Dicarbonylbis(η-cyclopentadienyl)titanium(II) Chemistry: Reactions with Organic Molecules containing C–Cl, P–Cl, O–H, and S–Cl Bonds; Synthesis, Properties, and Structures of η-Acyl Derivatives of Titanium(IV)

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The reaction of $[Ti(cp)_2(CO)_2]$ (1) (cp = η-C_5H_5) with acyl halides RCOCl (R = Me or Ph) gives acyl derivatives of titanium(IV), $[Ti(cp)_2(COR)Cl]$. Under the same conditions, the reaction of (1) with alkyl iodides gives the acyl derivatives $[Ti(cp)_2(COR)I]$ (R = Me, Et, Pr^i, or Bu^s). All the acyl derivatives are characterised by a low CO stretching frequency [ν(CO) at *ca.* 1 600 cm^{-1}]. *X*-Ray analysis of $[Ti(cp)_2(COMe)Cl]$ shows that the molecule has C_s symmetry with atoms Ti and Cl and the acetyl group lying in the crystallographic mirror plane. The Ti atom has distorted tetrahedral co-ordination, and it interacts strongly with the oxygen of the acetyl group which acts as a bidentate three-electron ligand. This structure explains the observed low CO stretching frequency for the acyl unit. Reaction with $MeSO_2Cl$ resulted in insertion of the $Ti(cp)_2$ unit into the S–Cl bond giving $[Ti(cp)_2(O_2SMe)Cl]$. Reactions of (1) with iodide, phenanthrene-9,10-quinone, and PPh_2Cl are also reported.

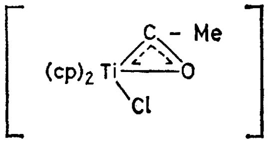
THE cyclopentadienyl ligand stabilises electron-rich metals, so providing highly reactive species for molecular activation.[1] Thus bis(cyclopentadienyl) derivatives of the early transition metals (Groups 4—6) exhibit high reactivity, such as carbenoid-like behaviour in C–H bond activation [2] and dinitrogen co-ordination.[3] The choice of these complexes as models in molecular activation can be further justified by the fact that the $M(cp)_2$ unit (cp = η-cyclopentadienyl) remains practically intact during several reactions, so there are only three orbitals which can be considered for the activation processes.[4] Dicarbonylbis(η-cyclopentadienyl)titanium(II),[5] $[Ti(cp)_2(CO)_2]$, can be considered as a typical example of this class of complexes. It is one of the rare examples of authentic stable titanium(II) species.[6] The presence of highly basic Ti^{II} is evident from the electrophilic nature of the substrates [7,8] which react with it and from consideration of its electronic configuration.[4] Many synthetic results of the reactions of $[Ti(cp)_2(CO)_2]$ can be formally interpreted as insertion into different covalent bonds or as addition to the multiple bond of the carbenoid unit $Ti(cp)_2$. In this paper we report the reactivity of $[Ti(cp)_2(CO)_2]$ toward organic molecules containing C–Cl, P–Cl, S–Cl, and O–H functional groups. The apparently anomalous pattern of the reaction in some cases points to the possible utilisation of complexes like $[M(cp)_2XY]$ in the functionalisation of organic molecules.[9] Part of this work has been briefly communicated.[10]

RESULTS AND DISCUSSION

Reactions with Acyl and Alkyl Halides.—Dicarbonylbis(η-cyclopentadienyl)titanium(II), $[Ti(cp)_2(CO)_2]$ (1), reacts with acyl chlorides at room temperature and in toluene solution losing the two CO groups to give the corresponding acylchlorotitanium(IV) derivatives, $[Ti(cp)_2(COR)Cl]$ (2), having ν(CO) at 1 620 (R = Me) and

$$\underset{(1)}{[Ti(cp)_2(CO)_2]} + RCOCl \xrightarrow{-2\,CO} \underset{(2)}{[Ti(cp)_2(COR)Cl]} \quad (1)$$

1 580 cm^{-1} (R = Ph). With long reaction times and stoicheiometric amounts of RCOCl, variable quantities of $[Ti(cp)_2Cl_2]$ are obtained. The products of reaction (1) are orange air-stable crystalline solids and have been characterised by elemental (Table 1) and spectroscopic analysis. The acyl derivatives (2) are unusually stable to heat and to oxidation if compared with the corresponding alkyl derivatives.[11] This is probably due to the interaction of the acyl oxygen with one empty orbital of the metal, as indicated by the anomalous i.r. stretching frequencies found for (2) and confirmed by *X*-ray structure analysis on $[Ti(cp)_2(COMe)Cl]$. Complexes (2) are insoluble in hydrocarbons and soluble in $CHCl_3$. Nucleophilic solvents, such as pyridine, induce a degree of decomposition, whose nature has not yet been determined.[12]



