Some Insertion Reactions into the Ti–Me bond of $[Ti(\eta^5-C_5Me_5)MeCl_2]$; Crystal Structures of $[Ti(\eta^5-C_5Me_5)(\eta^2-COMe)Cl_2]$ and $[\{Ti(\eta^5-C_5Me_5)\}_2(\mu-Cl)_2\{\mu-\eta^4-CH_2(2,6-Me_2C_6H_3N)C{=}C(NC_6H_3Me_2-2,6)CH_2\}]$ *

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Treatment of $[Ti(C_5Me_5)Cl_3]$ with trimethylaluminium gives $[Ti(C_5Me_5)MeCl_2]$, which reacts readily with CO, $CNC_6H_3Me_2$-2,6 and N_2CPh_2 to give the corresponding acyl $[Ti(C_5Me_5)(\eta^2-COMe)Cl_2]$, iminoacyl $[Ti(C_5Me_5)\{\eta^2-MeCN(C_6H_3Me_2-2,6)\}Cl_2]$ and hydrazonato $[Ti(C_5Me_5)\{\eta^2-N(Me)NCPh_2\}Cl_2]$ insertion products. The compound $[Ti(C_5Me_5)(\eta^2-COMe)Cl_2]$ reacts with PMe_3 to give $[Ti(C_5Me_5)\{\eta^2-OC(PMe_3)Me\}Cl_2]$ and $[Ti(C_5Me_5)\{OC(CNC_6H_3Me_2-2,6)Me\}Cl_2]$ has been identified by NMR spectroscopy as the product of a similar nucleophilic attack by $CNC_6H_3Me_2$-2,6. The reaction of $[Ti(C_5Me_5)\{\eta^2-MeCN(C_6H_3Me_2-2,6)\}Cl_2]$ with nucleophilic agents like $Li[N(SiMe_3)_2]$ leads to $[\{Ti(C_5Me_5)\}_2(\mu-Cl)_2\{\mu-\eta^4-CH_2(2,6-Me_2C_6H_3N)C{=}C(NC_6H_3Me_2-2,6)CH_2\}]$. The crystal structures of the latter and of $[Ti(C_5Me_5)(\eta^2-COMe)Cl_2]$ have been established by X-ray diffraction methods; the mononuclear compound shows a pseudo-square-pyramidal geometry with a strong Ti–[η^2-C(Me)O] interaction, while the dinuclear compound contains two $Ti(C_5Me_5)$ groups bridged by two chlorine atoms and by the new ligand $\eta^4-CH_2(2,6-Me_2C_6H_3N)C{=}C(NC_6H_3Me_2-2,6)CH_2$ reported here for the first time.

Insertion reactions are one of the most fundamental and widely encountered reactions in organometallic chemistry. In particular, the migratory insertion of carbon monoxide and related molecules into metal–carbon bonds has been intensively studied because of its relationship to several important catalytic processes.[1] In the case of lanthanides, actinides and early transition metals the so-formed acyls and related substances exhibit a particular reactivity which is being actively studied.[2] By far, most of the reported examples in this field have been bis(cyclopentadienyl) systems. Here we report the results of some insertion reactions with the formally electron-deficient titanium mono(pentamethylcyclopentadienyl) $[Ti(C_5Me_5)MeCl_2]$ **1** and the reactivity of the insertion products.

Results and Discussion

A hexane solution of $[Ti(C_5Me_5)MeCl_2]$ **1** was exposed to carbon monoxide (1 atm, *ca.* 10^5 Pa) giving a red solution and an orange precipitate. The solid was recrystallized from hexane–tetrahydrofuran (thf) (1 : 1) to give $[Ti(C_5Me_5)(\eta^2-COMe)Cl_2]$ **2** in 57% and $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu-O(Me)C{=}C(Me)O\}]$ **3** in 22% yields (see Scheme 1). The IR spectrum of **2** shows one absorption at 1554 cm^{-1} [ν(CO)], indicating the dihapto co-ordination of the acyl group. The ^1H NMR spectrum of **2** in C_6D_6 shows a shift of +0.46 ppm in the η^2-COMe signal with respect to that observed for the methyl group directly bound to titanium in **1** and the ^{13}C NMR spectrum confirms this bonding situation showing a peak for η^2-*C*OMe at δ 306.6.[2]

The enediolate derivative **3** is simultaneously formed in this reaction. Although its nature can be confirmed by mass spectrometry (**3**: *m*/*z* 594, **3**; 596, $[^{13}C_2]$**3**) and by comparison of its NMR parameters with those reported for some hafnium and lanthanide analogues,[3] its mode of formation remains unclear.

Crystal Structure of $[Ti(\eta^5-C_5Me_5)(\eta^2-COMe)Cl_2]$ **2**.—Given the lack of structural data about monocyclopentadienyl acyl derivatives of the early transition metals, the crystal structure of compound **2** was determined. Two views are shown in Fig. 1 together with the numbering scheme used; selected bond distances and angles are given in Table 1. The titanium atom is bonded to two terminal Cl atoms, to a C_5Me_5 ring in the η^5 fashion and to the COMe acyl group acting as a bidentate ligand. The titanium geometry can be considered to be pseudo-square pyramidal with the O and C(1) atoms of the acyl group and the two Cl atoms occupying the basal positions, and the centroid (CE) of the C_5Me_5 ring the apical position [the distance from CE is 2.020(6) Å]. Alternatively it may be described as distorted tetrahedral if the midpoint of the C(1)–O bond is considered to occupy one co-ordination site. The η^2 bonding of the acyl group is nearly symmetrical, the Ti–C(1) and Ti–O bond distances being 2.021(7) and 2.082(5) Å, respectively. The former distance is in the range observed for monopentamethylcyclopentadienyl alkyls, while the latter is rather short, *e.g.* 0.07 Å shorter than the average in $[Ti(C_5Me_5)(O_2CPh)_3]$.[4] It is noteworthy that in the bis(cyclopentadienyl) complex $[Ti(C_5H_5)_2(\eta^2-COMe)Cl]$ the η^2 bonding of the acyl group is much more asymmetrical, the Ti–C and Ti–O bond lengths being 2.07(2) and 2.194(14) Å, respectively.[5] The nature of the bonding of bidentate acyls with transition metals is mainly characterized by the difference (Δ) in the M–O and M–C distances. Small values of Δ have been taken as an indication of the strength of the dihapto co-ordination and the oxophilic character of the metal centre;[2,6] Δ is only 0.06 Å for **2**, and still lower and even negative values have been so far

