

Synthesis, characterization and reactions of some titanium aryloxides

R Gupta, A Singh & R C Mehrotra*

Department of Chemistry, University of Rajasthan
Jaipur 302 004

Received 2 August 1989; revised and accepted 15 November 1989

Titanium aryloxides of the type $TiCl_x(OR)_{4-x}$ [(where $x = 1, 2, 3$ or 4 ; ROH = 3, 5-dimethylphenol ($Ar'OH$), 3, 5-di-*t*-butylphenol ($Ar''OH$) and 2, 5-dimethylphenol ($Ar''OH$)] have been prepared and characterized by IR, PMR and molecular weight measurements. Molecular weight determinations exhibit an interesting variation in the molecular complexity depending upon the nature and extent of substituents on the aryloxy ligand. The Lewis acid behaviour of these new aryloxides has also been investigated.

The reactions of titanium tetrachloride with less hindered phenols afford tetrakis derivatives in a facile manner^{1,2}; in contrast, direct interaction of sterically hindered phenols give only chloride-aryloxide^{3,4} derivatives. Further, titanium aryloxide derivatives with less hindered phenols are generally oligomeric with bridging phenoxy groups; e.g. $TiCl_2(OPh)_2$ (ref. 5) and $[Ti(OPh)_4 \cdot PhOH]_2$ (ref. 6) have been characterized by X-ray crystallographic studies. A study of the coordination chemistry of titanium chloride aryloxides has also given interesting results^{7,8}.

Following the interesting observations in recent investigations on 2, 4, 6-trimethylphenoxides of titanium and zirconium⁹, we report herein synthesis and coordination chemistry of titanium derivatives with relatively less sterically-demanding phenoxide moieties.

Experimental

Solvents and various Lewis bases were rendered anhydrous before use by published procedure(s)¹⁰. Molecular weights were measured ebullioscopically (Gallenkamp apparatus) in benzene. IR ($4000-200\text{ cm}^{-1}$) and PMR spectra were recorded on a Perkin-Elmer grating spectrophotometer model 577 and 90 MHz Jeol FX 90Q instrument respectively.

As general synthetic procedures for chloride aryloxides of titanium and their molecular adducts were similar, only typical examples of each type are described in detail.

Synthesis of titanium monochloride-tris(3, 5-dimethylphenoxide) [$TiCl(OAr')_3$]

To a solution of $TiCl_4$ (1.8 g, 9.8 mmole) in benzene (~ 30 ml) was added a solution of 3, 5-dimethylphenol (3.6 g, 29.5 mmole) in benzene (20 ml). The reaction mixture was refluxed till evolution of HCl ceased (~ 12 hr). After removal of the solvent under reduced pressure, the product was recrystallized from *n*-hexane to give $TiCl(OAr')_3$ as a brown red crystalline solid (3.2 g, ~ 75 %).

A similar procedure was adopted for the preparation of other titanium derivatives of the type $TiCl_{(4-x)}(OR)_x$ [where $x = 1, 2, 3$ or 4 , ROH = 3, 5-dimethylphenol ($Ar'OH$), 3, 5-di-*t*-butylphenol ($Ar''OH$) or 2, 5-dimethylphenol ($Ar''OH$)].

Synthesis of $TiCl_2(OAr')_2(Py)_2$

Interaction of pyridine (0.98 g, 12.4 mmole) and $TiCl_2(OAr')_2$ (2.13 g, 5.9 mmole) in benzene (30 ml) was exothermic resulting in instantaneous precipitation of a light yellow coloured solid. The reaction mixture was stirred for 10 hr at room temperature and filtered to yield $TiCl_2(OAr')_2(Py)_2$ as a light yellow solid (2.31 g, ~ 80 %).

Synthesis of $TiCl_2(OAr')_2(THF)_2$

A solution of $TiCl_2(OAr')_2$ (1.15 g, 3.2 mmole) in THF (20 ml) was refluxed for 6 hr, concentrated to ~ 10 ml and *n*-hexane added. The reddish yellow precipitates of $TiCl_2(OAr')_2(THF)_2$ (0.41 g, 40%) thus obtained were filtered and recrystallized from a THF-*n*-hexane at -10° .