The high reactivity of (1) with electrophilic substrates is a quite general behaviour of this dicarbonyl derivative, and can be easily explained on the basis of the highly nucleophilic properties found for d^2-$[M(cp)_2X_2]$ systems. Reaction (1) can reasonably be interpreted as an S_N2-like substitution involving nucleophilic attack by the

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[1] B. R. Francis, M. L. H. Green, T. Luong-thi, and G. A. Moser, *J.C.S. Dalton*, 1976, 1339.

[2] J. E. Bercaw, *J. Amer. Chem. Soc.*, 1974, **96**, 5087.

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

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[5] J. G. Murray, *J. Amer. Chem. Soc.*, 1961, **83**, 1287.

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[7] C. Floriani and G. Fachinetti, *J.C.S. Dalton*, 1973, 1954; 1974, 2433; *J.C.S. Chem. Comm.*, 1974, 66.

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

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[10] C. Floriani and G. Fachinetti, *J.C.S. Chem. Comm.*, 1972, 790.

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[12] R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 2091.

$\mathrm{Ti^{II}}$ on the electrophilic carbon of the acyl chloride. Using (1) we have been able to insert, or add, the carbenoid unit $\mathrm{Ti(cp)_2}$ into different covalent bonds.[7,8] Because of the instability of its 14-electron configuration, $[\mathrm{Ti(cp)_2}]$ rearranges to different species,[13] so (1) can be regarded as the most authentic source of the $\mathrm{Ti(cp)_2}$ ' carbene,' which is stabilised by the two easily displaced CO groups. Insertion of carbon monoxide into the titanium–carbon σ bonds can be used as an alternative synthetic route for (2).[14]

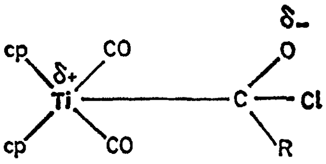


TABLE 1

Analytical data

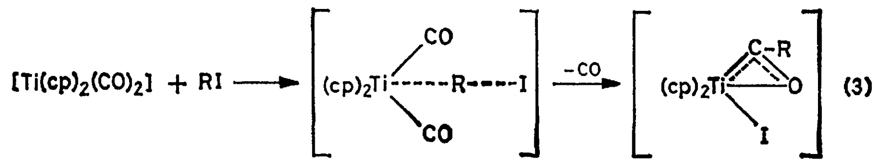
Complex	Analysis (%) [a] C	H	Halogen	M [a]
$[\mathrm{Ti(cp)_2(COMe)Cl}]$ (2; R = Me)	56.6 (56.1)	5.2 (5.1)	Cl 13.9 (13.8)	228 (256.5) [b]
$[\mathrm{Ti(cp)_2(COPh)Cl}]$ (2; R = Ph)	63.6 (64.0)	4.6 (4.7)	Cl 11.1 (11.2)	324 (318.5) [b]
$[\mathrm{Ti(cp)_2(COMe)I}]$ (3; R = Me)	41.0 (41.4)	3.8 (3.7)	I 36.1 (36.5)	
$[\mathrm{Ti(cp)_2(COEt)I}]$ (3; R = Et)	43.3 (43.1)	4.0 (4.1)	I 35.7 (35.1)	
$[\mathrm{Ti(cp)_2(COPr^i)I}]$ (3; R = $\mathrm{Pr^i}$)	44.9 (44.7)	4.6 (4.5)	I 34.0 (33.8)	
$[\mathrm{Ti(cp)_2(COBu^s)I}]$ (3; R = $\mathrm{Bu^s}$)	46.0 (46.2)	5.0 (4.9)	I 32.2 (32.6)	
$[\mathrm{Ti(cp)_2(O_2CMe)_2}]$ (5)	56.6 (56.8)	5.5 (5.4)		290 (296) [c]
$[\mathrm{Ti(cp)_2(O_2SMe)Cl}]$ (4)	45.1 (45.1)	4.4 (4.4)	Cl 11.8 (12.1) [d]	
$[\mathrm{Ti(cp)_2(C_{14}H_8O_2)}]$ (6)	74.1 (74.6)	4.7 (4.7)		382 (386) [c]
$[\mathrm{Ti(cp)_2I_2}]$ (7)	28.15 (27.8)	2.4 (2.31)	I 59.9 (58.8)	

[a] Calculated values are given in parentheses. [b] By osmometry in $\mathrm{CHCl_3}$. [c] By cryoscopy in benzene. [d] S 11.2 (10.9%).

