New Synthesis and Isocyano-complexes of Chloro(π-cyclopentadienyl)-titanium(III)

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A new synthesis of the complexes $[Ti(cp)_2Cl]_2$ (I) and $[Ti(cp)Cl_2]_2$ (II) *via* $[Ti(cp)_2(CO)_2]$ (cp = π-cyclopentadienyl) is reported. The reaction of complexes (I) and (II) with cyclohexyl isocyanide ($C_6H_{11}NC$) affords the first isocyano-complexes of titanium, $[Ti(cp)_2Cl(C_6H_{11}NC)]$ (V) and $[Ti(cp)Cl_2(C_6H_{11}NC)_2]$ (VI); complex (V) can also be obtained from the reaction between $[Ti(cp)_2(CH_2Ph)Cl]$ and $C_6H_{11}NC$.

THIS paper describes the synthesis of the complexes $[Ti(cp)_2Cl]_2$ [1] (I) and $[Ti(cp)Cl_2]_2$ [1] (II) (cp = π-cyclopentadienyl) from the ' oxidative addition ' of $[Ti(cp)_2Cl_2]$ and $TiCl_4$ to $[Ti(cp)_2(CO)_2]$.[2] The study can be regarded as an extension of research on the high reactivity of the nucleophile $[Ti(cp)_2(CO)_2]$ [3] towards a wide range of electrophilic reagents. Moreover, recent

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[1] R. S. P. Coutts and P. C. Wailes, *Adv. Organometallic Chem.*, 1970, **9**, 136.

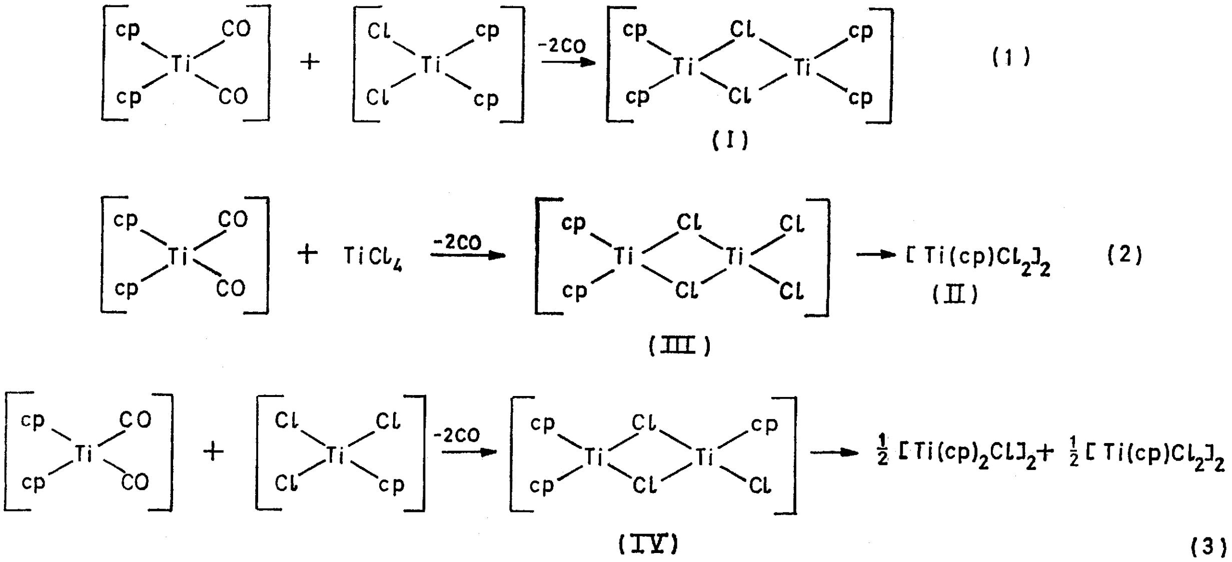
[2] J. G. Murray *J. Amer. Chem. Soc.*, 1961, **83**, 1287.

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

results of halogen-bridge splitting reactions involving complexes (I)[4] or (II)[5] and insertion reactions in titanium–carbon bonds[6-8] prompted us to report the reactions of (I), (II), and [Ti(cp)$_2$(R)Cl] with $C_6H_{11}NC$.

