A Novel Bonding Mode of the Diphenylureylene Ligand: Synthesis, Properties, and Structures of Mono-, Bi-, and Tri-nuclear Diphenylureylene Complexes of Bis(η-cyclopentadienyl)titanium

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The reaction of $[Ti(cp)_2(CO)_2]$ (1; cp = η-C_5H_5) with PhNCO (2) gives a trinuclear diphenylureylene complex $[\{Ti(cp)_2\}_3\{OC(NPh)_2\}_2]$ (3), where two $Ti(cp)_2\{OC(NPh)_2\}$ moieties are symmetrically linked to the central $Ti(cp)_2$ unit through the ligand oxygen atoms and each ureylene ligand chelates one titanium atom through the nitrogen atoms. The structural data and the i.r. spectrum, showing no band at >1 600 cm^{-1}, suggest the presence of an electronically delocalised diphenylureylene ligand. These results, together with the magnetic moment corresponding to two unpaired electrons, are in accord with the presence of two titanium(III) atoms and one titanium(IV) atom. Thermal rearrangement of (3) gives a binuclear titanium(III) complex, $[\{Ti(cp)_2\}_2\{OC(NPh)_2\}]$ (6), together with a mononuclear titanium(IV) complex $[Ti(cp)_2\{OC(NPh)_2\}]$ (5). An *X*-ray analysis has shown that the ureylene ligand in $[\{Ti(cp)_2\}_2\{OC(NPh)_2\}]\cdot C_6H_5Me$ (7) bridges two $Ti(cp)_2$ units both through the nitrogen and the oxygen atoms. The diphenylureylene moiety in (7) has the same structural features as observed in (3). Furthermore, the *X*-ray results for (3) and (7) show that the co-ordination geometries around the different titanium atoms are similar to that in many other $Ti(cp)_2$ complexes. Crystal data: (3), space group *C*2/*c* (monoclinic), *a* = 26.187(7), *b* = 8.865(3), *c* = 20.515(5) Å, *Z* = 4, *R* 0.095 for 805 reflections; (7), space group *Fdd*2 (orthorhombic), *a* = 19.138(2), *b* = 75.184(10), *c* = 8.553(2) Å, *Z* = 16, *R* 0.059 for 2 891 reflections.

IN metallorganic chemistry, attention was recently focused on the activation of heterocumulenes promoted by transition-metal complexes.[1] Heterocumulenes, such as isocyanates, ketenes, *etc.*, are powerful tools in organic synthesis and are exemplified by carbon dioxide, whose activation is an open question for inorganic chemists.[2] Isocyanates and ketenes can be assumed as models of the chemical behaviour of CO_2 in at least two aspects: (*a*) for the mode of attachment to the metal; (*b*) for the reactions of the co-ordinated species. The reaction of co-ordinated CO_2 to give carbonato-complexes and carbon monoxide[3,4] is very reminiscent of the activation of isocyanates induced by transition metals and for which ureylene complexes and CO are formed.[5] Moreover, the change in reactivity of such organic substrates on co-ordination to metals generally seems to imply the possibility of achieving C=C, C=N, and C=O bond breaking. Heterocumulenes present two different positions to attack by a metal, and for which different metal selectivities can be envisaged. The carbenoid-like basic metals, Rh^I, Ir^I, Pd^0, and Pt^0,[5] seem to have assumed the predominant role until now.

Here we report the reactions of the carbenoid-like $[Ti(cp)_2(CO)_2]$ (cp = η-cyclopentadienyl) with phenyl isocyanate which give rise to models for carbon dioxide activation. These reactions produce bis(cyclopentadienyl)titanium complexes containing a novel bonding mode of the ureylene ligand.[5]

EXPERIMENTAL

Unless otherwise stated, all the reactions described were carried out under an atmosphere of purified nitrogen. Infrared spectra were recorded on Perkin-Elmer 283 and 337 spectrometers. Absorption or evolution of CO was measured volumetrically as previously described.[6] Dicarbonylbis(η-cyclopentadienyl)titanium(II) was prepared by one of the methods previously reported.[7] Freshly distilled phenylisocyanate was employed. Magnetic-susceptibility measurements were made with a Faraday balance.

Preparation of 1,2 : 2,3-*Bis*[μ-*diphenylureylene*-NN′(*Ti*^{1} *or Ti*^{3}),O(*Ti*^{2})]-*tris*[*bis*(η-*cyclopentadienyl*)*titanium*], (3).—To a diethyl ether (250 cm^3) solution of $[Ti(cp)_2(CO)_2]$ (2.86 g, 12.2 mmol) was added neat liquid PhNCO (4.5 cm^3, 41.3 mmol). The resulting solution was kept at 25 °C. Copious gas evolution occurs suddenly, followed by precipitation of deep maroon crystals, which were filtered off at the end of the gas evolution (*ca.* 82%). Better crystals suitable for *X*-ray analysis were prepared using as solvent a 1 : 4 mixture of tetrahydrofuran (thf) and diethyl ether. The higher solubility in this mixture decreased the yield of (3) (Found: C, 70.65; H, 5.25; N, 5.85; Ti, 15.1. Calc. for $C_{56}H_{50}N_4O_2Ti_3$: C, 70.45; H, 5.25; N, 5.85; Ti, 15.1%). The i.r. spectrum shows strong absorptions in the 1 400—1 500 cm^{-1} region; χ_M^{corr} = 2 494 × 10^{-6} c.g.s. units at 296 K. The complex $[Ti(cp)_2(CO)_2]$ (0.160 g, 0.68 mmol) reacted with an isoctane (20 cm^3) solution of PhNCO (1.5 cm^3, 13.8 mmol) in gas-volumetric-analysis equipment at 21.2 °C to give 1.82 mmol of carbon monoxide [CO : Ti mol ratio: 2.67 : 1 (calc. 2.66 : 1)].

Reactions of (3).—*With* EtOH. The complex (0.24 g, 0.25 mmol) suspended in toluene (5 cm^3) was treated with EtOH (0.05 cm^3). A reaction took place immediately, giving a maroon solution and *NN*′-diphenylurea as a white crystalline solid (*ca.* 66%).

With Phenanthrene-9,10-*quinone*. To a thf (25 cm^3) solution of (3) (0.79 g, 0.83 mmol) was added solid phenanthrene-9,10-quinone(phenq) (0.17 g, 0.82 mmol). The reaction took place immediately forming $[Ti(cp)_2\{OC(NPh)_2\}]$ (5) as a microcrystalline green solid (*ca.* 80%). By the addition of hexane (50 cm^3) and cooling at −30 °C, deep green crystals were obtained, identical to an authentic sample of $[Ti(cp)_2(phenq)]$ (4).

