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SOME d^1-π-CYCLOPENTADIENYLTITANIUM COMPOUNDS WITH HALOGEN, ALKYL AND PHOSPHINE LIGANDS

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Summary

Reaction of the halides $(Cp_2TiCl)_2$ and $(CpTiCl_2)_n$ with Grignard or alkyllithium reagents leads to disproportion products. Such a disproportionation has been used to prepare $CpTiR_3$ ($Cp = \pi$-C_5H_5; R = Me, Me_3SiCH_2) and Cp_2TiR_2 ($R = Me_3SiCH_2$) from $(CpTiCl_2)_n$ and $(Cp_2TiCl)_2$. Evidence is presented that the tendency to disproportionation of d^1-titanium compounds, in which the metal is bonded only to carbon atoms, may account for the difficulty in isolating such substances. Preparations of the new compounds $CpTiCl_2 \cdot L_2$ [$L = Me_2PhP$, $MePh_2P$; $L_2 = (Me_2PCH_2)_2$ or $(Ph_2PCH_2)_2$] are described. The reactivity of $(C_5H_5)_3Ti$ and its stability with respect to disproportionation are discussed in the light of its structure.

Introduction

The compounds $(C_5H_5)_3Ti$ [1], Cp_2TiPh [2], $Cp_2Ti(\pi$-$C_3H_5)$ [3] and $[Cp_2Ti(C{\equiv}CPh)]_n$ [4] are the only moderately well-characterized examples of compounds of general formula Cp_nTiR_{3-n}. Recent reports by Shilov [5] and de Liefde Meijer [2] show that some of these and apparently related compounds such as $Cp_2Ti(i$-$C_3H_7)$ are of interest in connection with nitrogen fixation. This paper describes studies on series of compounds, the preparations and properties of which provide some insight into factors affecting reactivity and stability of species of general type Cp_nTiR_{3-n}.

Chemical studies

In view of the kinetic stability of substances containing the trimethylsilylmethyl functional group [6,7], attempts were made to prepare compounds of the form Cp_2TiR or $CpTiR_2$ ($R = Me_3SiCH_2$) by treating $(Cp_2TiCl)_2$ or $(CpTiCl_2)_n$ with stoichiometric amounts of Me_3SiCH_2MgCl or Me_3SiCH_2Li (eqns. 1 and 2).

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However, from these reactions at low temperatures (ca. —40°) yellow compounds Cp_2TiR_2 and $CpTiR_3$ were isolated, in about 50% yield. They were characterized by analysis and by IR and NMR spectroscopy. The data are given in Table 1 and the Experimental section. In addition to these tetravalent products, precipitates were also formed which appear to contain divalent titanium. The reactions were carried out at temperatures between —95° and 20° under an atmosphere of nitrogen or argon and the observations were similar in all cases. For example, when a petroleum ether solution of trimethylsilylmethyllithium and a toluene solution of $(Cp_2TiCl)_2$ were mixed at —95°, intensification and darkening of the green colour of the original solution occurred. Upon warming to —84°, this colour was discharged with appearance of a black precipitate, probably a divalent titanium species, and a yellow solution containing the compound $Cp_2Ti(CH_2SiMe_3)_2$.

$$(CpTiCl_2)_n + 2n\ RMgCl \rightarrow n/2\ CpTiR_3 + \text{divalent Ti species} + MgCl_2 \tag{1}$$

$$(Cp_2TiCl)_2 + 2\ RMgCl \rightarrow Cp_2TiR_2 + \text{divalent Ti species} + MgCl_2 \tag{2}$$

The isolation of both divalent and tetravalent titanium derivatives from reactions of trivalent starting materials indicates the occurrence of disproportionation. It is reasonable to suppose this disproportionation proceeds via dimerization of an initially formed trivalent species. To attempt to test this hypothesis, compounds were prepared in which dimerization would be restricted by occupation of potential sites for dimerization by other ligands. Such compounds are of the type $Cp_2TiCl \cdot L$ (I), where L = RNH_2 or R'_3P and R = H, Me, Et, Ph, C_3H_5; RNH_2 = py; $R'_3 = Me_2Ph$, $MePh_2$, and $CpTiCl_2 \cdot L_2$ (II), where L = Me_2PhP, $MePh_2P$ or $L_2 = (Me_2PCH_2)_2$, $(Ph_2PCH_2)_2$. The preparation and characterization of the compounds I, $Cp_2TiCl \cdot L$, have recently been reported elsewhere [8]. The new complexes II, $CpTiCl_2 \cdot L$, whose preparation is described here, were characterized by analysis, IR spectroscopy and, in one case, by molecular weight determination. The data are given in Table 1 and in the Experimental section. I and II react rapidly with ethyl-, allyl- and phenyl-magnesium bromides or with n-butyl- and phenyl-lithium, even at —90°, to give dark coloured mixtures from which the ligands, L, were isolated. No other tractable products could be obtained by application of the techniques of sublimation, extraction or column chromatography.