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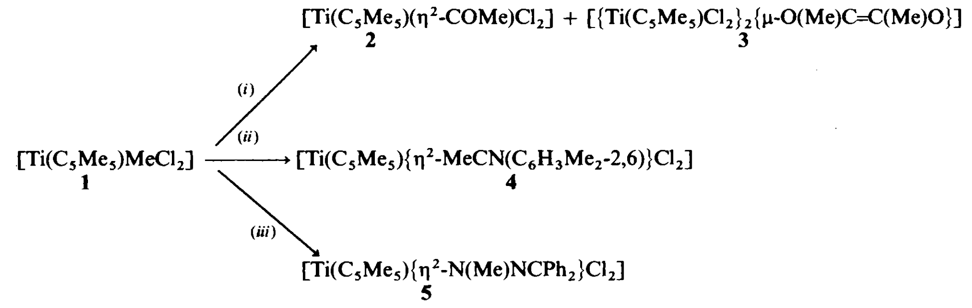
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) CO; (*ii*) $CNC_6H_3Me_2$-2,6; (*iii*) N_2CPh_2

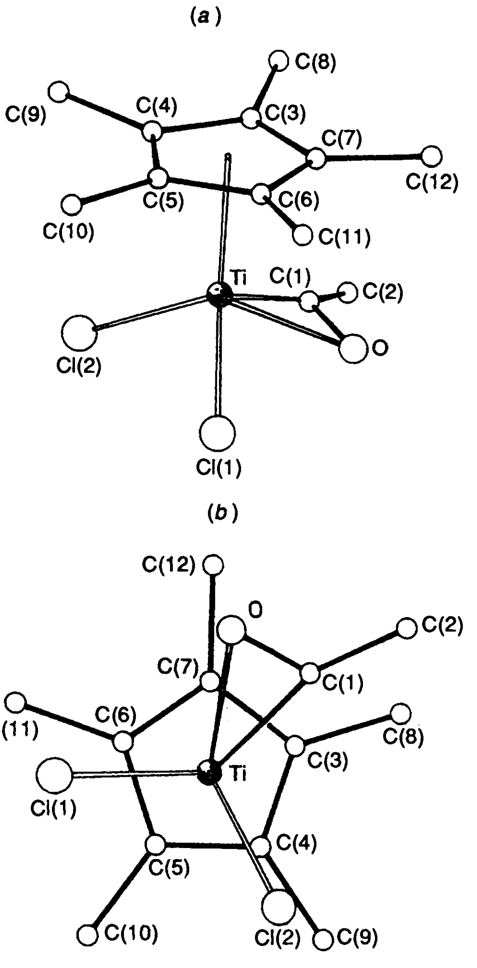


Fig. 1 (*a*) View of the structure of $[Ti(\eta^5-C_5Me_5)(\eta^2-COMe)Cl_2]$ **2** with the atomic numbering scheme. (*b*) View along the Ti–CE vector where CE is the centroid of the C_5Me_5 ring

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **2**

Ti–Cl(1)	2.312(2)	Ti–CE(1)	1.959(6)
Ti–Cl(2)	2.274(2)	Ti–CE(2)	2.020(6)
Ti–O	2.082(5)	O–C(1)	1.222(9)
Ti–C(1)	2.021(7)	C(1)–C(2)	1.505(10)
Cl(1)–Ti–Cl(2)	97.2(1)	Cl(2)–Ti–C(1)	93.9(2)
Cl(1)–Ti–CE(1)	102.5(2)	Cl(2)–Ti–O	116.8(1)
Cl(1)–Ti–CE(2)	117.6(2)	Cl(1)–Ti–C(1)	117.4(2)
Cl(2)–Ti–CE(1)	105.9(2)	Cl(1)–Ti–O	87.8(2)
Cl(2)–Ti–CE(2)	118.1(2)	Ti–O–C(1)	70.0(4)
CE(1)–Ti–CE(2)	113.2(2)	Ti–C(1)–O	75.4(4)
C(1)–Ti–CE(2)	109.9(3)	O–C(1)–C(2)	122.2(7)
O–Ti–CE(2)	114.2(2)	Ti–C(1)–C(2)	162.1(6)
O–Ti–C(1)	34.6(2)		

CE(1) is the middle point of the C(1)–O bond and CE(2) the centroid of the C(3)–C(7) cyclopentadienyl ring.

described only for some uranium and thorium acyls and for related derivatives of the type η^2-XCO (X = NR_2 or PR_2).[2]

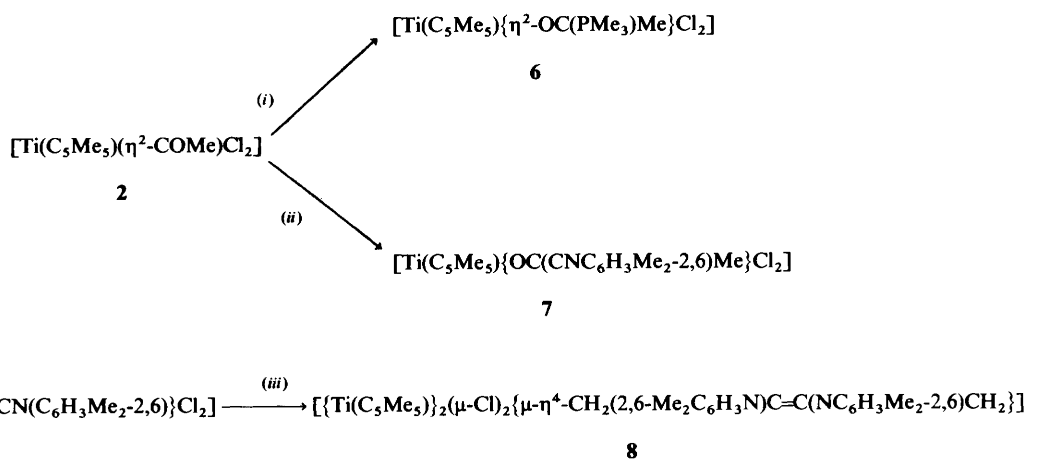
Reactions of compound **2** with nucleophiles reveal that the attack takes place preferentially on the more electrophilic acyl C(1) atom instead of the titanium. Thus PMe_3 reacts with a toluene solution of **2** to give the dark brown crystalline and stable ylide-like compound $[Ti(C_5Me_5)\{\eta^2-OC(PMe_3)Me\}Cl_2]$ **6**, similar to $[Ta(C_5Me_5)\{OC(PMe_3)(SiMe_3)\}Cl_3]$[7] and $[Mo(C_5H_5)\{OC(PMe_3)(C_6H_4Me\text{-}p)\}(NO)I]$.[8] The shifts of the ^{13}C NMR signal of the acyl C(1) atom from δ 306.6 for **2** to δ 83.0 for **6** and of the IR [ν(C=O)] frequency from 1554 to 1121 cm^{-1} are in agreement with the increase in electron density on the acyl C(1) atom upon co-ordination. Unfortunately, crystals of **6** were not suitable for an X-ray diffraction study.