Preparation of μ-*Diphenylureylene*-NN′O-*bis*[*bis*(η-*cyclopentadienyl*)*titanium*] (6).—A thf (25 cm^3) solution of $[Ti(cp)_2(CO)_2]$ (2.90 g, 12.40 mmol) was heated at 60 °C for

1.5 h in the presence of PhNCO (1.75 g, 14.70 mmol). Evolution of CO took place and the solution became deep blue. When the evolution of CO had stopped the solution was cooled at room temperature. Addition of diethyl ether (100 cm^3) gave deep blue crystals (*ca.* 80%) (Found: C, 69.55; H, 5.35; N, 4.55; Ti, 16.6. Calc. for $C_{33}H_{30}N_2OTi_2$: C, 69.95; H, 5.30; N, 4.95; Ti, 16.95%). The mass spectrum showed the parent peak at *m/e* 566. The only significant band in the i.r. spectrum (Nujol) appears at 1 525 cm^{-1}; $\mu_{eff.}$ (293 K) = 1.73 B.M. per titanium.*

$[Ti(cp)_2(CO)_2]$ (0.210 g, 0.90 mmol) reacted with a toluene (20 cm^3) solution of PhNCO (0.1 cm^3, 0.92 mmol) in a gas-volumetric-analysis equipment at 51 °C for 21 h to give 2.06 mmol of carbon monoxide (calc. 2.25 mmol). The reaction in toluene or the recrystallisation of (6) from toluene gave deep blue crystals of $[\{Ti(cp)_2\}_2\{OC(NPh)_2\}]\cdot 0.5C_6H_5Me$ (7), which were used for the *X*-ray analysis (Found: C, 70.9; H, 5.60; N, 4.10. Calc. for $C_{36.5}H_{34}N_2OTi_2$: C, 71.5; H, 5.55; N, 4.5%).

Preparation of Bis(η-*cyclopentadienyl*)(*diphenylureylene*-NN′)*titanium* (5).—Complex (3) (1.10 g, 1.15 mmol) suspended in toluene (25 cm^3) was heated at 90 °C for 0.5 h. A light green precipitate was formed, which was filtered off while hot, washed with toluene and dried (*ca.* 74%) (Found: C, 71.75; H, 5.20; N, 6.90; Ti, 12.45. Calc. for $C_{23}H_{20}N_2OTi$: C, 71.15; H, 5.15; N, 7.20; Ti, 12.35%). Complex (7) was obtained as deep blue crystals (*ca.* 47%) on cooling the toluene solution. The low yield of (7) can be explained by its relatively high solubility in toluene, from which further recovery was not attempted. Complex (5) is quite stable in air, but is sensitive to hydrolysis. The i.r. spectrum shows a strong band at 1 625 cm^{-1}.

Reaction of $[Ti(cp)_2(CO)_2]$ *with Complex* (5).—To a thf (10 cm^3) solution of $[Ti(cp)_2(CO)_2]$ (0.405 g, 1.73 mmol) was added solid (5) (0.30 g, 0.79 mmol) (practically insoluble in thf). On stirring, the green solid dissolved, the solution was concentrated, and by addition of diethyl ether (30 cm^3), (6) was obtained as deep blue crystals (*ca.* 53%).

X-*Ray Crystallography*.—*X*-Ray intensity data were collected on a Siemens single-crystal computer-controlled diffractometer by use of niobium-filtered Mo-K_α and nickel-filtered Cu-K_α radiation for complexes (3) and (7) respectively, and the ω—2θ scan technique.

Crystal data. (3), $C_{56}H_{50}N_4O_2Ti_3$, *M* = 954.8, Monoclinic, *a* = 26.187(7), *b* = 8.865(3), *c* = 20.515(5) Å, β = 105.09(4)°, *U* = 4 598.3 $Å^3$, *Z* = 4, D_c = 1.379 g cm^{-3}, *F*(000) = 1 984. Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 5.45 cm^{-1}, space group *Cc* or *C*2/*c*, the latter assumed in structural analysis.

(7), $C_{33}H_{30}N_2OTi_2\cdot 0.5C_7H_8$, *M* = 612.5, Orthorhombic, *a* = 19.138(2), *b* = 75.184(10), *c* = 8.553(2) Å, *U* = 12 306.7 $Å^3$, *Z* = 16, D_c = 1.322 g cm^{-3}, *F*(000) = 5 104. Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 46.7 cm^{-1}, space group *Fdd*2 from systematic absences.

Cell dimensions were determined from rotation and Weissenberg photographs. The values quoted were obtained by least-squares refinement of the 2θ values of 28 reflections (2θ > 22°) for (3) and 25 reflections (2θ > 70°) for (7).

Intensity data collection. The crystals used for data collection had dimensions *ca.* 0.50 × 0.18 × 0.34 (3) and 0.21 × 0.45 × 0.56 mm (7) respectively. They were mounted in thin-walled glass capillaries under a nitrogen atmosphere and aligned with the [010] and [001] axes [for (3) and (7), respectively] parallel to the spindle axis of the diffractometer. The intensities were measured with a drive speed related to the number of counts on the peak (lowest scan speed, 2.5° min^{-1}). A standard reflection, monitored every 20 reflections, did not change noticeably during data collection. The intensities were collected in the interval $5 < 2\theta < 44°$ for (3) and $6 < 2\theta < 140°$ for (7) using the five-point procedure. For (3), 2 827 independent reflections were measured, of which 813 having $I > 2\sigma(I)$ were considered observed and used in the analysis; for (7), the number of independent reflections was 3 031, 2 891 of which $[I > 2\sigma(I)]$ were included in the analysis. Corrections were applied for Lorentz and polarisation factors but not for absorption [μr = 0.1 and 0.7 for (3) and (7), respectively] and therefore the thermal coefficients are influenced by this omission, in particular for complex (7).

Structure determination and refinement. (*a*) *Complex* (3). The structure was solved by the heavy-atom method. The analysis of a three-dimensional Patterson map indicated that the vector distribution could be interpreted on the basis of the centrosymmetric space group *C*2/*c*, assuming one independent titanium atom, Ti(1), on a two-fold axis and the other one, Ti(2), in a general position. The successive Fourier map phased on these positions yielded the co-ordinates of the atoms of the ureylene ligand bridging the two metal atoms. Due to the presence of the C_2 symmetry, the molecule appeared to be trinuclear. The location of the cp carbon atoms was made difficult, especially for the ring around Ti(1), by the spreading of the electron density associated with these rings. High thermal motion or disorder could be responsible, which could suggest, however, the presence of pseudo-C_2 symmetry. After locating the cp carbon atoms in successive difference-Fourier syntheses, an attempt was made to refine the structure in the *Cc* space group with isotropic thermal parameters, using full-matrix least squares and a rigid-body constraint for the cp and Ph rings. This refinement did not converge, due to the very high correlations between all the corresponding positional parameters in the two symmetry-related parts of the molecule. Refinement was therefore continued in the *C*2/*c* space group with the three cp and the two independent Ph rings treated as rigid groups, using full-matrix least squares, first isotropically down to *R* 0.159, then anisotropically for the two titanium atoms and the ureylene atoms down to the final *R* 0.095 for 805 reflections (eight reflections probably affected by counting errors were rejected). The hydrogen atoms were introduced in the last cycle in calculated positions and refined with the rigid-body constraint. An electron-density synthesis for the final rigid-group model showed no unusual features with no peaks above the general background. This model was considered satisfactory, although poorly refined, in view of the large number of variables with respect to the number of observations. The function minimised during all least-squares calculations was $\Sigma w|\Delta F|^2$ with unit weights. Atomic scattering factors used were taken from ref. 8 for Ti, ref. 9 for C, N, and O, and ref. 10 for H. The computer programs used were those of ref. 11. The final positions for the atoms are listed in Table 1.

