

NOVEL REACTIONS OF MONOCYCLOPENTADIENYLTITANIUM(III) DIHALIDES WITH ORGANIC CARBONYL GROUPS

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SUMMARY

Cyclopentadienyltitanium(III) dihalides, CpTiX_2 (where $\text{X} = \text{Cl}$ or Br), or their tetrahydrofuranates, $\text{CpTiX}_2 \cdot \text{THF}$, have been brought into reaction with organic compounds containing the carbonyl group (benzophenone, acetophenone, acetone, and benzaldehyde). The physical and chemical properties of the yellow crystalline products suggest that organotitanium(IV) derivatives are formed by an intramolecular "redox" process. Evidence for reversibility of the reaction is offered in the case of benzophenone complexes.

INTRODUCTION

Monocyclopentadienyltitanium(III) dihalides have been shown to form normal coordination type complexes with ethers^{1,2}, alcohols², and a range of nitrogen donors³. It was expected that ketones and aldehydes would form coordination complexes similar to those of both titanium(IV)⁴⁻⁶ and titanium(III) halides^{7,8}. The reaction of ketones with titanium(III) chloride^{7,8} gives complexes of general formulae $\text{TiCl}_3 \cdot n\text{R}_2\text{CO}$ ($\text{R} = \text{Me}$, Et , and Ph ; $n = 2$ or 3). These compounds have visible spectral, and magnetic data consistent with octahedral titanium(III) species. Coordination results in a lowering of the carbon-oxygen stretching frequency ($\approx 50\text{--}100 \text{ cm}^{-1}$) in the $\text{C}=\text{O}$ region. This characteristic lowering of the carbonyl stretching frequency has been observed also in the spectra of the keto complexes formed by titanium(IV) chloride⁴⁻⁶.

RESULTS AND DISCUSSION

The reaction of a ketone or aldehyde with CpTiX_2 or $\text{CpTiX}_2 \cdot \text{THF}$ ($\text{X} = \text{Cl}$ or Br) in a mixed solvent of THF/diethyl ether resulted in a colour change from mauve or blue, for CpTiCl_2 or CpTiBr_2 , and from blue or green, for $\text{CpTiCl}_2 \cdot \text{THF}$ or $\text{CpTiBr}_2 \cdot \text{THF}$, to a brown solution and a yellow crystalline precipitate. The yellow precipitates, after washing with ether and drying, analysed for 1/1 complexes (see Table 1). The complexes, apart from those formed from benzophenone, were slightly

TABLE I
ANALYTICAL DATA

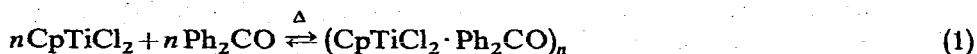
Compound	Colour	Analysis found (calcd.) (%)				Mol. wt. found (calcd.)
		C	H	Halide	Ti	
[CpTiCl ₂ ·(CH ₃) ₂ CO] ₂ (I)	Yellow	40.1 (39.7)	4.7 (4.6)	29.8 (29.3)	19.9 (19.8)	(484)
[CpTiBr ₂ ·(CH ₃) ₂ CO] ₂ (II)	Yellow	29.2 (28.9)	3.4 (3.3)	48.0 (48.2)	14.6 (14.5)	618 (662)
[CpTiCl ₂ ·Ph(CO ₃)CO] ₂ (III)	Yellow	51.2 (51.4)	4.2 (4.3)	23.1 (23.3)	15.9 (15.8)	554 (608)
[CpTiBr ₂ ·Ph(CH ₃)CO] ₂ (IV)	Yellow	38.2 (39.7)	3.3 (3.3)	39.6 (40.7)	11.9 (12.2)	791 (786)
[CpTiCl ₂ ·Ph ₂ CO] _n (V)	Greenish yellow	59.1 (59.1)	4.1 (4.1)	18.9 (19.4)	13.1 (13.1)	^a (366)
[CpTiBr ₂ ·Ph ₂ CO] _n (VI)	Greenish yellow	43.0 (47.5)	3.9 (3.3)	36.9 (35.1)	10.7 (10.5)	^a (455)
[CpTiCl ₂ ·PhCHO] ₂ (VII)	Yellow	49.9 (49.7)	3.8 (3.8)	24.0 (24.4)	16.6 (16.5)	544 (580)
[CpTiBr ₂ ·PhCHO] ₂ (VIII)	Yellow	37.8 (38.0)	2.9 (2.9)	40.9 (42.2)	12.7 (12.7)	702 (758)

