Structure and Properties of Carbonylbis(η-cyclopentadienyl)(η-diphenylacetylene)titanium: The First Titanium Complex containing a Two-carbon η-Bonded Ligand

By **Giuseppe Fachinetti, Carlo Floriani,* Fabio Marchetti,** and **Marcello Mellini,** Istituto di Chimica Generale and Istituto di Mineralogia, Università di Pisa, 56100 Pisa, Italy

The reaction of $[\mathrm{Ti(cp)_2(CO)_2}]$ (cp = η-C_5H_5) with diphenylacetylene gives mononuclear $[\mathrm{Ti(cp)_2(C_2Ph_2)(CO)}]$ characterised by ν(CO) at 1 995 and ν(C≡C) at 1 780 cm^{-1}. The new complex shows high catalytic activity in the hydrogenation of olefins and acetylenes at room temperature under 1 atm of H_2. At >30 °C and in solutions of aromatic hydrocarbons it decomposes to $[\mathrm{Ti(cp)_2(CO)_2}]$ and $[\overline{\mathrm{Ti(cp)_2(CPh{:}CPh{\cdot}CPh{:}C}}\mathrm{Ph})]$. Its stability in the solid state has allowed an *X*-ray structural analysis: orthorhombic, space group $P2_12_12_1$, *a* = 18.464(5), *b* = 13.301(4), *c* = 7.822(4) Å, *Z* = 4, and D_c = 1.49 g cm^{-3}. Full-matrix least-squares refinement has led to a final *R* value of 0.067 based on 1 647 independent observed reflections. The titanium atom is η-bonded to two C_5H_5 rings and η-bonded to the diphenylacetylene ligand. The two ' eclipsed ' C_5H_5 rings are bent back to make room in the horizontal (molecular) plane for a CO ligand and a ' σ,π '-bonded C_2Ph_2 molecule. The Ti–C(CO) and C–O bond lengths [2.050(8) and 1.130(10) Å] are consistent with the CO being bonded to titanium as in $[\mathrm{Ti(cp)_2(CO)_2}]$. The Ti–C($C_2Ph_2$) bond lengths [2.107(7) and 2.230(7) Å], together with the C=C bond distance [1.285(10) Å] and C≡C–Ph deformation angles [138.8(7) and 145.8(7)°], suggest a metallocyclopropene structure for the titanium–diphenylacetylene interaction.

HIGHLY reactive free radicals or carbene-like metallic species are provided by bent bis(η-cyclopentadienyl) derivatives of early transition metals (Groups 4 or 5) in low oxidation states.[1-3] Examples of activation of dinitrogen and C–H have been realised using bis(cyclopentadienyl)-titanium, -zirconium, and -tungsten derivatives.[2-6] In bis(cyclopentadienyl) Group 4 chemistry one of the main problems is to find the source of the carbenoid-like 14-electron system, M(cp)$_2$. No definitive proof has been produced, until now, for the existence of a bis(η-cyclopentadienyl)titanium(II) unit in the so-called ' titanocenes.' [7]

We have used $[\mathrm{Ti(cp)_2(CO)_2}]$ (cp = η-C_5H_5) as an authentic source of this moiety.[8] Synthetic results of many reactions of $[\mathrm{Ti(cp)_2(CO)_2}]$ can be ascribed to the addition of the Ti(cp)$_2$ unit to an unsaturated system, as well as to its insertion into a covalent bond. The presence of the CO ligands causes an abrupt change in the reactivity of $[\mathrm{Ti(cp)_2(CO)_2}]$ compared with the ' titanocenes,' and affects the choice of the molecule to be activated, which must be fundamentally electrophilic. Another candidate for furnishing the Ti(cp)$_2$ unit and showing a high degree of reactivity is $[\mathrm{Ti(cp)_2(C_2Ph_2)(CO)}]$, reported herein. Moreover, it is the only authentic example, structurally identified, of a titanium compound containing a two-carbon η^2-bonded unit. An η interaction between titanium and a carbon–carbon multiple bond has been so often invoked, in polymerisation processes, catalytic hydrogenation, and insertion reactions,[9] that it was automatically accepted, even when there were no structurally identified η-olefin, or η-acetylene complexes of titanium.[10] The activation of the C≡C bond promoted on co-ordination to titanium has been studied in its reaction with H_2. Part of this work has been briefly communicated.[11]

EXPERIMENTAL

All the reactions were carried out under an atmosphere of purified nitrogen, carbon monoxide, or hydrogen. Solvents were purified by standard methods. Infrared spectra were recorded on Perkin-Elmer 282 and 337 spectrometers, and n.m.r. spectra on Varian T-60 and EM-360 spectrometers. Absorption or evolution of gases was measured volumetrically as previously described.[12] Dicarbonylbis(η-cyclopentadienyl)titanium(II) was prepared by one of the methods previously reported.[13] Only one example of catalytic hydrogenation is reported in detail, the hydrogenation of other olefins being carried out under similar conditions.