(*b*) *Complex* (7). The structure was solved by the heavy-atom method. The co-ordinates of the two independent titanium atoms were found from a vector-distribution analysis of a Patterson map. All the non-hydrogen atoms were located in a successive difference-Fourier synthesis which showed the presence of a toluene molecule of crystal-

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

lisation situated on a two-fold axis. Refinement was by block-diagonal least squares, isotropically down to R 0.111, anisotropically down to R 0.078. The function minimised was $\Sigma w|\Delta F|^2$ with unit weights, and a small improvement to R 0.071 was obtained by applying the weighting scheme proposed by Cruickshank,[12] $w^{-1} = A + B|F_o| + C|F_o|^2$ with $A = 18.653\ 8$, $B = 0.294\ 380$, and $C = 0.001\ 161\ 45$, deduced from the $\langle \Delta F \rangle$ against $|F|$ distribution.[13] At this stage a difference-Fourier map showed the positions of 23 hydrogen atoms. Those marked with an asterisk in the Table of atomic co-ordinates were introduced in their geometrical positions. No attempt was made to locate the

TABLE 1

Atomic co-ordinates ($\times 10^4$) for complex (3) with estimated standard deviations in parentheses

	x/a	y/b	z/c
Ti(1)	0	5 037(9)	2 500
Ti(2)	1 911(2)	8 384(7)	3 503(3)
O(1)	0 490(9)	6 534(21)	2 966(8)
N(1)	1 183(9)	8 055(26)	2 739(10)
N(2)	1 311(10)	6 952(25)	3 690(13)
C(16)	0 963(15)	7 156(37)	3 106(15)
C(1)	0 647(10)	5 097(26)	1 810(13)
C(2)	0 770(10)	3 827(26)	2 244(13)
C(3)	0 324(10)	2 854(26)	2 097(13)
C(4)	−0 075(10)	3 523(26)	1 573(13)
C(5)	0 125(10)	4 910(26)	1 395(13)
C(6)	1 702(10)	9 883(23)	4 353(10)
C(7)	1 395(10)	10 434(23)	3 723(10)
C(8)	1 746(10)	11 031(23)	3 365(10)
C(9)	2 271(10)	10 848(23)	3 775(10)
C(10)	2 243(10)	10 139(23)	4 385(10)
C(11)	2 558(11)	6 445(32)	3 823(12)
C(12)	2 206(11)	5 912(32)	3 219(12)
C(13)	2 230(10)	6 920(32)	2 690(12)
C(14)	2 598(11)	8 076(32)	2 968(12)
C(15)	2 800(11)	7 783(32)	3 668(12)
C(21)	1 235(9)	6 044(21)	4 237(12)
C(22)	0 969(9)	6 621(21)	4 691(12)
C(23)	0 878(9)	5 703(21)	5 202(12)
C(24)	1 052(9)	4 210(21)	5 259(12)
C(25)	1 317(9)	3 634(21)	4 805(12)
C(26)	1 408(9)	4 551(21)	4 294(12)
C(31)	0 931(8)	8 779(24)	2 111(12)
C(32)	1 268(8)	9 425(24)	1 762(12)
C(33)	1 058(8)	10 121(24)	1 140(12)
C(34)	0 512(8)	10 171(24)	0 867(12)
C(35)	0 175(8)	9 525(24)	1 216(12)
C(36)	0 385(8)	8 829(24)	1 838(12)
H(1)	0 897(10)	6 062(26)	1 800(13)
H(2)	1 146(10)	3 668(26)	2 628(13)
H(3)	0 320(10)	1 757(26)	2 339(13)
H(4)	−0 440(10)	2 971(26)	1 333(13)
H(5)	−0 083(10)	5 631(26)	1 000(13)
H(6)	1 547(10)	9 370(23)	4 739(10)
H(7)	0 974(10)	10 401(23)	3 538(10)
H(8)	1 648(10)	11 508(23)	2 867(10)
H(9)	2 637(10)	11 161(23)	3 654(10)
H(10)	2 575(10)	9 840(23)	4 811(10)
H(11)	2 640(11)	5 979(32)	4 326(12)
H(12)	1 960(11)	4 846(32)	3 220(12)
H(13)	1 978(11)	6 644(32)	2 169(12)
H(14)	2 670(11)	8 887(32)	2 627(12)
H(15)	3 079(11)	8 477(32)	3 960(12)
H(22)	0 819(9)	7 761(21)	4 631(12)
H(23)	0 684(9)	6 171(21)	5 564(12)
H(24)	1 028(8)	3 558(21)	5 702(12)
H(25)	1 508(9)	2 535(21)	4 907(12)
H(26)	1 643(9)	4 124(21)	3 974(12)
H(32)	1 691(8)	9 382(24)	1 972(12)
H(33)	1 319(8)	10 593(24)	0 863(12)
H(34)	0 349(8)	10 691(24)	0 381(12)
H(35)	−0 248(8)	9 578(24)	1 009(12)
H(36)	0 124(8)	8 367(24)	2 118(12)

TABLE 2

Atomic co-ordinates ($\times 10^4$) for complex (7), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Ti(1)	0 485(1)	2 111(1)	9 552(01)
Ti(2)	−0 559(1)	1 652(1)	7 500(01)
O	0.008(1)	1 878(1)	8 519(04)
N(1)	0.538(2)	1 677(1)	7 098(06)
N(2)	1 125(2)	1 938(1)	8 205(5)
C(37)	0 611(2)	1 826(1)	7 885(6)
C(1)	0 406(3)	2 257(1)	7 137(9)
C(2)	0 872(3)	2 358(1)	8 126(10)
C(3)	0 472(4)	2 427(1)	9 339(11)
C(4)	−0.222(4)	2 369(1)	9 186(10)
C(5)	−0 258(4)	2 266(1)	7 818(10)
C(6)	0 968(5)	2 188(1)	1 2101(10)
C(7)	1 224(3)	2 029(1)	11 745(9)
C(8)	0 680(4)	1 913(1)	11 689(7)
C(9)	0 051(3)	2 002(1)	12 004(8)
C(10)	0 253(6)	2 177(1)	12 278(9)
C(11)	−1 361(3)	1 856(1)	6 473(8)
C(12)	−1 673(3)	1 684(1)	6 304(11)
C(13)	−1 249(4)	1 588(1)	5 286(10)
C(14)	−0 698(4)	1 691(1)	4 774(8)
C(15)	−0 755(3)	1 861(1)	5 515(7)
C(16)	−0 702(5)	1 566(1)	10 222(9)
C(17)	−1 267(3)	1 512(1)	9 494(11)
C(18)	−1 053(5)	1 375(1)	8 368(10)
C(19)	−0 338(5)	1 360(1)	8 516(10)
C(20)	−0 133(3)	1 480(1)	9 678(10)
C(21)	1 097(2)	1 564(1)	6 677(7)
C(22)	1 034(3)	1 464(1)	5 313(9)
C(23)	1 549(3)	1 343(1)	4 894(10)
C(24)	2 134(3)	1 323(1)	5 790(10)
C(25)	2 206(3)	1 421(1)	7 120(10)
C(26)	1 680(3)	1 540(1)	7 584(8)
C(31)	1 751(2)	1 948(1)	7 369(7)
C(32)	2 367(3)	1 992(1)	8 157(8)
C(33)	2 997(3)	2 007(1)	7 394(9)
C(34)	3 026(3)	1 982(1)	5 802(9)
C(35)	2 419(3)	1 942(1)	4 998(8)
C(36)	1 786(3)	1 926(1)	5 758(7)
C(41)	0 000(—)	0 000(—)	0 951(14)
C(42)	0 340(3)	0 131(1)	0 146(11)
C(43)	0 348(4)	0 131(1)	−1 470(14)
C(44)	0 000(—)	0 000(—)	−2 345(21)
C(45)	0 000(—)	0 000(—)	2 761(20)
H(1)	0 670(40)	2 210(10)	6 160(100)
H(2)	1 440(30)	2 390(10)	8 170(100)
H(3) *	0 680(30)	2 510(10)	10 390(90)
H(4) *	−0 640(30)	2 400(10)	9 940(90)
H(5)	−0 660(30)	2 210(10)	7 360(110)
H(6)	1 300(40)	2 280(10)	12 230(130)
H(7)	1 750(30)	2 000(10)	11 570(90)
H(8) *	0 720(40)	1 760(10)	11 370(110)
H(9)	−0 520(30)	1 990(10)	11 900(90)
H(10) *	−0 130(40)	2 280(10)	12 620(110)
H(11)	−1 520(30)	1 950(10)	7 400(100)
H(12)	−2 230(30)	1 690(10)	6 650(90)
H(13) *	−1 350(30)	1 450(10)	4 870(100)
H(14)	−0 250(30)	1 680(10)	3 950(90)
H(15) *	−0 380(30)	1 970(10)	5 450(100)
H(16) *	−0 710(30)	1 670(10)	11 220(100)
H(17)	−1 780(30)	1 520(10)	9 880(100)
H(18)	−1 460(30)	1 310(10)	7 570(100)
H(19)	0 100(40)	1 300(10)	8 050(90)
H(20)	0 380(30)	1 510(10)	10 300(100)
H(22)	0 560(30)	1 480(10)	4 780(110)
H(23) *	1 460(30)	1 270(10)	3 890(80)
H(24)	2 550(30)	1 270(10)	5 190(80)
H(25)	2 730(40)	1 400(10)	7 440(100)
H(26)	1 710(30)	1 590(10)	8 650(90)
H(32)	2 300(30)	2 020(10)	9 330(90)
H(33)	3 470(30)	2 030(10)	7 760(90)
H(34)	3 480(40)	2 000(10)	5 460(90)
H(35)	2 590(30)	1 910(10)	4 080(100)
H(36)	1 350(30)	1 910(10)	5 230(90)
H(42) *	0 610(30)	0 250(10)	0 770(100)
H(43) *	0 670(40)	0 230(10)	−2 050(100)
H(44)	0 000(1)	0 000(1)	−3 740(160)