The preparation of alkyl derivatives of trivalent mono-π-cyclopentadienyltitanium compounds was attempted. An ethereal suspension of $(CpTiCl_2)_n$ was treated with a 2/1 molar ratio of methylmagnesium bromide or methyllithium at room temperature. A gas which was vigorously evolved was shown by its IR spectrum to be methane. A black precipitate was formed leaving a yellow coloured solution from which the compound $CpTiMe_3$ was isolated (eqn.3). This was identified by the IR and NMR spectra (Table 1).

$$(CpTiCl_2)_n + 2n\ MeMgBr \rightarrow n/2\ CpTiMe_3 + MeH + MgBr_2 + \text{divalent Ti} \tag{3}$$

The black precipitate, which is soluble in aromatic hydrocarbons, reacts rapidly with water to form Ti_2O_3 and a non-condensable, explosive gas, presumably hydrogen since it is IR inactive, is evolved. The evolution of hydrogen suggests that the black precipitate contains formally divalent titanium. Useful information could not be obtained from either the ^1H NMR or IR spectra of the black precipitate. A suspension of the black material turns white when treated with dry hydrogen chloride and a yellow colour appears in the supernatant liquid. The white precipitate was shown to be magnesium chloride and the yellow compound $CpTiCl_3$ was isolated from the ether solution.

Reaction between $(Cp_2TiCl)_2$ and methylmagnesium chloride or methyllithium does not give Cp_2TiMe_2. Instead, a dark coloured precipitate and a yellow solution are formed. The yellow solution reacts rapidly at 20° with carbon monoxide to form the known $Cp_2Ti(CO)_2$. This was identified by comparison of its IR spectrum with that of an authentic sample [9]. The yellow solution reacts with molecular nitrogen at temperatures below —50° to give an ink-blue solution, the colour of which is discharged upon warming. No blue colour is formed if the solutions are degassed before cooling or if argon is present instead of molecular nitrogen. The yellow substance appears to sublime at 40° in vacuo onto a probe cooled to —78°; however, this sublimate did not react with dinitrogen or carbon monoxide.

Since some complexes of the type Cp_2TiR react with molecular nitrogen, we were interested to find whether the formally analogous compound $(C_5H_5)_3Ti$ would react similarly. Crystals of the compound were obtained as described from $(Cp_2TiCl)_2$ and NaCp [1] and were subsequently treated with molecular nitrogen in toluene at temperatures down to —95°. No colour change was observed. This suggested that some substantial difference exists between the stereochemistry about titanium in Cp_2TiPh and $(C_5H_5)_3Ti$, and that in the latter there is effectively no vacant coordination site to which the nitrogen molecule can bond. In support of this, it was observed that $(C_5H_5)_3Ti$ does not react with pyridine, except at temperatures above 85°, and then with decomposition.

Attempts were made to oxidize $(C_5H_5)_3Ti$ under mild conditions with $FeCl_3$, $AgBF_4$ and $AgPF_6$ to give the diamagnetic cation $[(C_5H_5)_3Ti]^+$. With $FeCl_3$, a reaction occurred according to eqn.4 and with $AgBF_4$ and $AgPF_6$ the product Cp_2TiF_2 [10] was isolated in good yield. The ^1H NMR spectrum of Cp_2TiF_2 is reported here.

$$2\,(C_5H_5)_3Ti + 2\,FeCl_3 \rightarrow 2\,Cp_2TiCl_2 + Cp_2Fe + FeCl_2 \qquad (4)$$

The crystal and molecular structure of $(C_5H_5)_3Ti$ has been determined and it is found that there are two normal *pentahapto*-cyclopentadienyl rings while the third C_5H_5 ring, which is also planar, is attached to the metal by only two carbon atoms (see Fig.1) [11].

Discussion

Many inorganic derivatives of trivalent titanium which disproportionate readily, such as $[TiCl_3 \cdot THF]_2$ [12] or $[Ti(NMe_2)_3]_2$ [13] are dimeric or oligomeric while those which do not disproportionate, such as $TiBr_3 \cdot 2NMe_2$ [14], are monomeric. The evidence above suggests that generally alkyls of the type Cp_2TiR also disproportionate by a mechanism involving the dimers.