Acyl derivatives can be obtained from the reaction of (1) with alkyl iodides [equation (2); R = Me, Et, $\mathrm{Pr^i}$, or $\mathrm{Bu^s}$]. Reaction (2) is carried out in toluene solution at room temperature. The quantity of carbon monoxide evolved corresponds to 1 mol per Ti atom. The other CO group is inserted into the Ti–C bond. Reaction (2)

$$\underset{(1)}{[\mathrm{Ti(cp)_2(CO)_2}]} + \mathrm{RI} \xrightarrow[\text{toluene}]{-\mathrm{CO}} \underset{(3)}{[\mathrm{Ti(cp)_2(COR)I}]} \quad (2)$$

is strongly dependent on the nature of the halogen. As expected for normal leaving-group behaviour, the qualitative reaction rates observed are in the order I ≫ Br > Cl. The mechanism is presumably analogous to that proposed for the oxidative addition of MeI to $[\mathrm{Rh(cp)(CO)(PPh_3)}]$.[15] The products of reaction (2) are orange air-stable crystalline solids and have been characterised by elemental analysis (Table 1) and i.r. and n.m.r. spectroscopy. The very slow reaction of the alkyl chlorides is probably due, at least in part, to the poor stabilisation of the high-energy chloride ion by the weakly polar solvent toluene. The observed reaction between (1) and $\mathrm{PhCH_2Cl}$ gave $\mathrm{(PhCH_2)_2}$ and $[\mathrm{Ti(cp)_2Cl_2}]$ as the only products of the reaction. The explanation of some of the chemical and spectroscopic properties of the acyl derivatives (2) and (3) will be evident from the X-ray structure of $[\mathrm{Ti(cp)_2(COMe)Cl}]$.



(1) (3)

Structure of $[\mathrm{Ti(cp)_2(COMe)Cl}]$.—The final interatomic distances and angles are given in Table 2. The Figure shows the atom-labelling scheme used. Crystallographic requirements impose $C_s(m)$ symmetry on the molecule. The mirror plane bisects the cp–Ti–cp angle and contains the ligands Cl and COMe. The Ti atom has a distorted tetrahedral co-ordination (Table 2). The structure of $[\mathrm{Ti(cp)_2(COMe)Cl}]$ is very similar to that of $[\mathrm{Zr(cp)_2(COMe)Me}]$.[16]

The cyclopentadienyl rings, related by the mirror plane and hence eclipsed, are planar and inclined at an angle of 49.3°. Intramolecular contacts of 2.97 and 2.90 Å were found for the distances C(4) $\cdots$ C(4′) and C(5) $\cdots$ C(5′) respectively. The average cp ring C–C distance is 1.43 Å, with an average ring angle of 108°. The Ti–C(cp) distances vary from 2.36 to 2.41 Å (mean 2.39 Å). The Ti–cp(centroid) distance is 2.06 Å, while the cp(centroid)–Ti–cp(centroid) angle is 131.6°. This

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

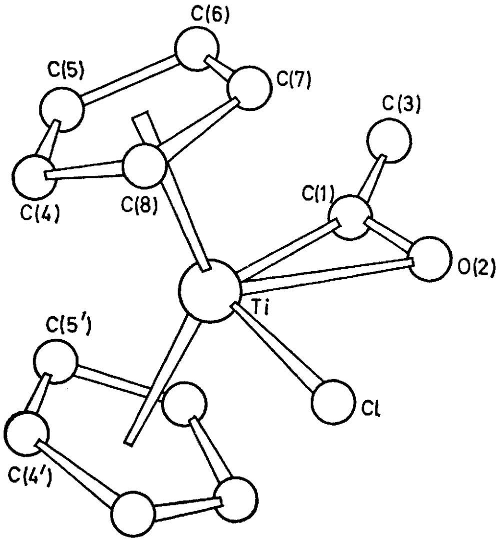
[14] G. Fachinetti and C. Floriani, *J. Organometallic Chem.*, 1974, **71**, C5.

[15] A. J. Hart Davies and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.