The reaction of a benzene solution of compound **2** with $CNC_6H_3Me_2$-2,6 was carried out in a NMR tube. As shown in Scheme 2, the final solution contains the ketenimine complex $[Ti(C_5Me_5)\{OC(CNC_6H_3Me_2\text{-}2,6)Me\}Cl_2]$ **7** as evidenced by its ^1H and ^{13}C NMR spectra which are similar to those reported for related derivatives of Th and Zr.[9] Compound **7** was identified in solution but not isolated in the solid.

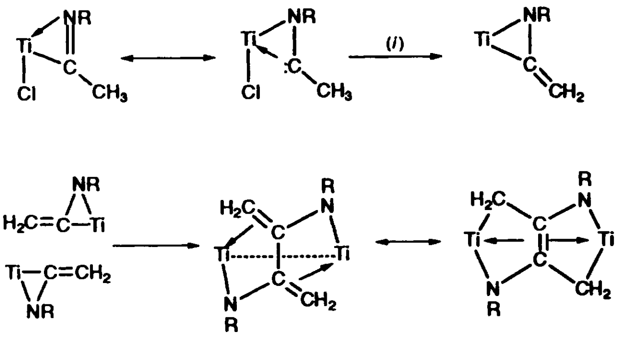
Similar insertion reactions also take place when hexane solutions of compound **1** react with $CNC_6H_3Me_2$-2,6 and N_2CPh_2 leading respectively to the complexes $[Ti(C_5Me_5)\{\eta^2-MeCN(C_6H_3Me_2\text{-}2,6)\}Cl_2]$ **4** and $[Ti(C_5Me_5)\{\eta^2-N(Me)NCPh_2\}Cl_2]$ **5**. Their IR spectra show the [ν(C=N)] absorption at 1635 for **4** and at 1535 cm^{-1} for **5**, indicating dihapto co-ordination to the metal centre. The IR and NMR behaviour of **5** is analogous to that reported for $[(C_5Me_5)Me\{\eta^2-N(Me)NCPh_2\}Ti(\mu-O)Ti(C_5Me_5)Me_2]$ indicating the formation of a dihapto co-ordinated benzophenone methylhydrazonate (1 −) ligand.[10]

Reactions of compound **4** with CO and $CNC_6H_3Me_2$-2,6 do not take place and only the starting material is recovered. Treatment of **4** with $Li[N(SiMe_3)_2]$ in thf at −40 °C results in deprotonation of the methyl of the iminoacyl group, bonding of the resulting methylene group to a second metal centre and simultaneous coupling between the two iminoacyl carbon atoms to give a dinuclear complex $[\{Ti(C_5Me_5)\}_2(\mu-Cl)_2\{\mu-\eta^4-CH_2(2,6-Me_2C_6H_3N)C{=}C(NC_6H_3Me_2\text{-}2,6)CH_2\}]$ **8**, identified by an X-ray study. The reaction probably takes place through the intermediate steps shown in Scheme 3.

The ^1H NMR spectrum of compound **8** in C_6D_6 shows a resonance at δ 1.82 due to the methyl protons of the C_5Me_5 group, one multiplet between δ 6.92 and 7.03 assignable to the $Me_2C_6H_3$ protons, and two resonances at δ 1.98 and 2.38 which correspond to two inequivalent $Me_2C_6H_3$ groups. Additional resonances at δ 1.59 and 1.92 [d, $^2J(H_AH_B)$ = 5.6 Hz] must be assigned to diastereotopic protons of the CH_2 groups. The mass [m/z = 628 (M^+)] and ^{13}C-{^1H} NMR spectra confirm the dimeric structure of **8**.



Scheme 2 (*i*) PMe_3; (*ii*) $CNC_6H_3Me_2$-2,6; (*iii*) $Li[N(SiMe_3)_2]$ − LiCl



Scheme 3 (*i*) $Li[N(SiMe_3)_2]$ − LiCl − $HN(SiMe_3)_2$

Crystal Structure of $[\{Ti(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}Cl)_2\{\mu\text{-}\eta^4\text{-}CH_2(2,6\text{-}Me_2C_6H_3N)C{=}C(NC_6H_3Me_2\text{-}2,6)CH_2\}]\cdot 0.5C_6H_{14}$ **8**.—Single crystals of compound **8** were grown from hexane by slow cooling to −40 °C, and incorporated a disordered hexane molecule. A view of the molecular structure is shown in Fig. 2 together with the numbering scheme used; selected bond distances and angles are given in Table 2. Complex **8** contains two $Ti(C_5Me_5)$ fragments joined through two symmetrical chloride bridges and through two N and two C atoms from the new tetradentate $\mu\text{-}\eta^4\text{-}CH_2(2,6\text{-}Me_2C_6H_3N)C{=}C(NC_6H_3Me_2\text{-}2,6)CH_2$ ligand.