Preparations.— *Carbonylbis(η-cyclopentadienyl)(η-diphenylacetylene)titanium* (3). A heptane (600 cm^3) solution of $[\mathrm{Ti(cp)_2(CO)_2}]$ (7.9 g, 33.8 mmol) was treated with an excess of solid C_2Ph_2 (14.0 g, 78.7 mmol) at room temperature. Carbon monoxide evolved was eliminated gently *in vacuo* over 3 h, during which time (3) separated as a yellow crystalline solid. This was washed with hexane (50 cm^3) and dried *in vacuo* (*ca.* 80%) [Found: C, 78.2; H, 5.25%; *M* (cryoscopy in benzene) 356. Calc. for $C_{25}H_{20}TiO$: C, 78.1; H, 5.20%; *M* 384], ν(CO) at 1 998 cm^{-1} in heptane and 1 995 cm^{-1} in Nujol, ν(CC) in Nujol at 1 780 cm^{-1}; ^{1}H n.m.r. in C_6D_6 τ 2.9 (10 H, m, Ph) and 5.0 (10 H, s, cp).

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* One of the C_5H_5 groups acts as two-carbon three-electron ligand in $\mathrm{Ti(C_5H_5)_3}$ (C. R. Lucas, M. Green, R. A. Forder, and K. Prout, *J.C.S. Chem. Comm.*, 1973, 97).

[1] J. W. Lauher and R. Hoffmann, *J. Amer. Chem. Soc.*, 1976, **98**, 1729.

[2] C. Giannotti and M. L. H. Green, *J.C.S. Chem. Comm.*, 1972, 1114.

[3] J. L. Thomas, *J. Amer. Chem. Soc.*, 1973, **95**, 1838 and refs. therein.

[4] J. L. Bercaw, *J. Amer. Chem. Soc.*, 1974, **96**, 5087 and refs. therein.

[5] J. M. Manriquez, R. D. Sanner, R. E. March, and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1976, **98**, 3042.

[6] N. J. Cooper and M. L. H. Green, *J.C.S. Chem. Comm.*, 1974, 761.

[7] G. P. Pez, *J. Amer. Chem. Soc.*, 1976, **98**, 8072 and refs. therein.

[8] G. Fachinetti, C. Floriani, and H. Stoeckli-Evans, *J.C.S. Dalton*, 1977, 2297 and refs. therein.

[9] W. H. Boon and M. D. Rausch, *J.C.S. Chem. Comm.*, 1977, 397.

[10] D. G. Sekutowski and G. D. Stucky, *J. Amer. Chem. Soc.*, 1976, **98**, 1376.

[11] G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1974, 66.

[12] F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1962, **1**, 30.

[13] G. Fachinetti, G. Fochi, and C. Floriani, *J.C.S. Chem. Comm.*, 1976, 230 and refs. therein.

Treatment of (3) (0.515 g) with toluene (30 cm^3) containing I_2 (0.8 g) resulted in rapid evolution of CO. A black-violet solid formed suddenly, shown to be $[Ti(cp)_2I_2]$ (*ca.* 72%). The solution was evaporated to dryness and the solid washed with pentane. The pentane solution, after treatment with a solution of $Na_2[S_2O_3]$ and drying, gave on evaporation C_2Ph_2 (*ca.* 87%).

Bis(η-Cyclopentadienyl)(1,2,3,4-tetraphenylbutadienylene)-titanium (4). The complex $[Ti(cp)_2(CO)_2]$ (1.2 g, 5.13 mmol) and C_2Ph_2 (2.0 g, 11.23 mmol) were heated under reflux in pentane for 3 d. The deep green crystalline solid formed was collected and washed with pentane (80%). This was shown to be identical to that reported [14] (Found: C, 85.4; H, 5.65. Calc. for $C_{38}H_{30}Ti$: C, 85.4; H, 5.60%).

Catalytic Hydrogenation.—Complex (3) (0.15 g, 0.39 mmol) was dissolved in heptane (50 cm^3) to which 1,4-diphenylbutadiene (1.5 g, 7.2 mmol) was added. Absorption of H_2 at 1 atm * and 20 °C for 10—15 min was followed by dissolution of the 1,4-diphenylbutadiene. The final solution when exposed to the atmosphere precipitated inorganic titanium species, which were filtered off. The remaining solution was evaporated to dryness. Thin-layer chromatography showed the presence of trace amounts of $(PhCH_2)_2$ and of 1,4-diphenylbutane as the main product. The solid recrystallised from ethanol gave 1,4-diphenylbutane (1.2 g, 80%), m.p. 53—54 °C.

The hydrogenation of styrene, *trans*-stilbene, oct-1-ene, and diphenylacetylene was carried out under similar conditions. Within a few minutes the unsaturated substrates were completely hydrogenated to the corresponding saturated hydrocarbons only, no by-products being formed except trace amounts of $(PhCH_2)_2$.