methyl hydrogens of the toluene molecule which must be statistically distributed for symmetry requirements. All the hydrogen atoms were refined isotropically in the last cycle. The final *R* was 0.059. Atomic scattering factors used were taken from ref. 9 for Ti, O, N, and C and from ref. 10 for H. The computer programs used were those of ref. 14. The final positions for the atoms are given in Table 2. All the calculations were made on a CYBER 7600 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale (Bologna).

Observed and calculated structure factors together with the thermal parameters for the two complexes are listed in Supplementary Publications No. SUP 22442 (29 pp.).* The most relevant bond distances and angles and the equations of molecular planes are given in Tables 3—5.

TABLE 3

Bond distances (Å) and angles (°) in complex (3)

Ti(1)–C(1)	2.48(3)	Ti(1)–C(4)	2.29(3)
Ti(1)–C(2)	2.46(3)	Ti(1)–C(5)	2.38(3)
Ti(1)–C(3)	2.35(3)	Average	2.39(1)
Ti(2)–C(6)	2.37(2)	Ti(2)–C(9)	2.39(2)
Ti(2)–C(7)	2.38(2)	Ti(2)–C(10)	2.37(2)
Ti(2)–C(8)	2.39(2)	Average	2.38(1)
Ti(2)–C(11)	2.38(3)	Ti(2)–C(14)	2.35(3)
Ti(2)–C(12)	2.44(3)	Ti(2)–C(15)	2.33(3)
Ti(2)–C(13)	2.43(3)	Average	2.39(1)
Ti(1)–O(1)	1.92(2)	Ti(2)–N(2)	2.13(3)
Ti(1)–Cp(1)	2.06(3)	Ti(2)–Cp(2)	2.05(2)
Ti(2)–N(1)	2.15(2)	Ti(2)–Cp(3)	2.06(3)
C(16)–O(1)	1.32(4)	N(1)–C(31)	1.44(3)
C(16)–N(1)	1.33(4)	N(2)–C(21)	1.44(3)
C(16)–N(2)	1.32(4)		
O(1)–Ti(1)–O(1′)	92.5(9)	O(1)–Ti(1)–Cp(1′)	108.8(9)
O(1)–Ti(1)–Cp(1)	105.6(1.0)	Cp(1)–Ti(1)–Cp(1′)	129.4(1.0)
N(1)–T(2)–N(2)	59.4(9)	N(2)–Ti(2)–Cp(2)	110.0(1.0)
N(1)–Ti(2)–Cp(2)	107.1(1.0)	N(2)–Ti(2)–Cp(3)	107.6(1.1)
N(1)–Ti(2)–Cp(3)	108.1(1.0)	Cp(2)–Ti(2)–Cp(3)	137.8(1.1)
Ti(1)–O(1)–C(16)	150.1(2.1)	N(1)–C(16)–N(2)	107.4(3.1)
O(1)–C(16)–N(1)	130.6(2.7)	C(16)–N(1)–C(31)	127.7(2.5)
O(1)–C(16)–N(2)	122.0(2.8)	Ti(2)–N(1)–C(16)	95.8(1.8)
Ti(2)–N(1)–C(31)	134.9(1.7)	Ti(2)–N(2)–C(16)	97.0(2.1)
C(16)–N(2)–C(21)	125.8(2.7)	Ti(2)–N(2)–C(21)	137.2(1.9)
N(1)–C(31)–C(32)	116.0(2.0)	N(2)–C(21)–C(22)	120.7(1.9)
N(1)–C(31)–C(36)	123.9(2.1)	N(2)–C(21)–C(26)	119.3(2.1)

Primed atoms at the symmetry-related position $\bar{x}, y, \frac{1}{2} - z$.

All the average values were calculated using the formulae $\mu_{\text{av.}} = (\mu_i/\sigma_i^2)/\Sigma_i\sigma_i^{-2}$ and $\sigma_{\text{av.}} = (\Sigma_i\sigma_i^{-2})^{-\frac{1}{2}}$ where μ_i are the individual observations and σ_i their standard deviations.

RESULTS AND DISCUSSION

The complex $[\mathrm{Ti(cp)_2(CO)_2}]$ (cp = η-C_5H_5) reacts with a large excess of PhNCO in diethyl ether or in a hydrocarbon solution at room temperature, losing carbon monoxide, with the overall stoicheiometry (1).

$$\underset{(1)}{3[\mathrm{Ti(cp)_2(CO)_2}]} + \underset{(2)}{4\,\mathrm{PhNCO}} \longrightarrow \underset{(3)}{[\{\mathrm{Ti(cp)_2}\}_3\{\mathrm{OC(NPh)_2}\}_2]} + 8\,\mathrm{CO} \qquad (1)$$

Complex (3) can be obtained as a maroon crystalline solid from oxygenated solvents, as well as a powder from hydrocarbons, in which it is very slightly soluble. While (3) is thermally stable in the solid state, it rearranges on heating in solution. The presence of the intact unit $\mathrm{Ti(cp)_2}$ in (3) is deduced from the hydrolysis which gives $[\mathrm{Ti(cp)_2Cl_2}]$ and *NN*′-diphenylurea. Although the latter compound confirms the presence of a diphenylureylene residue, this was not indicated by the i.r. spectrum, in which there were no bands at $>1\,600$ cm^{-1}. The *X*-ray structural analysis showed the molecular complexity and the relative arrangements of the different units in (3). The

TABLE 4

Bond distances (Å) and angles (°) for complex (7)