RESULTS

The synthesis of the complex [Ti(cp)$_2$Cl]$_2$, (I), was carried out by mixing equimolar quantities of the complexes [Ti(cp)$_2$(CO)$_2$] and [Ti(cp)$_2$Cl$_2$] in thf (thf = tetrahydrofuran) or toluene at room temperature. After 2 days the i.r. CO stretching bands of [Ti(cp)(CO)$_2$] (1975 and 1897 cm^{-1}) had disappeared and a high yield (80%) of a crystalline solid, found to be [Ti(cp)$_2$Cl]$_2$, was obtained. The synthesis of the complex [Ti(cp)Cl$_2$]$_2$, (II), was carried out by mixing equimolar quantities of [Ti(cp)$_2$(CO)$_2$] and $TiCl_4$ in toluene. The immediate disappearance of the carbonyl species, followed by the formation of a green-maroon product, (III), not isolated, was observed. Heating complex (III) for many hours at 100 °C in either xylene or toluene, gave *ca.* 60% yield of [Ti(cp)Cl$_2$]$_2$. The synthesis of complexes (I) and (II) can be represented by equations (1) and (2). The presence of the asymmetric intermediate (III) is assumed; attempts to isolate (III) or (IV) from the reaction between the complexes [Ti(cp)$_2$-(CO)$_2$] and [Ti(cp)Cl$_3$] [equation (3)] were unsuccessful. Reaction (3) was carried out in toluene at room temperature yielding a green solution containing complexes (I) and (II), the latter as a slightly soluble mauve solid.



The reaction of complexes (I) and (II) with cyclohexyl isocyanide in toluene gave, upon addition of heptane, complexes (V) and (VI), respectively, as green crystalline solids. The analytical data (Table) agree with the above formulae. Complexes (V) and (VI) showed one single band (toluene solution or Nujol mull) in the CN stretching region at 2180 and 2200 cm^{-1}, respectively. The complexes are monomeric in benzene solution. Magnetic moments (Table) are in agreement, both for (V) and (VI), with one unpaired electron located on the magnetically dilute titanium(III). The reaction of complex (V) with oxygen yielded, *inter alia*, cyclohexyl isocyanide and cyclohexyl isocyanate.

Following an interest in the insertion of unsaturated molecules in titanium–carbon bonds, the reaction between the complex [Ti(cp)$_2$(CH$_2$Ph)Cl] and $C_6H_{11}NC$ was attempted. Contrary to results obtained with SO_2,[7] NO,[8] and CO with several alkyl derivatives,[6] no insertion products were found and *ca.* 95% yield of complex (V) and bibenzyl resulted [equation (6)]. Reaction (6) is very fast in toluene solution; complex (V) can be recrystallised from the reaction mixture on addition of heptane.

Analytical and magnetic results for chloro(π-cyclopentadienyl)titanium(III) derivatives

Complex	Analytical data: %found (% calc.) C	H	Cl	N	μ_{eff} (293 K) B.M.
(I) [Ti(cp)$_2$Cl]$_2$	56·7(56·2)	4·7(4·7)	16·8(16·7)		
(II) [Ti(cp)Cl$_2$]$_2$	32·2(32·6)	2·6(2·7)	37·1(38·6)		
(V) [Ti(cp)$_2$Cl(C$_6$H$_{11}$NC)]	63·6(63·2)	6·3(6·5)	11·3(11·0)	4·4(4·3)	1·74
(VI) [Ti(cp)Cl$_2$(C$_6$H$_{11}$NC)$_2$]	56·7(56·7)	6·7(6·7)	17·6(17·7)	6·5(6·9)	1·73

cp = π-Cyclopentadienyl.

DISCUSSION

Reactions (1)—(3) can be regarded as the results of acid–base interactions, followed by electron transfer, between basic titanium(II) and acidic titanium(IV).[9] Our recent report on oxidative additions to the complex

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[4] M. L. H. Green and C. R. Lucas, *J.C.S. Dalton*, 1972, 1000.

[5] R. S. P. Coutts, R. L. Martin, and P. C. Wailes, *Austral. J. Chem.*, 1972, **25**, 1401.

[6] C. Floriani and G. Fachinetti, *Abs. 14th Internat. Conf. Co-ordination Chem.*, Toronto, 1972, p. 707.

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

[8] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometallic Chem.*, 1972, **34**, 155.

