\eta^1(C=O)}$ in the range 1611–1594 cm⁻¹ due to the much greater donor character of C₅Me₅ compared with C₅H₅.

The IR spectra of **3a** and **3b** recorded in solid state and in solution (CH₂Cl₂) were identical, indicating that η^2 bonding was preserved in solution. This η^2 bond character was preserved in the IR spectrum even when a ten-fold excess of pyridine was added to a CH₂Cl₂ solution of **3b**.

In the ¹³C NMR spectrum (Table 2), the acyl carbon C₂₃ of **3b** exhibits a resonance at $\delta = 301.4$ ppm. This is the lowest value ever found for an acyl carbon [14], indicating positive charge on the C₂₃ atom. This value is comparable only with carbene carbons in organometallic compounds [16,17]. Hoffman and coworkers [13] have proposed a “carbenium-type” character for η^2 acyl groups in acyl complexes of Group IV metals and

actinides on the basis of crystallographic data and MO calculations.

The IR C≡N frequency in [BPh₃CN] group (Table 1) increases by about 40 cm⁻¹ on coordination in **3a** and **3b**. An increase of $\nu_{C=N}$ in linear C≡N → M groups is characteristic of all nitrile adducts [18,19].

In the ¹³C NMR spectrum, the nitrile carbon atom C₃ resonance at 124(m) ppm is normal for linear nitrile complexes [14]. The broadening of this signal is due to coupling with the ¹⁰B and ¹¹B isotopes of the [BPh₃CN] group.

3. Conclusions

The compound Cp₂Ti(η^2 COⁱPr)BPh₃CN contains an η^2 acyl group whose chemical shift (301.4 ppm) is the most deshielded of any known titanium complex, and is consistent with a significant carbenoid character. This 18e complex is pentacoordinate and zwitterionic, with the nitrogen of the anionic BPh₃CN ligand bound to titanium. Studies of the reactivity of these complexes will be the object of further work.

4. Experimental section

All experiments were carried out under argon. Solvents were distilled from sodium (hexane) or calcium hydride (dichloromethane) or magnesium with 5 Å molecular sieves (methanol).

Infrared spectra were recorded as Nujol mulls or in CH₂Cl₂ on a BOEM MB 100 Michelson spectrometer.

Table 2
¹³C NMR data for **3b**

		C ⁺ D ₂ Cl ₂ without ¹ H-heteronuclear decoupling	CD ₂ Cl ₂ ¹³ C NMR spectrum	CD ₃ C ⁺ OCD ₃ ¹³ C NMR spectrum
CO(t)		301.4	301.1 t	302.1 [†] 206.1
B–C (of Ph)		153(b)	154(b)	156(b)
Ph (C <i>meta</i>)	¹ J _{CH} 155 Hz	133.7 d of t	133.8	135.0
	² J _{CH} 7.2			
Ph (C <i>ortho</i>)	¹ J _{CH} 156 Hz	126.5 d of d	126.7	127.4
	² J _{CH} 7.2			
CN	¹ J _{CH} 159 Hz	124.0 d of t	124.1	124.8
	² J _{CH} 7.2			
Ph (C <i>para</i>)	¹⁰ B and ¹¹ B	117.1 m (w)	117.1	121.1
Cp	¹ J _{CH} 177 Hz	109.0 d of qt	109.1	110.5
	² or ³ J _{CH} 6.0			
		[‡] 53.1		
CH(CH ₃) ₂	¹ J _{CH} 127 Hz	44.4 d of m	44.4	45.4
	² J _{CH} 4.5			
CH(CH ₃) ₂	¹ J _{CH} 130 Hz	18.4 q of m	18.4	18.8
	² or ³ J _{CH} 4.9			

d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, b = broad, w = weak.

NMR spectra were measured on a Bruker AM 250 instrument.

Conductivities were determined using a Philips GM4249/01 and cells GM 4221. Elemental analyses were carried out by CNRS Laboratory. $\text{Cp}_2\text{Ti}(\text{CO})_2$ and NaBPh_3CN were made according to known procedures. All other reagents were used as purchased.

$\text{Cp}_2\text{Ti}(\eta^2\text{COMe})\text{I}$ (**2a**): a solution of 1 g (0.0043 mol) $\text{Cp}_2\text{Ti}(\text{CO})_2$ in 25 ml hexane was treated with 1.3 g (0.01 mol) of CH_3I at room temperature and the mixture stirred for 1 h. During this time CO was evolved and a brown powder was separated by filtration (yield 100%).

For IR data see Table 1.

$\text{Cp}_2\text{Ti}(\eta^2\text{CO}^i\text{Pr})\text{I}$ (**2b**): this product was made as for **2a** using I^iPr (yield 100%).