Both metal centres (Figs. 3 and 4) may be considered to possess a typical 'four-legged piano-stool' environment, with angles in the range of 72.9(2)–87.8(5)° between the legs and with distances of 2.05(2) Å from the metal to the centroid of the C_5Me_5 ring. The N(11)C(11)C(12)C(22)C(21)N(12) skeleton is only roughly planar with the two strictly planar moieties N(11)C(11)C(12)C(22) and N(12)C(12)C(11)C(21) tilted by 16.0(8)°. The bond lengths C(11)–C(21), C(12)–C(22) and C(11)–C(12), 1.45(3), 1.43(3) and 1.40(3) Å respectively, and N(11)–C(11) and N(12)–C(12), 1.41(3) and 1.43(2) Å, are indicative of extensive delocalization of the double bonds over the N(11)C(11)C(12)C(22)C(21)N(12) skeleton. The Ti(1)–C(11), Ti(1)–C(12), Ti(2)–C(11) and Ti(2)–C(12) distances, in the range 2.391(17)–2.475(19) Å, are consistent with a possible π interaction, as in other $Ti(C_5Me_5)$ complexes.[11] Finally, the Ti–N distances, 1.946(15) and 1.953(15) Å, are comparable to Ti–N(Me), 1.949(6) Å, found in $[(C_5Me_5)Me\{\eta^2\text{-}N(Me)NCPh_2\}Ti(\mu\text{-}O)Ti(C_5Me_5)Me_2]$.[10]

Experimental

All manipulations and reactions were carried out using standard Schlenk techniques and a HE-63-P Vacuum Atmospheres glove-box, under an atmosphere of argon. Hexane was refluxed over Na/K alloy and distilled under N_2, tetrahydrofuran over sodium–benzophenone and toluene over sodium. The compound $[Ti(C_5Me_5)Cl_3]$ was prepared by published procedures.[12] Infrared spectra were recorded on a Perkin Elmer 883 spectrometer and ^1H and ^{13}C NMR spectra on a Varian Unity FT-300 spectrometer [300 (^1H), 75 MHz (^{13}C)]. Electron-impact mass spectra were obtained at 70 eV (*ca.* 1.12×10^{-17} J) with a Hewlett-Packard 5988 spectrometer. Carbon and hydrogen analyses were carried out with a Perkin Elmer 240B microanalyser.

$[Ti(C_5Me_5)MeCl_2]$ **1**.—A suspension of $[Ti(C_5Me_5)Cl_3]$ (2.43 g, 8.40 mmol) in hexane (100 cm^3) at −78 °C was treated with $AlMe_3$ (5.06 cm^3, 1.66 mol dm^{-3} in hexane, 8.40 mmol) to give an orange suspension. The mixture was allowed to warm to room temperature and stirred vigorously for 18 h. The resulting dark green solution was decanted from the black solid formed and filtered over Celite. Cooling to −20 °C overnight afforded orange crystals which were washed with cold hexane (yield: 1.60 g, 71%) (Found: C, 48.85; H, 6.70. $C_{11}H_{18}Cl_2Ti$ requires C, 49.10; H, 6.75%). NMR (C_6D_6): ^1H, δ 1.61 (3 H, TiMe) and 1.75 (15 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 131.0 (C_5Me$_5$), 78.2 (TiMe) and 13.1 (C_5*Me*$_5$).

$[Ti(C_5Me_5)(\eta^2\text{-}COMe)Cl_2]$ **2**.—A solution of compound **1** (0.40 g, 1.49 mmol) in hexane (15 cm^3) was exposed to carbon monoxide (1 atm) at 0 °C. A change from orange to red was observed over 10 min, and an orange microcrystalline precipitate was formed, which was filtered off and dried *in vacuo*. The orange solid was extracted with hexane–thf (1 : 1, 10 cm^3) and filtered, giving a dark red solution. Cooling to −40 °C overnight gave $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu\text{-}O(Me)C{=}C(Me)O\}]$ **3** as a dark brown solid (yield 0.10 g, 22%). The red solution was reduced in volume to 5 cm^3 and cooled to −40 °C overnight, giving red crystals of **2**, which were filtered off and washed with a small amount of cold hexane before drying *in vacuo* (yield 0.25 g, 57%) (Found: C, 48.70; H, 6.10. $C_{12}H_{18}Cl_2OTi$ **2** requires C, 48.50; H, 6.10%). IR (Nujol): 1554m cm^{-1} [ν(CO)]. NMR (C_6D_6): ^1H, δ 2.07 (3 H, MeCO) and 1.74 (15 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 306.6 (Me*C*O), 128.8 (C_5Me$_5$), 27.0 (*Me*CO) and 12.8 (C_5*Me*$_5$). Complex **3** (Found: C, 48.45; H, 6.00. $C_{24}H_{36}Cl_4O_2Ti_2$ requires C, 48.50; H, 6.10%). NMR (C_6D_6): ^1H, δ 2.14 [3 H, C(Me)O] and 1.85 (15 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 152.8 [*C*(Me)O], 131.8 (C_5Me$_5$), 17.2 [C(*Me*)O] and 12.6 (C_5*Me*$_5$). Mass spectrum: *m/z* 594 (M^+).

In a similar experiment a solution of compound **1** (0.30 g, 1.12 mmol) in hexane (5 cm^3) was exposed to ^{13}CO (1 atm) at 0 °C. The compounds [^{13}C]**2** (0.17 g, 51%) and [$^{13}C_2$]**3** (0.09 g, 27%) were obtained (Found: C, 48.40; H, 6.20. $C_{12}H_{18}Cl_2OTi$