[16] G. Fachinetti, C. Floriani, F. Marchetti, and S. Merlino, *J.C.S. Chem. Comm.*, 1976, 522.

geometry is similar to that in many other Ti(cp)$_2$ complexes.[17,18]

The bond angles associated with the acetyl group are greatly distorted. The Ti–C(1)–O(2) angle is only 79.7°, which may be compared to 78.6° found for the same angle in [Zr(cp)$_2$(COMe)Me].[16] The Ti–C(1)–C(3) angle is 154°, while angle C(3)–C(1)–O(2) is 126°. As in [Zr(cp)$_2$(COMe)Me], the bond lengths in the acetyl group may be interpreted in terms of this group acting as a three-electron ligand [angle C(1)–Ti–O(2) 32°], with a Ti · · · O(2) bond distance of 2.19 Å.[19] To support this there seems to be a shortening of the Ti–C(acetyl) bond (2.07 Å) compared to the average Ti–C(σ) distance of 2.14 Å found in Ti(CH$_2$Ph)$_4$.[20]



Molecular structure of [Ti(cp)$_2$(COMe)Cl]

In [M(cp)$_2$X$_2$] complexes the X–Ti–X angle varies from 94 to 97°.[21] In [Ti(cp)$_2$(COMe)Cl] the Cl–Ti–C(1) angle is 112.1° compared to the C(methyl)–Zr–C(1) angle of 110.8° in [Zr(cp)$_2$(COMe)Me].[16] The presence of the acyl group acting as a three-electron ligand may be more general than suspected, and can provide the explanation for the very low CO stretching frequency normally found for acyl derivatives of the early transition metals.[4] The η structure for the acyl group is preserved in solution, as shown by the unchanged position of the acyl CO band in the i.r. spectrum. This conclusion cannot be extended to basic competing solvents because of the instability of the acyl derivatives (2) and (3) in such solvents.[12] The other very interesting feature of the structure is the unusually long Ti–Cl bond distance (2.50 compared to 2.36 Å previously observed [17]). This bond-lengthening effect can be ascribed to the interaction of the acyl oxygen with the metal, and can be generalised as a consequence of the passage from a 16- to an 18-electron configuration in [M(cp)$_2$X$_2$] systems. This fact can be very useful in interpreting the chemistry of such systems (M = Zr$^{\mathrm{IV}}$ or Ti$^{\mathrm{IV}}$) in many kinds of reactions, such as insertions or the functionalisation of organic molecules.

TABLE 2

(*a*) Final positional parameters ($\times$ 10^4) and (*b*) bond lengths (Å) and angles (°), with their standard deviations in parentheses

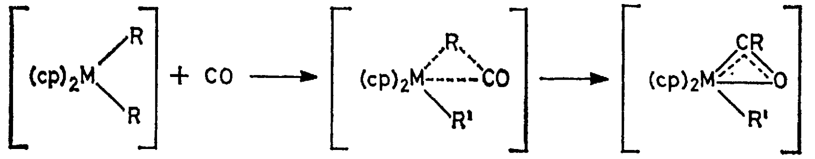
(*a*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ti	3 725(2)	¼	3 034(4)
Cl	5 321(3)	¼	4 758(8)
C(1)	2 580(13)	¼	5 011(26)
O(2)	3 236(10)	¼	6 131(20)
C(3)	1 547(15)	¼	5 540(34)
C(4)	3 986(12)	1 271(13)	280(21)
C(5)	2 992(12)	1 298(11)	724(20)
C(6)	2 844(11)	813(13)	2 634(25)
C(7)	3 774(14)	526(12)	3 431(26)
C(8)	4 473(11)	802(10)	1 932(24)

(*b*)

Ti · · · O(2)	2.194(14)	C(7)–C(8)	1.44(2)
Ti–Cl	2.494(6)	C(8)–C(4)	1.42(2)
Ti–Cl(1)	2.07(2)	Ti–C(4)	2.40(1)
C(1)–O(2)	1.18(2)	Ti–C(5)	2.36(1)
C(1)–C(3)	1.47(3)	Ti–C(6)	2.39(2)
C(4)–C(5)	1.41(2)	Ti–C(7)	2.40(2)
C(5)–C(6)	1.43(2)	Ti–C(8)	2.41(1)
C(6)–C(7)	1.44(2)		
C(1)–Ti–O(2)	32.0(4)	C(5)–C(4)–C(8)	107.9(6)
Cl–Ti–C(1)	112.2(3)	C(4)–C(5)–C(6)	108.8(6)
Cl–Ti–O(2)	80.2(2)	C(5)–C(6)–C(7)	107.9(8)
C(1)–O(2)–Ti	68.3(7)	C(6)–C(7)–C(8)	106.5(8)
Ti–C(1)–O(2)	79.7(6)	C(7)–C(8)–C(1)	108.9(9)
Ti–C(1)–C(3)	154.0(16)		
C(3)–C(1)–O(2)	126.3(13)		