^a See text.

soluble in THF, CHCl₃ and toluene or benzene, and virtually insoluble in diethyl ether and petrol. All were considered hydrolytically unstable and were therefore handled under anaerobic conditions.

Solid state reflectance spectra in the visible and UV regions displayed no absorptions attributable to *d-d* transitions. In THF the yellow benzophenone complexes dissolved to give green solutions with spectra similar to CpTi^{III}X₂·THF (X = Cl or Br), the remainder of the complexes dissolved to give yellow solutions with spectra again devoid of *d-d* bands. All compounds were virtually diamagnetic with χ_{M0} values < 120.

Ebulliometric molecular weight determinations in toluene showed the compounds to be dimeric although the benzophenone complexes showed anomalous behaviour. In the boiling solvent thermal decomposition took place, and in the case of compound (V) an insoluble purple material remained (probably CpTiCl₂, see later in discussion), and a deflection was registered equivalent to the approximate molecular weight of the free ketone (benzophenone). The toluene solution from the molecular weight determination was taken off with a syringe and reduced to dryness. An IR spectrum of the residue showed the presence of C=O groups, suggesting that the reaction is reversible [eqn (1)].



Infrared data

Infrared spectra were recorded for the eight compounds in the range 4000–250 cm⁻¹ using KBr disks. The total absence of the strong $\nu(\text{C}=\text{O})$ stretching band,

which occurs in the free ligand spectra at $\approx 1700 \text{ cm}^{-1}$, is the most significant item of evidence observed. This excludes the possibility of a normal coordination type complex involving attachment to the metal via the oxygen atom of the carbonyl group, as such interactions have been reported to cause maximum shifts of the C=O stretching frequency of the order of 150 cm^{-1} ⁴⁻⁶

The region $1200\text{--}1600 \text{ cm}^{-1}$ in which the free ligand exhibits rich absorption, was also depleted of many bands; in particular, the strong to very strong bands between $1200\text{--}1270 \text{ cm}^{-1}$ which are also associated with contributions from C-O stretching modes. As is exemplified in Fig. 1, the spectra of the new complexes show no strong bands above 1200 cm^{-1} , and most of the new absorptions associated with C-O frequencies occur in the narrow range $1000\text{--}1150 \text{ cm}^{-1}$, a region in which the metal alkoxides absorb strongly.

