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SYNTHESIS AND PROPERTIES OF MONOCYCLOPENTADIENYLTITANIUM COMPOUNDS

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Summary

The pentacoordinated complexes $(RCp)TiCl_2(acac)$ (R = H, Me, Ph_2CH) have been prepared by photolysis of $(RCp)_2TiCl_2$ and acetylacetone in THF and the hexacoordinated compounds $(RCp)TiCl(acac)_2$ by the reaction of $(RCp)_2TiCl_2$ and acetylacetone in the presence of triethylamine in isobutyronitrile. The hexacoordinated complexes $(RCp)TiCl(oq)_2$ (R = H, Me, Ph_2CH; oq = 8-oxyquinolate) have been prepared by the direct interaction of $(RCp)_2TiCl_2$ and 8-hydroxyquinoline in isobutyronitrile; these compounds can be obtained more quickly by photolysis of the same starting materials in THF solution.

Introduction

The synthesis of β-diketonate chelates of titanium(IV) generally involves the reaction of dicyclopentadienyltitanium halides with β-diketones in the presence of a base such as triethylamine, or reaction of halides with the sodium salt of a β-diketone [1–5]. By this means several dicyclopentadienyltitanium compounds of the type $[Cp_2Tike]^+ X^-$ (where ke = β-diketone, X = uninegative anion like ClO_4^-, BF_4^-, $FeCl_4^-$, etc.) and monocyclopentadienyltitanium compounds of the type $CpTiCl(ke)_2$ have been synthesized. However, the reaction of dichlorodicyclopentadienyltitanium(IV) with 8-hydroxyquinoline gives $CpTiCl(oq)_2$ (oq = 8-oxyquinolate) in the absence of triethylamine because the 8-hydroxyquinoline group acts as HCl acceptor [6].

Several authors [7–11] have observed the photolability of the η-cyclopentadienyl ligand on dichlorodicyclopentadienyltitanium, and Brubaker Jr. et al. [8–10] have obtained $CpTiCl_2(OR)$ (R = Me, i-Pr, n-Pr) by photolysis of Cp_2TiCl_2 in the

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presence of alcohols. We describe below the photochemical reactions of $(RCp)_2TiCl_2$ (R = H, Me, Ph_2CH) with chelating ligands containing a replaceable hydrogen atom, such as acetylacetone and 8-hydroxyquinoline, and also the reactions of $(RCp)_2TiCl_2$ with the same ligands in isobutyronitrile without photolysis.

Results and discusion

The photolysis of a THF solution of $(RCp)_2TiCl_2$ (R = H, Me, Ph_2CH) in the presence of acetylacetone (acacH) led to cleavage of the Ti–Cp bond and formation of $(RCp)TiCl_2(acac)$. The photogenerated $Cp^{\cdot}$ radical might abstract a hydrogen atom from an acetylacetone molecule to give an acac$^{\cdot}$ radical, which subsequently combines with $(RCp)TiCl_2$ to give $(RCp)TiCl_2(acac)$. The use of toluene as solvent leds to similar results. However, treatment of $(RCp)_2TiCl_2$ (R = Me, Ph_2CH) at room temperature with an excess of acetylacetone in isobutyronitrile in the presence of Et_3N yielded compounds of the type $(RCp)_2TiCl(acac)_2$. Newton et al. [1] have previously prepared $CpTiCl(acac)_2$ in acetonitrile as solvent. However the use of isobutyronitrile as solvent makes it easier to separate the products. In the absence of Et_3N the starting material can be recovered in 90% yield after a week of stirring. In contrast, the reactions of 8-hydroxyquinoline (Hoq) with $(RCp)_2TiCl_2$ (R = Me, Ph_2CH) in isobutyronitrile gave $(RCp)TiCl(oq)_2$, in the absence of added base the 8-hydroxyquinoline itself acting as hydrogen chloride acceptor; the reaction was complete after 3 days stirring. The same compounds were obtained in a few fours when a solution of $(RCp)_2TiCl_2$ (R = H, Me, Ph_2CH) and 8-hydroxyquinoline in THF was irradiated with a medium pressure mercury lamp; in these case the removal of hydrogen chloride by 8-hydroxyquinoline and the cleavage of the Ti–Cp bond by photolysis cause the reaction to proceed rapidly.

The compounds obtained are air-sensitive but they can be manipulated to air in the solid state for short periods of time without appreciable decomposition. In solution they are more air-sensitive. Analytical and conductance data for the compounds obtained are listed in Table 1. The molar conductivities in acetone correspond to non-electrolytes [12]. The compounds are soluble in THF, chloroform, acetone, toluene and insoluble in petroleum ether (b.p. 40–70 °C) and hexane. The diphenylmethylcyclopentadienyl derivatives are more soluble than the methylcyclopentadienyl, and the latter are more soluble than the cyclopentadienyl derivatives.