The first step in the insertion of carbon monoxide is its co-ordination to the metal [14,22] which thus achieves a closed-shell configuration [equation (4): M = Zr, R = R′ = alkyl; M = Ti, R′ = halide]. On the basis of the structures described, CO addition labilises one of the alkyl residues, so promoting its migration.[16,22] The



(4)

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[17] T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organometallic Chem.*, 1975, **102**, 457 and refs. therein.

[18] A. C. Villa, A. G. Manfredotti, and C. Guastini, *Acta Cryst.*, 1976, **B32**, 909 and refs. therein.

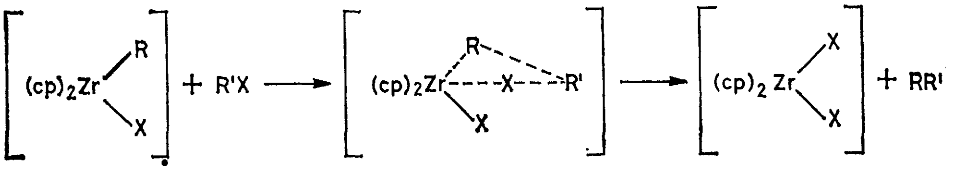
[19] H. Stoechli-Evans, *Helv. Chim. Acta*, 1975, **58**, 373; R. Allman, V. Batzel, R. Pfeil, and G. Schmid, *Z. Naturforsch.*, 1976, **B31**, 1329.

[20] G. R. Davies, J. A. J. Jarvis, and B. T. Kilbourn, *Chem. Comm.*, 1971, 1511; I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Amer. Chem. Soc.*, 1971, **93**, 3787.

[21] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and C. V. Rees, *Acta Cryst.*, 1974, **B30**, 2290.

[22] G. Fachinetti, S. Del Nero, and C. Floriani, *J.C.S. Dalton*, 1976, 203; G. Fachinetti, G. Fochi, and C. Floriani, *ibid.*, 1977, 1946.

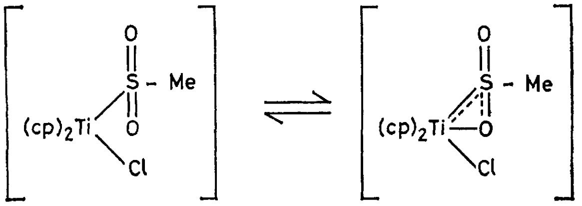
functionalisation of an alkyl group bonded to zirconium in $[Zr(cp)_2(R)X]$ can be explained on the same basis. The Lewis-acid properties of Zr^{IV} enhance the electrophilic nature of R′, *via* co-ordination of R′X, and this parallels the labilisation of the nucleophile-like R which then migrates to R′ [equation (5): R = alkyl, X = halogen; $R'X = X_2$, MeCOX, *etc.*].[23]



(5)

$$\underset{(1)}{[Ti(cp)_2(CO)_2]} + MeSO_2Cl \xrightarrow{-2\,CO} \underset{(4)}{[Ti(cp)_2(SO_2Me)Cl]} \quad (6)$$

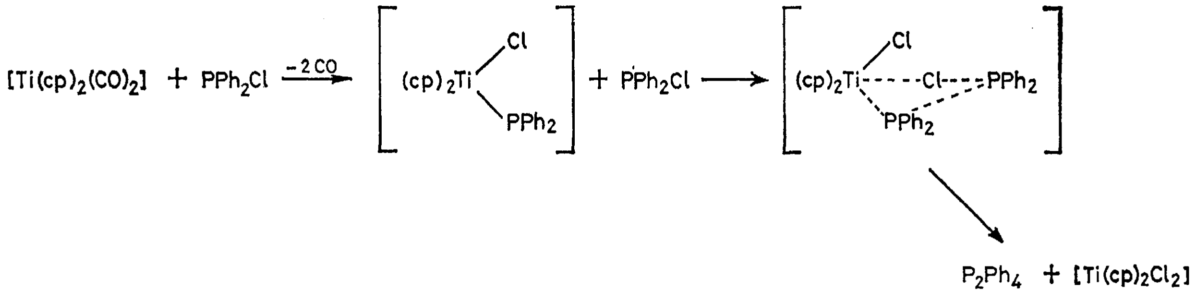
Reactions with Molecules containing S–Cl *and* P–Cl *Bonds.*—Methanesulphonyl chloride, $MeSO_2Cl$, reacts with (1) at low temperature in toluene solution giving the corresponding titanium(IV) derivative $[Ti(cp)_2(SO_2Me)Cl]$ (4). Complex (4) has the same spectroscopic properties as the product obtained from the insertion of SO_2 into the Ti–Me σ bond[24] (Table 1). The splitting of the cp and Me bands in the ^1H n.m.r. spectrum was interpreted as resulting from an equilibrium between an *O* and *OO′* bonding[24] as well as between *S* and *OS* bonding. The form (A) is reminiscent of the η structure of the acyls reported.