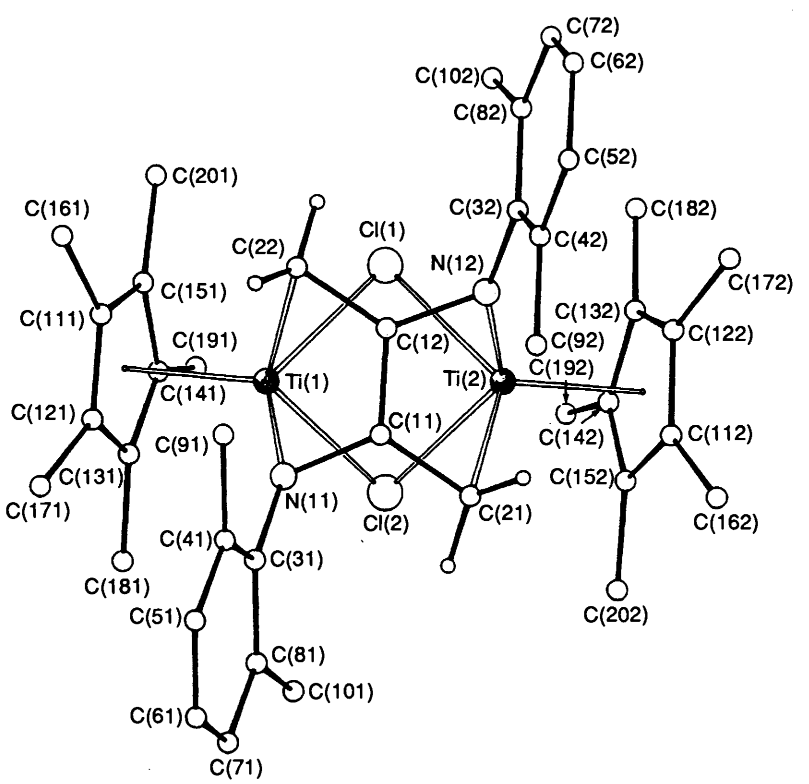


Fig. 2 View of the structure of [{Ti(η^5-C$_5$Me$_5$)}$_2$(μ-Cl)$_2${μ-η^4-CH$_2$(2,6-Me$_2$C$_6$H$_3$N)C=C(NC$_6$H$_3$Me$_2$-2,6)CH$_2$}]·0.5C$_6$H$_{14}$ **8** with the atomic numbering scheme

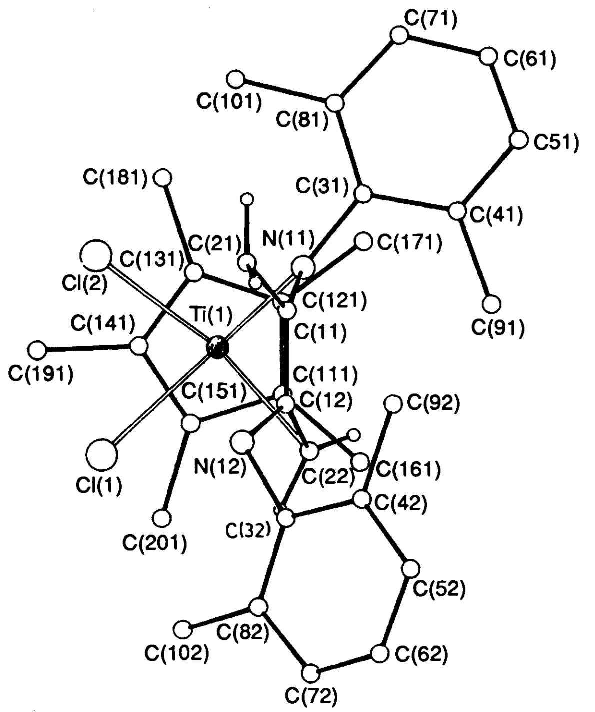


Fig. 3 View along the Ti(1)–CE(1) vector of the environment of the Ti(1) atom in compound **8**

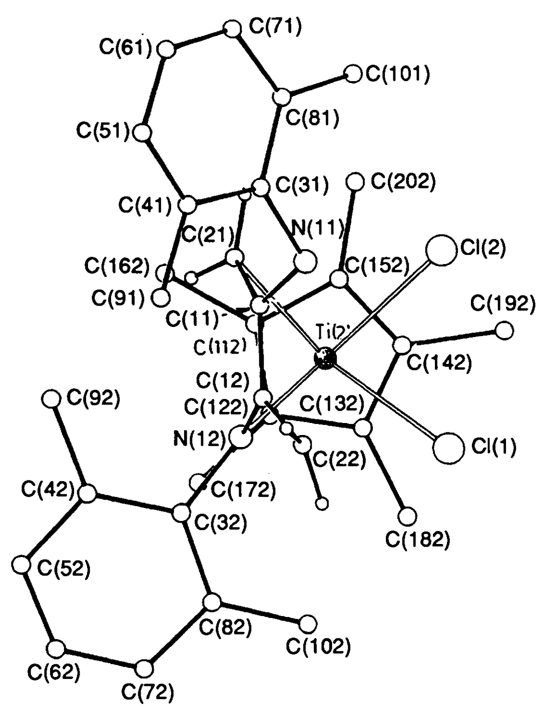


Fig. 4 View along the Ti(2)–CE(2) vector of the environment of the Ti(2) atom in compound **8**

[^{13}C]**2** requires C, 48.70; H, 6.10%). IR (Nujol): 1523m cm^{-1} [ν(CO)]. NMR (C$_6$D$_6$): ^{1}H, δ 2.07 (d, $^2J_{CH}$ = 6.3 Hz, MeCO) and 1.74 (15 H, C$_5$Me$_5$); ^{13}C-{^{1}H}, δ 306.6 (Me*C*O), 128.8 (*C*$_5$Me$_5$), 27.0 (d, $^1J_{CC}$ = 19 Hz, *Me*CO) and 12.8 (C$_5$*Me*$_5$). Complex [^{13}C$_2$]**3** (Found: C, 48.60; H, 6.20. C$_{24}$H$_{36}$Cl$_4$O$_2$Ti$_2$ requires C, 48.70; H, 6.10%). Mass spectrum: *m/z* 596 (*M*$^+$).