Ti(1)–C(1)	2.344(9)	Ti(1)–C(4)	2.386(10)
Ti(1)–C(2)	2.342(10)	Ti(1)–C(5)	2.362(9)
Ti(1)–C(3)	2.383(11)	Average	2.362(4)
Ti(1)–C(6)	2.438(9)	Ti(1)–C(9)	2.400(7)
Ti(1)–C(7)	2.429(8)	Ti(1)–C(10)	2.425(8)
Ti(1)–C(8)	2.387(8)	Average	2.414(4)
Ti(2)–C(11)	2.345(8)	Ti(2)–C(14)	2.365(7)
Ti(2)–C(12)	2.377(7)	Ti(2)–C(15)	2.344(8)
Ti(2)–C(13)	2.358(9)	Average	2.359(3)
Ti(2)–C(16)	2.432(8)	Ti(2)–C(19)	2.399(10)
Ti(2)–C(17)	2.419(9)	Ti(2)–C(20)	2.410(9)
Ti(2)–C(18)	2.405(10)	Average	2.415(4)
Ti(1)–O	2.164(9)	Ti(2)–O	2.196(9)
Ti(1)–N(2)	2.126(7)	Ti(2)–N(1)	2.136(5)
Ti(1)–Cp(1)	2.035(10)	Ti(2)–Cp(3)	2.029(8)
Ti(1)–Cp(2)	2.114(8)	Ti(2)–Cp(4)	2.107(10)
O–C(37)	1.334(6)	N(1)–C(21)	1.413(8)
N(1)–C(37)	1.314(10)	N(2)–C(31)	1.397(6)
N(2)–C(37)	1.323(8)		
C(1)–C(2)	1.445(10)	C(3)–C(4)	1.404(11)
C(1)–C(5)	1.400(10)	C(4)–C(5)	1.405(12)
C(2)–C(3)	1.390(12)	Average	1.411(5)
C(6)–C(7)	1.327(11)	C(8)–C(9)	1.403(10)
C(6)–C(10)	1.379(15)	C(9)–C(10)	1.391(11)
C(7)–C(8)	1.359(10)	Average	1.372(5)
C(11)–C(12)	1.431(10)	C(13)–C(14)	1.380(11)
C(11)–C(15)	1.421(9)	C(14)–C(15)	1.431(10)
C(12)–C(13)	1.392(11)	Average	1.413(4)
C(16)–C(17)	1.312(11)	C(18)–C(19)	1.379(14)
C(16)–C(20)	1.349(11)	C(19)–C(20)	1.398(11)
C(17)–C(18)	1.468(12)	Average	1.378(5)
O–Ti(1)–N(2)	61.7(2)	O–Ti(2)–N(1)	60.7(2)
O–Ti(1)–Cp(1)	111.5(3)	O–Ti(2)–Cp(3)	109.8(4)
O–Ti(1)–Cp(2)	108.3(4)	O–Ti(2)–Cp(4)	108.4(3)
N(2)–Ti(1)–Cp(1)	110.6(3)	N(1)–Ti(2)–Cp(3)	113.2(3)
N(2)–Ti(1)–Cp(2)	110.1(3)	N(1)–Ti(2)–Cp(4)	107.5(3)
Cp(1)–Ti(1)–Cp(2)	132.7(4)	Cp(3)–Ti(2)–Cp(4)	133.9(4)
Ti(1)–O–C(37)	92.2(4)	Ti(1)–N(2)–C(37)	94.2(4)
Ti(2)–O–C(37)	92.3(4)	Ti(1)–N(2)–C(31)	137.6(6)
Ti(1)–O–Ti(2)	175.3(2)	C(31)–N(2)–C(37)	124.5(6)
O–C(37)–N(1)	111.5(5)	Ti(2)–N(1)–C(37)	95.6(4)
O–C(37)–N(2)	111.9(6)	Ti(2)–N(1)–C(21)	137.1(6)
N(1)–C(37)–N(2)	136.7(5)	C(21)–N(1)–C(37)	124.2(4)
N(1)–C(21)–C(22)	118.2(5)	N(2)–C(31)–C(32)	119.3(5)
N(1)–C(21)–C(26)	123.5(6)	N(2)–C(31)–C(36)	122.9(5)

The two phenyl rings show D_{6h} symmetry within experimental error; the C–C bond distances and the C–C–C bond angles average 1.380(4), 1.384(4) Å and 119.9(3), 119.9(2)° respectively.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 5

Equations of least-squares planes and, in square brackets, distances (Å) from these planes

Complex (3) *

Plane (1): ureylene ligand N(1), C(16), N(2), O(1)
$0.4706X' - 0.8000Y' - 0.3721Z' = -6.9611$
[N(1) −0.001, C(16) 0.003, N(2) −0.001, O(1) −0.001, C(21) 0.009, C(31) −0.204, Ti(2) −0.092, Ti(1) −0.918]

Plane (2): cyclopentadienyl ring C(1), C(2), C(3), C(4), C(5)
$0.5573X' - 0.4750Y' - 0.6811Z' = -4.1825$
[Ti(1) −2.055]

Plane (3): cyclopentadienyl ring (C6), C(7), C(8), C(9), C(10)
$0.1639X' - 0.8962Y' - 0.4122Z' = -11.0567$
[Ti(2) 2.049]

Plane (4): cyclopentadienyl ring C(11), C(12), C(13), C(14), C(15)
$0.8164X' - 0.5440Y' - 0.1941Z' = -0.7760$
[Ti(2) −2.056]

Plane (5): phenyl ring C(21), C(22), C(23), C(24), C(25), C(26)
$-0.7403X' - 0.2893Y' - 0.6069Z' = -7.3615$

Plane (6): phenyl ring C(31), C(32), C(33), C(34), C(35), C(36)
$0.1656X' - 0.8698Y' - 0.4648Z' = -8.4957$

Complex (7)

Plane (1): ureylene ligand O, N(1), N(2), C(37)
$-0.2137X + 0.5210Y - 0.8264Z = 1.3311$
[O 0.000, N(1) −0.001, N(2) 0.001, C(37) −0.002, Ti(1) −0.012, Ti(2) 0.067]

Plane (2): cyclopentadienyl ring C(1), C(2), C(3), C(4), C(5)
$-0.2013X + 0.8185Y - 0.5381Z = 10.4444$
[C(1) 0.004, C(2) −0.009, C(3) 0.011, C(4) −0.008, C(5) 0.002, Ti(1) −2.036]

Plane (3): cyclopentadienyl ring C(6), C(7), C(8), C(9), C(10)
$-0.1150X + 0.1991Y - 0.9732Z = -7.0120$
[C(6) 0.001, C(7) 0.003, C(8) −0.004, C(9) 0.005, C(10) −0.005, Ti(1) 2.114]

Plane (4): cyclopentadienyl ring C(11), C(12), C(13), C(14), C(15)
$-0.5497X + 0.3306Y - 0.7671Z = 1.8013$
[C(11) −0.003, C(12) 0.008, C(13) −0.009, C(14) 0.004, C(15) 0.000, Ti(2) −2.028]

Plane (5): cyclopentadienyl ring C(16), C(17), C(18), C(19), C(20)
$0.1270X + 0.7082Y - 0.69457Z = 2.0983$
[C(16) −0.003, C(17) 0.005, C(18) −0.004, C(19) 0.002, C(20) 0.000, Ti(2) 2.107]

Plane (6): phenyl ring C(21), C(22), C(23), C(24), C(25), C(26)
$0.4611X + 0.7221Y - 0.5157Z = 6.5102$
[C(21) 0.004, C(22) 0.007, C(23) −0.11, C(24) 0.002, C(25) 0.011, C(26) −0.012]

