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Complexes of Titanium(IV) Chloride with Monodentate Schiff Bases

José A. García-Vázquez*, Manuel López-Becerra and José R. Masaguer

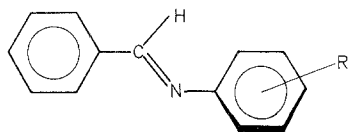
Departamento de Química Inorgánica. Universidad Autónoma. Cantoblanco. Madrid-34. Spain

Summary

The reaction of titanium tetrachloride with *N*-phenyl benzalaldimine and some of its monomethylated and dimethylated derivatives, L, yields complexes of general formulae $\text{TiCl}_4 \cdot 2\text{L}$ and/or $\text{TiCl}_4 \cdot \text{L}$ depending on L. These complexes have been characterized by analysis and by i.r., Raman and ^1H n.m.r. spectroscopy.

Introduction

Although much work has been done on complexes of Schiff bases with transition metal ions^(1–3) comparatively little has been reported on complexes of early transition metals in which the Schiff base is monodentate. Here we describe the preparation and characterization of the Schiff bases derived from benzaldehyde and aniline (Figure).



[R = H (1), 2-Me (2), 3-Me (3), 4-Me (4), 2,3-(Me)₂ (5), 2,4-(Me)₂ (6), 2,5-(Me)₂ (7), 2,6-(Me)₂ (8), 3,4-(Me)₂ (9); or 3,5-(Me)₂ (10)] and their complexes with titanium tetrachloride.

Experimental

Titanium tetrachloride and organic solvents were purified and dried by standard literature methods. Schiff bases were prepared by heating equimolecular amounts of the amine (0.04 mole) and aldehyde (0.04 mole) in benzene (30 cm³) under reflux until the theoretical amount of water had been collected in a Dean-Stark trap, and were purified by distillation under reduced pressure.

Titanium tetrachloride and the complexes being extremely sensitive to humidity, all manipulations were carried out in a rigorously dried apparatus and handled in a dry-box, which was continuously flushed with dry nitrogen.

Preparation of complexes

A solution of the TiCl_4 was added dropwise to a solution of the Schiff base in the same solvent under continuous stirring and the mixture was kept stirring at room temperature for about 10–20 h. The precipitate was filtered off, washed with CCl_4 and cyclohexane, and dried *in vacuo* at room temperature. One-to-one adducts were obtained by using a slight excess of TiCl_4 (molar ratio 1 : 1) and CCl_4 as solvent, whereas the one-to-two adducts were prepared by using a slight excess of Schiff base (molar ratio 1 : 2) and ethyl acetate as solvent.

Titanium was estimated gravimetrically as TiO_2 . Chloride was determined as AgCl and the C, H and N determined conventionally. Molecular weight determinations were made cryoscopically in nitrobenzene.

Physicochemical measurements

I.r. spectra were recorded as Nujol mulls between CsI plates (4000–250 cm⁻¹) and polyethylene windows (500–180 cm⁻¹) on a Perkin-Elmer IR-180 spectrophotometer. Raman spectra were recorded on a Jarrell-Ash spectrophotometer model 25-300, using a He-Ne laser (25 mw, 623.8 nm line) with the samples in capillary tubes in order to avoid hydrolysis. ^1H n.m.r. spectra were obtained in DMSO-d_6 at room temperature on a Varian XL-100-15 instrument operated at 100 MHz with tetramethylsilane as internal standard.

Results and Discussion

The analytical data (Table 1) show that the interaction of TiCl_4 with Schiff bases that do not have methyl groups in the *ortho*-positions in the aniline ring give two types of complex, $\text{TiCl}_4 \cdot 2\text{L}$ and $\text{TiCl}_4 \cdot \text{L}$, depending on the solvent and the molar ratio of reactants used. The complexes TiCl_4L were the only products obtained with the other Schiff bases, all attempts to prepare the 1 : 2 complexes being unsuccessful. This is due to the steric effects of the *ortho*-methyl groups. The molecular weights of 1 : 1 complexes are consistent with dinuclear structures.

The high intensity band in the region 1623–1639 cm⁻¹ in the ligands attributable to the C=N stretch is found in the region 1645–1662 cm⁻¹ in the complexes (Table 2) showing that the coordination has taken place through the imine nitrogen^(4–5) and as result of this the bond order of carbon to nitrogen link is

* Author to whom all correspondence should be addressed.

Table 1. Analytical data for titanium(IV) complexes.