[Ti(C$_5$Me$_5$){η^2-MeCN(C$_6$H$_3$Me$_2$-2,6)}Cl$_2$] **4**.—A solution of CNC$_6$H$_3$Me$_2$-2,6 (0.47 g, 3.61 mmol) in hexane (10 cm^3) was added dropwise to compound **1** (0.97 g, 3.61 mmol) in hexane (30 cm^3) at room temperature to give an orange solution. An orange microcrystalline precipitate formed over a few minutes and was filtered off, washed with cold hexane

Table 2 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound **8**

Ti(1)–Cl(1)	2.516(6)	Ti(2)–Cl(1)	2.500(6)
Ti(1)–Cl(2)	2.511(6)	Ti(2)–Cl(2)	2.519(6)
Ti(1)–N(11)	1.946(15)	Ti(2)–N(12)	1.953(15)
Ti(1)–C(22)	2.235(19)	Ti(2)–C(21)	2.224(18)
Ti(1)–CE(1)	2.05(2)	Ti(2)–CE(2)	2.05(2)
Ti(1)–C(11)	2.391(17)	Ti(2)–C(11)	2.475(19)
Ti(1)–C(12)	2.443(19)	Ti(2)–C(12)	2.414(17)
N(11)–C(11)	1.41(3)	N(12)–C(12)	1.43(2)
N(11)–C(31)	1.42(3)	N(12)–C(32)	1.44(2)
C(11)–C(21)	1.45(3)	C(12)–C(22)	1.43(3)
C(11)–C(12)	1.40(3)		
CE(1)–Ti(1)–Cl(1)	110.5(6)	CE(2)–Ti(2)–Cl(1)	114.7(6)
CE(1)–Ti(1)–Cl(2)	115.3(7)	CE(2)–Ti(2)–Cl(2)	109.5(6)
CE(1)–Ti(1)–N(11)	116.0(8)	CE(2)–Ti(2)–N(12)	116.6(7)
CE(1)–Ti(1)–C(22)	112.7(8)	CE(2)–Ti(2)–C(21)	114.2(8)
Cl(1)–Ti(1)–Cl(2)	72.9(2)	Cl(1)–Ti(2)–Cl(2)	73.0(2)
Cl(1)–Ti(1)–N(11)	133.5(5)	Cl(2)–Ti(2)–N(12)	133.8(5)
Cl(1)–Ti(1)–C(22)	80.7(5)	Cl(2)–Ti(2)–C(21)	81.2(5)
Cl(2)–Ti(1)–N(11)	86.8(4)	Cl(1)–Ti(2)–N(12)	87.8(5)
Cl(2)–Ti(1)–C(22)	130.7(5)	Cl(1)–Ti(2)–C(21)	129.9(5)
N(11)–Ti(1)–C(22)	82.1(6)	N(12)–Ti(2)–C(21)	80.0(7)
Ti(1)–N(11)–C(11)	89.3(11)	Ti(2)–N(12)–C(12)	89.7(10)
Ti(1)–N(11)–C(31)	154.4(13)	Ti(2)–N(12)–C(32)	152.9(13)
C(11)–N(11)–C(31)	116.2(15)	C(12)–N(12)–C(32)	116.8(14)
Ti(1)–C(22)–C(12)	80.3(11)	Ti(2)–C(21)–C(11)	81.7(11)
N(11)–C(11)–C(12)	116.3(16)	N(12)–C(12)–C(11)	113.4(15)
N(11)–C(11)–C(21)	120.9(17)	N(12)–C(12)–C(22)	124.8(16)
C(21)–C(11)–C(12)	120.2(16)	C(11)–C(12)–C(22)	120.5(17)
Ti(1)–Cl(1)–Ti(2)	77.4(2)	Ti(1)–Cl(2)–Ti(2)	77.1(2)

CE(1) and CE(2) are the centroids of the C(111)–C(151) and C(112)–C(152) cyclopentadienyl rings respectively.

Table 3 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of compound **2**

Atom	*X/a*	*Y/b*	*Z/c*
Ti	794(1)	717(1)	2377(1)
Cl(1)	2855(2)	1156(2)	1386(2)
Cl(2)	2322(2)	403(2)	3851(1)
O	326(5)	−529(3)	1401(4)
C(1)	−47(7)	−739(5)	2260(6)
C(2)	−653(10)	−1786(5)	2530(7)
C(3)	−1862(7)	1057(5)	2787(5)
C(4)	−821(7)	1754(5)	3335(5)
C(5)	−99(7)	2384(5)	2638(5)
C(6)	−683(7)	2103(5)	1634(5)
C(7)	−1754(7)	1275(5)	1728(5)
C(8)	−3019(8)	335(6)	3232(6)
C(9)	−664(9)	1863(6)	4474(5)
C(10)	1084(8)	3230(5)	2901(6)
C(11)	−324(9)	2609(6)	652(5)
C(12)	−2737(8)	735(6)	848(5)

(2×5 cm^3) and dried *in vacuo* (yield 1.03 g, 72%) (Found: C, 59.85; H, 6.75; N, 3.50. $\mathrm{C_{20}H_{27}Cl_2NTi}$ requires C, 60.00; H, 6.80; N, 3.50%). IR (Nujol): 1635m cm^{-1} [ν(CN)]. NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 7.24 (m, 3 H, $\mathrm{C_6H_3}$), 2.70 (3 H, MeCN), 2.34 (15 H, $\mathrm{C_5Me_5}$) and 2.19 (6 H, $\mathrm{C_6H_3}\mathit{Me}_2$); ^{13}C-{^{1}H}, δ 243.2 (Me*C*N), 142.4, 130.1, 128.4, 126.6 ($\mathrm{C_6H_3}$), 128.4 ($\mathit{C}_5\mathrm{Me_5}$), 21.0 (*Me*CN), 18.9 ($\mathrm{C_6H_3}\mathit{Me}_2$) and 13.1 ($\mathrm{C_5}\mathit{Me}_5$).

$[\mathrm{Ti(C_5Me_5)\{\eta^2\text{-}N(Me)NCPh_2\}Cl_2}]$ **5**.—Similarly, the brown complex **5** was prepared from $\mathrm{Ph_2CN_2}$ (0.29 g, 1.49 mmol) and **1** (0.40 g, 1.49 mmol). Yield 0.45 g, 65% (Found: C, 62.40; H, 6.10; N, 6.20. $\mathrm{C_{24}H_{28}Cl_2N_2Ti}$ requires C, 62.20; H, 6.10; N, 6.05. IR (Nujol): 1535m cm^{-1} [ν(CN)]. NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 7.68 (m, 2 H, $\mathrm{C_6H_5}$), 7.30 (m, 8 H, $\mathrm{C_6H_5}$), 3.01 (3 H, $\mathrm{MeN_2}$) and 1.98 (15 H, $\mathrm{C_5Me_5}$); ^{13}C-{^{1}H}, δ 141.8 ($\mathit{C}\mathrm{Ph_2}$), 138.3, 135.7, 130.2, 129.0, 128.8, 128.7, 128.1, 127.7 ($\mathrm{C}\mathit{Ph}_2$), 130.3 ($\mathit{C}_5\mathrm{Me_5}$), 45.0 ($\mathrm{MeN_2}$) and 12.9 ($\mathrm{C_5}\mathit{Me}_5$).