(7)

(A)

The reaction between (1) and chlorodiphenylphosphine gave, almost quantitatively, $[Ti(cp)_2Cl_2]$ and Ph_2PPPh_2. This reaction can be used as an efficient alternative synthesis for the tetraphenyldiphosphane.[25] This synthetic result can be reasonably explained on the basis of equation (8).



(8)

Reactions with Molecules containing Active Protons and with Phenanthrene-9,10-*quinone*.—Complex (1) is normally unreactive with alcohols, even under very drastic conditions. It reacts very slowly with carboxylic acids in toluene solution. The reaction with $MeCO_2H$ was carried out both in toluene solution and with pure acetic acid, giving $[Ti(cp)_2(O_2CMe)]$ (5) with simultaneous evolution of carbon monoxide and hydrogen. The reaction leading to (5) can be interpreted in terms of intermediate formation of a titanium hydride species which is unstable in the presence of acetic acid. Complex (5) was obtained as a yellow-maroon crystalline solid, soluble in aromatic hydrocarbons, monomeric in benzene, and highly unstable to hydrolysis. Its reaction with HCl gave quantitatively $[Ti(cp)_2Cl_2]$ and acetic acid. The complex was completely characterised by its analytical (Table 1) and spectroscopic data which were practically identical to those already reported.[26]

The reaction of (1) with phenanthrene-9,10-quinone in toluene gave a deep green solution, from which (6) crystallised out as deep-green crystals on addition of heptane. Complex (6) is very soluble in aromatic hydrocarbons, monomeric in benzene (*M* 382), and stable in air in the solid state. The lowering of the CO stretching band to 1 440—1 490 cm^{-1} points to the reduction of the quinone to the corresponding phenanthrenediolate unit.[27] Reaction (10) parallels other metal-carbenoid additions to phenanthrene-9,10-quinone, such as those of $[Pt(PPh_3)_2]$ and $[Ir(CO)Cl(PPh_3)_2]$.[28] Phenanthrene-9,10-quinone can be considered as a dioxygen-like molecule in many aspects. For the other cited metal

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[23] D. W. Hart and J. Schwartz, *J. Amer. Chem. Soc.*, 1974, **96**, 8115.

[24] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometallic Chem.*, 1971, **33**, 181.

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[26] P. C. Wailes, R. S. P. Coutts, and H. Weigold, 'Organometallic Chemistry of Titanium, Zirconium and Hafnium,' Academic Press, New York, 1974, p. 68.

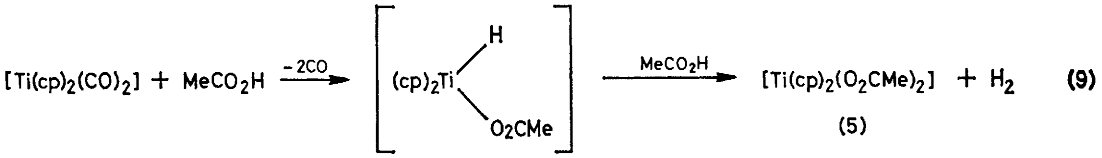
[27] C. Floriani, G. Fachinetti, and F. Calderazzo, *J.C.S. Dalton*, 1973, 765; C. Floriani, R. Henzi, and F. Calderazzo, *ibid.*, 1972, 2640.

[28] J. S. Valentine and D. Valentine, *J. Amer. Chem. Soc.*, 1970, **92**, 5795.

carbenoids the reaction with oxygen gave similar synthetic results, that is a 1 : 1 adduct, but for (1) the reaction with molecular oxygen did not give an isolable dioxygen complex.