For IR data see Table 1.

$\text{Cp}_2\text{Ti}(\eta^2\text{COMe})(\text{NCBPh}_3)$ (**3a**): a solution of 0.5 g (0.0015 mol) $\text{Cp}_2\text{Ti}(\eta^2\text{COMe})\text{I}$ in 10 ml of CH_3OH was mixed at room temperature with a solution of 1 g (0.003 mol) of NaBPh_3CN in 10 ml of methanol. After 12 h, light yellow crystals stable in air were filtered (yield 90%).

For IR data see Table 1.

Anal. Found: C, 76.09; H, 5.69. $\text{C}_{31}\text{H}_{28}\text{BNOTi}$ Calc.: C, 76.13; H, 5.72%.

Table 3
Relevant crystallographic data for compound **3a**

Formula	$\text{C}_{33}\text{H}_{32}\text{BNOTi}$
FW	517.34
Crystal dimensions (mm ³)	0.10 × 0.10 × 0.50
Color	Light yellow
Space group	$P\bar{1}$
<i>a</i> (Å)	10.663(4)
<i>b</i> (Å)	12.264(7)
<i>c</i> (Å)	12.415(9)
α (deg)	94.91(5)
β (deg)	106.36(5)
γ (deg)	113.67(4)
<i>V</i> (Å ³)	1389.9(24)
<i>Z</i>	2
Temperature (°C)	20
Monochromator	Graphite
$\lambda(\text{Mo K}\alpha)$ (Å)	0.71069
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	3.35
<i>d</i> _{calc} (g cm ⁻³)	1.27
2 θ range (deg)	1 < 2 θ < 23
Scan width (deg)	0.80 + 0.34 tan θ
Scan speed (deg min ⁻¹)	1.83 ≪ 5.5
Diffractionmeter	Enraf-Nonius CAD4
No. of reflections collected	4235
No. of unique reflections	3862
No. of reflections with <i>I</i> > 3 σ (<i>I</i>)	1057
<i>R</i>	0.0675
<i>R</i> _w	0.0742

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w(F_c)^2} \right]^{1/2}$$

Table 4
Atomic coordinates of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-COR})\text{B}(\text{C}_6\text{H}_5)_3\text{CN}]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ti(1)	0.3827(4)	0.3432(3)	0.1869(3)	0.0656
N(2)	0.384(1)	0.517(1)	0.183(1)	0.0567
C(3)	0.368(1)	0.604(1)	0.188(1)	0.0413
C(5)	0.496(2)	0.843(1)	0.275(1)	0.0518
C(6)	0.505(2)	0.942(2)	0.344(2)	0.0720
C(7)	0.636(2)	1.043(2)	0.399(2)	0.0811
C(8)	0.763(2)	1.051(2)	0.391(2)	0.0823
C(9)	0.760(2)	0.955(2)	0.322(2)	0.0671
C(10)	0.629(2)	0.855(2)	0.266(1)	0.0662
C(11)	0.223(2)	0.697(1)	0.265(1)	0.0235
C(12)	0.112(2)	0.729(2)	0.235(1)	0.0596
C(13)	0.014(2)	0.706(2)	0.293(2)	0.0859
C(14)	0.024(2)	0.650(2)	0.380(2)	0.0705
C(15)	0.136(2)	0.616(2)	0.415(2)	0.0876
C(16)	0.236(2)	0.641(2)	0.356(2)	0.0756
C(17)	0.275(2)	0.737(1)	0.068(1)	0.0534
C(18)	0.159(2)	0.640(2)	-0.016(1)	0.0620
C(19)	0.096(2)	0.642(2)	-0.128(2)	0.0835
C(20)	0.149(2)	0.755(2)	-0.158(1)	0.0569
C(21)	0.263(2)	0.855(2)	-0.080(2)	0.0714
C(22)	0.324(2)	0.851(1)	0.029(2)	0.0673
C(23)	0.260(2)	0.254(2)	0.280(2)	0.0818
C(25)	0.181(3)	0.155(2)	0.335(2)	0.1073
C(26)	0.182(3)	0.204(2)	0.443(2)	0.1217
C(27)	0.198(3)	0.050(2)	0.319(3)	0.1430
C(28)	0.575(2)	0.451(2)	0.365(2)	0.1093
C(29)	0.627(2)	0.487(2)	0.275(2)	0.0890
C(30)	0.625(2)	0.394(3)	0.209(2)	0.1208
C(31)	0.573(3)	0.291(2)	0.255(3)	0.1223
C(32)	0.542(2)	0.326(2)	0.351(2)	0.0991
C(33)	0.205(4)	0.303(3)	0.009(3)	0.1442
C(34)	0.158(3)	0.210(4)	0.048(3)	0.1201
C(35)	0.242(4)	0.154(2)	0.049(2)	0.1383
C(36)	0.349(3)	0.216(3)	0.017(2)	0.1221
C(37)	0.329(4)	0.319(2)	-0.007(2)	0.1098
B(4)	0.345(2)	0.728(2)	0.204(2)	0.0435
O(24)	0.248(1)	0.350(1)	0.287(1)	0.0819
Du1	0.2566	0.2404	0.0232	
Du2	0.5884	0.3898	0.2910	