Results and discussion

The reaction of $TiCl_4$ with phenol, depending upon the stoichiometric amounts of an appropriate phenol, resulted in the formation of mono-, bis-, tris- and tetrakis- $(TiCl_{(4-x)}(OR)_x)$; where $x = 1, 2, 3$ or 4) derivatives under refluxing conditions. The reactions are rather slow and require about 14-16 hr for completion. However, in the case of more hindered phenols³ like 2, 6-diphenylphenol and 2,6-di-*t*-butylphenol substitution proceeds only upto the formation of the bis-product $TiCl_2(OAr)_2$ even after prolonged refluxing.

Interaction of $TiCl_{(4-x)}(OAr')_x$ with Lewis bases such as pyridine or THF resulted in the formation of molecular adducts of the type $TiCl_{(4-x)}(OAr')_xL_n$ (where $x = 1, 2$ or 3 ; L = Py or THF, $n = 2$; $x = 4$, L = Py, $n = 2$; $x = 4$, L = THF, $n = 1$; $Ar'OH = 3, 5$ -di-

Table 1—Analytical and physical properties of titanium aryloxides and the adducts

Sl. Compound No. colour	Found (Calc.)		
	% Ti	% Cl	Mol. wt
1. TiCl(OAr') ₃ Red	10.6 (10.7)	7.9 (7.9)	399 (447)
2. TiCl ₂ O(Ar') ₂ Brown red	13.1 (13.3)	19.4 (19.6)	653 (361)
3. TiCl ₃ OAr' Brown red	17.2 (17.4)	38.6 (38.7)	528 (275)
4. Ti(OAr') ₄ Orange red	8.7 (9.0)	—	—
5. TiCl(OAr') ₃ (Py) ₂ Light yellow	8.0 (7.9)	6.0 (5.9)	—
6. TiCl ₂ (OAr') ₂ (Py) ₂ Light yellow	9.2 (9.2)	13.5 (13.7)	—
7. TiCl ₃ (OAr')(Py) ₂ Light yellow	11.0 (11.1)	24.4 (24.6)	—
8. Ti(OAr') ₄ (Py) ₂ Orange red	6.9 (6.9)	—	—
9. TiCl ₂ (OAr') ₂ (THF) ₂ Orange yellow	9.5 (9.5)	13.8 (14.1)	—
10. TiCl(OAr') ₃ (THF) ₂ Orange red	8.1 (8.1)	6.0 (6.0)	—
11. Ti(OAr') ₄ (THF) Orange red	7.9 (7.9)	—	—
12. TiCl ₃ (OAr')(THF) ₂ Brown red	11.4 (11.4)	25.3 (25.4)	—
13. TiCl ₃ (OAr'') Dark red	13.1 (13.3)	29.5 (29.6)	812 (360)
14. TiCl ₂ (OAr'') ₂ Dark red	9.1 (9.0)	13.2 (13.0)	455 (533)
15. TiCl(OAr'') ₃ Orange red	6.6 (6.8)	4.9 (5.0)	—
16. Ti(OAr'') ₄ Yellowish orange	5.4 (5.5)	—	—
17. TiCl ₃ (OAr''') Brown red	17.1 (17.4)	38.6 (38.7)	555 (275)
18. TiCl(OAr''') ₃ Orange red	10.6 (10.7)	7.8 (7.9)	—
19. TiCl ₂ (OAr''') ₂ Red	13.2 (13.3)	19.5 (19.6)	342 (361)
20. Ti(OAr''') ₄ Red	9.1 (9.0)	—	—

^a Abbreviations: Py = pyridine; THF = tetrahydrofuran; Ar'OH = 3,5-dimethylphenol, Ar''OH = 3,5-di-*t*-butylphenol, Ar'''OH = 2, 5-dimethylphenol.

methylphenol). These aryloxide derivatives are coloured solids (light yellow to reddish brown). The colour of all these compounds can be ascribed to charge transfer bands in the visible region. Most of these complexes are soluble in common organic solvents (e.g. benzene, *n*-hexane, etc.), except their pyridine adducts (Table 1).

Most of these aryloxo complexes of titanium appear to be 5- or 6-coordinated. The chloride aryloxide derivatives of titanium of the type [TiCl₃(OR)] (where

ROH = Ar'OH, Ar''OH and Ar'''OH) and [TiCl₂(O-Ar')₂] are dimeric involving aryloxide bridging.