EXPERIMENTAL

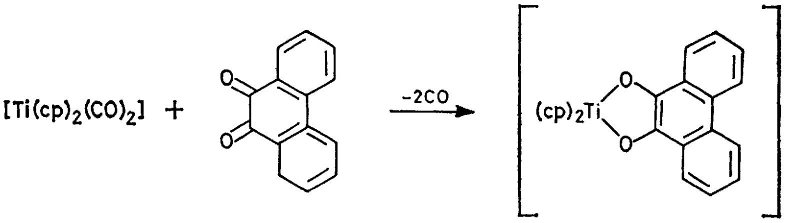
Unless otherwise stated, all the reactions were described carried out under an atmosphere of purified nitrogen or carbon monoxide; solvents were purified by standard methods. Infrared spectra were recorded on Perkin-Elmer 283 and 337 spectrometers, and n.m.r. spectra on a Varian T-60 spectrometer. Absorption or evolution of CO was measured volumetrically as previously described.[29] Some of the typical reactions are described in detail, the preparation of the other complexes being carried out under similar conditions. Dicarbonylbis(η-cyclopentadienyl)titanium(II) was prepared by one of the methods previously reported.[30]



(9)

Structure Analysis and Refinement.—The rod-like orange-red crystals of [Ti(cp)$_2$(COMe)Cl] were stable in air. Preliminary oscillation, Weissenberg, and precession photographs indicated an orthorhombic cell.

Crystal data. $C_{12}H_{13}ClOTi$, $M = 256.4$, $a = 13.85(2)$, $b = 12.07(2)$, $c = 6.74(1)$ Å, $U = 1\,127$ Å^3, space group $Pn2_1a$ or $Pnma$ (the latter confirmed by successful refinement), $D_m = 1.52$, $Z = 4$, $D_c = 1.51$ g cm^{-3}, $F(000) = 528$, μ(Cu-K_α) = 86 cm^{-1}.



(10)

(6)

Reflections corresponding to the layers *hk*0—5 and *h*0*l*—*h*2*l* were recorded by the equi-inclination Weissenberg method, using nickel-filtered Cu-K_α radiation (λ 1.541 8 Å) on multiple-film packs. The films were scanned by the S.R.C. service, with an Optronics P-1000 Photoscan. Intensities were corrected for Lorentz-polarisation effects but not for absorption. A total of 438 unique observed reflections was obtained after interlayer scaling and merging of equivalent reflections.

The positions of all the non-hydrogen atoms were obtained from Patterson and Fourier syntheses. Refinement was initially by cycles of isotropic full-matrix least squares, followed by cycles of anisotropic block-diagonal least squares. Atomic-scattering factors were taken from ref. 31. No attempt was made to locate the hydrogen atoms. The Cl atom and the acetyl group [C(1), O(2),C(3)], which lie in the crystallographic mirror plane, have high β_{22} anisotropic vibrational components. However, the refinement was only successful when the structure was considered to be ordered in space group *Pnma*. Hence the molecule possesses C_s symmetry.

Refinement was terminated at R 0.082 and R' 0.104 (average parameter shift $\leqslant 0.2\sigma$). The weighting scheme used in the final stages of refinement was $w^{\frac{1}{2}} = 1$ if $F_o \leqslant 24$, otherwise $w^{\frac{1}{2}} = 24/F_o$. The final positional parameters are given in Table 2. Observed and calculated structure factors, final anisotropic vibrational parameters, and spectroscopic data are listed in Supplementary Publication No. SUP 22125 (6 pp.).* All the calculations were carried out using a system of programs supplied by Professor M. R. Truter, Rothampsted Experimental Station.[32]

Preparations.— *Acetylchlorobis*(η-*cyclopentadienyl*)-*titanium*(IV) (2; R = Me). A toluene (25 cm^3) solution of [Ti(cp)$_2$(CO)$_2$] (1) (1.28 g, 5.48 mmol) was treated at room temperature with MeCOCl (2 cm^3, 28 mmol). In a few minutes, slow evolution of carbon monoxide took place. After 2 h the acetyl derivative began to crystallise from the solution which was kept at room temperature with stirring for 1 d. The orange crystalline complex was filtered off and washed with toluene (30 cm^3), yield *ca*. 80%. The complex [Ti(cp)$_2$(COMe)Cl] is stable in air in the solid state. A $CHCl_3$ solution of the complex when treated with HCl gave, almost quantitatively, [Ti(cp)$_2$Cl$_2$]. When stoicheiometric amounts of MeCOCl and longer reaction times, or heptane as solvent, were used variable quantities of [Ti(cp)$_2$Cl$_2$] were obtained.