The IR spectra of these compounds show the characteristic absorption bands of η^5-bonded cyclopentadienyl groups. The methylcyclopentadienyl and diphenylmethylcyclopentadienyl derivatives also show the characteristic bands of the methyl and diphenylmethyl groups, respectively. In the case of the acetylacetonate compounds the presence of intense infrared bands between 1500 and 1600 cm^{-1} suggests that the ligand is chelated throught the two keto oxygens. The infrared spectra together with the molar conductivities (the compounds are non-electrolytes) suggest a coordination number of six (the cyclopentadienyl ring being regarded as occupying only one coordination site) for the $(RCp)TiCl(acac)_2$ compounds, similar to the $CpTiCl(acac)_2$ previously described, and a coordination number of five for the $(RCp)TiCl_2(acac)$ compounds. Table 2 shows the carbonyl stretching frequencies of the acetylacetonate compounds. The IR spectra of the $(RCp)TiCl(oq)_2$ complexes are very similar, and indicate the presence of bidentate 8-oxyquinolate and η^5-bonded cyclopentadienyl groups.

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA

Compound	Colour	Elemental analyses (Found (calcd.) (%))			Molar conductivity [a] λ_M (ohm^{-1} cm^2 mol^{-1})
		C	H	N	
$CpTiCl_2(acac)$	orange	42.20 (41.72)	4.79 (4.39)		8.77
$(MeCp)TiCl_2(acac)$	orange	44.12 (44.45)	4.95 (4.71)		14.62
$(Ph_2CHCp)TiCl_2(acac)$	yellow	63.18 (61.47)	5.41 (4.90)		9.45
$(MeCp)TiCl(acac)_2$	yellow	53.46 (53.25)	6.00 (5.82)		13.15
$(Ph_2CHCp)TiCl(acac)_2$	yellow	65.87 (65.56)	5.41 (5.68)		11.29
$(MeCp)TiCl(oq)_2$	red	58.92 (59.26)	4.11 (3.90)	5.98 (5.76)	14.86
$(Ph_2CHCp)TiCl(oq)_2$	orange	71.54 (71.70)	4.77 (4.48)	4.11 (3.98)	10.34

[a] In acetone (10^{-3} *M* solutions).

The ^1H NMR spectra of all the compounds show a resonance or groups of resonances between 5.90 and 6.88 ppm due to the cyclopentadienyl protons. For the methylcyclopentadienyl compounds an additional resonance at 2.3 ppm due to the methyl protons was observed. The diphenylmethylcyclopentadienyl derivatives show a resonance at ca. 7.20 ppm due to the phenyl protons and an additional resonance at ca. 5.70 ppm assigned to the CH protons.

The ^1H NMR spectra of the acetylacetonate compounds show two resonances at ca. 2 ppm and ca. 5.60 ppm assigned to the methyl and the γ protons of the acac ligand respectively. These signals appear as multiplets at room temperature indicating the presence of several isomers in solution. The 8-oxyquinolate derivates show a complex signal between 6.60 and 8.30 ppm due to the 8-oxyquinolate protons. The ^1H NMR spectral data for all the new complexes are listed in Table 3.

In conclusion, the photochemical reactions of $(RCp)_2TiCl_2$ in the presence of

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF THE ACETYLACETONATE COMPOUNDS

Compound	ν(C=O)
$CpTiCl_2(acac)$	1525 vs
	1560 vs
$(MeCp)TiCl_2(acac)$	1525 vs
	1560 vs
$(Ph_2CHCp)TiCl_2(acac)$	1520 vs
	1565 vs
$(MeCp)TiCl(acac)_2$	1515 vs
	1540 vs
$(Ph_2CHCp)TiCl(acac)_2$	1519 vs
	1582 vs

TABLE 3

^{1}H NMR DATA (δ, ppm)

Compound	C_5H_5	C_6H_5	$CH(C_5H_5)$	$CH_3(C_5H_5)$	CH(acac)	CH_3(acac)	oq
$CpTiCl_2$(acac)	6.88 s				5.80 m	2.15 m	
$(MeCp)TiCl_2$(acac)	6.35 m			2.31 s	5.80 m	2.00 m	
$(Ph_2CHCp)TiCl_2$(acac)	6.25 m 5.90 m	7.20 m	5.60 s		5.80 m	2.00 m	
$(MeCp)TiCl(acac)_2$	6.32 m			2.20 s	5.60 m	2.00 m	
$(Ph_2CHCp)TiCl(acac)_2$	6.40 m 5.95 m	7.23 m	5.70 s		5.50 m	1.90 m	
$(MeCp)TiCl(oq)_2$	6.38 m			2.37 s			6.60–8.30
$(Ph_2CHCp)TiCl(oq)_2$	6.25 m 5.96 m	7.25 m	5.78 d				7.00–8.30

acetylacetone lead to pentacoordinated compounds of the type $(RCp)TiCl_2$(acac) whereas the reactions of $(RCp)_2TiCl_2$ in the presence of acetyacetone and triethylamine give hexacoordinated compounds of the type $(RCp)TiCl(acac)_2$.