X-*Ray Data Collection and Structure Determination for Complex* (3).—*Crystal data.* $C_{25}H_{20}OTi$, $M = 383.9$, $a = 18.464(5)$, $b = 13.301(4)$, $c = 7.822(4)$ Å, $U = 1\,921.0$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.49$ g cm^{-3}, $F(000) = 800$, $\mu = 4.75$ cm^{-1}, crystal dimensions 0.42 × 0.25 × 0.13 mm.

A single crystal of the complex was sealed in a Lindemann glass capillary. Rotation and Weissenberg photographs showed orthorhombic symmetry; the space group was uniquely determined as $P2_12_12_1$ (D_2^4, no. 19) on the basis of systematic extinctions in $h00$ for $h = 2n + 1$, in $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$. The lattice parameters, determined by photographic methods, were refined with a Philips PW-1100 automatic single-crystal diffractometer by least-squares fitting of θ values for 25 reflections having $\theta > 20°$, using graphite-monochromatised Mo-K_α radiation (λ 0.710 7 Å).

Intensity data were collected on the same diffractometer with the same radiation at a scan width of 1.20° and scan speed 0.05° s^{-1}, and using a θ—2θ scan over the range $3 \leqslant \theta \leqslant 34°$. As a check of the stability of the instrument and the crystal, three reflections were monitored every 3 h; the fluctuation was within ±2%. Of the 2 034 available reflections, 387 were omitted since they had $I_{top} - 2(I_{top})^{\frac{1}{2}} < I_{back}$, with I_{top} and I_{back} indicating peak and background intensity, respectively. Of the 1 647 collected reflections, 122 were classified as unobserved, having $F_o < 3\sigma(F_o)$, where $\sigma(F_o)$ was estimated from counting statistics. Lorentz and polarisation corrections were applied in the usual way; neither absorption nor dispersion corrections were made.

The Ti atom position was determined from a Patterson map; two successive Fourier syntheses located all the atoms in the unit cell except the hydrogen atoms. Full-matrix least-squares refinement using the ORFLS program,[15a] with isotropic thermal parameters, reduced the R factor to 0.11. Further refinement, with anisotropic thermal parameters and reflections weighted according to $1/\sigma(F_o)^2$, led to R 0.083. After introducing hydrogen atoms in calculated positions (B isotropic 6.0 Å^2), further refinement of Ti, C, and O atoms led to R 0.067 and $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.073$. A final ΔF synthesis did not show any peak having electronic intensity >0.3 Å^{-3}. Scattering factors for neutral atoms were taken from ref. 15*b*. Final values of the atomic positional parameters are reported in Tables 1 and 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22310 (11 pp.).†

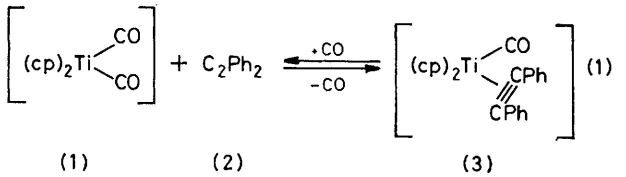
TABLE 1

Final atomic parameters of heavy atoms with estimated standard deviations in parentheses

	X	*Y*	*Z*
Ti	0.410 95(6)	0.134 75(9)	0.797 63(17)
O	0.254 9(3)	0.036 6(5)	0.834 6(13)
C(1)	0.409 5(6)	0.202 3(6)	0.515 4(11)
C(2)	0.478 9(5)	0.181 8(7)	0.553 4(11)
C(3)	0.485 3(4)	0.076 0(7)	0.567 3(11)
C(4)	0.417 5(6)	0.032 5(6)	0.541 5(11)
C(5)	0.370 4(5)	0.110 9(7)	0.508 3(12)
C(6)	0.371 7(6)	0.207 3(7)	1.064 0(13)
C(7)	0.342 8(6)	0.263 4(8)	0.928 3(17)
C(8)	0.396 5(9)	0.310 1(7)	0.844 5(14)
C(9)	0.458 4(7)	0.234 9(8)	0.920 9(19)
C(10)	0.445 2(6)	0.223 4(7)	1.050 3(16)
C(11)	0.481 1(3)	0.034 6(5)	0.924 9(9)
C(12)	0.420 6(3)	−0.013 0(4)	0.930 3(10)
C(13)	0.556 1(3)	0.023 3(5)	0.988 4(9)
C(14)	0.612 8(4)	0.078 5(6)	0.905 0(12)
C(15)	0.683 8(4)	0.067 0(7)	0.967 5(12)
C(16)	0.699 6(4)	0.007 7(6)	1.105 7(14)
C(17)	0.646 2(4)	−0.045 0(6)	1.189 1(15)
C(18)	0.574 5(4)	−0.037 7(5)	1.128 3(13)
C(19)	0.384 2(3)	−0.104 4(5)	0.982 1(10)
C(20)	0.342 6(4)	−0.160 4(5)	0.867 7(12)
C(21)	0.309 7(4)	−0.249 7(6)	0.918 8(13)
C(22)	0.316 4(4)	−0.283 8(6)	1.084 1(17)
C(23)	0.357 6(5)	−0.228 2(6)	1.200 1(14)
C(24)	0.388 7(4)	−0.138 4(6)	1.149 4(10)
C(25)	0.309 5(4)	0.072 9(5)	0.813 9(15)