Plane (7): phenyl ring C(31), C(32), C(33), C(34), C(35), C(36)
$-0.1755X + 0.9746Y - 0.1391Z = 12.8211$
[C(31) −0.012, C(32) 0.010, C(33) −0.001, C(34) −0.005, C(35) 0.002, C(36) 0.007]

Plane (8): toluene molecule C(41), C(42), C(43), C(44), C(45), C(42′), C(43′)
$-0.8319X + 0.5549Y - 0.0001Z = 0.0000$
[C(41) 0.000, C(42) 0.005, C(43) −0.007, C(44) 0.000, C(45) 0.000, C(42′) −0.005, C(43′) 0.008]

Plane (9): O, N(1), N(2), C(37), Ti(1), Ti(2)
$-0.1966X + 0.5300Y - 0.8249Z = 1.4884$
[O −0.018, N(1) −0.016, N(2) 0.023, C(37) −0.005, Ti (1) 0.002, Ti(2) 0.014]

* The transformation matrix from monoclinic X, Y, Z to orthogonal X',Y',Z' is:

$$\begin{matrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{matrix}$$

preparation, physical properties, and reactions of (3) will be discussed on this basis.

The Structure of (3).—The structure of (3) consists of trinuclear molecules (C_2 symmetry), where two $\mathrm{Ti(cp)_2\{OC(NPh)_2\}}$ moieties are symmetrically linked to the central $\mathrm{Ti(cp)_2}$ unit through the carbonyl oxygen atoms. Figure 1 shows a view of the molecular structure together with the numbering scheme. Unfortunately, the significance of the Ti–C(cp) bond distances is debatable, since the disorder (or high thermal motion) prevents the accurate location of the rings. This notwithstanding, it is possible to infer that the co-ordination geometry around the two independent metal atoms is similar to that found in other well determined structures.[15]

The main features of the titanium co-ordination are: (*a*) the plane of σ bonds is nearly orthogonal to that containing the metal-to-ring normals; (*b*) the cyclopentadienyl rings exhibit an almost staggered configuration around Ti(2), while the configuration around Ti(1) is neither staggered nor eclipsed (Figure 2); (*c*) the distances from the titanium atoms to the ring centres are Ti(1)–cp(1) 2.06(3), Ti(2)–cp(2) 2.05(2), Ti(2)–cp(3) 2.06(3) Å; (*d*) the cp(centroid)–Ti–cp(centroid) angles are 129.4(1.0) and 13.8(1.1)° around Ti(1) and Ti(2), respectively; (*e*) Ti–N bond distances fall in the usual range, while an unusually short Ti(1)–O(1) distance [1.92(2) Å] [16] is observed.

The ureylene ligand defines a plane (Table 5) from which Ti(2) and Ti(1) are displaced by −0.092 and −0.918 Å, respectively. The angles associated with C(16) indicate an approximate sp^2 geometry. The bond lengths and angles of this ureylene ligand can be compared in Table 6 with those of other bridging ureylene ligands.[17,18] The lengthening of the C–O bond distances coupled with a significant shortening of the C–N bond distances suggests that diphenylureylene is present both in (3) and (7) as a delocalised ligand. This electronic delocalisation all over the ligand reduces the C–O bond order, with the consequent absence of any CO band at >1 600 cm^{-1} in the i.r. spectrum. The assignment of a formal oxidation number to the titanium atoms must take into account both the structural data and the magnetic properties of (3). The most likely possibility, which agrees with the magnetic moment of 1.72 B.M. at

TABLE 6

Bond lengths (Å) and angles (°) associated with ureylene ligands

	$\mathrm{[\{Fe(CO)_3\}_2\{OC(NPh)_2\}]}$ [a]	$\mathrm{[\{Fe(CO)_3\}_2\{OC(NMe)_2\}]}$ [b]	Complex (3)	Complex (7)
C–O	1.20	1.21(3)	1.32(4)	1.334(6)
C–N [c]	1.41	1.36(3)	1.33(4)	1.314(10)
C–N	1.41	1.43(3)	1.32(4)	1.323(8)
N–C(R)	1.43 [d]	1.55(3) [e]	1.44(3)	1.397(6)
N–C(R)	1.44	1.49(3)	1.44(3)	1.413(8)
O–C–N		126.1(26)	122.0(2.8)	111.5(5)
O–C–N		135.6(26)	130.6(2.7)	111.9(6)
N–C–N	98	98.3(25)	107.4(3.1)	136.7(5)

[a] J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Comm.*, 1967, 1149. [b] Ref. 18. [c] Crystallographically non-equivalent N atoms. [d] R = Ph. [e] R = Me.

296 K for two titanium atoms per unit, as well as for all the cp rings η^5-bonded to the titanium atoms, requires that Ti(1) is titanium(IV) while Ti(2) is titanium(III). In the presence of a non-delocalised diphenylureylene ligand, we expect Ti(1) to be titanium(II) and Ti(2) to be titanium(IV). However, the magnetic moment is lower (2.43 *vs.* 2.83 B.M.) than expected for a d^2 high-spin system, and furthermore this hypothesis would require a cp ring η^3-bonded to Ti(1),[19] for which we have no evidence.

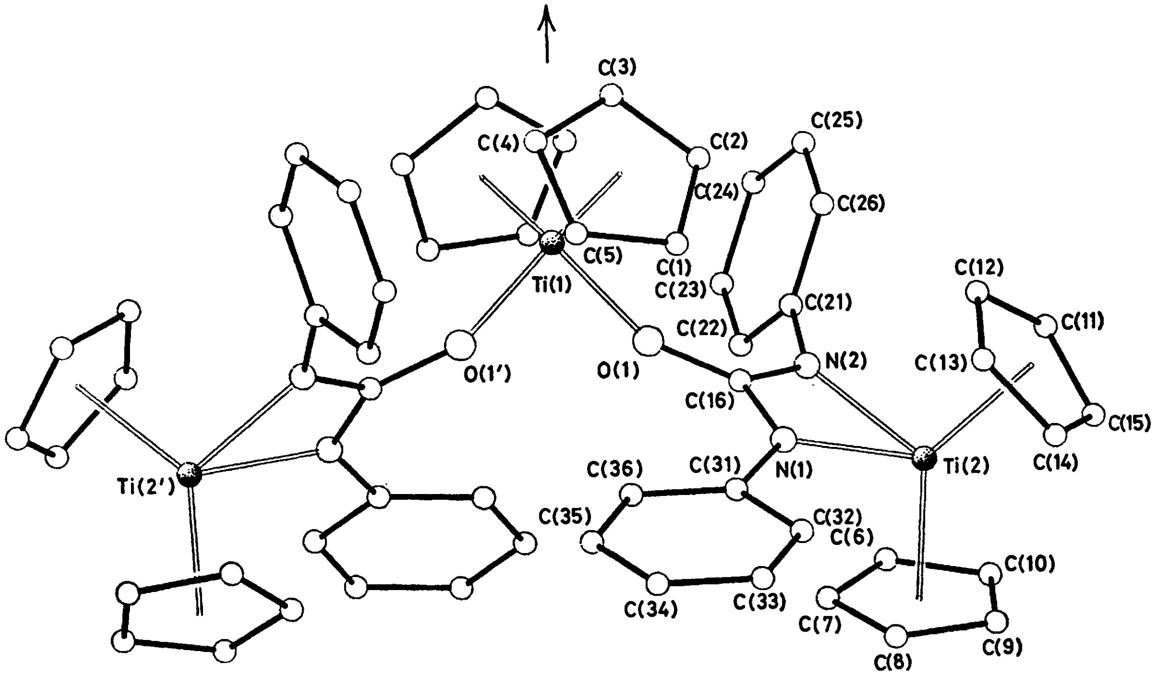


FIGURE 1 A view of the molecular structure of complex (3). Primed atoms are at the symmetry-related position $\bar{x}, y, \frac{1}{2}-z$