Benzoylchlorobis(η-*cyclopentadienyl*)*titanium*(IV) (2; R = Ph). Pure PhCOCl (1.8 cm^3, 15.6 mmol) was added to a toluene solution (30 cm^3) of (1) (1.37 g, 5.85 mmol). Slow evolution of CO took place within minutes and continued for 10 h, when a yellow-orange crystalline solid separated. This was collected and washed with toluene (25 cm^3), yield *ca*. 80%.

Acetylbis(η-*cyclopentadienyl*)*iodotitanium*(IV) (3; R = Me). Pure MeI (1.0 cm^3, 16.2 mmol) was added to a toluene solution (30 cm^3) of (1) (1.53 g, 6.54 mmol) at room temperature. Slow evolution of gas occurred over several hours, and the solution was kept *in vacuo* for 1—2 d,

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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

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

[31] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[32] *X*-Ray ARC, Library of Programs for an IBM 1130 Computer, *J. Appl. Cryst.*, 1973, **6**, 309.

during which orange crystals of the acyl derivative precipitated from the solution. These were washed with toluene, yield *ca.* 80%. Volumetric measurements indicated the evolution of 1.02 mol of CO per Ti atom.

Bis(acetato)bis(η-cyclopentadienyl)titanium(IV) (5). Complex (1) (0.6 g, 2.56 mmol) was dissolved in acetic acid (20 cm^3). Slow evolution of gas occurred and continued for several hours. After 1 d the acetic acid solution was evaporated to dryness and the residue recovered with toluene (25 cm^3) to give a yellow-maroon solution. By addition of heptane (50 cm^3) and cooling a crystalline yellow-maroon solid was obtained, which was washed with heptane (30 cm^3), yield *ca.* 50%. The complex $[Ti(cp)_2(O_2CMe)_2]$ is readily hydrolysed in the presence of hydrochloric acid to $[Ti(cp)_2Cl_2]$. The reaction can be carried out very slowly, using a toluene solution of $MeCO_2H$, but with the same result.

Chlorobis(η-cyclopentadienyl)(methylsulphinato)titanium(IV) (4). A toluene (25 cm^3) solution of $MeSO_2Cl$ (0.171 cm^3, 2.2 mmol) was added to a toluene (20 cm^3) solution of (1) (0.51 g, 2.18 mmol) cooled to −5 °C. The reaction was very rapid and after 2 h the solution was red-orange. The solution was concentrated to 10 cm^3 and by addition of heptane (10 cm^3) a red-orange microcrystalline solid was obtained (*ca.* 78%).

Reaction of Chlorodiphenylphosphine with Complex (1).—A heptane (75 cm^3) solution of (1) (1.12 g, 4.79 mmol) was treated with PPh_2Cl (1.8 cm^3, 5.07 mmol) at room temperature. After 30 min gas was evolved and a red microcrystalline solid started to separate. After 12 h a white solid crystallised together with the red one. The toluene was heated until the white solid dissolved, and the red solid was filtered off. This was identified as $[Ti(cp)_2Cl_2]$ (1.1 g, 4.41 mmol). From the toluene solution on cooling a crystalline white solid was recovered and by comparison with an authentic sample (i.r. and m.p. 120 °C) was shown to be P_2Ph_4 (1.1 g, 2.97 mmol).[25]

*Bis(η-cyclopentadienyl)(phenanthrene-*9,10*-diolato)-titanium*(IV) (6).—Phenanthrene-9,10-quinone (0.93 g, 4.47 mmol) was added to a toluene (25 cm^3) solution of (1) (1.06 g, 4.53 mmol). On stirring the suspension (the phenanthrenequinone is slightly soluble in toluene), rapid evolution of CO occurred and the solid dissolved. After 1 h a deep green solution was obtained. The toluene solution was concentrated to 10 cm^3 and by addition of heptane (100 cm^3) a deep green microcrystalline solid was obtained (*ca.* 85%). The solid is quite soluble in hydrocarbons and is stable in air, m.p. 155 °C.

Bis(η-cyclopentadienyl)di-iodotitanium(IV).—A toluene solution (10 cm^3) of iodine (0.66 g, 2.62 mmol) was added to a toluene solution (10 cm^3) containing (1) (0.63 g, 2.67 mmol). At the end of the addition a black crystalline solid was formed, which was washed with toluene and dried (*ca.* 50%).

We thank C.N.R. (Roma) for support, and the Fonds National Suisse de la Recherche Scientifique for support to H. S-E.

[6/2292 *Received, 17th December,* 1976]