$[\mathrm{Ti(C_5Me_5)\{\eta^2\text{-}OC(PMe_3)Me\}Cl_2}]$ **6**.—A solution of $\mathrm{PMe_3}$ (0.0377 cm^3, 1 mol dm^{-3} in toluene, 0.377 mmol) was added to compound **2** (0.10 g, 0.377 mmol) in toluene (10 cm^3) at room temperature. A change from orange to brown was observed over 5 min. The mixture was stirred for 2 h, and reduced in volume to 5 cm^3. Cooling to −40 °C overnight afforded a dark brown microcrystalline precipitate (yield 0.12 g, 95%) (Found: C, 48.40; H, 7.20. $\mathrm{C_{15}H_{27}Cl_2OPTi}$ requires C, 48.30; H, 7.30%). NMR ($\mathrm{C_6D_6}$–[$^2\mathrm{H_8}$]thf): ^{1}H, δ 2.04 (15 H, $\mathrm{C_5Me_5}$), 1.59 (d, 3 H, $^3J_{\mathrm{PH}} = 14.4$, OCMe) and 1.13 (d, $^2J_{\mathrm{PH}} = 13.2$ Hz, 9 H, $\mathrm{PMe_3}$); ^{13}C-{^{1}H}, δ 124.5 ($\mathit{C}_5\mathrm{Me_5}$), 83.0 (d, $^1J_{\mathrm{PC}} = 54.7$, O*C*Me), 22.2 (d, $^2J_{\mathrm{PC}} = 23.7$, OC*Me*), 11.8 ($\mathrm{C_5}\mathit{Me}_5$) and 9.4 (d, $^1J_{\mathrm{PC}} = 52.9$ Hz, $\mathrm{PMe_3}$).

$[\mathrm{Ti(C_5Me_5)\{OC(CNC_6H_3Me_2\text{-}2,6)Me\}Cl_2}]$ **7**.—Hexadeuteriobenzene (0.5 cm^3) was added to a 5 mm NMR tube containing compound **2** (0.030 g, 0.10 mmol) and $\mathrm{CNC_6H_3Me_2}$-2,6 (0.013 g, 0.10 mmol). Within 5 min the red solution afforded the product quantitatively according to ^{1}H NMR spectroscopy. The product is thermally stable in solution for 96 h at 90 °C. NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 6.88 (m, 3 H, $\mathrm{C_6H_3}$), 2.29 (6 H, $\mathrm{C_6H_3}\mathit{Me}_2$), 1.94 (15 H, $\mathrm{C_5Me_5}$) and 1.88 (3 H, OCMe); ^{13}C-{^{1}H}, δ 206.7 (C*C*N), 141.3, 130.5, 129.0, 126.4 ($\mathrm{C_6H_3}$), 131.6 ($\mathit{C}_5\mathrm{Me_5}$), 118.6 (*C*CN), 19.0 ($\mathrm{C_6H_3}\mathit{Me}_2$), 17.3 (OC*Me*) and 12.5 ($\mathrm{C_5}\mathit{Me}_5$).

$[\{\mathrm{Ti(C_5Me_5)}\}_2(\mu\text{-}\mathrm{Cl})_2\{\mu\text{-}\eta^4\text{-}\mathrm{CH_2(2,6\text{-}Me_2C_6H_3N)C{=}C(NC_6H_3Me_2\text{-}2,6)CH_2}\}]$ **8**.—A solution of compound **4** (0.17 g, 0.42 mmol) in thf (15 cm^3) was treated with Li[N(SiMe$_3$)$_2$] (0.07 g, 0.42 mmol) in thf (10 cm^3) at −40 °C to give a red solution. The mixture was allowed to warm to room temperature and stirred for 1 h. Volatiles were removed under reduced pressure and the resulting dark brown solid was extracted with hexane (4×5 cm^3). The combined filtered extracts were reduced in volume to 5 cm^3 and cooled to −40 °C. Dark blue crystals formed overnight and were filtered off and washed with cold hexane (3 cm^3) (yield 0.11 g, 72%) (Found: C, 65.85; H, 7.30; Cl, 10.05; N, 3.45. $\mathrm{C_{40}H_{52}Cl_2N_2Ti_2}$ requires C, 66.05; H, 7.20; Cl, 9.75; N, 3.85%). NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 7.03–6.92 (m, 3 H, $\mathrm{Me_AMe_BC_6}\mathit{H}_3$), 2.38 (3 H, $\mathit{Me}_\mathrm{A}\mathrm{Me_BC_6H_3}$), 1.98 (3 H, $\mathrm{Me_A}\mathit{Me}_\mathrm{B}\mathrm{C_6H_3}$), 1.92 [d, 1 H, $^2J(\mathrm{H_AH_B}) = 5.6$, $\mathrm{C}\mathit{H}_\mathrm{A}\mathrm{H_B}$], 1.82 (15 H, $\mathrm{C_5Me_5}$) and 1.59 [d, 1 H, $^2J(\mathrm{H_AH_B}) = 5.6$ Hz, $\mathrm{CH_A}\mathit{H}_\mathrm{B}$]; ^{13}C-{^{1}H}, δ 152.2, 136.2, 135.6, 129.5, 128.5, 125.3 ($\mathrm{Me_AMe_B}\mathit{C}_6\mathrm{H_3}$), 122.8 ($\mathit{C}_5\mathrm{Me_5}$), 114.3 ($\mathrm{CH_2}\mathit{C}{=}\mathit{C}\mathrm{CH_2}$), 69.3 (μ-η^4-$\mathit{C}\mathrm{H_2C{=}C}\mathit{C}\mathrm{H_2}$), 22.1 ($\mathit{Me}_\mathrm{A}\mathrm{Me_BC_6H_3}$), 21.4 ($\mathrm{Me_A}\mathit{Me}_\mathrm{B}\mathrm{C_6H_3}$) and 12.6 ($\mathrm{C_5}\mathit{Me}_5$).

