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Preliminary communication

Hydrolysis of (pentamethylcyclopentadienyl)titanium(IV) carbamates. X-ray structure of $[\{Cp^*Ti(\eta^2\text{-}O_2CNEt_2)\}_2(\mu\text{-}O)_2]$

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Abstract

Complexes $[Cp^*Ti(NR_2)_3]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me or Et) react with CO_2 to give the corresponding insertion products $[Cp^*Ti(\eta^2\text{-}O_2CNR_2)_3]$ (R = Me (**1**), Et (**2**)). When solutions of **1**–**2** are exposed to wet air a hydrolytic process takes place and leads to the formation of the $[\{Cp^*Ti(\eta^2\text{-}O_2CNR_2)\}_2(\mu\text{-}O)_2]$ (R = Me (**3**), Et (**4**)). The molecular structure of **4** has been established by single crystal X-ray analysis.

Keywords: Titanium; Carbamate complexes; μ-oxo complexes; X-ray diffraction

Amido derivatives of the first transition metal groups are good starting materials to study insertion of small molecules into the metal–nitrogen bond [1] and it is well known that insertion of CO_2 leads to get the corresponding carbamate complexes [2]. We recently reported the synthesis and characterization of several mono(pentamethylcyclopentadienyl) amido derivatives of titanium(IV) [3] and now are studying the insertion processes of CO_2 and isoelectronic molecules into the Ti–N bond.

When toluene solutions of $[Cp^*Ti(NR_2)_3]$ (R = Me or Et) are exposed to CO_2 (≈ 1 atm), insertion takes place rapidly to give $[Cp^*Ti(\eta^2\text{-}O_2CNR_2)_3]$ (R = Me (**1**), Et (**2**)) [4] (See Scheme 1).

The IR spectra of complexes **1**–**2** show the characteristic absorption of the bidentate $\eta^2\text{-}O_2CNR_2$ moieties [2], with very strong bands at 1559 and 1539 cm^{-1}, respectively. The ^1H and ^{13}C-NMR spectra confirm the insertion of CO_2 in all the Ti–N bonds in the starting materials.

If complexes **1**–**2** are exposed to wet air, hydrolysis takes place in few minutes leading to the carbamate products $[\{Cp^*Ti(\eta^2\text{-}O_2CNR_2)\}_2(\mu\text{-}O)_2]$ (R = Me (**3**), Et (**4**)) [5]. (see Scheme 1). Both complexes still have IR stretching vibrations for the $\eta^2\text{-}O_2CNR_2$ groups, at 1574 and 1550 cm^{-1}, respectively. Another pair of bands, at 682 and 639 cm^{-1} for **3** and 672 and 615 cm^{-1} for **4**, can be assigned to the non-linear Ti–O–Ti bonding system [6]. Signals in the ^1H and ^{13}C-NMR spectra of complexes **3**–**4** are consistent with the presence of only one $\eta^2\text{-}O_2CNR_2$ group on each titanium. It is possible to suggest that two oxygen atoms bridge two metal centres, consistent with the dimeric nature of these complexes found by mass spectrometry.

Although various organometallic oxides containing the Cp^*Ti unit have been studied [7], only for

$$\begin{tikzcd}
{[Cp^*Ti(NR_2)_3]} \arrow[d, "CO_2"'] \\
{[Cp^*Ti(\eta^2\text{-}O_2CNR_2)_3]} \arrow[d, "H_2O"', "-CO_2,\ -HNR_2"] \\
{[\{Cp^*Ti(\eta^2\text{-}O_2CNR_2)\}_2(\mu\text{-}O)_2]}
\end{tikzcd}$$

Scheme 1.