Ligand No.	% Found (Calcd.) Ti	Cl	C	H	N	Colour
TiCl₄ · 2L						
(1)	8.7(8.7)	25.2(25.7)	56.0(56.6)	4.0(4.0)	5.0(5.1)	yellow
(3)	8.4(8.3)	25.0(24.4)	58.0(58.1)	4.2(4.4)	4.4(4.5)	yellow
(4)	8.2(8.3)	24.3(24.4)	57.6(58.1)	4.0(4.4)	4.3(4.5)	yellow
(9)	7.8(7.9)	23.0(23.3)	59.2(59.2)	5.3(5.0)	4.4(4.6)	yellow
(10)	8.0(7.9)	23.1(23.3)	59.6(59.2)	5.2(5.0)	4.3(4.6)	yellow
TiCl₄ · L						
(1)	13.0(12.9)	38.1(38.2)	42.0(42.1)	2.9(3.0)	3.5(3.8)	green
(2)	12.4(12.4)	37.0(36.8)	43.2(43.7)	3.2(3.4)	3.8(3.6)	yellow
(3)	12.6(12.4)	36.6(36.8)	43.1(43.7)	3.6(3.4)	3.6(3.6)	yellow
(4)	12.1(12.4)	37.3(36.8)	43.3(43.7)	3.0(3.4)	3.5(3.6)	brown
(5)	12.2(12.0)	35.9(35.5)	46.5(45.2)	3.7(3.8)	3.8(3.5)	brown
(6)	11.8(12.0)	35.7(35.5)	45.0(45.2)	4.0(3.8)	3.5(3.5)	yellow
(7)	11.8(12.0)	35.6(35.5)	44.7(45.2)	4.0(3.8)	4.0(3.5)	yellow
(8)	12.4(12.0)	35.9(35.5)	43.8(45.2)	3.6(3.8)	3.5(3.5)	brown
(9)	12.4(12.0)	35.5(35.5)	44.1(45.2)	4.2(3.8)	3.1(3.5)	yellow
(10)	12.1(12.0)	35.2(35.5)	46.1(45.2)	4.3(3.8)	3.6(3.5)	yellow

Table 2. I.r. (Raman) spectra results in the $\nu(\text{C}=\text{N})$ region (cm^{-1}).

Ligand No.	Ligand	TiCl ₄ · 2L	TiCl ₄ L
(1)	1628vs (1624s)	1657vs	1654vs
(2)	1630vs (1628vs)	—	1645m
(3)	1631vs (1628vs)	1652vs (1647s)	1650s
(4)	1628vs (1623s)	1657vs (1654s)	1651vs
(5)	1631s (1629s)	—	1646vs
(6)	1630vs (1629vs)	—	1645vs
(7)	1630vs (1634vs)	—	1646vs
(8)	1639vs (1638vs)	—	1646vs
(9)	1629vs (1625m)	1657vs (1662s)	1652s
(10)	1628s (1623s)	1657s (1661s)	1654s

Table 3. I.r. and Raman spectra (cm^{-1}) of complexes TiCl₄ · 2L.

Ligand No.	$\nu(\text{Ti}-\text{N})$ A _{2u} (i.r.)	A _{1g} (R)	$\nu(\text{Ti}-\text{Cl})$ E _u (i.r.)	A _{1g} (R)	B _{1g} (R)
(1)	348m	—	320vs,br	—	—
(3)	354m	228m	323vs,br	304s	243m
(4)	338m	—	325s	—	—
(9)	345sh	206m	330vs	308s	239w
(10)	340sh	205w	326vs	306s	234w

Table 4. I.r. spectra (cm^{-1}) of complexes TiCl₄ · L.

Ligand No.	$\nu(\text{Ti}-\text{Cl})$
(1)	400s, 360vs, 330sh
(2)	350sh, 335vs,br
(3)	395m, 355vs, 335vs
(4)	400s, 350vs,br
(5)	380s, 340sh, 325s
(6)	395m, 360sh, 340vs,br
(7)	395vs, 335s,br, 325sh
(8)	390s, 365s, 325vs,br
(9)	390sh, 350vs,br, 326sh
(10)	370sh, 355vs,br, 320vs

increased⁽⁶⁾. This shift may be due to a polarization effect and to a modification of the conjugation of imine group with the phenyl ring of the benzal portion which leads to the accumulation of the electronic charge in the C=N bond, as a consequence of the coordination of the metal.

For the adducts of the type TiCl₄ · 2L, where L is monodentate, there are two probable configurations: one is a *cis*-form with C_{2v} symmetry for the skeleton and the other is a *trans*-form with D_{4h} symmetry. For the *cis*-configuration we can expect four Ti-Cl (2A₁ + B₁ + B₂) and two Ti-N (A₁ + B₂) stretching vibrations, coincident in both the i.r. and Raman spectra. For the *trans*-configurations, the mutual exclusion rule is expected to hold and we can expect one Ti-Cl (E_u) and one Ti-N (A_{2u}) stretching vibrations in the i.r. spectra and two Ti-Cl (A_{1g} + B_{1g}) and one Ti-N (A_{1g}) stretching vibration in the Raman spectrum. The spectra (Table 3) suggest that these complexes have the *trans*-configuration (D_{4h} symmetry). The i.r. spectra of these adducts are dominated by a strong band between 320 and 330 cm⁻¹, accompanied by a medium band or a shoulder to higher frequency. These bands occur in the same spectral region as $\nu(\text{Ti}-\text{Cl})$ vibrations of six-coordinated adducts of titanium tetrachloride⁽⁷⁾. We therefore assign the strong band to the $\nu(\text{Ti}-\text{Cl})$ E_u mode. The other band may arise from solid-state splitting of the E_u mode and/or a $\nu(\text{Ti}-\text{N})$ mode. The latter is not unreasonable since the Sn-N stretching bands of SnX₄ · 2L (where X = Cl or Br and L is PhN=CHPh) have been assigned in the 315–290 cm⁻¹ region^(8,9). An intense Raman line, noncoincident with the strong i.r. band and at lower frequency accompanied by a weaker line at ca. 60 cm⁻¹ to lower frequency, appears in each case. The strong Raman line and its weaker counterpart can be assigned to the Ti-Cl stretching (A_{1g} and B_{1g}, respectively). The band at ca. 220 cm⁻¹ is tentatively assigned to the Ti-N stretching mode.