RESULTS AND DISCUSSION

Chemical Studies.—Carbon monoxide can be reversibly displaced in $[Ti(cp)_2(CO)_2]$ (1) by diphenylacetylene [equation (1)]. Complex (3) separates as a yellow crystalline solid from heptane, in which it is slightly soluble, when CO is continuously pumped off. Under a



(1) (2) (3)

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* Throughout this paper: 1 atm = 101 325 Pa.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[14] K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Japan*, 1966, **39**, 1178.

[15] (*a*) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Report ORNL–TM–305, 1962; (*b*) 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

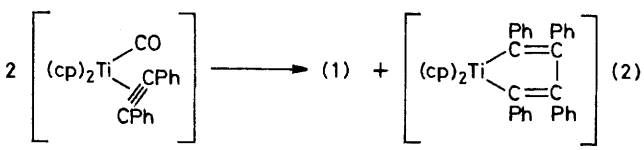
CO atmosphere, (3) absorbs CO giving back (1) rapidly.

TABLE 2

Atomic parameters of hydrogen atoms (calculated positions). For the thermal factors B a fixed value of 6.0 was assumed

Atom	X	Y	Z
H(1)	0.397	0.284	0.481
H(2)	0.525	0.246	0.580
H(3)	0.534	0.041	0.586
H(4)	0.413	−0.041	0.534
H(5)	0.311	0.111	0.473
H(6)	0.342	0.161	1.155
H(7)	0.298	0.264	0.915
H(8)	0.402	0.368	0.757
H(9)	0.524	0.312	0.905
H(10)	0.496	0.201	1.149
H(14)	0.603	0.135	0.819
H(15)	0.727	0.106	0.901
H(16)	0.754	0.007	1.157
H(17)	0.661	−0.078	1.289
H(18)	0.543	−0.081	1.206
H(20)	0.341	−0.119	0.748
H(21)	0.288	−0.298	0.837
H(22)	0.301	−0.354	1.136
H(23)	0.370	−0.249	1.327
H(24)	0.417	−0.090	1.253

Complex (3) [ν(CO) at 1 995 and ν(CC) at 1 780 cm^{-1} in Nujol] is characterised by a short range of stability (temperature and solvent). The decomposition of (3) [reaction (2)] occurring in solution is accelerated by the presence of aromatic hydrocarbons and at temperatures >30 °C (monitored by n.m.r. and i.r. spectra).

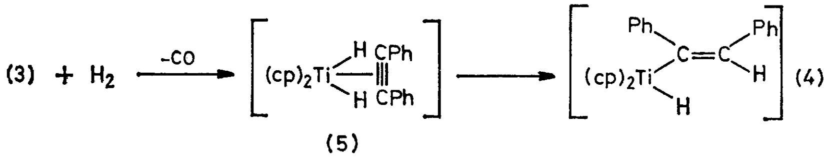


(3) (4)

It was previously reported that reaction (1) gives complex (4) as the only product.[14] Indeed, when the reaction is carried out at temperatures >30 °C and in aromatic solvents, (3) is observed only transiently, the final product always being (4). Complex (3) should be considered as an intermediate in the formation of a not yet identified bis(diphenylacetylene) complex affording the metallocycle (4). It was suggested that a metallocyclic compound similar to (4) might be an intermediate in the reaction of ‘ titanocenes ’ with ethylene.[16] Reaction of CO with butane-1,4-diyltitanium gave the elimination of the C_4 unit as cyclobutanone, while (4), under the same conditions, did not give tetraphenylcyclopentadienone. The best synthetic route to (4), using this kind of reaction, is to heat (1) under reflux in the presence of C_2Ph_2 in pentane [equation (3)]. The labilisation of CO in complex (1) promoted by an electrophilic reagent is a quite general behaviour of this

$$[\mathrm{Ti(cp)_2(CO)_2}] + 2\,\mathrm{C_2Ph_2} \xrightarrow{\text{pentane}} [\overline{\mathrm{Ti(cp)_2(CPh{:}CPh{\cdot}CPh{:}CPh})}] \quad (3)$$

dicarbonyl. Depending on the π-acceptor properties of the ligand, the substitution can be stopped at the first CO. With azobenzene,[17] diphenylketene,[18] or acetylenes substituted with highly electron-attracting groups,[19] partial substitution of CO cannot be observed.