The green colour observed at —90° upon mixing solutions of $(Cp_2TiCl)_2$ and trimethylsilylmethyllithium may have been due to a trivalent titanium species that disproportionates at —84° to give the isolated products. No dispro-

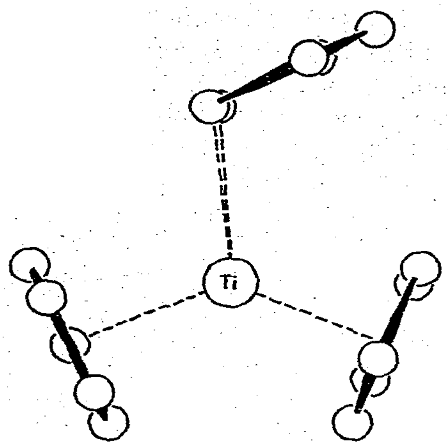

Fig. 1.

portionation is observed for the species $CpTiCl_2 \cdot L_2$ and $Cp_2TiCl \cdot L$ in which dimerization could be inhibited by the ligands, L. The stability of $(C_5H_5)_3Ti$ may be understood similarly, since the *bihapto*-(C_5H_5) ring could restrict dimerization.

Experimental

All operations were carried out under inert atmospheres of nitrogen or argon and all solvents were freshly distilled from calcium hydride prior to use. Proton NMR spectra were recorded on a Japan Electron Optics Instrument operating at 60 MHz and IR spectra were obtained as Nujol mulls on a Perkin Elmer 457 instrument.

Reactions of $(Cp_2TiCl)_2$ with Me_3SiCH_2MgCl or Me_3SiCH_2Li

The green compound $(Cp_2TiCl)_2$ (1.68 g) was suspended in ether (100 ml) at −40° and Me_3SiCH_2MgCl (7.9 mmol) in ether (20 ml) was slowly added.

TABLE 1

ANALYTICAL DATA FOR THE d^1-π-CYCLOPENTADIENYLTITANIUM COMPOUNDS

Compound	Colour	M.p. (°C)[a]	^{1}H NMR[b]
$Cp_2Ti(CH_2SiMe_3)_2$	Yellow	100 s	4.25(s) 10[c]; 9.17(s) 4[d]; 10.00(s) 18[e]
$CpTi(CH_2SiMe_3)_3$	Yellow	60 s	4.18(s) 5[c]; 8.17(s) 6[d]; 9.97(s) 27[e]
$CpTiMe_3$	Yellow	20 s	4.13(s) 5[c]; 8.86(s) 9[e]
Cp_2TiF_2	Yellow	230 s	3.56(t); $J_{F,H} = 1.6$[c]
$CpTiCl_2 \cdot 2Me_2PhP$	Green	134 d	Paramagnetic
$CpTiCl_2 \cdot 2MePh_2P$	Green	125 d	Paramagnetic
$CpTiCl_2 \cdot$diphos	Green	143 d	Paramagnetic
$CpTiCl_2 \cdot$dmpe	Green	209 d	Paramagnetic

[a] M.p. were determined in vacuo in sealed capillaries and are uncorrected. s = sublimes, d = decomposes.
[b] In benzene-d_6 vs. TMS internal standard. Data given as: τ, (multiplicity), coupling in Hz, relative area, assignment, where [c] Cp, [d] CH_2, [e] Me.

After stirring for 3 h, the solvent was removed in vacuo at 0°. The residue was extracted with petroleum ether at 0° and the extract chilled to −78° giving yellow crystals. Yield 48%. The reaction was repeated in toluene at −80° with a petroleum ether solution of Me_3SiCH_2Li. Yield 37%. IR absorptions characteristic of π-cyclopentadienyl ligands are seen at 3080, 1010 and 795 cm^{-1} [10] while bands arising from the trimethylsilylmethyl group occur at 1250 and 850 cm^{-1}. (Found: C, 61.2; H, 9.0. $Cp_2Ti(CH_2SiMe_3)_2$ calcd.: C, 61.3; H, 9.15%.)

Reactions of $(CpTiCl_2)_n$

With Me_3SiCH_2MgCl or Me_3SiCH_2Li. The purple compound $(CpTiCl_2)_n$ (1.3 g) was suspended in ether (100 ml) at −35° and Me_3SiCH_2MgCl (14.2 mmol) in ether (35 ml) was slowly added. After stirring for 3 h, the solvent was removed in vacuo at −35° and the extract chilled to −78° giving yellow crystals in 45% yield. The reaction was repeated in petroleum ether with Me_3SiCH_2Li. Yield 43%. IR absorptions characteristic of the π-cyclopentadienyl and trimethylsilylmethyl ligands are seen in the usual regions (see above). (Found: C, 54.4; H, 10.3. $CpTi(CH_2SiMe_3)_3$ calcd.: C, 54.5; H, 10.2%.)