Crystal Structure Determination of the Complexes $[\mathrm{Ti(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}COMe)Cl_2}]$ **2** *and* $[\{\mathrm{Ti(\eta^5\text{-}C_5Me_5)}\}_2(\mu\text{-}\mathrm{Cl})_2\{\mu\text{-}\eta^4\text{-}\mathrm{CH_2(2,6\text{-}Me_2C_6H_3N)C{=}C(NC_6H_3Me_2\text{-}2,6)CH_2}\}]\cdot 0.5\mathrm{C_6H_{14}}$ **8**.—The small size and poor quality of the crystals of compound **8** gave a limited number of observed reflections and prevented an accurate structure determination.

Crystal data. $\mathrm{C_{12}H_{18}Cl_2OTi}$ **2**, $M = 297.08$, monoclinic, space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $a = 8.389(2)$, $b = 13.000(4)$, $c = 13.109(4)$ Å, $\beta = 94.34(2)°$, $U = 1425.5(7)$ Å^3, $Z = 4$, $D_c = 1.384$ g cm^{-3}, $F(000) = 616$, μ(Mo-Kα) = 9.51 cm^{-1}.

$\mathrm{C_{40}H_{52}Cl_2N_2Ti_2 \cdot 0.5C_6H_{18}}$, $M = 770.66$, tetragonal, space group $I4_1/a$ (no. 88, origin at $\bar{1}$ at 0, $\frac{1}{4}$, $\frac{1}{8}$ from $\bar{4}$), $a = 18.518(8)$, $c = 49.722(10)$ Å, $U = 170\,50(11)$ Å^3, $Z = 16$, $D_c = 1.201$ g cm^{-3}, $F(000) = 6544$, μ(Cu-Kα) = 46.02 cm^{-1}.

Data were collected at room temperature on Philips PW 1100 (**2**) and Siemens AED (**8**) single-crystal diffractometers using graphite-monochromated Mo-Kα radiation ($\bar{\lambda} = 0.710\,73$ Å) (**2**) and nickel-filtered Cu-Kα radiation ($\bar{\lambda} = 1.541\,84$ Å) and the θ–2θ scan mode. All reflections with θ in the ranges 3–24 (**2**) and 3–60° (**8**) were measured; of 2255 (**2**) and 6202 (**8**) inde-

Table 4 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of compound **8**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ti(1)	2786(2)	4902(2)	1122(1)
Ti(2)	1960(2)	5686(2)	655(1)
Cl(1)	3257(3)	5313(3)	673(1)
Cl(2)	2486(3)	6219(3)	1078(1)
N(11)	1821(8)	4777(7)	1269(3)
N(12)	1731(8)	4703(7)	541(3)
C(11)	1534(9)	4841(9)	1007(4)
C(21)	1060(10)	5436(10)	936(4)
C(31)	1309(11)	4702(10)	1481(4)
C(41)	953(11)	4013(11)	1515(4)
C(51)	451(11)	3915(12)	1726(4)
C(61)	290(13)	4470(13)	1892(5)
C(71)	581(11)	5149(12)	1863(5)
C(81)	1108(11)	5272(11)	1659(4)
C(91)	1128(11)	3397(11)	1335(4)
C(101)	1417(11)	6023(11)	1626(4)
C(111)	3546(12)	4042(12)	1334(4)
C(121)	3220(12)	4436(12)	1536(4)
C(131)	3440(11)	5143(12)	1518(4)
C(141)	3910(11)	5194(11)	1306(4)
C(151)	3994(12)	4524(12)	1185(5)
C(161)	3564(14)	3223(13)	1280(5)
C(171)	2766(14)	4138(13)	1768(5)
C(181)	3277(14)	5732(14)	1716(5)
C(191)	4347(15)	5843(14)	1212(5)
C(201)	4485(14)	4298(13)	965(5)
C(12)	1885(10)	4449(9)	805(4)
C(22)	2453(10)	3956(10)	872(4)
C(32)	1580(11)	4165(11)	340(4)
C(42)	890(11)	3838(11)	351(4)
C(52)	694(13)	3282(12)	163(4)
C(62)	1210(13)	3106(12)	−22(5)
C(72)	1863(13)	3390(12)	−33(5)
C(82)	2099(13)	3942(12)	146(4)
C(92)	324(11)	4061(11)	556(4)
C(102)	2833(13)	4239(12)	140(5)
C(112)	1117(11)	6400(10)	416(4)
C(122)	1543(11)	6061(11)	224(4)
C(132)	2239(12)	6340(12)	253(4)
C(142)	2229(12)	6818(11)	465(4)
C(152)	1559(10)	6860(10)	578(4)
C(162)	292(12)	6360(13)	448(5)
C(172)	1242(12)	5620(12)	−5(5)
C(182)	2844(14)	6182(14)	65(5)
C(192)	2892(13)	7252(14)	560(5)
C(202)	1317(13)	7372(13)	788(5)

pendent reflections, 1193 (**2**) and 1505 (**8**), having $I \geqslant 2\sigma(I)$, were considered observed and used in the analyses. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collections. The individual profiles were analysed following Lehmann and Larsen.[13] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied to the data of **8** (maximum and minimum transmission factors 1.194 and 0.777).[14]

The structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms for compound **2** and for only Ti, Cl, N and C(11), C(12), C(21) and C(22) for **8**. Some peaks were found in the final ΔF map of **8** due to the presence of a disordered hexane molecule of solvation, but it was not possible to obtain an acceptable image of the solvent. The ten biggest peaks, practically of the same height, were considered as carbon atoms and refined, with occupancy factors of 0.25. All hydrogen atoms of **2** were placed at their calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. All hydrogen atoms of **8**, except the four methylenic ones at C(11) and C(21) which were clearly localized and refined, were placed at their geometrically calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement of **2** with $g = 0.0038$ at convergence, while unit weights were used in all stages of refinement of **8**. Final *R* and *R'* values were 0.0428 and 0.0538 (**2**) and 0.0709 and 0.0764 (**8**). The SHELX 76 and SHELXS 86 systems of computer programs were used.[15] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 16. Final atomic coordinates for the non-hydrogen atoms of **2** are given in Table 3 and for the non-hydrogen atoms except those of the disordered hexane molecule of **8** in Table 4. All calculations were carried out on the CRAY X-MP 8/432 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

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

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