(5)

The isolation and study of titanium η-acetylene complexes such as (3) is relevant to the titanocene-based catalysed reactions of mono-olefins and acetylenes. Complex (3) is highly active in catalysing hydrogenation of carbon–carbon double and triple bonds under very mild conditions, while it is inactive toward N=N (azobenzene) and C=N (benzonitrile) functions. The hydrogenations are carried out at 1 atm of H_2 in solutions of aliphatic hydrocarbons at 10—20 °C, aromatic solvents and higher temperatures promoting reaction (2). Olefins hydrogenated under these conditions were styrene, 1,4-diphenylbutadiene, *trans*-stilbene, and oct-1-ene. All were reduced, quantitatively, to the corresponding saturated hydrocarbons, within a few minutes, using a catalyst–substrate molar ratio in the range 2×10^{-2}—$5 \times 10^{-2} : 1$. This catalyst must be handled with rigorous exclusion of oxygen.

While $[\mathrm{Ti(cp)_2(CO)_2}]$ is completely inactive under mild conditions, it promotes the catalytic hydrogenation of acetylenes under rather drastic conditions.[14] This can be ascribed, on the basis of our results, to the formation of an intermediate active η-acetylene complex rather than to a titanocene species.[20]

Both complexes (1) and (3) are expected to be excellent candidates for oxidative-addition reactions with different reagents,[8,21] including H_2. Complex (1), which is unreactive with H_2 at room temperature, induces the hydrogenation of CO to CH_4 at very high temperatures only,[22] while (3) reacts easily with H_2 at room temperature giving $(PhCH_2)_2$ and trace amounts of (1). The difference between (1) and (3) may depend on their rather different

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[16] J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1976, **98**, 6529.

[17] G. Fachinetti, G. Fochi, and C. Floriani, *J. Organometallic Chem.*, 1973, **57**, C51.

[18] G. Fachinetti, C. Biran, C. Floriani, A. C. Villa, and C. Guastini, *J. Amer. Chem. Soc.*, 1978, **100**, 1921.

[19] G. Fachinetti and C. Floriani, unpublished work. The molecular complexity of these adducts is not yet clear.

[20] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1972, **94**, 1219.

[21] G. Fachinetti and C. Floriani, *J.C.S. Dalton*, 1973, 1954; 1974, 2433.

[22] J. C. Huffman, J. G. Stone, W. C. Krusell, and K. G. Caulton, *J. Amer. Chem. Soc.*, 1977, **99**, 5829.

electronic properties. Thus (1) requires highly electrophilic reagents, whereas the presence of C_2Ph_2 and CO together around titanium provides suitable electronic conditions for realising the addition and transfer of H_2. The addition of H_2 to (3) could give the corresponding dihydride (5), which then hydrogenates acetylenes or olefins by the usual steps (addition, insertion, and elimination).[23] Some steps of this process are sketched in reaction (4). Justifications for each step can be found in the well documented bis(cyclopentadienyl)titanium chemistry.[8,24] Thus it has been known for some time that low-valent titanocene species can function as olefin-hydrogenation catalysts. They are reduced species of $[Ti(cp)_2Cl_2]$ with sodium dihydronaphthylide,[25] reduced forms of $[Ti(cp)_2Cl_2]$ supported on polystyrene,[26] solutions formed by treating bis(cyclopentadienyl)(η-1-methylallyl)titanium with H_2,[27] and much more recently $[(cp)_2Ti(\mu\text{-}\sigma : \eta\text{-}C_5H_4)Ti(cp)]$ (6) and its solvated species.[28,29] However, complexes (3) and (6) are the only well defined materials that have been shown to have such catalytic properties. The marked difference between the two is mainly in their mono- and di-metallic natures. It was suggested that the mechanism of the reduction of olefins involves the collaboration of the two metal centres in (6).[29] The nature of (3), on the other hand, suggests that the complete reaction probably takes place at one metal centre. In this regard, the action of (3) is much more reminiscent of the titanocene species diluted by attachment to a polymeric matrix [26] than of