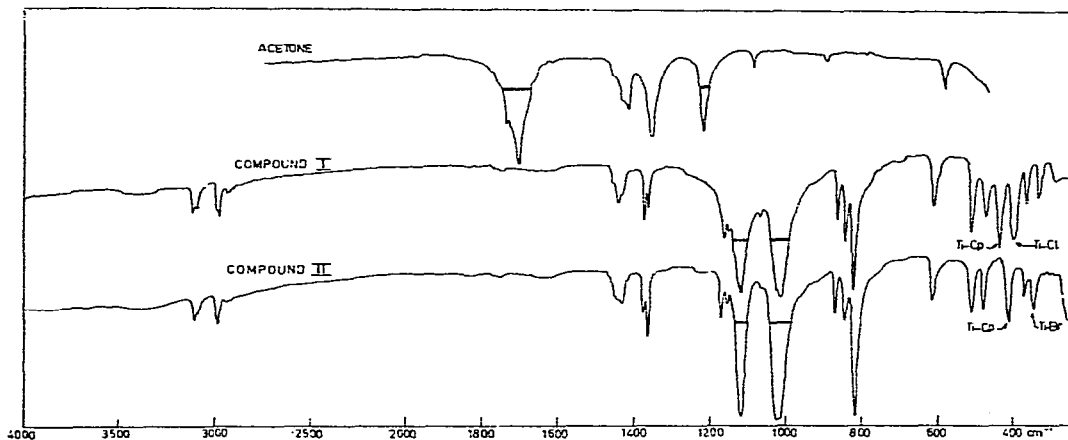


Fig. 1. Infrared spectra of acetone complexes.

The presence of π -bonded cyclopentadienyl ligands was shown by the simultaneous appearance of four bands in the regions $3100\text{--}3000 \text{ cm}^{-1}$ (C-H stretch), $1400\text{--}1450 \text{ cm}^{-1}$ (C-C skeletal stretch), 1000 ± 20 (C-H deformation), and $780 \pm 70 \text{ cm}^{-1}$ (C-H deformation)⁹. The C-H deformation band normally found at $1010 \pm 16 \text{ cm}^{-1}$ was masked by strong absorptions due to other ligand vibrations.

Below 600 cm^{-1} absorption bands due to the vibrations of metal-halide, metal-oxygen, and metal-cyclopentadienyl are expected in addition to bands due to internal vibration of the ligands. Tentative assignments in this region are given in Table 2.

The assignment of the titanium-halogen stretching vibration is strengthened by the fact that the chloride derivatives show a very strong band at $404 \pm 4 \text{ cm}^{-1}$ which is absent in all bromide derivatives. The usual range quoted for $\text{Ti}^{\text{IV}}\text{-Cl}$ stretching modes is $360\text{--}390 \text{ cm}^{-1}$ for six-coordinate compounds, and one could expect some rise in frequency due to decrease in coordination number. The bromide derivatives on the other hand possess a medium to strong band at $335\text{--}370 \text{ cm}^{-1}$ which is not present in the chloride derivatives.

There are few reports of infrared data for monocyclopentadienyltitanium(IV) derivatives in this low wavelength region; however a recent publication¹⁰ has made

TABLE 2
INFRARED DATA

Compound	Band position ^a		Ti-O	Ti-O	Ti-Cp	Ti-Cl	Ligand bands	Ti-Cl	TiBr
	Ti-O	Ti-O							
(I)	516 s	480 m	442 s	406 s	373 m	340 m	350 m		
(II)	512 s	484 s	415 s	400 vs 410 (sh)	373 m	330 vw			
(III)	528 s	465 m	423 s	400 vs 410 (sh)	378 m				
(IV)	536 s	472 m (br)	445 m 425 w	408 vs	394(sh) 385 m	325 w-m	345 m-s		
(V)	522 m-s 506 w	470 m	449 s		390 (sh) 365 m				
(VI)	522 s 508 w-m	470 s	425 s		390 m 380 (sh)		335 m-s		
(VII)	540 m 525 m	460(sh) 450(sh)	440 s	404 vs 410(sh)	365 m 360(sh)	350 vw	370 s 345(sh)		
(VIII)	540 w(sh) 535 s	470 m (br)	425 s						

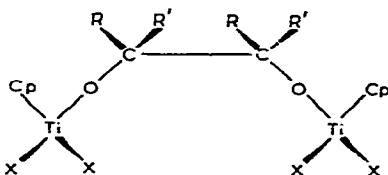
^a With tentative assignments.

assignments to the IR bands of CpTiCl_3 using approximate normal coordinate analyses. The strong bands at 412 and 332 cm^{-1} were assigned to metal-chloride stretching vibrations in good agreement with the data above. The very strong band at 345 cm^{-1} in the spectrum of CpTiBr_3 can be assumed to be the Ti-Br stretching mode, once again in agreement with the results of the present study.