[9] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.

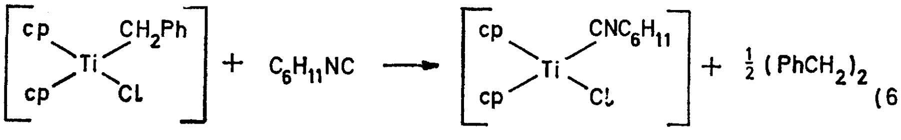
$[\mathrm{Ti(cp)_2(CO)_2}]$ pointed out the basicity of titanium in this d^2 system, especially in nucleophilic displacements on organic acyl and alkyl halides.[3] On the other hand, the nucleophilic character of $[\mathrm{Ti(cp)_2(CO)_2}]$ is suggested by the basic properties shown by similar d^2 systems having bent cyclopentadienyl structures, such as $[\mathrm{Mo(cp)_2H_2}]$ and $[\mathrm{W(cp)_2H_2}]$.[10] In the case of the complex $[\mathrm{Ti(cp)_2(CO)_2}]$ (1975 and 1897 cm^{-1} in heptane), the CO stretching frequencies can be regarded as a rough indication of the nucleophilicity of the metal atom.

$$[\mathrm{Ti(cp)_2Cl}]_2 + 2\mathrm{C_6H_{11}NC} \xrightarrow[\text{heptane}]{\text{toluene}} 2[\mathrm{Ti(cp)_2Cl(C_6H_{11}NC)}] \qquad (4)$$

(V)

$$[\mathrm{Ti(cp)Cl_2}]_2 + 4\mathrm{C_6H_{11}NC} \xrightarrow[\text{heptane}]{\text{toluene}} 2[\mathrm{Ti(cp)Cl_2(C_6H_{11}NC)_2}] \qquad (5)$$

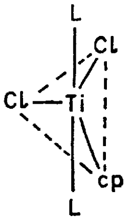
(VI)



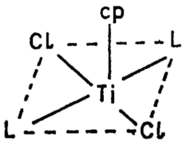
(6)

(V)

Reactions (4) and (5) are examples of the recently reported halogen-bridge splitting in complexes (I)[4] and (II)[5] with many different N, P, and O ligands. Complexes (V) and (VI) seem to be the only reported isocyano-complexes of titanium. The high wavenumber values [2180 (V) and 2200 cm^{-1} (VI)] for the C≡N stretching vibrations are in agreement with good σ-donation from carbon to titanium and the very poor back-bonding ability of titanium(III). This may explain the failure to obtain the corresponding monocarbonyl derivative.[4] The presence of only one C≡N stretching band in solid state or in solution for complexes (V) and (VI), together with the magnetic moments (Table) and molecular-weight values, suggest for (V) four- and for (VI) five-co-ordination around the metal atom. In the case of complex (V) a pseudo-tetrahedral arrangement of the ligands is obvious. The single C≡N stretching band may suggest for the di-isocyano-derivative (VI) either a trigonal-bipyramidal (A) or a square-pyramidal (B) arrangement of the ligands around the titanium atom, with the two isocyano-groups *trans* to each other (pseudo-C_{2v} symmetry).



(A)



(B)

$\mathrm{L = C_6H_{11}NC}$

An unexpected behaviour of complexes (I) and (II) is in the greater preference for carbon than for oxygen ligands, as shown by the invariance of the i.r. spectra of (V) and (VI) on going from toluene to thf solution.

EXPERIMENTAL

All reactions and operations described in this paper were carried out in an atmosphere of purified nitrogen. Solvents were deaerated and dried by standard methods. I.r. spectra were measured with a Perkin-Elmer model 337 grating spectrophotometer. Magnetic susceptibilities were measured with a Gouy balance. Molecular weights were determined cryoscopically in benzene.

Preparations.— *Bis[chlorobis(π-cyclopentadienyl)titanium*(III)], (I). The complex dichlorobis(π-cyclopentadienyl)-titanium(IV) (0·53 g, 2·13 mmol) was added to a solution of dicarbonylbis(π-cyclopentadienyl)titanium(II) (0·5 g, 2·13 mmol) in thf or toluene (50 cm^3). The suspension was stirred for 2 days at room temperature to complete dissolution of the solid. When the solvent was slowly evaporated under reduced pressure, the solution gave dark green crystals which dried *in vacuo* (*ca.* 80%).