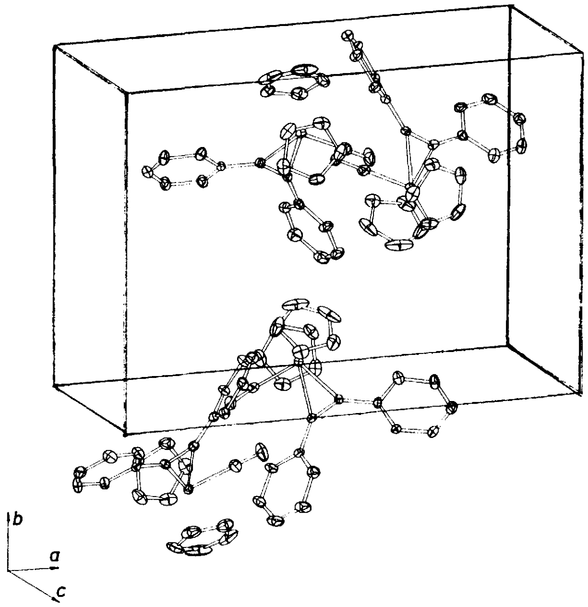

FIGURE 1 Crystal packing of complex (3). Relative to the reference molecule at x,y,z, the molecules in the Figure are at: x,y,z; $\frac{1}{2} - x,y,\frac{1}{2} + z$; $\frac{1}{2} + x,\frac{1}{2} - y,-z$; $1 - x,\frac{1}{2} + y,\frac{1}{2} - z$

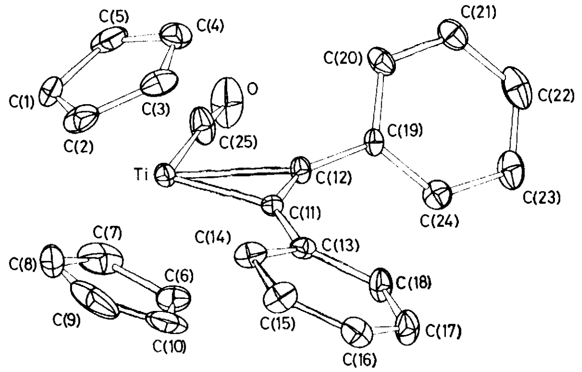

FIGURE 2 Molecular structure of complex (3)

TABLE 3

Bond lengths (Å) for complex (3)

Titanium-atom co-ordination		
	Ti–C(1)	2.384(9)
	Ti–C(2)	2.369(10)
	Ti–C(3)	2.397(9)
	Ti–C(4)	2.425(9)
	Ti–C(5)	2.405(10)
	Ti–ct 1 *	2.083
	Ti–C(6)	2.408(10)
	Ti–C(7)	2.357(12)
	Ti–C(8)	2.375(10)
	Ti–C(9)	2.384(13)
	Ti–C(10)	2.386(12)
	Ti–ct 2	2.084
	Ti–C(11)	2.107(7)
	Ti–C(12)	2.230(7)
	Ti–C(25)	2.050(8)
	C(11)–C(12)	1.285(10)
	C(25)–O	1.130(10)
	C(11)–C(13)	1.480(10)
	C(12)–C(19)	1.447(10)
cp_1		
	C(1)–C(2)	1.343(15)
	C(1)–C(5)	1.416(14)
	C(2)–C(3)	1.416(14)
	C(3)–C(4)	1.394(14)
	C(4)–C(5)	1.382(14)
cp_2		
	C(6)–C(7)	1.403(16)
	C(7)–C(8)	1.341(19)
	C(8)–C(9)	1.333(22)
	C(9)–C(10)	1.324(18)
	C(10)–C(6)	1.378(16)
Ph_1		
	C(13)–C(14)	1.435(11)
	C(14)–C(15)	1.407(12)
	C(15)–C(16)	1.369(14)
	C(16)–C(17)	1.373(13)
	C(17)–C(18)	1.411(12)
	C(18)–C(13)	1.403(12)
Ph_2		
	C(19)–C(20)	1.395(12)
	C(20)–C(21)	1.393(12)
	C(21)–C(22)	1.375(17)
	C(22)–C(23)	1.396(15)
	C(23)–C(24)	1.384(12)
	C(24)–C(19)	1.387(12)

* ct 1 is the centroid of the cyclopentadienyl ring which contains C(1)—C(5); ct 2 is that of C(6)—C(10). cp_1, cp_2, Ph_1, and Ph_2 are crystallographically non-equivalent cyclopentadienyl and phenyl rings.

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[23] A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1973, **95**, 7262.

[24] G. Fachinetti and C. Floriani, *J. Organometallic Chem.*, 1974, **71**, C5.

[25] E. E. Van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, *J.C.S. Chem. Comm.*, 1972, 481.

[26] W. D. Bonds, C. H. Brubaker, E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, *J. Amer. Chem. Soc.*, 1975, **97**, 2128.

[27] H. A. Martin and R. O. De Jongh, *Rec. Trav. chim. belges*, 1971, **90**, 713.

[28] G. P. Pez and S. C. Kwan, *J. Amer. Chem. Soc.*, 1976, **98**, 8079.

[29] G. P. Pez, *J.C.S. Chem. Comm.*, 1977, 560.

the ' titanocenes,' for which always a bimetallic structure is assumed.