Russian workers have made an extensive study of the metal-Cp stretching frequency in compounds of the general formula $\text{CpTi}(\text{OEt})_n\text{Cl}_{3-n}$, where $n=0-3$ ¹¹, and have established that in such compounds the Ti-Cp band occurs between $420-441\text{ cm}^{-1}$. Further work showed the effect of halogen exchange on such compounds. In going from CpTiCl_3 to CpTiBr_3 the band at 441 cm^{-1} shifted to 425 cm^{-1} ; the bands assigned to Cp-Ti stretch in $\text{CpTi}(\text{OEt})\text{Cl}_2$ and $\text{CpTi}(\text{OEt})\text{Br}_2$ similarly showed a shift of 18 cm^{-1} to lower frequency. These results are confirmed by the present findings.

The alcoholate², and etherate^{1,2} complexes of $\text{CpTi}^{\text{III}}\text{X}_2$ were shown to have weak bands in the regions 565 ± 25 and $475 \pm 5\text{ cm}^{-1}$, assigned to metal-oxygen stretching frequencies. Some polymeric titanium(III) compounds also show two bands at $\approx 550\text{ cm}^{-1}$ and between $470-490\text{ cm}^{-1}$ which have been tentatively assigned as Ti-O stretching bands¹². Kriegsmann and Leicht have assigned Ti-O vibrational modes in titanium(IV) alkoxides in the range $650-400\text{ cm}^{-1}$ ¹³. Again such assignments would tend to support the tentative assignments to Ti-O stretching modes (Table 2) given in this investigation.

Analytical, molecular weight, and infrared data are thus in agreement with a dimeric, 1/1 ratio compound containing alkoxide-type ligands. The structure of compounds (I)-(IV), (VII) and (VIII) can thus be considered to be of the type shown below, or its isomeric forms.



NMR data confirmed that isomeric forms exist for these compounds and attempted isolation of the individual isomers is in progress.

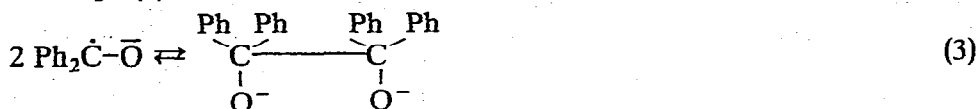
Compounds (V) and (VI) differ from the others in their chemical behaviour. It has been established by IR and NMR that the hydrolysis or alcoholysis of these compounds yield benzophenone, whereas hydrolysis of say compound (I) yields pinacol (IR, NMR), the expected dialcohol from the dimeric structure above. Similarly, compounds (V) and (VI) dissolve in THF to give $\text{CpTiX}_2 \cdot \text{THF}$ ($\text{X}=\text{Cl}$ or Br) and free benzophenone, whereas all of the other compounds dissolve without reaction. Thermally, (V) and (VI) decompose even in benzene or toluene at 40° to CpTiX_2 ($\text{X}=\text{Cl}$ or Br) and benzophenone (as demonstrated in attempted ebulliometric molecular weight determinations), whereas all of the other products gave dimeric values for their molecular weight at 110° (boiling toluene).

The reduction of carbonyl groups in aldehydes and ketones has been extensively studied in organic chemistry and a comprehensive literature is available¹⁴. These reductions have been effected mainly with Group I, II or III metals. The re-

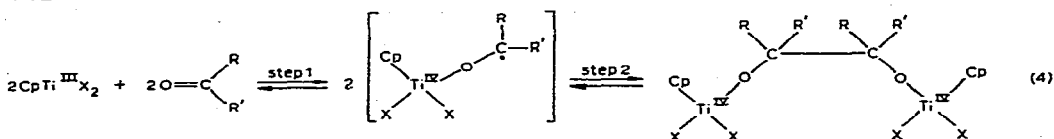
duction of organic carbonyl compounds accompanying the dissolution of Na in liquid ammonia has also been widely explored^{15,16}. The addition of an electron results in an anion radical [eqn. (2)].



