

On the water promoted reaction of titanium isopropoxide with carbon dioxide†

Rajshekhar Ghosh, Munirathinam Nethaji and Ashoka G. Samuelson*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India.

E-mail: ashoka@ipc.iisc.ernet.in; Fax: +09180 – 3601552; Tel: +09180 – 2932663

Received (in Cambridge, UK) 24th June 2003, Accepted 10th September 2003

First published as an Advance Article on the web 22nd September 2003

Insertion of carbon dioxide into titanium isopropoxide takes place only in the presence of trace quantities of water to give an isopropyl carbonato cluster which has been crystallographically characterised.

Cobalt complexes such as [Co(TCT)(OR)]BPh₄ (R = Et, Ph; TCT = *cis,cis*-1,3,5-tris(cinnamylideneamino)cyclohexane)¹ activate carbon dioxide *via* insertion, although the ethoxide complex loses carbon dioxide even in a stream of argon. In a recent paper, the dimeric zinc complex [Zn₂Br₄(μ-OCHRCH₂NC₅H₅)₂] (R = H, CH₃) was shown to insert carbon dioxide and then convert epoxides into cyclic carbonates.² Reversible carbon dioxide insertion into the rhenium oxygen bond has been demonstrated with complexes like *fac*-(CO)₃L₂-ReOCH₃ (L = PMe₃; L₂ = diars) to give the complex *fac*-(CO)₃L₂Re(OC(O)OCH₃).³ Several alkyl vanadium(III) alkoxide complexes like RV(O^{*i*}Bu)₂XMgO^{*i*}Bu (X = Cl, Br) also insert carbon dioxide reversibly.⁴ Molybdenum systems like Mo₂(O^{*i*}Pr)₄(L)₄ (L = PMe₃, HO^{*i*}Pr)⁵ react with carbon dioxide to give Mo₂(O₂CO^{*i*}Pr)₄ and Mo₂(O₂CO^{*i*}Pr)₄(PMe)₄. Copper(I) alkoxides of the type ROCu(PPh₃)₂⁶ (R = C₂H₅, C₆H₅CH₂) react with carbon dioxide at low temperatures giving a complex of the formula ROCu(O)OCu(PPh₃)₂; whereas when R is ^{*i*}Bu, in ROCuL_{*n*} (L = PEt₃, ^{*i*}BuNC) the insertion is reversible.⁷

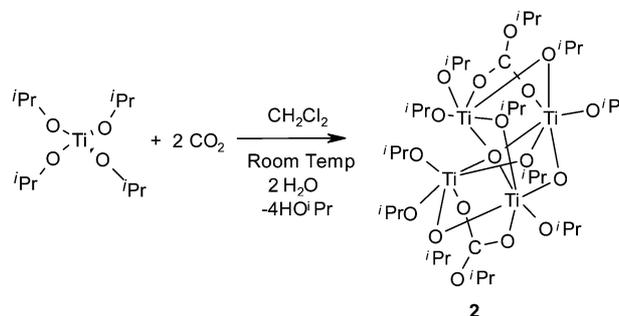
We report here our studies on the reaction of carbon dioxide with titanium isopropoxide. While reactions with heterocumulenes and titanium isopropoxide are known,⁸ the reactions of CO₂ are not. In fact supercritical CO₂ is used as a solvent for Ti(O^{*i*}Pr)₄.⁹ The insertion of CO₂ was first attempted with dry CO₂, and titanium isopropoxide dissolved in dry tetrahydrofuran. Under these conditions there was no reaction. A serendipitous discovery of the insertion was made when the reaction was attempted with commercial CO₂ which was not dried prior to use. An insertion product was suspected on the basis of a new IR band at 1618 cm⁻¹. Subsequent control experiments showed that the insertion of CO₂ proceeds only in the presence of trace quantities of moisture. Large quantities of moisture convert titanium isopropoxide into titanium dioxide.[‡]

Apart from IR spectroscopy, the carbonato species was characterized by a resonance at 159 ppm in ¹³C NMR. A titration experiment with CO₂ showed that about 0.5 eq. of carbon dioxide is taken up per equivalent of titanium isopropoxide. An inverse gated ¹³C{¹H} experiment on the reaction mixture confirmed that the integral of the peak at 159 ppm, which corresponds to the carbonato carbon, is approximately 1/8th of that of the isopropoxide methine carbons which included the free isopropanol liberated in the process.

A reaction was subsequently carried out in methylene chloride (Scheme 1), which permitted crystallisation of the carbon dioxide inserted complex. It was crystallographically characterised (Fig. 1), and found to be a tetrameric titanium complex with each cluster having two carbon dioxide units inserted into Ti–O^{*i*}Pr bonds.§ The carbonato ligands are inequivalent in the cluster and are distinguishable in solution

also. The ¹³C peak at 159 ppm shows two closely separated resonances.

The presence of two oxo bridges in the cluster suggests one plausible pathway by which water is promoting the insertion. The other pathway for the activation of carbon dioxide is protonation of CO₂ as noted by Lau and co-workers.¹⁰ To see whether the insertion of CO₂ is driven by a proton source or by the formation of the oxo bridge, the reaction was done in the presence of isopropanol and dry CO₂. Once again no insertion was observed under these conditions. To rule out protonation by water, titanium isopropoxide was reacted with 0.5 eq. of water followed by removal of isopropanol formed. Subsequently dry carbon dioxide was admitted leading to the formation of **2**. This suggests that generation of the oxo cluster is sufficient to generate the carbonato cluster and the protonation of carbon dioxide may not be an essential requirement for observing the insertion reaction.



Scheme 1 Insertion of carbon dioxide.

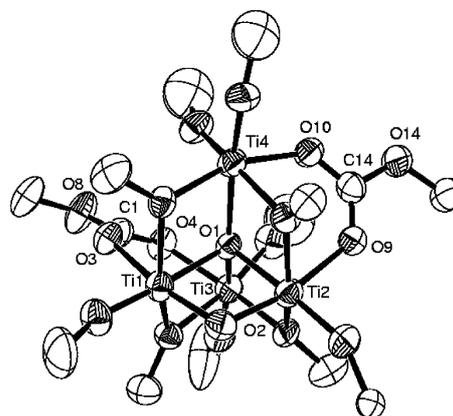


Fig. 1 ORTEP view of **2** with 50% probability ellipsoids (isopropoxide methyl and hydrogen atoms omitted for clarity). Important bond lengths [Å] and angles [°]: Ti(1)–Ti(2) 2.9499(20), Ti(1)–Ti(3) 3.1734(18), Ti(1)–Ti(4) 3.2050(18), Ti(2)–Ti(3) 3.2030(16), Ti(2)–Ti(4) 3.1675(15), Ti(3)–Ti(4) 3.9457(14), Ti(1)–O(3) 2.1485(42), Ti(3)–O(4) 2.0447(47), Ti(2)–O(9) 2.1586(52), Ti(4)–O(10) 2.0405(53), O(3)–C(1) 1.2590(81), O(4)–C(1) 1.2501(96), O(8)–C(1) 1.3465(87), O(9)–C(14) 1.2462(69), O(10)–C(14) 1.2740(85), O(14)–C(14) 1.339(10), O(3)–C(1)–O(4) 127.75(66), O(9)–C(14)–O(10) 127.42(66).

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b3/b307217g/>