TABLE 4

Bond angles (°) for non-hydrogen atoms in complex (3)

Titanium-atom co-ordination		
	C(11)–Ti–C(12)	34.3(3)
	C(11)–Ti–C(25)	106.1(3)
	C(12)–Ti–C(25)	71.9(3)
	Ti–C(25)–O	174.9(1.0)
	C(12)–C(11)–C(13)	138.8(7)
	Ti–C(11)–C(13)	142.9(5)
	Ti–C(11)–C(12)	78.1(5)
	Ti–C(12)–C(19)	146.5(6)
	Ti–C(12)–C(11)	67.6(4)
	C(11)–C(12)–C(19)	145.8(7)
	ct 1–Ti–ct 2	133.5(5)
cp_1		
	C(2)–C(1)–C(5)	108.7(9)
	C(1)–C(2)–C(3)	107.4(9)
	C(2)–C(3)–C(4)	109.0(8)
	C(3)–C(4)–C(5)	106.3(8)
	C(4)–C(5)–C(1)	108.6(9)
cp_2		
	C(7)–C(6)–C(10)	103.5(9)
	C(6)–C(7)–C(8)	109.6(1.1)
	C(7)–C(8)–C(9)	107.4(1.1)
	C(8)–C(9)–C(10)	109.9(1.3)
	C(9)–C(10)–C(6)	109.71(1.1)
Ph_1		
	C(14)–C(13)–C(18)	118.3(7)
	C(13)–C(14)–C(15)	117.7(8)
	C(14)–C(15)–C(16)	122.3(8)
	C(15)–C(16)–C(17)	121.1(8)
	C(16)–C(17)–C(18)	118.6(9)
	C(17)–C(18)–C(13)	121.9(8)
Ph_2		
	C(20)–C(19)–C(24)	117.7(7)
	C(19)–C(20)–C(21)	120.7(9)
	C(20)–C(21)–C(22)	120.8(9)
	C(21)–C(22)–C(23)	119.1(9)
	C(22)–C(23)–C(24)	119.8(10)
	C(23)–C(24)–C(19)	121.8(8)

Structural Properties.—The crystal structure of (3) comprises discrete molecules separated by van der Waals contacts (Figure 1). The molecular structure and atom-numbering system is shown in Figure 2. Each titanium atom is η^5-bonded to two C_5H_5 rings that are bent back to make a cavity in the horizontal, not crystallographic, mirror (molecular) plane for a CO ligand and a ' σ,π '-bonded diphenylacetylene ligand. The molecule has no crystallographic symmetry, but nearly has $C_s(m)$ idealised point symmetry when the Ph groups are not included. The $C_s(m)$ symmetry requires eclipsing of the C_5H_5 rings. Selected sets of interatomic distances and angles are given in Tables 3 and 4.

(*a*) *The Cyclopentadienyl groups*. The two cyclopentadienyl rings are closely planar, and although C–C ring bond lengths vary from 1.324(18) to 1.416(14) Å (Table 3) this variation is probably not significant since the carbon atoms of the cyclopentadienyls have rather high temperature factors, evidence of their low thermal rigidity. In compounds containing η-C_5H_5 rings it is not uncommon to witness a large librational motion of the ring which has the effect of shortening the C–C(cp) bond lengths below the expected (1.43 Å) value.[30,31] The two C_5H_5 rings exhibit, rather unusually, a nearly eclipsed configuration. The Ti–C(cp) bond lengths [2.357(10)—2.425(9) Å, mean 2.39(2) Å] are quite similar to those found in other well determined structures,[8,10,30,32,33] so the two rings may be considered to be bonded to titanium in a true η^5 fashion.

(b) *Titanium-atom co-ordination*. The distances from titanium to the ring centres are 2.083 and 2.084 Å, which may be compared with many other titanium–ring centre distances which are nearly constant, especially for titanium(IV) derivatives.[10] A significant shortening of the Ti-ct distances was observed only for Ti^{II} (2.02 Å) in $[Ti(cp)_2(CO)_2]$ [32] and for Ti^{III} (2.03 Å) in $[Ti(cp)_2(BH_4)]$.[34] The value found is at the upper limit for titanium(IV) derivatives. The centroid–metal–centroid angle [133.5(5)°] is similar to that found in many other $Ti(cp)_2$ complexes.[8,32–35] Ti, C(11), C(12), and C(25) define the molecular plane, with deviations from the least-squares plane being <0.04 Å. The Ti–C(11) and Ti–C(12) bond distances [2.107(7) and 2.230(7) Å] are particularly noteworthy, because this is the first η^2 C–C system co-ordin-

TABLE 5

The C=C bond lengths, deformation angles, and ν(C≡C) stretching in diphenylacetylene complexes