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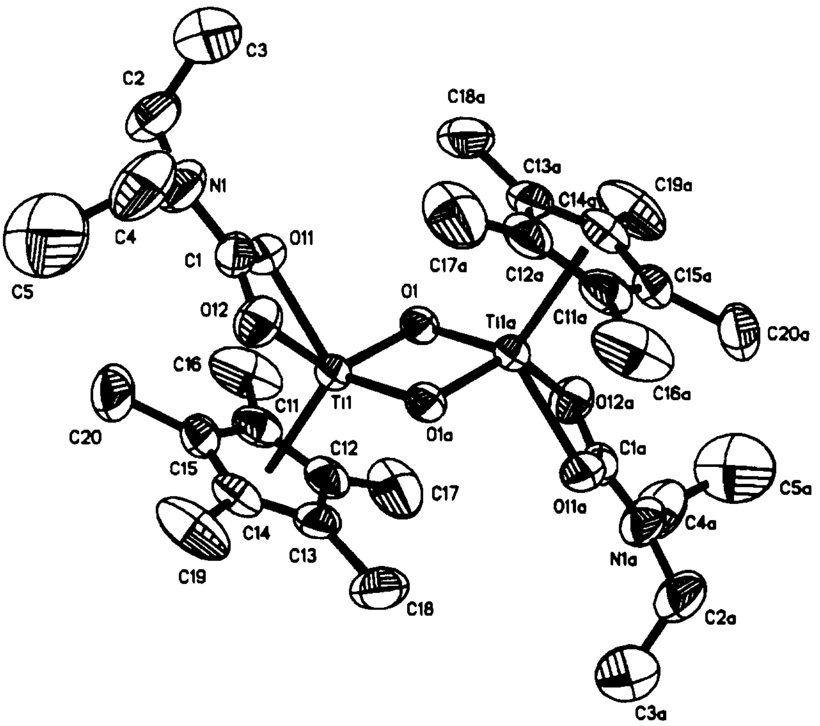

Fig. 1. ORTEP of compound **4** with 50% of probability

$[\{Cp^*Ti(acac)O\}_2]$ [8] has a $(\mu\text{-}O)_2$ bridging system been proposed, and compound **4** is the first to be analyzed by X-ray diffraction [9]. Fig. 1 shows a molecule of compound **4**, and selected bond lengths and angles are in Table 1. This complex contains two $Cp^*Ti(\eta^2\text{-}O_2CNR_2)O$ units related by a centre of symmetry, with a four-legged piano-stool configuration at each titanium.

Table 1
Selected bond lengths [Å] and angles [°] for **4**

Ti(1)–O(1)	1.852(2)	Ti(1)–O(1)A	1.844(2)
Ti(1)–O(11)	2.119(2)	Ti(1)–O(12)	2.115(2)
O(11)–C(1)	1.273(3)	O(12)–C(1)	1.272(3)
N(1)–C(1)	1.350(3)	N(1)–C(2)	1.471(5)
N(1)–C(4)	1.431(5)	C(2)–C(3)	1.475(6)
C(4)–C(5)	1.491(8)	Ti(1)–Cp*(1)	2.064
Ti(1) ··· Ti(1)A	2.761(1)		
O(1)–Ti(1)–O(1)A	83.30(7)	O(12)–Ti(1)–O(1)A	88.88(7)
O(1)–Ti(1)–O(12)	131.65(8)	O(1)A–Ti(1)–O(11)	130.16(7)
O(1)–Ti(1)–O(11)	88.00(7)	O(12)–Ti(1)–O(11)	61.77(8)
Ti(1)A–O(1)–Ti(1)	96.70(7)	C(1)–O(11)–Ti(1)	90.4(2)
C(1)–O(12)–Ti(1)	90.6(2)	C(1)–N(1)–C(4)	120.5(3)
C(1)–N(1)–C(2)	120.1(3)	C(4)–N(1)–C(2)	119.3(3)
O(12)–C(1)–O(11)	117.3(2)	O(12)–C(1)–N(1)	121.1(3)
O(11)–C(1)–N(1)	121.6(3)	N(1)–C(2)–C(3)	113.5(4)
N(1)–C(4)–C(5)	113.2(4)	Cp*(1)–Ti(1)–O(1)	115.9
Cp*(1)–Ti(1)–O(11)	111.0	Cp*(1)–Ti(1)–O(12)	110.1
Cp*(1)–Ti(1)–O(1)A	116.9		

Symmetry transformations used to generate equivalent atoms: A $-x+1/2, -y+1/2, -z$. Cp* is the centroid of the C_5Me_5 ring.

Bond lengths and angles in the $Ti_2(\mu\text{-}O)_2$ core are in the same range that those reported in the literature for $[\{\{\eta^5\text{-}C_5H_2)(SiMe_3)_3\text{-}1,2,4\}TiCl\}_2(\mu\text{-}O)_2]$ [6b], $[\{Ti(acac)_2\}_2(\mu\text{-}O)_2]$ [10a], $K_4[\{TiO(cat)_2\}_2]\cdot 9H_2O$ [10b], $[\{Cp''Ti(O)Cl\cdot CH_2Cl_2\}_2]$ [10c], $[\{Ti(\mu\text{-}O)(OC_6H_3\text{-}2,6Pr^i_2)_2(NC_5H_4\text{-}4NC_4H_8)\}_2]$ [10d], $[\{TiCl(\mu\text{-}O)(12\text{-}crown\text{-}4)\}_2][SbCl_6]_2\cdot 2CH_2Cl_2$ [10e]. The Ti–O(carbamate) bond lengths [2.119(2) and 2.115(2)Å] are similar to that observed in $[Ti(NMe_2)_2(O_2CNMe_2)_2]$ [2.115Å(av)] [2b].