An aromatic or non-enolizable aliphatic ketone can react to give a "ketyl" (which is a radical ion). The solution is paramagnetic and in the case of benzophenone a series of complex equilibria has been shown to exist in solution. One such equilibrium is shown in eqn. (3):



In the present investigation one can consider the organotitanium(III) derivative (d^1 system) as a source of electron donation. The formation of the dimeric products obtained can then be explained using the steps in eqns. (2) and (3) [see eqn. (4)].



In the cases in which stable intermediates are not expected, the reaction goes to completion via step 2, and can be considered irreversible [compounds (I)–(IV), (VII) and (VIII)]. When the ketone is benzophenone [(V) and (VI)], the intermediate ketyl can be stabilized by electron delocalization and offers an opportunity to reverse step 2 under suitable conditions. This may well explain the anomalous behaviour of compounds (V) and (VI), and their ability to regenerate the C=O group after formation of the alkoxide type bond to the metal.

EXPERIMENTAL

General

All manipulations were carried out in an N_2 -filled evacuable glove box, or in a stream of purified argon, using a Schlenk system. Infrared spectra were run in KBr disks, on a Perkin-Elmer 521 spectrophotometer. Visible spectra were measured in solution on a Beckman DK2 spectrophotometer and in the solid state on a Beckman DK2A spectrophotometer with a diffuse reflectance attachment. Magnetic susceptibilities were determined by the Gouy method.

Analysis

Titanium was estimated by ashing a sulphated pellet of the sample. C, H and halide were determined by the Australian Microanalytical Service using weighed pellets sealed in Al capsule.

Reagents

CpTiX_2 or $\text{CpTiX}_2 \cdot \text{THF}$ ($\text{X} = \text{Cl}$ or Br) were prepared from CpTiX_3 by

reduction with Zn^1 . Acetone and acetophenone were purified by drying over molecular sieves and distilling under argon. Analytical grade benzophenone was used without further purification as was a fresh sample of benzaldehyde. Diethylether and THF were distilled from $LiAlH_4$ under argon.

Reactions

1. General method

Reactions were carried out by the addition of approximately 1–2 g samples of the solid halide or tetrahydrofuranate to a solution of the ketone or aldehyde ($\approx 50\%$ in excess of 1/1 mole ratio) in 30 ml of diethyl ether and 10 ml of THF, at room temperature. The reaction mixture was stirred, and usually within several minutes the solid had dissolved to give a brown solution, after which slow precipitation of yellow crystalline products occurred. The crystalline precipitates were filtered off and washed several times with ether, and then pumped dry. The yields of pure product ranged from 15–90%. (Table 1 gives the analytical data).

2. Reversibility of benzophenone reaction with $CpTiX_2$

(A). $(CpTiCl_2 \cdot Ph_2CO)_n$ (3.0 g) was dissolved in THF (30 ml) giving a green solution and blue crystals. The latter were filtered off, washed with diethyl ether (3×10 ml) and then pumped dry, giving 0.5 g of mauve solid which was identified as $CpTiCl_2$ by IR and Ti analysis. (Found: Ti, 25.8. $CpTiCl_2$ calcd.: Ti, 26.0%.) The green filtrate on pumping to low bulk precipitated a yellow solid which was filtered off and washed with benzene. This solid was an impure sample of the original adduct. The benzene/THF filtrate was pumped dry and extracted with diethyl ether to give 0.5 g of impure $Ph_2C=O$ identified by IR and NMR spectra.

The ratio of $CpTiCl_2/Ph_2C=O$ is approximately 1/1, in agreement with the proposed stoichiometry. Obviously there is an equilibrium reaction which accounts for the incomplete reversal.

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