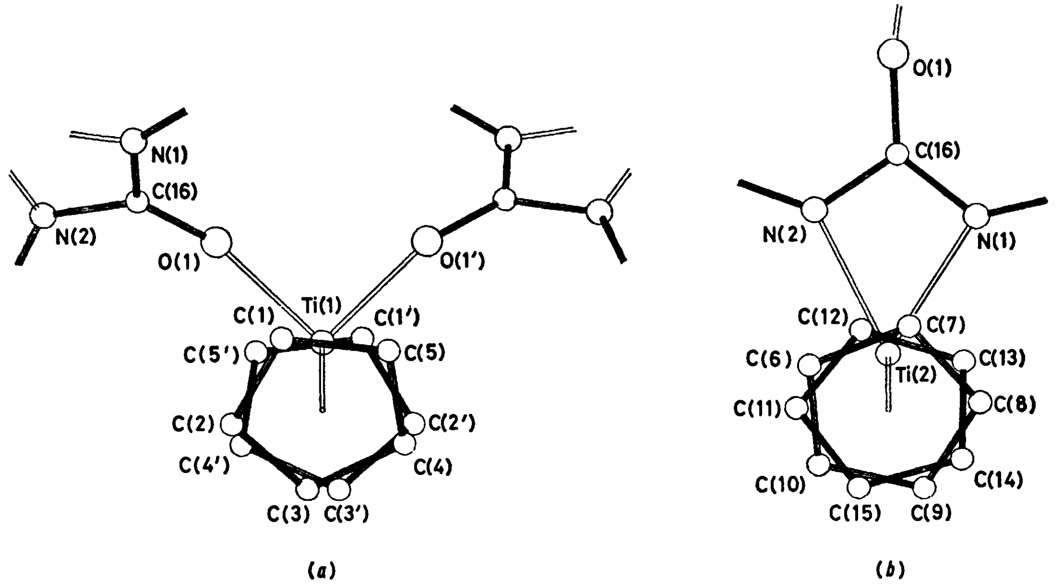
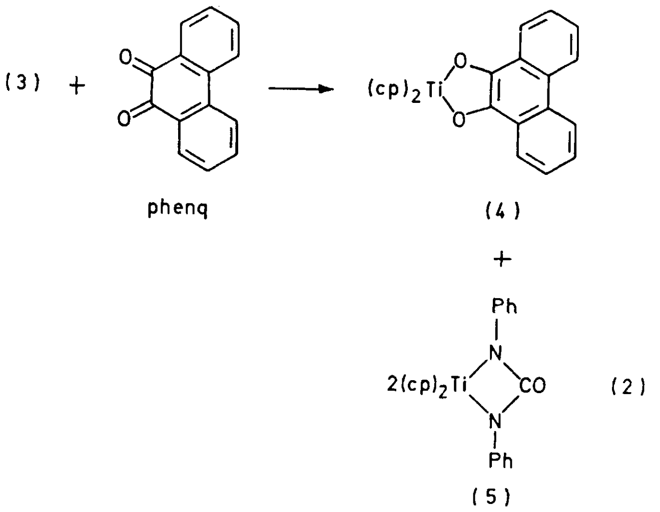
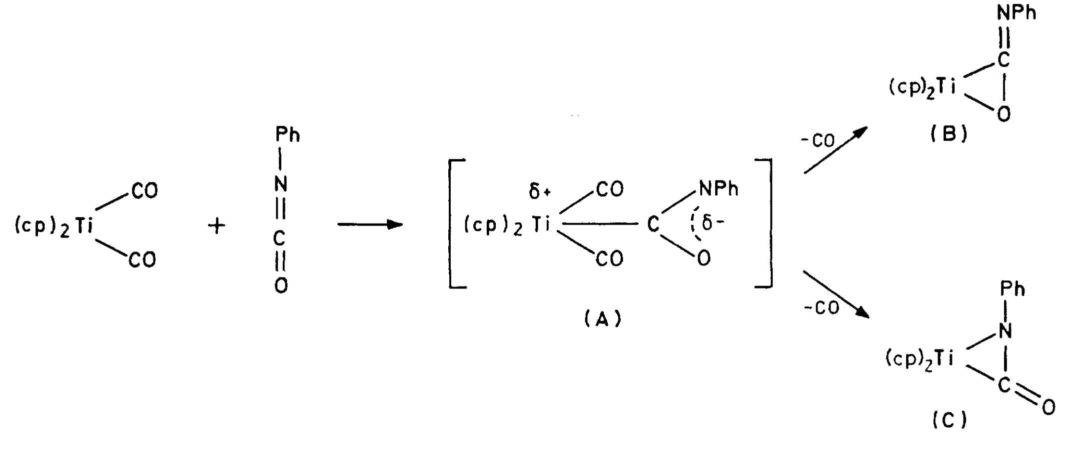


FIGURE 2 Projection of the environments of the two titanium atoms in (3) on to the plane perpendicular to the lines cp(1)–cp(1') and cp(2)–cp(3) for (*a*) and (*b*) respectively

The reaction occurring between the trinuclear complex (3) and phenanthrene-9,10-quinone, which complexes one of the three Ti(cp)$_2$ units and sets free the mononuclear diphenylureylene complex (5), is shown in (2). The different solubility of complexes (4) and (5) allows their separation (see Experimental section). An alternative synthesis of (5) and its properties will be presented below.

Some comments, at this point, must be devoted to the preparation of (3) and consequently of the other products reported in this paper. Phenyl isocyanate, which is an electrophilic substrate, passes the ' compatibility ' test with $[Ti(cp)_2(CO)_2]$, whose nucleophilic basic nature was recently explored.[16] So the first step of the reaction between (1) and (2) can reasonably be interpreted as a S_N2-type substitution involving nucleophilic attack by Ti^{II} on the electrophilic carbon of the isocyanate, followed by the addition of the Ti(cp)$_2$ unit to C=O, (B), or N=C, (C), unsaturated system. The supposed intermediate (A) is very similar to the 1 : 1 adduct which was isolated in the reaction between a nucleophilic phosphorus(III) compound and a substituted isocyanate.[20] Both (B) and (C) can explain the metal-induced breaking of the N=C bond reported in the alkyl and aryl isocyanate metallorganic chemistry.[5] It must be pointed out, however, that there are very few examples of η^2-C,N bonding to metals,[21,22] and no example of an η^2-C,O bonded isocyanate, even if the second possibility is not unexpected for metals like titanium.