In contrast, only compounds of the type $(RCp)TiCl(oq)_2$ were obtained from the reaction of $(RCp)_2TiCl_2$ with 8-hydroxyquinoline with and without irradiation.

Experimental

All preparations were carried out under dry, oxygen-free nitrogen, using standard Schlenk vacuum techniques. All solvents were dried before use by standard procedures.

Elemental analyses for C, H and N were performed by Elemental Microanalyses Limited, Devon (England) or by Centro Nacional de Química Orgánica, C.S.I.C., Madrid (Spain). Infrared Spectra in the 4000–200 cm^{-1} region were recorded as KBr discs or Nujol nulls between CsI plates on a Perkin–Elmer 325 Spectrometer. ^{1}H NMR Spectra were determined using a Varian EM-390 90 MHz Spectrometer in deuterochloroform (with TMS as internal standard). Preparative photolyses were carried out in a standard borosilicate glass or quartz apparatus cooled by top water. The lamps used were 100 W medium-pressure mercury lamps supplied by Hanovia Co. Ltd.

The compounds $(MeCp)_2TiCl_2$ and $(Ph_2CHCp)_2TiCl_2$ were prepared as previously described [13,14].

Photolysis of Cp_2TiCl_2 in the presence of acetylacetone

A solution of Cp_2TiCl_2 (0.25 g, 1 mmol) and acetylacetone (1 ml, 9.7 mmol) in THF (100 ml) was photolyzed at room temperature for 28 h. After filtration the solvent was removed to leave a red-orange oil. The oil was extracted (3 × 25) with toluene, the toluene solution was concentrated and petroleum ether (b.p. 40–70 °C) was added until the solution became cloudy. The solution was cooled overnight, kept in a refrigerator and the resulting orange precipitate was filtered off, washed with petroleum ether (40–70 °C), and dried under vacuum, to give 0.21 g (76%) of $CpTiCl_2$(acac).

Photolysis of $(MeCp)_2TiCl_2$ in the presence of acetylacetone

A solution of $(MeCp)_2TiCl_2$ (0.44 g, 1.5 mmol) and acetylacetone (1 ml, 9.7

mmol) in THF was irradiated at room temperature for 42 h. After filtration the solvent was removed to leave an orange oil, which was extracted with diethyl ether (2×20). The extract was filtered and concentrated and kept for 12 h in a refrigerator. The orange solid, (MeCp)$TiCl_2$(acac), was washed with hexane and petroleum ether (40–70 °C) then dried in vacuum (0.32 g, 68%).

Photolysis of $(Ph_2CHCp)_2TiCl_2$ in the presence of acetylacetone

A THF solution of $(Ph_2CHCp)_2TiCl_2$ (0.4 g, 0.7 mmol) and acetylacetone (1 ml, 9.7 mmol) was irradiated for 23 h. The red-yellow solution was filtered and the filtrate was evaporated under reduced pressure to leave a yellow oil. Extraction with diethyl ether gave a yellow solution; this was concentrated and petroleum ether (40–70 °C) was added until the mixture became cloudy, and the solution was kept in a refrigerator for 12 h (Ph_2CHCp)$TiCl_2$(acac) separated as a yellow solid, which was washed with hexane and petroleum ether (40–70 °C) and dried in vacuum (0.15 g, 49%).

Reaction of $(MeCp)_2TiCl_2$ with acetylacetone

A solution of $(MeCp)_2TiCl_2$ (0.25 g, 0.9 mmol) in isobutyronitrile was treated with acetylacetone (0.2 ml, 1.9 mmol) and triethylamine (0.1 ml, 0.7 mmol). The solution was stirred for 24 h, during which a white solid separated and the initial dark-red colour changed to orange. The solution was filtered and the precipitate was identified as triethylammonium chloride. The filtrate was evaporated under reduced pressure to give an orange solid, which was extracted with benzene. The extract was filtered and concentrated and petroleum ether (40–70 °C) was added. The solution was kept in a refrigerator for 12 h to give (MeCp)TiCl$(acac)_2$ as an orange solid.