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References and notes

[1] M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, *Metal and Metalloid Amides* Ellis Horwood, 1980.

[2] (a) M.H. Chisholm and M.W. Extine, *J. Am. Chem. Soc., 99* (1977) 782; (b) M.H. Chisholm and M.W. Extine, *J. Am. Chem. Soc., 99* (1977) 792; (c) M.H. Chisholm, L-S Tan and J.C. Huffman; *J. Am. Chem. Soc., 104* (1982) 4879; (d) G. Wilkinson; R.D. Gillard; J.A. McCleverty (eds.) *Comprehensive Coordination Chemistry*; Pergamon, Vol. 2, Oxford U.K. 1987, and references therein.

[3] A. Martin, M. Mena, P.R. Raithby, R. Serrano and C. Yélamos, *J. Organomet. Chem.*, *467* (1994) 79.

[4] Compound **1**: A solution of [Cp*Ti(NMe$_2$)$_3$] (0.54 g, 1.71 mmol) in toluene (40 ml) was exposed to carbon dioxide (1 atm) at 0°C. A change from red to yellow was observed after stirring 30 min at room temperature. The volatiles were removed in vacuo and the yellow solid **1** was obtained in 95% yield (0.73 g). $\nu(O_2CN) = 1559$(vs)cm^{-1}. ^{1}H-NMR (C_6D_6, 20°C, δ): 2.13 (s, 15H, C_5Me_5), 2.55 (s, 18H, O_2CNMe_2). $^{13}C\{^1H\}$-NMR (C_6D_6, 20°C, δ): 11.3 (C_5Me_5), 34.3 (O_2CNMe_2), 128.5 (C_5Me_5), 167.0 (O_2CNMe_2). Anal.: Found: C, 50.62; H, 7.21; N, 9.06. $C_{19}H_{33}N_3O_6Ti$ Calc. C, 51.01; H, 7.43; N, 9.39% MS: *m/e* [assignment, rel. int.(%)]: 359 [(M-O_2CNMe_2)$^+$, 3], 312 [(M-Cp*)$^+$, 17].

Compound **2**: As for **1**, 0.55 g (1.38 mmol) of [Cp*Ti(NEt$_2$)$_3$] stirred for 2 h lead to 0.71 g (97%) of yellowish green solid **2**. $\nu(O_2CN) = 1535$(vs)cm^{-1}. ^{1}H-NMR (C_6D_6, 20°C, δ): 0.97 (t, 7.1Hz, 18H, $O_2CN(CH_2\text{-}Me)_2$), 2.15 (s, 15H, C_5Me_5), 3.11 (q, 7.1Hz, 12H, $O_2CN(CH_2\text{-}Me)_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 20°C, δ): 11.5 (C_5Me_5), 14.1 ($O_2CN(CH_2\text{-}Me)_2$), 39.6 ($O_2CN(CH_2\text{-}Me)_2$), 123.7 (C_5Me_5), 167.1 (O_2CNEt_2). Anal.: Found: C, 56.16; H, 8.39; N, 7.62. $C_{25}H_{45}N_3O_6Ti$ Calc. C, 56.49; H, 8.53; N, 7.91% MS: *m/e* [assignment, rel. int.(%)]: 416 [(M-O_2CNEt_2)$^+$, 24], 397 [(M-Cp*)$^+$, 100].

[5] Compound **3**: A solution of 0.5 g (1.12 mmol) of **1** in 60 ml of hexane was exposed to wet air for 1 h, then concentrated to half volume and cooled to −40°C for 12 h giving 0.28 g (87%) of yellow crystals of **3**. $\nu(O_2CN) = 1574$(vs)cm^{-1}, ν(Ti–O–Ti) = 682(m), 639(m)cm^{-1}. ^{1}H-NMR (C_6D_6, 20°C, δ): 2.08 (s, 30H, C_5Me_5), 2.70 (s, 12H, O_2CNMe_2). $^{13}C\{^1H\}$-NMR (C_6D_6, 20°C, δ): 11.4 (C_5Me_5), 34.5 (O_2CNMe_2), 123.8 (C_5Me_5), 166.1 (O_2CNMe_2). Anal.: Found: C, 54.23; H, 7.33; N, 4.86. $C_{26}H_{42}N_2O_6Ti_2$ Calc. C, 54.36; H, 7.37; N, 4.88% MS: *m/e* [assignment, rel. int.(%)]: 574 [M$^+$, 2], 439 [(M-Cp*)$^+$, 100].