For the 1 : 1 adducts we propose a dimeric halogen-bridged structure, in agreement with molecular weight measurements in nitrobenzene. Similar 1 : 1 adducts with TiCl₄ and monodentate ligands have been obtained previously and explained through halide bridging^(10–13). These compounds there may also be *cis* or *trans*. These adducts (Table 4) display three bands in the region 400–300 cm⁻¹, assigned to the terminal

Table 5. ^1H n.m.r. data (ppm) of the ligands and complexes.

Ligand No.	Ligand $-\text{CH}=\text{N}$	$\text{TiCl}_4 \cdot 2\text{L}$	$\text{TiCl}_4 \cdot \text{L}$	Ligand: Found (Calcd.) Me	$\text{TiCl}_4 \cdot 2\text{L}$	$\text{TiCl}_4 \cdot \text{L}$
(1)	8.61	8.76	9.45			
(2)	8.49		8.55	2.32		2.43
(3)	8.58	8.72	9.39	2.34	2.34	2.34
(4)	8.61	8.80	9.25	2.32	2.32	2.32
(5)	8.45		8.59	2.27(2.24) ^{b)} , 2.24(2.22) ^{a)}		2.72
(6)	8.48		8.65	2.29(2.27) ^{c)} , 2.28(2.27) ^{a)}		2.37 ^{a)} , 2.28 ^{b)}
(7)	8.49		8.63	2.30(2.29) ^{b)} , 2.25(2.27) ^{a)}		2.36 ^{a)} , 2.28 ^{c)}
(8)	8.30		8.50	2.08(2.27)		2.42
(9)	8.60	8.86	9.46	2.25(2.24) ^{b)} , 2.23(2.22) ^{c)}	2.23	2.23
(10)	8.58	8.83	9.49	2.30(2.29)	2.30	2.30

^{a)} *ortho*; ^{b)} *meta*; ^{c)} *para*.

Ti–Cl stretching vibrations, one of which is broad and can be considered to be a combination of two bands. There is also a possibility that some of these bands are due to the Ti–N stretching vibrations. However, the total number of bands observed is quite close to the number of expected bands for a *trans*-configuration with C_{2h} symmetry⁽¹³⁾.

No bridged Ti–Cl stretching vibrations were observed possibly because they appear in a region where the ligands show intense bands.

The ^1H n.m.r. spectra of the free Schiff bases and their complexes with TiCl_4 are given in Table 5.

Except for base (8), the methyl proton chemical shift is almost independent of its position in the ring. The observed changes in the dimethyl derivatives are due largely to the interaction of the methyls. The experimental values may be compared with those calculated from the observed positions in the monomethyl derivatives by adding a contribution for the other methyl group ($Z_{\text{ortho}} = -0.1$; $Z_{\text{meta}} = -0.05$ and $Z_{\text{para}} = -0.05$ ⁽¹⁴⁾). The lack of deshielding observed for the *ortho*-methyl group in bases (2), (5), (6) and (7) can be explained by twisting of the aniline ring out of the plane of the molecule. A similar conclusion has been reached by other workers^(15–18) for the base (1). The observed shielding of the *ortho*-methyl groups in the ligand (8) relative to the analogous substituent in the bases (2), (5), (6) and (7), however indicates that in the base (8) there is a significant conformational change, in which the methyl groups are located more directly in the shielding zone of the imine bond⁽¹⁷⁾.

On the other hand, *meta*- or *para*-substitution has almost no effect on the position of the methine proton signal. *Ortho*-substitution, however, produces a shift upfield (ca. 0.13 for the bases (2), (5), (6) and (7), and 0.34 for the base (8)). This shift can be interpreted as due to the inductive effect of the methyl groups⁽¹⁹⁾ and the conformational change⁽²⁰⁾.

On complexing, the following changes occur. (a) The methine proton signals all shift downfield. This is evidence for coordination through the imine nitrogen^(21, 22). This coordination produces an inductive effect which causes the downfield

shift of the signal. In addition, as the coordination seems to produce an increase in the π -electron density of the $\text{C}=\text{N}$ bond (*vide supra*) the deshielding anisotropy on the imine hydrogen increases. (b) In the 1:1 complexes the lowest values for the methine proton chemical shift arise from *ortho*-substituted bases. These complexes have the lowest $\text{C}=\text{N}$ stretches. This is evidence of the steric effect caused by the *ortho*-methyl group.

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