Complex	C≡C bond (Å)	C≡C–Ph angle (°)	ν(C≡C) band (cm^{-1})	Ref.
$[Pt(C_2Ph_2)(PPh_3)_2]$	1.32(9)	140	1 740, 1 768	*a*
$[Ni(C_2Ph_2)(CNBu^t)_2]$	1.28(2)	149	1 810	*b*
$[Nb(cp)(C_2Ph_2)_2(CO)]$	1.35(2)	138		*c*
$[Nb(cp)(C_2Ph_2)(C_4Ph_4)(CO)]$	1.26(4)	142	1 780	*d*
$[W(C_2Ph_2)_3(CO)]$	1.30	140	1 702	*e*
$[W(cp)Ph(C_2Ph_2)O]$	1.29(3)	143.5(4)	1 748	*f*
$[Pt(C_2Ph_2)_2]$	1.280(6)	153	1 881	*g*
$[Ti(cp)_2(C_2Ph_2)(CO)]$	1.285(10)	138.8(7), 145.8(7)	1 780	*h*

[a] G. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometallic Chem.*, 1967, **7**, P9. [b] R. S. Dickson and J. A. Ibers, *J. Organometallic Chem.*, 1972, **36**, 191. [c] A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Comm.*, 1969, 277. [d] A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Comm.*, 1969, 739. [e] R. M. Laine, R. E. Moriarty, and R. Bau, *J. Amer. Chem. Soc.*, 1972, **94**, 1402. [f] N. G. Bokiy, Yu. V. Gatilov, Yu. T. Struchkov, and N. A. Ustynyuk, *J. Organometallic Chem.*, 1973, **54**, 213. [g] M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1976, 759. [h] Present work.

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[30] E. F. Epstein, I. Bernal, and H. Kopf, *J. Organometallic Chem.*, 1971, **26**, 229; *Inorg. Chim. Acta*, 1973, **7**, 211; B. R. Davis and I. Bernal, *J. Organometallic Chem.*, 1971, **30**, 75.

[31] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Cryst.*, 1974, **B30**, 2286.

[32] J. L. Atwood, K. E. Stone, H. G. Alt, D. G. Hrncir, and M. D. Rausch, *J. Organometallic Chem.*, 1977, **132**, 367.

[33] J. L. Atwood, W. E. Hunter, H. Alt, and M. D. Rausch, *J. Amer. Chem. Soc.*, 1976, **98**, 2454.

[34] K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, 1973, **12**, 232.

[35] A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal, and I. Bernal, *Canad. J. Chem.*, 1975, **53**, 1622.

ated to titanium. The values fall in the range of known Ti–C(sp)^2 distances: 2.172(5) and 2.141(5) Å in [Ti(cp)$_2$-(CPh:CPh·CPh:CPh)] [33] and 2.27 Å in [Ti(cp)$_2$Ph$_2$].[36] The significant difference between the two values can be, tentatively, attributed to steric hindrance due to the proximity of CO to C(12), causing a lengthening of the Ti–C(12) bond distance.

(*c*) *Carbon monoxide and diphenylacetylene*. Significant values associated with the Ti–CO unit are the Ti–C(25) and C(25)–O bond lengths [2.050(8) and 1.130(10) Å] which are in good agreement with the same values reported for [Ti(cp)$_2$(CO)$_2$] [2.030(11) and 1.15(1) Å for Ti–C and C–O].[32] The slightly higher Ti–C and shorter C–O bond lengths in (**3**) may eventually be interpreted on the basis of a higher oxidation state for titanium for which less efficient back donation is possible. The Ti–C(25)–O system is practically linear [174.9(10)°]. Bond lengths and angles within the phenyl rings fall in the usual range (Tables 3 and 4). The following features of the C$_2$Ph$_2$ ligand are of primary importance: C(11)–C(12) 1.285(10) Å; C(13)–C(11)–C(12) 138.8(7)°; and C(11)–C(12)–C(19) 145.8(7)°. The C–C bond lengths and deformation angles in various C$_2$Ph$_2$ complexes are summarised in Table 5. The extent of the lengthening and the bending of C≡C–Ph angle reflects a major contribution by π back donation and a minor contribution from σ and π donation.[37] Table 5 indicates that the majority of the C–C bond distances lie in a relatively small range around 1.28 Å, and the deformation angles are *ca.* 143°. These features seem to indicate that the C$_2$Ph$_2$ is behaving as a bidentate ligand in a metallocyclopropene structure (as a limiting form). This description is also justified by the ν(C≡C) stretching vibration (1 780 cm^{-1} *cf.* 2 223 cm^{-1} for the free ligand). The enhanced formal oxidation state of titanium may be indicated by the relatively high CO stretching frequency (1 995 cm^{-1}). The phenyl rings are closely planar and the angles formed by the phenyl planes with the molecular plane are 23.9 and 47.4° for the phenyls attached at C(11) and at C(12) respectively.

We thank the C.N.R. (Roma) for support.

[7/1999 *Received*, 14*th November*, 1977]

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[36] V. Kocman, J. C. Rucklidge, R. J. O'Brien, and W. Santo, *Chem. Comm.*, 1971, 1340.

[37] S. Otsuka and A. Nakamura, *Adv. Organometallic Chem.*, 1976, **14**, 245.