Compound **4**: Similarly to **3**, complex **4** was obtained in 91% yield. $\nu(O_2CN) = 1550$(vs)cm^{-1}, ν(Ti–O–Ti) = 672(m), 615(m)cm^{-1}. ^{1}H-NMR ($CDCl_3$, 20°C, δ): 1.19 (t, 6.9Hz, 12H, $O_2CN(CH_2\text{-}Me)_2$), 1.90 (s, 30H, C_5Me_5), 3.38 (q, 8H, 6.9Hz, $O_2CN(CH_2\text{-}Me)_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 20°C, δ): 11.2 (C_5Me_5), 13.9 ($O_2CN(CH_2\text{-}Me)_2$), 39.9 ($O_2CN(CH_2\text{-}Me)_2$), 123.7 (C_5Me_5), 164.8 (O_2CNEt_2). Anal.: Found: C, 56.98; H, 7.96; N, 4.51. $C_{30}H_{50}N_2O_6Ti_2$ Calc. C, 57.15; H, 7.99; N, 4.44% MS: *m/e* [assignment, rel. int.(%)]: 631 [M$^+$, 2], 496 [(M-Cp*)$^+$, 100].

[6] (a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Complexes*, 4th edn. Wiley, New York, 1986; (b) J. Okuda and E. Herdtweck, *Inorg. Chem.*, *30* (1991) 1516.

[7] (a) S.I. Troyanov, V. Varga and K. Mach, *J. Organomet. Chem.*, *402* (1991) 201; (b) T. Carofiglio, C. Floriani, A. Sgamellotti, M. Rosi, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, (1992) 1081; (c) F. Bottomley, *Polyhedron*, *11* (1992) 1707; (d) R. Andrés, M. Galakhov, A. Martin, M. Mena and C. Santamaria, *Organometallics*, *13* (1994) 2159.

[8] P. Gómez-Sal, A. Martin, M. Mena, P. Royo and R. Serrano, *J. Organomet. Chem.*, *419* (1991) 77.

[9] Measurements were performed at 20°C using MoKα radiation ($\lambda = 0.71065$ Å) and a graphite-orientated monochromator on an ENRAF-Nonius CAD4 diffractometer. $C_{30}H_{50}N_2O_6Ti_2$, $M = 630.52$, monoclinic, space group C2/c. Unit cell dimensions: $a = 17.022(3)$Å, $b = 13.127(4)$Å, $c = 15.305(3)$Å, $\beta = 94.19(1)°$, $V = 3411(1)$Å^3, from the least squares refinement of 25 centred reflections ($7 < 2\theta < 12$), $Z = 4$, $D_{calc} = 1.228$ g/cm^3, μ(Mo Kα) = 0.508 mm^{-1}, $F(000) = 1344$. The structure was solved by direct methods with SHELX-86 and refined by blocked full-matrix least-squares analysis on F^2 with SHELXL-93. All calculations were performed on an ALPHA AXP Digital Workstation. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions in the last cycles of refinement. 3917 reflections collected, 3703 independent reflections, goodness-of-fit 0.954, refinement converged with $R1 = 0.0423$ and $wR2 = 0.1356$ [$I > 2\sigma(I)$], and for all data $R1 = 0.1041$, $wR2 = 0.2458$. (max./min. rest electron density 0.420/−0.378eÅ^{-3}).

Full list of atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

[10] (a) G.D. Smith, C.N. Caughlan and J.A. Campbell, *Inorg. Chem.*, *11* (1972) 2989; (b) B.A. Borgias, S.R. Cooper, Y.B. Kohl and K.N. Raymond, *Inorg. Chem.*, *23* (1984) 1009; (c) T.J. Clark, T.A. Nile, D. McPhail and A.T. McPhail, *Polyhedron 8* (1989) 1804; (d) J.E. Hill, P.E. Fanwick and I.P. Rothwell, *Acta Cryst.*, *C47* (1991) 541; (e) G.R. Willey, J. Palin and N.W. Alcock, *J. Chem. Soc., Dalton Trans.*, (1992) 1117.