It is usually accepted that, when a metal induces N–C bond cleavage in co-ordinated isocyanate, the addition of a formal metal nitrene to another molecule of isocyanate affords the ureylene ligand co-ordinated to the metal.[5,23] The presence of a metal nitrene unit, sometimes invoked in this reaction, was not confirmed. Alternatively, it can be proposed that the metal-promoted isocyanate transformation into a ureylene ligand may first involve a dimerisation. In fact, dimerisation of diphenylketene and carbon dioxide, which are analogous to isocyanates, was observed in their reaction with $[Ti(cp)_2(CO)_2]$ [24] and also with an iridium(I) complex.[4]

When (3) is heated in toluene, (5) crystallises out from the solution as a light green crystalline solid, while (6) can be recovered as deep blue crystals on cooling the toluene solution. Complex (6) obtained from reaction

$$\underset{(3)}{[\{Ti(cp)_2\}_3\{OC(NPh)_2\}_2]} \longrightarrow \underset{(5)}{[Ti(cp)_2\{OC(NPh)_2\}]} + \underset{(6)}{[\{Ti(cp)_2\}_2\{OC(NPh)_2\}]} \quad (3)$$

(3) contains half a molecule of toluene of crystallisation [complex (7)]. A direct synthesis of (6) involves heating (1) with an equimolar thf solution of PhNCO [equation (4)], where (6) is obtained as a deep blue crystalline solid

$$2[Ti(cp)_2(CO)_2] + 2\ PhNCO \xrightarrow{-CO} \underset{(6)}{[\{Ti(cp)_2\}_2\{OC(NPh)_2\}]} \quad (4)$$

by addition of OEt_2 to the thf solution. When reaction (4) is carried out in toluene, or (6) is recrystallised from toluene, deep blue crystals of (7) were obtained. The mass spectrum supported the binuclear nature of (6), with the parent peak appearing at m/e 566. The magnetic moment, 1.73 B.M. (293 K) per titanium, corresponds to that of Ti^{III}. While hydrolysis of (6) gave *NN'*-diphenylurea, the presence of a strong CO band at 1 530 cm^{-1} (Nujol) was believed to be due to an *O*-bonded ureylene ligand, as confirmed by the *X*-ray analysis.

The Structure of (7).—Figure 3 shows the binuclear unit and the numbering scheme. The diphenylureylene ligand bridges the two Ti(cp)$_2$ units through both the nitrogen and oxygen atoms. The Ti, O, and N atoms define a plane nearly orthogonal to that containing the metal-to-ring normals. The cyclopentadienyl rings are planar and neither purely eclipsed nor staggered (Figure 4). The Ti–C distances for the two cp around each Ti are significantly different (Table 4), while the mean C–C distances in the four rings are at the limits of significance.

The observed trend in Ti–C bond distances was previously pointed out for other bis(cyclopentadienyl)titanium derivatives.[15,25] The Ti–cp(centroid) distances range

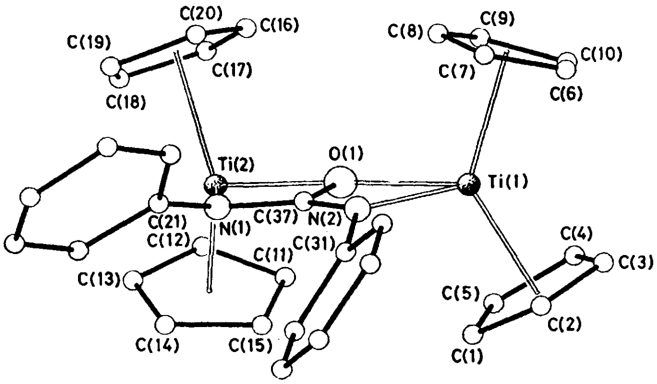


FIGURE 3 A view of the molecular structure of complex (7)

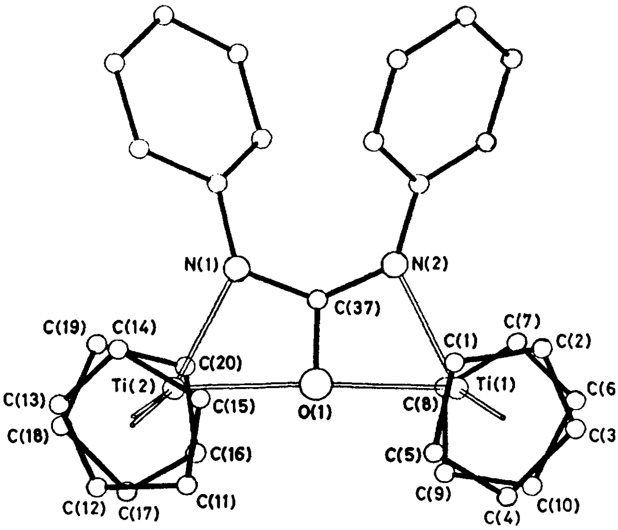
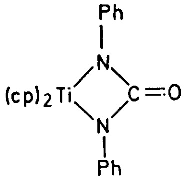


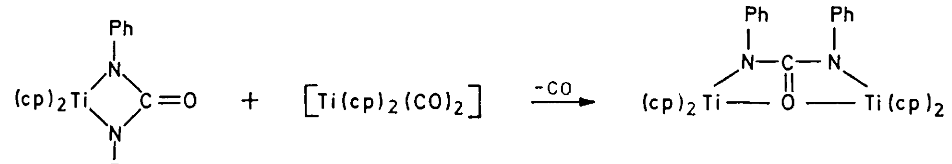
FIGURE 4 Projection of complex (7) on to the plane perpendicular to the cp(1)–cp(2) line

from 2.029(8) to 2.114(8) Å, while the cp(centroid)–Ti–cp(centroid) angles vary from 132.7(4) to 133.9(4)°. This geometry is similar to that in many other $Ti(cp)_2$ complexes.[15] The bond distances and angles associated with the diphenylureylene ligand are compared in Table 6 with those of other ureylene complexes. The Ti–N distances [2.126(7) and 2.136(5) Å] are quite similar to those in (3), while a significant lengthening of the Ti–O bonds is observed [Ti(1)–O 2.164(9) and Ti(2)–O 2.196(9) Å]. The last two values compare well with that found in $[Ti(cp)_2(COMe)Cl]$ for a similar Ti–O=C interaction [Ti–O 2.194(14) Å].[16] Atoms O, C(37), N(1), and N(2) define a plane from which Ti(2) is displaced by 0.067 Å (Table 5). The synergic lengthening of the C–O, and shortening of the C–N, bond distances can be interpreted assuming that the three atoms N–C–O act as a pseudo-allylic ligand. The bond angles associated with the ureylene ligand are greatly distorted, in this case (Table 6), because of the constraint imposed by the special arrangement between the two metal centres. Within the organic portion of the structure and the toluene, present as a molecule of crystallisation, the bond distances and angles seem particularly consistent.

Complex (5) is the third kind of ureylene complex which can be obtained from the reaction of $[Ti(cp)_2(CO)_2]$ with PhNCO. We could not find a direct synthesis to (5), which is always obtained from thermal [reaction (3)] or chemical [reaction (2)] transformation of (3). In spite of the green colour, (5) is a diamagnetic derivative of Ti^{IV}. Its poor solubility prevented a molecular-weight determination in solution, and its low volatility precluded an assignment of the molecular complexity from the mass spectrum which gave significant fragments only at *m*/*e* 372, 389, 464, and 566. The hydrolysis gave *NN'*-diphenylurea and $[Ti(cp)_2Cl_2]$, while the i.r. spectrum showed the presence of a free, or very weakly bonded, C=O unit [ν(CO)(Nujol) at 1 625 cm^{-1}]. The considerations outlined above justify the following mononuclear structure for (5). We think that reactions (3) and (4) may be explained from the results of reaction (5).



When a thf solution of (1) is treated with a suspension of (5) a deep blue solution is obtained from which (6) is recovered in high yield. Reactions like (5) between (1) and bis(cyclopentadienyl)titanium(IV) derivatives are excellent synthetic routes to many binuclear bis(cyclopentadienyl)titanium(III) complexes.[26] Reaction (3) may occur through a similar intramolecular redox process.



(6) (5)

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