Bis[dichloro(π-cyclopentadienyl)titanium(III)], (II). $\mathrm{TiCl_4}$ (1·76 g, 9·3 mmol) was dissolved in dry xylene (200 cm^3), then slowly added to a solution of the complex $[\mathrm{Ti(cp)_2(CO)_2}]$ (2·17 g, 9·3 mmol) in xylene (100 cm^3). During the addition, rapid CO evolution was observed, and at the end a black-green solid was obtained. The suspension was heated for 16 h at 100 °C and the colour of the solid changed from green to mauve. The solid was purified by dissolving in thf, from which blue-green crystals were obtained (*ca.* 60%). On drying *in vacuo* at 50 °C the colour changed to mauve.

Chloro(cyclohexyl isocyanide)bis(π-cyclopentadienyl)titanium(III) (V): *Method A*. The complex dichlorobis(π-cyclopentadienyl)titanium(IV) (0·66 g, 2·65 mmol) was added to dicarbonylbis(π-cyclopentadienyl)titanium(II) (0·62 g, 2·65 mmol) in toluene (100 cm^3) and the mixture was stirred for 2 days, when a green solution was obtained. The addition of cyclohexyl isocyanide (0·58 g, 5·3 mmol) to this solution resulted in a change of colour from light to

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[10] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 4854.

dark green. After evaporating most of the toluene and addition of heptane (100 cm^3), a green solid crystallised out from the solution (*ca.* 80%). The *complex* is soluble in benzene or toluene. $M = 348$ (calc.: 322·5). I.r. spectrum (toluene solution): ν(CN) 2180; (Nujol mull) 3095m, 2180vs, 1320m, 1260w, 1155w, 1125w, 1075w, 1020vs sh, 928w, 910w, 895w, 835vs (broad), 790vs (broad), and 525w cm^{-1}.

Method B. To a toluene solution (25 cm^3) of the complex $[Ti(cp)_2(CH_2Ph)Cl]$ (1·1 g, 3·6 mmol), was added $C_6H_{11}NC$ (0·44 g, 4·1 mmol). Within 15 min the colour changed from black-violet to green. After 2 h, on the addition of heptane (100 cm^3), light green *crystals* were obtained (*ca.* 95%). The filtered solution, evaporated to dryness, gave pure $(PhCH_2)_2$ (m.p. 52 °C) by sublimation. The amount of $(PhCH_2)_2$ was determined *via* g.l.c. and found to be 0·31 g (1·7 mmol).

Dichlorobis(cyclohexyl isocyanide)(π-cyclopentadienyl)titanium(II), (VI). Cyclohexyl isocyanide (0·67 g, 6·15 mmol) was added to a suspension of the complex $[Ti(cp)Cl_2]_2$ (0·54 g, 1·47 mmol) in toluene (25 cm^3). All the mauve solid dissolved immediately and the colour of the solution became blue-green. Upon addition of heptane (50 cm^3), blue-green crystals were obtained after 1 h. They were washed with heptane and dried (*ca.* 90%). No free isocyanide was found (i.r.) in the filtered solution. The *complex* is soluble in benzene or toluene. $M = 373$ (calc: 402). I.r. spectrum (in toluene): ν(CN) 2000; (Nujol mull) 2000vs, 1323m, 1195w, 1157w, 1130w, 1015ms, 930w, 907m, 895m, 870w, 840w, 812s, 795s, 545vw, 530vw, and 490w cm^{-1}.

Reaction of $[Ti(cp)_2(CO)_2]$ *with* $[Ti(cp)Cl_3]$.—A toluene (100 cm^3) solution of the complex $[Ti(cp)_2(CO)_2]$ (1·12 g, 4·8 mmol) was slowly added to toluene (100 cm^3) containing $[Ti(cp)Cl_3]$ (1·08 g, 4·8 mmol). At the end of the addition a precipitate began to form. After 2 h the solution was dark green. The mauve solid was collected by filtration, washed, and dried *in vacuo*. It was shown to be $[Ti(cp)Cl_2]_2$ by microanalysis. After evaporating most of the toluene, a green solid crystallised out from the solution, the elemental analysis of which corresponded to that of $[Ti(cp)_2Cl]_2$.

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