Infrared spectra (nujol, 4000-200 cm⁻¹) of titanium aryloxides of the type TiCl_(4-x)(OR)_x (x = 1, 2 or 3, OR = OAr', OAr'' and OAr''') exhibit structurally significant bands in the regions of 430-500, 320-375 and 1150-1180 cm⁻¹, assignable to νTi-O, νTi-C and νC-O respectively. The shift to lower wavenumber (Δν = 80 cm⁻¹) from free phenolic νC-O is thus evident.

The νC=N mode of free pyridine at 1578 cm⁻¹ is shifted to 1600 ± 10 cm⁻¹ in the pyridine adducts, indicating coordination of pyridine nitrogen to a metal centre¹¹. The bands at 285 ± 5 cm⁻¹ may be possibly due to ν(M←N). The bands characteristic of νTi-O have been observed in the range of 430-460 cm⁻¹.

In the THF adducts of TiCl_(4-x)(OAr')_x (x = 1, 2 or 3), νTi-Cl modes appear at 340 ± 5 cm⁻¹ and the νC—O—C of free THF occurring at 1070 cm⁻¹ is shifted to lower wavenumbers (Δν = ~30 cm⁻¹) in the adducts, indicating THF coordination through the oxygen¹².

The PMR spectrum of TiCl₂(OAr')₂ exhibits signals at δ2.23, 6.47 and 6.60 due to CH₃ and *ortho* and *para* aromatic protons respectively. The position of the methyl proton signal is almost unaltered as compared to that of the parent ligand (δ2.22), but signals due to *ortho* and *para* aromatic protons are shifted downfield by ~0.07 ppm compared to that of free ligand occurring at δ6.40 and 6.53 respectively.

The THF adduct TiCl₂(OAr')₂(THF)₂ exhibits in its PMR spectrum a singlet at δ2.23 due to methyl protons, while the *ortho* and *para* aromatic protons are observed as a broad signal centred at δ6.52. The α and β protons of coordinated THF appear as broad signals at δ3.8 and 1.9 respectively. These appear to be shifted slightly (~0.05 ppm) downfield, with respect to the corresponding signals in the free THF.

The PMR spectrum of Ti(OAr')₄(Py)₂ displayed a broad signal in the region of δ7.36-8.92 for the pyridine ring protons, while methyl and aromatic protons of aryloxy ligand were observed at δ2.23 and 6.51 respectively.

The PMR spectrum of TiCl₂(OAr'')₂(Ar''OH = 3, 5-di-*t*-butyl-phenol) exhibits-*t*-Bu protons at δ1.29, aromatic protons as a doublet at 6.78 (J = 2.00 Hz) and a triplet at 7.09 (J = 2.00 Hz) for *ortho* and *para* aromatic protons respectively.

The PMR spectrum of TiCl₃(OAr''') exhibits signals for *ortho* and *meta* methyl protons at δ2.27 and 2.40, respectively, while *o*-, *m*- and *p*-protons are observed as complex multiplets in the range of δ6.65-7.14 (arising from overlapping doublets).

Acknowledgement

One of us (R G) gratefully acknowledges the Rajasthan University, Jaipur for a J R F under the S A P.

References

- 1 Verma I D & Mehrotra R C, *J Indian chem Soc.*, 38 (1961) 147.
- 2 Nayar V S V & Peacock R D, *J chem Soc.*, (1964) 2827.
- 3 Dilworth R J, Hanich J, Magda J B & Joachim S, *J organometal Chem.*, 315(1) (1986) C9-12.
- 4 Latesky S L, Keddington J, McMullen A K, Rothwell I P & Huffman J C, *Inorg Chem.*, 24 (1985) 995.
- 5 Watenpaugh K & Coughlan C N, *Inorg Chem.*, 5 (1966) 1782.
- 6 Svetich G W & Vog A A, *Acta Crystallogr.*, B28 (1972) 1760.
- 7 Gordon D & Wallbridge M G H, *Inorg chim Acta.*, 111 (1986) 77.
- 8 Malhotra K C & Martin R L, *J organometal Chem.*, 239 (1982) 159 and references therein.
- 9 Shah A, Singh A & Mehrotra R C, *Polyhedron*, 5 (1986) 1285.
- 10 Perrin D D, Armarego W L F & Perrin D R, *Purification of laboratory chemicals* (Oxford, New York), 1980.
- 11 Ouellette T J & Haendler H M, *Inorg Chem.*, 8 (1969) 1777.
- 12 Benner L S & Root C A, *Inorg Chem.*, 11 (1972) 652.