$\text{Cp}_2\text{Ti}(\eta^2\text{CO}^i\text{Pr})(\text{NCBPh}_3)$ (**3b**): this product was made as for **3a** using 0.5 g (0.0013 mol) of $\text{Cp}_2\text{Ti}(\eta^2\text{CO}^i\text{Pr})\text{I}$ and 0.7 g (0.0026 mol) of NaBPh_3CN in 10 ml of methanol (yield 100%).

For IR and ¹³C NMR data see Tables 1 and 2.

Anal. Found: C, 76.85; H, 6.09; Ti, 9.58. $\text{C}_{33}\text{H}_{32}\text{BNOTi}$ Calc.: C, 76.67; H, 6.19; Ti, 9.26%.

¹H NMR (250 MHz, acetone): δ (ppm) 7.35, 7.34, 7.11, 7.06, 7.05 (m, $\text{B}(\text{C}_6\text{H}_5)_3$), 5.91 (s, C_5H_5), 3.34 (hept, CH), 1.55, 1.53 (d, $(\text{CH}_3)_2$).

Recrystallisation of the crude product from CH_2Cl_2 gave crystals suitable for X-ray structure determination.

$\text{Cp}_2\text{Ti}(\eta^2\text{CO}^i\text{Pr})(\text{NCBPh}_3)$ could also be obtained by mixing 0.5 g (0.0013 mol) of $\text{Cp}_2\text{Ti}(\eta^2\text{CO}^i\text{Pr})\text{I}$ in 20 ml of methanol with a solution of 0.17 g (0.0013 mol) of TCNE and 0.88 g (0.0026 mol) of NaBPh_4 in

Table 5
 $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-COR})\text{B}(\text{C}_6\text{H}_5)_3\text{CN}]$, bonds and angles