Reaction of $(Ph_2CHCp)_2TiCl_2$ with acetylacetone

Acetylacetone (0.2 ml, 1.9 mmol) and triethylamine (0.1 ml, 0.7 mmol) were added to a isobutyronitrile solution of $(Ph_2CHCp)_2TiCl_2$ (0.32 g, 0.52 mmol), and the mixture was stirred for 18 h. The white precipitate formed was filtered off and identified as triethylammonium chloride. The solution was pumped to dryness to leave a yellow oil, which was extracted with benzene. The extract was concentrated and petroleum ether (40–70 °C) was added. The yellow precipitate of (Ph_2CHCp)-TiCl$(acac)_2$ was filtered off, washed with petroleum ether (40–70 °C), and dried in vacuum.

Photolysis of Cp_2TiCl_2 in the presence of 8-hydroxyquinoline

A solution of Cp_2TiCl_2 (0.25 g, 1 mmol) and 8-hydroxyquinoline (1.16 g, 8 mmol) in THF (100 ml) was irradiated at room temperature for 18 h. The precipitate formed was filtered off and identified as 8-hydroxyquinolinium chloride. The dark red solution was pumped to dryness to leave a red solid, which heated to 200 °C/0.1 mmHg gave a small amount of a sublimate of 8-hydroxyquinolinium chloride and a red residue of CpTiCl$(Oq)_2$. This was recrystallized from THF to give red crystals (0.4 g, 91.6%). The IR and ^1H NMR spectra were identical with those described by Newton et al. [6].

Photolysis of $(MeCp)_2TiCl_2$ in the presence of 8-hydroxyquinoline

By the above procedure (MeCp)TiCl$(oq)_2$ (0.34 g, 85%) was obtained by irradia-

tion of $(MeCp)_2TiCl_2$ (0.25 g, 0.9 mmol) in THF in the presence of 8-hydroxyquinoline (0.39 g, 2.7 mmol).

Photolysis of $(Ph_2CHCp)_2TiCl_2$ in the presence of 8-hydroxyquinoline

$(Ph_2CHCp)TiCl(oq)_2$ (0.22 g, 87%) was obtained by irradiation of $(Ph_2CHCp)_2TiCl_2$ (0.25 g, 0.43 mmol) and 8-hydroxyquinoline (0.18 g, 1.3 mmol) by the same procedure.

Reaction of $(MeCp)_2TiCl_2$ with 8-hydroxyquinoline

A solution of $(MeCp)_2TiCl_2$ (0.25 g, 0.9 mmol) in isobutyronitrile (50 ml) was treated with 8-hydroxyquinoline. The mixture was stirred at room temperature for 72 h, then filtered. The precipitate was identified as 8-hydroxyquinolinium chloride. The filtrate was evaporated under reduced pressure. The red crystals of $(MeCp)TiCl(oq)_2$ were washed with petroleum ether (40–70 °C) and dried in vacuum (0.31 g, 77.7%).

Reaction of $(Ph_2CHCp)_2TiCl_2$ with 8-hydroxyquinoline

Following the above procedure $(Ph_2CHCp)TiCl(oq)_2$ (0.21 g, 81%) was obtained from the reaction of $(PhCHCp)_2TiCl_2$ (0.25 g, 0.43 mmol) with 8-hydroxyquinoline (0.18 g, 1.3 mmol) in isobutyronitrile for 80 h.

References

1 M.J. Frazer and W.E. Newton, Inorg. Chem., 10 (1971) 2137.
2 D.A. White, J. Inorg Nucl. Chem., 33 (1971) 691
3 G. Doyle and R.S. Tobias, Inorg. Chem., 6 (1967) 1111.
4 G. Doyle and R.S. Tobias, Inorg. Chem., 7 (1968) 2484.
5 D.N. Sen and V.N. Kantak, J Ind Chem Soc., 46 (1969) 358
6 J. Charalambous, M.J. Frazer and W.E. Newton, J. Chem. Soc A, (1971) 2487
7 R.W. Harrigan, G.S. Hammond and H.B. Gray, J. Organomet. Chem., 81 (1974) 79
8 E. Vitz and C.H Brubaker Jr., J. Organomet. Chem., 84 (1974) C16
9 E. Vitz, P.J Wagner and C.H Brubaker Jr., J. Organomet. Chem., 107 (1976) 301
10 Z.T Tsai and C.H. Brubaker Jr., J Organomet Chem., 166 (1979) 199.
11 P.B. Brindley, A.G. Davies and J A-A. Hawari, J. Organomet. Chem., 250 (1983) 247
12 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
13 L.T Reynolds and G. Wilkinson, J Inorg Nucl. Chem., 9 (1959) 86.
14 M.F. Sullivan and W.F. Little, J. Organomet. Chem., 8 (1967) 277.