With MeMgCl or MeLi. The compound $(CpTiCl_2)_n$ (2.95 g) was suspended in ether (150 ml) at room temperature and MeMgCl (32 mmol) in ether (16 ml) was slowly added. The mixture was stirred for 2 h, during the first few minutes of which vigorous gas evolution occurred. The solvent was then removed in vacuo at 20° and the residue extracted with petroleum ether. The extract was chilled to −78° giving yellow crystals. Yield 47%. The reaction was repeated in ether using methyllithium. Yield 44%. The IR spectrum of the product exhibits strong bands at 1450, 1025, 815 and 510 cm^{-1}. (Found: C, 60.5; H, 9.5. $CpTiMe_3$ calcd.: C, 60.8; H, 8.9%.)

Dichlorobis(dimethylphenylphosphine)(π-cyclopentadienyl)titanium

The purple compound $(CpTiCl_2)_n$ (0.4 g) was suspended in toluene (60 ml) and dimethylphenylphosphine (0.6 g) was added. After stirring at room temperature for 12 h, volatiles were removed in vacuo at 50°. The residue was washed several times with petroleum ether and was recrystallized from diethyl ether. Yield 85%. In addition to IR absorptions at 3110, 1009 and 810 cm^{-1} due to the π-cyclopentadienyl ligand, absorptions at 1280, 900 and 750 cm^{-1} are also seen.

The analogous $CpTiCl_2 \cdot 2MePh_2P$ was similarly prepared in 85% yield. (Found: C, 54.6; H, 6.05; P, 13.65; Ti, 10.8; Cl, 15.8. $CpTiCl_2 \cdot 2PMe_2Ph$ calcd.: C, 54.8; H, 5.9; P, 13.5; Ti, 10.4; Cl, 15.4%.) (Found: C, 63.3, H, 5.4. $CpTiCl_2 \cdot 2PMePh_2$ calcd.: C, 63.7; H, 5.35%.) Mol. wt. (cryoscopic in benzene, found 399; $CpTiCl_2 \cdot 2PMe_2Ph$ calcd., 460.

Dichloro[1,2-bis(dimethylphosphino)ethane](π-cyclopentadienyl)titanium

The purple compound $(CpTiCl_2)_n$ in tetrahydrofuran was treated with stoichiometric amounts of 1,2-bis(dimethylphosphino)ethane at room temperature. After stirring for 12 h, the solvent was removed in vacuo at room temperature. Green crystals separate from the concentrated solution which were washed with petroleum ether and dried in vacuo.

The analogue $CpTiCl_2 \cdot$ diphos was similarly prepared except that all the tetrahydrofuran was removed and a saturated toluene solution of the residue was prepared at room temperature. Green crystals were grown in this solution by slow removal of the solvent (50%) in vacuo at 35°. Yield 60%. The usual π-cyclopentadienyl absorption bands occur in the IR spectra of these compounds and in addition bands were observed at 738, 728, 690 and 510 cm^{-1} (diphos) and at 1197, 948, 740 and 722 cm^{-1} (dmpe). (Found: C, 39.7; H, 6.8; P, 18.4; Ti, 14.1; Cl, 21.1. $CpTiCl_2 \cdot$dmpe calcd.: C, 39.55; H, 6.3; P, 18.55; Ti, 14.3; Cl, 21.2%.) (Found: C, 63.8; H, 4.9; P, 10.6. $CpTiCl_2 \cdot$diphos calcd.: C, 63.9; H, 5.0; P, 10.6%.)

Reactions of $(C_5H_5)_3Ti$

With ferric chloride. The compound $(C_5H_5)_3Ti$ (0.522 g) in ether (100 ml) was treated at room temperature with $FeCl_3$ (0.348 g) in ether (50 ml). The mixture turned red and a precipitate formed. The solvent was removed in vacuo at 30° and from the residue ferrocene (0.185 g) was sublimed at 100° in vacuo. The residue from the sublimation was washed repeatedly with a mixture of ether and tetrahydrofuran until the washings were colourless. The solvent was removed from the washings and the red residue was shown to be Cp_2TiCl_2. The off-white residue which remains after removal of Cp_2TiCl_2 was shown to be $FeCl_2$. Yields ca. 90%.

With silver hexafluorophosphate or silver tetrafluoroborate. Silver hexafluorophosphate (1.27 g) or silver tetrafluoroborate (0.98 g) in benzene (150 ml) was added to tris(cyclopentadienyl)titanium (1.22 g) in benzene (60 ml). The mixture was stirred for 1 h and then allowed to settle. The supernatant liquid was discarded. The precipitate was extracted with acetone and the extracts were chilled to −78° to obtain yellow plates which were recrystallized from benzene. Yield 70%. (Found: C, 55.1; H, 4.7. $Cp_2\ TiF_2$ calcd.: C, 55.6; H, 4.7%.)

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