Ti(1)–N(2)	2.13(1)	Ti(1)–O(24)	2.17(1)			
Ti(1)–C(23)	2.04(2)					
Ti(1)–C(28)	2.37(2)	Ti(1)–C(33)	2.33(3)			
Ti(1)–C(29)	2.34(2)	Ti(1)–C(35)	2.38(2)			
Ti(1)–C(30)	2.33(2)	Ti(1)–C(34)	2.33(3)			
Ti(1)–C(31)	2.33(2)	Ti(1)–C(36)	2.35(2)			
Ti(1)–C(32)	2.35(2)	Ti(1)–C(37)	2.27(2)			
C(3)–B(4)	1.64(2)	C(5)–B(4)	1.59(2)			
C(11)–B(4)	1.62(2)	C(17)–B(4)	1.67(2)			
N(2)–C(3)	1.14(2)	C(5)–C(6)	1.37(2)			
C(5)–C(10)	1.40(2)	C(6)–C(7)	1.37(2)			
C(7)–C(8)	1.35(2)	C(8)–C(9)	1.38(2)			
C(9)–C(10)	1.37(2)	C(11)–C(12)	1.36(2)			
C(11)–C(16)	1.38(2)	C(12)–C(13)	1.38(2)			
C(13)–C(14)	1.34(2)	C(14)–C(15)	1.38(2)			
C(15)–C(16)	1.41(2)	C(17)–C(18)	1.38(2)			
C(17)–C(22)	1.46(2)	C(18)–C(19)	1.37(2)			
C(19)–C(20)	1.40(2)	C(20)–C(21)	1.36(2)			
C(21)–C(22)	1.34(2)	C(23)–C(25)	1.51(2)			
C(23)–O(24)	1.23(2)	C(25)–C(26)	1.41(3)			
C(25)–C(27)	1.37(2)	C(28)–C(29)	1.40(3)			
C(28)–C(32)	1.42(3)	C(29)–C(30)	1.34(3)			
C(30)–C(31)	1.41(3)	C(31)–C(32)	1.40(3)			
C(33)–C(34)	1.25(5)	C(33)–C(37)	1.33(3)			
C(35)–C(34)	1.33(4)	C(35)–C(36)	1.28(3)			
C(36)–C(37)	1.40(3)					
C(3)–N(2)–Ti(1)	169.1(13)	C(5)–B(4)–C(3)	110.8(13)			
C(11)–B(4)–C(3)	104.8(12)	C(11)–B(4)–C(5)	114.2(14)			
C(17)–B(4)–C(3)	103.6(13)	C(17)–B(4)–C(5)	113.0(13)			
C(17)–B(4)–C(11)	109.7(12)	B(4)–C(3)–N(2)	176.8(16)			
B(4)–C(5)–C(6)	122.8(15)	B(4)–C(5)–C(10)	122.3(15)			
B(4)–C(11)–C(12)	123.6(13)	B(4)–C(11)–C(16)	118.5(13)			
B(4)–C(17)–C(18)	124.0(15)	B(4)–C(17)–C(22)	123.0(15)			
C(23)–O(24)–Ti(1)	67.5(10)	C(25)–C(23)–Ti(1)	160.8(14)			
O(24)–C(23)–Ti(1)	78.7(11)	O(24)–C(23)–C(25)	120.4(16)			
C(26)–C(25)–C(23)	111.9(20)	C(27)–C(25)–C(23)	115.9(19)			
C(27)–C(25)–C(26)	120.0(24)	C(10)–C(5)–C(6)	114.8(16)			
C(7)–C(6)–C(5)	121.5(17)	C(8)–C(7)–C(6)	122.4(19)			
C(9)–C(8)–C(7)	118.8(18)	C(10)–C(9)–C(8)	118.1(17)			
C(13)–C(12)–C(11)	121.7(15)	C(9)–C(10)–C(5)	124.5(17)			
C(16)–C(11)–C(12)	117.8(16)	C(14)–C(13)–C(12)	120.8(18)			
C(15)–C(14)–C(13)	120.3(17)	C(16)–C(15)–C(14)	118.4(17)			
C(15)–C(16)–C(11)	121.0(16)	C(22)–C(17)–C(18)	112.9(16)			
C(19)–C(18)–C(17)	126.7(17)	C(20)–C(19)–C(18)	116.4(18)			
C(21)–C(20)–C(19)	120.6(16)	C(22)–C(21)–C(20)	122.1(17)			
C(21)–C(22)–C(17)	121.3(16)					
C(32)–C(28)–C(29)	104.7(20)	C(30)–C(29)–C(28)	112.1(22)			
C(31)–C(30)–C(29)	106.8(22)	C(32)–C(31)–C(30)	108.2(22)			
C(31)–C(32)–C(28)	108.1(22)	C(37)–C(33)–C(34)	109.8(30)			
C(36)–C(35)–C(34)	110.3(28)	C(35)–C(34)–C(33)	108.6(30)			
C(37)–C(36)–C(35)	105.3(23)	C(36)–C(37)–C(33)	105.6(23)			
Ti1	Du1	2.05	Du1	Ti1	Du2	134.4
	Du2	2.01				
N2	Du1	3.30				
	Du2	3.23				
C23	Du1	3.17				
	Du2	3.17				
Du1	Du2	3.75				

methanol at room temperature. Light yellow crystals were filtered out after 12 h (yield 100%).

IR and NMR data are identical with those of **3b**.

5. X-ray data collection, structure determination and refinement

Suitable crystals were grown by a slow recrystallization from CH₂O₁₂ at room temperature. A yellow single crystal was chosen, with approximate dimensions 0.10 × 0.10 × 0.53 mm³.

Diffracted intensities were collected on an Enraf-Nonius four-circle diffractometer (CAD4, ω - 2θ scans) at room temperature with graphite monochromated Mo K α radiation. Final lattice parameters (Table 3) were determined from least-squares refinement with $[(\sin \theta)/\lambda]^2$ values for 25 reflections ($15^\circ < \theta < 16^\circ$). The crystal structure was solved by direct method SHELXS [20] and refined with anisotropic thermal parameters. All hydrogen atoms, except two, were located by difference Fourier synthesis. The structure was refined by least-squares techniques with approximation (in two blocks corresponding to molecules A and B respectively) to the normal matrix using CRYSTALS [21]. All heavy atoms were refined anisotropically. H atoms were placed in calculated positions (H–C–H = 109°; H–C–C = 120°; C–H = 0.96 Å) and were not further refined but calculated after each cycle. They were assigned isotropic thermal parameters 20% higher than those of C atoms to which they were attached. In the final cycles of the refinement the H atoms are fixed on “riding” positions. The scattering factors employed in all structure factor calculations were those from the *International Tables for X-Ray Crystallography*, Vol. IV, tabulated in CRYSTALS.

The positional parameters for all atoms from the least-squares cycle are provided in Table 4. Selected interatomic distances and angles and their e.s.d.s, which were calculated from the estimated standard errors of the fractional coordinates, are summarized in Table 5.

Tables of refined thermal parameters, specific least-squares planes and the observed and calculated structure factors of the compound are available as supplementary material.

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